

Influence of microbial community composition and metabolism on air–sea $\Delta p\text{CO}_2$ variation off the western Antarctic Peninsula

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ABSTRACT: We studied CO_2 and O_2 dynamics in the western Antarctic Peninsula (WAP) waters in relation to (1) phytoplankton biomass, (2) microbial community primary production and respiration, and (3), for the first time, phytoplankton composition, during summer and fall in 3 consecutive years (2002, 2003 and 2004). The areal average of $\Delta p\text{CO}_2$ (the difference between surface seawater and atmospheric partial pressure of CO_2) for the 3 yr was significantly negative ($-20.04 \pm 44.3 \mu\text{atm}$, $p < 0.01$) during the summer to fall period in the region, possibly indicating a CO_2 sink. In the southern WAP (i.e. south of Anvers Island), $\Delta p\text{CO}_2$ was significantly negative ($-43.60 \pm 39.06 \mu\text{atm}$) during fall. In the northern WAP (north of Anvers Island), $\Delta p\text{CO}_2$ values showed a more complex distribution during summer and fall (-4.96 ± 37.6 and $21.71 \pm 22.39 \mu\text{atm}$, respectively). Chlorophyll *a* (chl *a*) concentration averaged $1.03 \pm 0.25 \mu\text{g l}^{-1}$ and was higher in the south of the peninsula. Phytoplankton composition influenced chl *a* concentration with higher and lower values for diatom- and phytoflagellate-dominated communities, respectively. A significant negative correlation existed between chl *a* and $\Delta p\text{CO}_2$. From incubation experiments performed in the northern WAP, respiration was low (averaging $5.1 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$), and the net community production (NCP) correlated negatively with $\Delta p\text{CO}_2$ and positively with % O_2 saturation. However, despite the high NCP values measured, $\Delta p\text{CO}_2$ was significantly positive in the northern WAP during the summer to fall period. Strong mixing and lower chl *a* concentration may explain this result. In contrast, $\Delta p\text{CO}_2$ was significantly negative in the southern WAP, possibly because of high surface water chl *a* concentration.

KEY WORDS: CO_2 sinks · CO_2 sources · Phytoplankton biomass · Phytoplankton composition · Primary production · Community respiration

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INTRODUCTION

The Southern Ocean contributes up to 15% of the global ocean primary production (Huntley et al. 1991) and has been considered among the most

important CO_2 sinks on Earth, being responsible for 24% (i.e. $0.39 \text{ Pg C yr}^{-1}$) of the global ocean CO_2 uptake (Takahashi et al. 2002). However, Takahashi et al. (2009) recently showed that the Southern Ocean CO_2 sink is smaller than previously thought

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(0.05 Pg C yr⁻¹, i.e. 4% of the global ocean CO₂ uptake), in agreement with views developed by atmospheric scientists (Bousquet et al. 2000, Peylin et al. 2002). In addition, over the last decades, the Southern Ocean CO₂ sink seems to have decreased in capacity (Metzl 2009), probably because of global warming (Le Quéré et al. 2007, 2010). However, coastal and shelf waters, such as the western Antarctic Peninsula (WAP) and the Ross Sea, are among the most productive waters of the Southern Ocean (Ferreira et al. 2004, Ducklow et al. 2006) and may still represent important CO₂ sinks (Agustí et al. 2004, Arrigo et al. 2008).

Within the Southern Ocean, the WAP has experienced some of the most rapid warming on Earth over the last 50 yr (Marshall et al. 2002, Vaughan et al. 2003, Turner et al. 2005). This warming has affected both air (Turner et al. 2005) and sea temperatures (Gille 2002, 2008, Meredith & King 2005, Whitehouse et al. 2008), and, along with increasing upwelling of warm Upper Circumpolar Deep Water onto the WAP shelf (Martinson et al. 2008), has triggered a change in sea-ice dynamics (i.e. a decrease in the extent and duration of sea-ice cover; Stammerjohn et al. 2008), all of which may have affected its potential as a CO₂ sink through physical, chemical, and biological processes.

Polar waters are considered to be rectified (1-way) annual CO₂ sinks because sea ice is present during winter when production is at a minimum, and absent during summer when production is at a maximum (Yager et al. 1995, Ducklow et al. 2007). This represents a rectification of the typical (ice-free, low latitude) seasonal cycle of air–sea CO₂ flux. Because of the observed changes in sea-ice dynamics (Stammerjohn et al. 2008), the rectified sink hypothesis for WAP waters is now being questioned (Wang et al. 2009). Indeed, if, in the future, sea ice is absent during low production periods, and therefore during times when the ocean acts as a CO₂ source, WAP waters may no longer be a rectified CO₂ sink.

Moreover, global change will continue to have an impact on marine organisms in the WAP, affecting the timing and magnitude of phytoplankton spring blooms (Montes-Hugo et al. 2009), the composition of communities at various trophic levels, such as phytoplankton (Moline et al. 2004, Montes-Hugo et al. 2009), zooplankton (Loeb et al. 1997, Atkinson et al. 2004), and top predators (Ducklow et al. 2007), and therefore the trophic interactions within the food web (Schofield et al. 2010). In turn, these effects may have an impact on the net community production (NCP, i.e. the rate of carbon fixation by photosynthesis rela-

tive to remineralization by respiration), on the transfer of carbon through the food web and on sedimentation processes. In polar ecosystems such as the WAP, air–sea CO₂ gas exchanges are driven by either physical (e.g. deep-water formation) or biological processes (e.g. primary production or respiration, Carrillo et al. 2004). Therefore, through its impact on microbial organisms, global change may also have an indirect impact on CO₂ dynamics.

The objective of the present study was to study the potential biological contribution to atmosphere–ocean CO₂ variability in the WAP. Three consecutive surveys were conducted on board the Argentinean icebreaker 'Almirante Irizar' during the austral summer and fall of 2002, 2003 and 2004. This was the first time air–sea CO₂ and O₂ exchanges were studied along the WAP (from the South Shetland Islands to Marguerite Bay) in relation to (1) phytoplankton biomass, (2) microbial community metabolism, and (3) phytoplankton composition.

MATERIALS AND METHODS

Study area

The WAP consists of 3 sub-regions (continental slope, shelf, and coastal regions, Fig. 1a; for a review of the WAP ecosystem, see Ducklow et al. 2007). These zones include the permanently open ocean zone, the sea-ice zone, and the coastal continental shelf zone (Tréguer & Jacques 1992, Smith et al. 1998). In the WAP, the coastal zone is the most productive, and the continental slope is the least productive (Ducklow et al. 2006). In addition, the dynamics of phytoplankton in the WAP are strongly subjected to the dynamics of sea ice (Garibotti et al. 2003), whose retreat brings water column stability (Garibotti et al. 2005b). For this study, we define the northern (southern) WAP as waters north (south) of Anvers Island (as defined by Montes-Hugo et al. 2009; Fig. 1a).

Sampling

Sampling was performed in the WAP on 9 occasions from January 2002 to April 2004 on board the Argentinean icebreaker 'Almirante Irizar' within the framework of the ARG AU (Programme de coopération entre la France et l'ARGentine pour l'étude de l'océan Atlantique AUstral) cooperative research program (see Table 1 and Fig. 1b for the

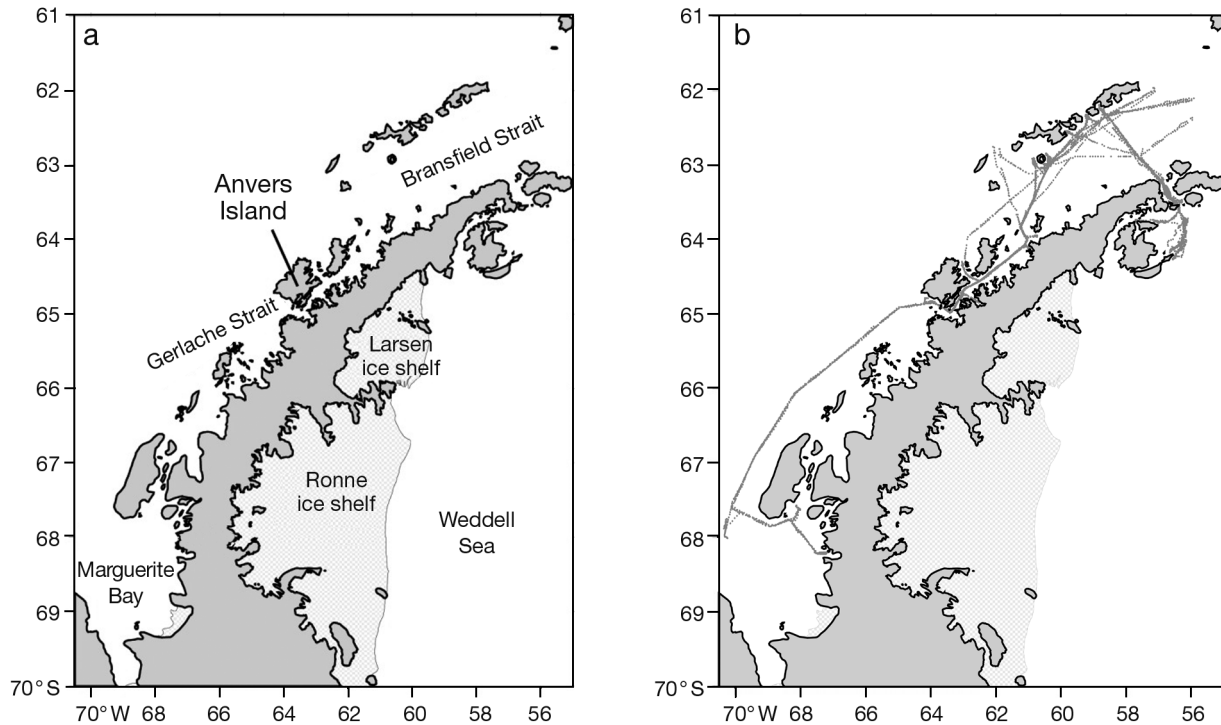


Fig. 1. (a) Western Antarctic Peninsula (WAP), and (b) ARGAU cruise itineraries (see ‘Materials and methods: Sampling’ for details)

dates and itineraries of the 9 cruises). The north of the peninsula was sampled both during the summer (before 21 March) and fall (after 21 March) while the south of the peninsula was only sampled during fall. The sampling methods of the ARGAU missions were described by Schloss et al. (2007) and Bianchi et al. (2005). Roughly, they consisted of a continuous acquisition and recording of meteorological, atmospheric, and seawater data. Incident photosynthetic available radiation (PAR) and the partial pressure of atmospheric CO_2 ($p\text{CO}_2$) were recorded continuously. The atmospheric $p\text{CO}_2$ was determined from an air intake placed on the bow of the ship. The air went through a flow-through equilibrator and an infrared analyzer (Siemens, Type Ultramat 5F) which was calibrated every 6 h with 3 gas standards con-

taining 270.0, 361.0, and 489.9 ppm mole fraction of CO_2 . The atmospheric $p\text{CO}_2$ was further corrected for warming effects using temperature data obtained from high-accuracy sensors that were placed in the equilibrator and the air intake. In addition, a surface seawater intake (placed at a depth of 9 m on the ship’s exterior) allowed the continuous measurement of surface seawater $p\text{CO}_2$, temperature, salinity, and *in vivo* fluorescence. The surface seawater $p\text{CO}_2$ was obtained from the infrared analyzer described above and was corrected for atmospheric pressure variations, drift, and moisture effects as in Bianchi et al. (2005). The surface seawater $p\text{CO}_2$ was determined with a precision of $1 \mu\text{atm}$ (Metzl et al. 1995). The difference between atmospheric and surface seawater $p\text{CO}_2$ was later computed as $\Delta p\text{CO}_2$, which contributes to CO_2 fluxes and ultimately to CO_2 sinks (if $\Delta p\text{CO}_2 < 0$) and CO_2 sources (if $\Delta p\text{CO}_2 > 0$).

Discrete samples were collected every 3 h from the seawater intake to determine dissolved oxygen concentration (following the Winkler method and using an automatic potentiometer Mettler DL21 titrator; $N = 137, 114,$ and 62 for the 2002, 2003, and 2004 missions, respectively). Discrete samples were also collected every 3 h to determine chlorophyll *a* (chl *a*) concentration (determined with a spectrophotometer; $N = 129, 116,$ and 63 for 2002, 2003, and 2004,

Table 1. Dates of the 9 ARGAU cruises (see Fig. 1) in the western Antarctic Peninsula in 2002, 2003, and 2004

2002	2003	2004
3–14 February	11–16 February	14–16 February
9–22 March	6–28 March	17 March–7 April
14–22 April	11–27 April	
	4–5 May	

respectively), nutrient concentrations (i.e. nitrite, nitrate, phosphate, and silicate; $N = 132, 114,$ and 62 for 2002, 2003, and 2004, respectively), and microscopic counts (performed under an inverted microscope; $N = 12$ and 8 for 2002 and 2003, respectively) and to perform incubation experiments to determine the NCP, gross primary production (GPP), and community respiration (R) of the surface planktonic community ($N = 14, 19,$ and 7 for 2002, 2003, and 2004, respectively).

For the analysis of nutrient concentrations, duplicate samples were filtered through Whatman GF/F filters and kept frozen at -20°C until analysis. Nitrate, nitrite, and silicate concentrations were determined with a Technicon II[®] automatic analyzer. Phosphate concentration was determined manually following the method of Strickland & Parsons (1972). For microscopic analyses, the biovolume of cells was calculated using the geometric shapes proposed by Hillebrand et al. (1999) and corrected to account for cell shrinkage caused by fixation of samples (Montagnes et al. 1994). The carbon content of cells was calculated with 2 different carbon-to-volume ratios for diatoms (which were composed of nano- and microphytoplankton) and for phytoflagellates (an arbitrary group composed of both flagellates and dinoflagellates and including both pico- and nanophytoplankton) according to Menden-Deuer & Lessard (2000). Incubations were run in replicates with 3 clear and 2 to 3 dark bottles incubated between 6 and 24 h to measure GPP and NCP as well as R .

Samples for incubation were collected at a depth of 9 m using the ship's intake. The same water was further circulated through the incubation system to keep samples at *in situ* water temperature. In 2002 and 2003, the irradiance in the incubation system simulated PAR at the sampling depth, corresponding to ~50% of incident PAR as measured by a PUV-500 profiler spectroradiometer (Biospherical Instruments) in the water column before the incubation experiments. In 2004, incubation bottles were exposed to natural light and were therefore wrapped with neutral filters to reach ~50% of the sea-surface irradiance, corresponding to the irradiance measured at the sampling depth. The initial and final oxygen concentrations in the clear and dark bottles were determined as described above using the Winkler method. NCP was calculated as the difference between the initial and final oxygen concentration in the clear bottles. R was calculated as the difference between the initial and final oxygen concentration in the dark bottles. GPP was calculated as $R + \text{NCP}$. NCP and R

were computed as daily estimates by multiplying hourly estimates by 24 following the method of Agustí et al. (2004). Daily GPP estimates were computed as $\text{GPP} (\text{d}^{-1}) = \text{GPP} (\text{h}^{-1}) \times \text{DL}$, where DL is day length (h). Finally, the GPP: R ratio (i.e. the metabolic balance) was used to discriminate between autotrophic ($\text{GPP}:R > 1$) and heterotrophic communities ($\text{GPP}:R < 1$). This method had a strong analytical precision with an average coefficient of variation of 0.29% between replicates.

% O_2 saturation was calculated following García & Gordon (1992) and using the solubility coefficients of Benson & Krause (1984) and the salinity and temperature data measured from the continuous sampling system. Areal averages were used to describe data averages over the sampling areas. Data were log transformed to meet the assumptions of normality and homoscedasticity, and model II linear regression analyses were performed to describe relationships between variables. In addition, 1-sample t -tests were used to determine whether ΔpCO_2 and % O_2 saturation were significantly different from 0 and 100%, respectively, for the years 2002, 2003, and 2004 and for all 3 cruises pooled together. Finally, ANOVAs were run to determine differences between seasons and between the northern and southern WAP for all variables. Data are represented as averages \pm SE.

RESULTS

Surface water temperature and salinity

Sea surface temperature over the whole WAP showed very little interannual variability, with an areal average of $0.33 \pm 0.97^{\circ}\text{C}$ over all 3 years (Table 2). As expected, sea surface temperature decreased significantly from February to May ($r = -0.24$, $p < 0.01$; data not shown). Moreover, during fall, the southern peninsula (with an average of $-0.18 \pm 0.77^{\circ}\text{C}$ over all 3 years) was significantly colder ($p < 0.01$) than the northern peninsula (with an average of $0.28 \pm 0.83^{\circ}\text{C}$ over all 3 years; Table 2 and Fig. 2a).

The areal average of surface water salinity over the whole WAP was 33.63 ± 0.41 over all 3 years (Table 2). Surface water salinity in the northern WAP did not change significantly from summer to fall, with respective areal averages of 34.02 ± 0.21 and 34.04 ± 0.25 (Table 2). However, during fall, surface water salinity was significantly higher ($p < 0.01$) in the north than in the south (with an areal average of 33.28 ± 0.26 in the south, Fig. 2b).

Table 2. Areal average (\pm SE) of sea surface temperature ($^{\circ}\text{C}$) and salinity (see ‘Materials and methods: Sampling’ for details). WAP: western Antarctic Peninsula

Year	Whole WAP		Summer north		Fall north		Fall south	
	Temp.	Salinity	Temp.	Salinity	Temp.	Salinity	Temp.	Salinity
2002	-0.04 ± 1.46	33.65 ± 0.39	1.22 ± 1.03	33.99 ± 0.24	0.33 ± 0.6	34.15 ± 0.19	-0.74 ± 0.4	33.31 ± 0.16
2003	0.36 ± 0.77	33.61 ± 0.39	1.02 ± 1.08	34.08 ± 0.15	0.16 ± 0.75	33.92 ± 0.27	0.3 ± 0.59	33.34 ± 0.36
2004	0.47 ± 0.64	33.64 ± 0.33	0.66 ± 0.85	34.03 ± 0.15	0.17 ± 0.85	33.97 ± 0.23	0.46 ± 0.33	33.35 ± 0.27
2002, 2003, and 2004	0.33 ± 0.97	33.63 ± 0.41	1.07 ± 1.1	34.02 ± 0.21	0.28 ± 0.83	34.04 ± 0.25	-0.18 ± 0.77	33.28 ± 0.26

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

Over all years, % O_2 saturation ranged from 76.66 to 148.17%, with an areal average of $93.98 \pm 2.1\%$ (Table 3, Fig. 2c). In 2002, the WAP was supersaturated with respect to oxygen in the north in summer (average of $101.07 \pm 2.85\%$) and undersaturated in both the north ($93.56 \pm 3.51\%$) and south ($93.26 \pm 1.4\%$) during fall (Table 3). In 2003 and 2004, WAP

waters were mostly undersaturated with respect to oxygen, except for a few locations in the northern WAP in summer. The % O_2 saturation in the north was significantly higher during summer than during fall ($p < 0.01$, Table 3). In addition, % O_2 saturation was significantly higher in the south than in the north during fall ($p < 0.01$).

The atmospheric $p\text{CO}_2$ averaged $372.2 \pm 0.7 \mu\text{atm}$ from 2002 to 2004, while the sea $p\text{CO}_2$ was much

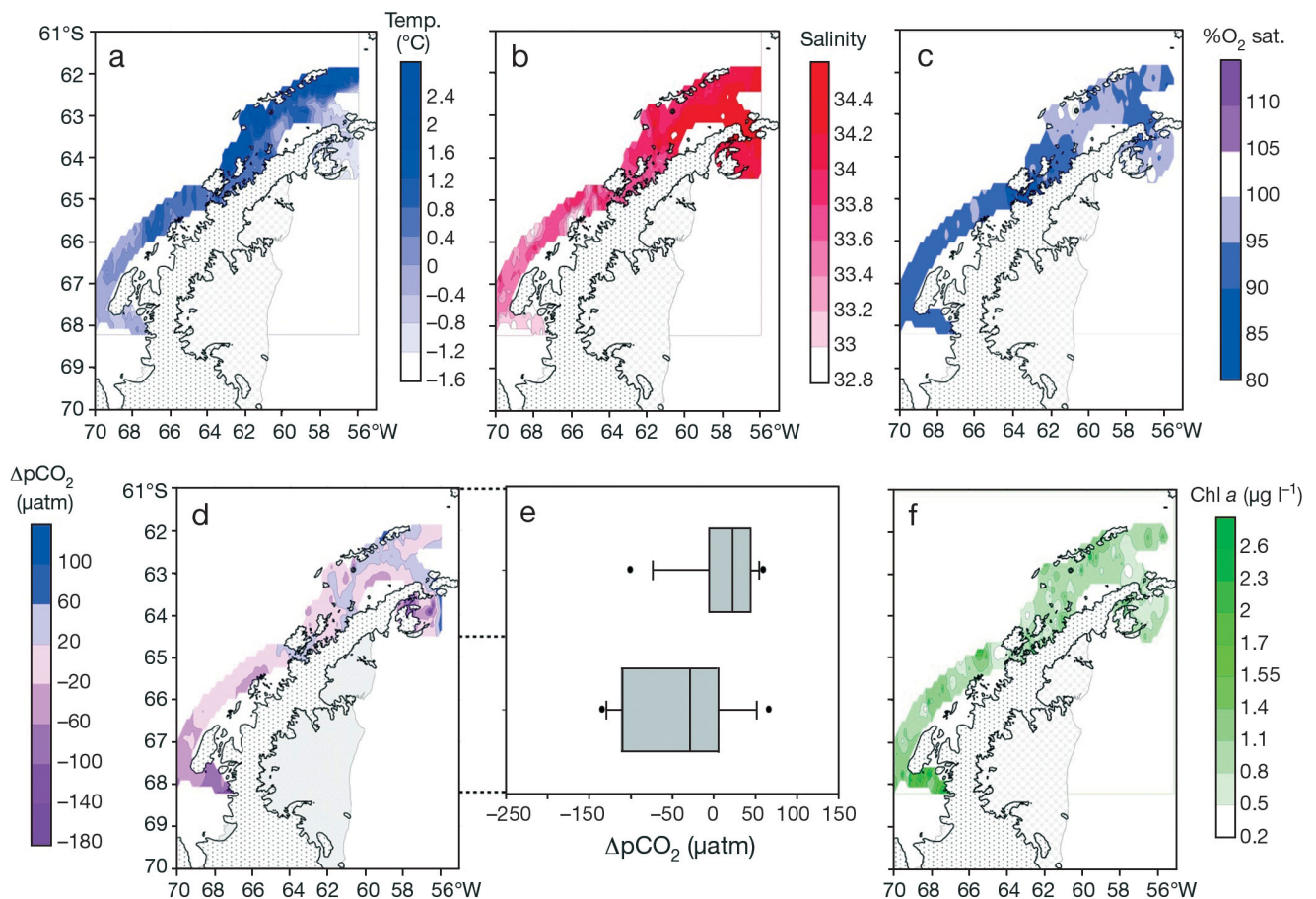


Fig. 2. (a) Sea surface temperatures ($^{\circ}\text{C}$), (b) sea surface salinity, (c) % O_2 saturation, and (d) $\Delta p\text{CO}_2$ along the western Antarctic Peninsula (WAP) in 2002, 2003, and 2004 (combined). (e) Box plots describing the $\Delta p\text{CO}_2$ data in the northern and southern WAP. The box plots indicate the 5th and 95th percentile (dots), the lower and upper quartiles, and the median. (f) Chl a along the WAP in 2002, 2003, and 2004 (combined). To avoid distortion, chl a values $> 3 \mu\text{g l}^{-1}$ were not used in (f)

Table 3. Areal average (\pm SE) of $\Delta p\text{CO}_2$ (μatm), % O_2 saturation (sat O_2), and chl *a* ($\mu\text{g l}^{-1}$) (see 'Materials and methods: Sampling' for details). WAP: western Antarctic Peninsula

ARGAU cruise	Whole WAP			Summer north		
	Sat O_2	$\Delta p\text{CO}_2$	Chl <i>a</i>	Sat O_2	$\Delta p\text{CO}_2$	Chl <i>a</i>
2002	96.19 \pm 3.37	-27.13 \pm 42.31	0.78 \pm 0.28	101.07 \pm 2.85	-27.88 \pm 39.59	0.91 \pm 0.27
2003	91.48 \pm 2.44	0.01 \pm 39.20	1.08 \pm 0.25	93.78 \pm 3.37	18.62 \pm 19.51	0.88 \pm 0.4
2004	93.33 \pm 1.26	-14.03 \pm 41.81	1.65 \pm 0.32	95.06 \pm 2.56	19.59 \pm 32.07	1.41 \pm 0.21
2002, 2003, and 2004	93.98 \pm 2.10	-20.04 \pm 44.30	1.03 \pm 0.25	98.39 \pm 2.35	-4.96 \pm 37.6	0.98 \pm 0.24
ARGAU cruise	Fall north			Fall south		
	Sat O_2	$\Delta p\text{CO}_2$	Chl <i>a</i>	Sat O_2	$\Delta p\text{CO}_2$	Chl <i>a</i>
2002	93.56 \pm 3.51	23.31 \pm 23.17	0.42 \pm 0.2	93.26 \pm 1.40	-49.26 \pm 30.27	1.01 \pm 0.38
2003	89.27 \pm 1.66	35.59 \pm 16.22	0.94 \pm 0.17	94.74 \pm 0.98	-31.30 \pm 37.97	1.39 \pm 0.48
2004	91.20 \pm 1.18	17.96 \pm 18.33	1.57 \pm 0.56	93.73 \pm 0.55	-42.93 \pm 45.8	1.79 \pm 0.16
2002, 2003, and 2004	90.99 \pm 1.99	21.71 \pm 22.39	0.85 \pm 0.22	94.02 \pm 0.54	-43.60 \pm 39.06	1.31 \pm 0.32

more variable and ranged from 176.3 to 503.2 μatm . Over the 3 yr, the areal average of $\Delta p\text{CO}_2$ in the WAP was negative (-20.04 ± 44.3 μatm , contributing to a CO_2 sink) during the summer to fall period ($p < 0.01$, Table 3). However, $\Delta p\text{CO}_2$ showed important variations among years, and although variation in the data is high, it could have led the WAP to be a significant CO_2 sink in 2002 and in 2004 (areal averages of -27.13 ± 42.31 and -14.03 ± 41.81 μatm , respectively, $p < 0.01$) while a balanced CO_2 budget was observed in 2003 (areal average of 0.01 ± 39.2 μatm).

For all years, a south to north gradient in $\Delta p\text{CO}_2$ seemed to exist as shown in Fig. 2d and the box plots in Fig. 2e. During summer, $\Delta p\text{CO}_2$ was negative in the north ($p < 0.01$), contributing to an atmospheric CO_2 sink in 2002 only (with areal averages of -27.88 ± 39.59 , 18.62 ± 19.51 , and 19.59 ± 32.07 μatm for 2002, 2003, and 2004, respectively). In addition, in the north, $\Delta p\text{CO}_2$ was significantly lower during summer (with an average of -4.96 ± 37.6 μatm) than during fall (21.71 ± 22.39 μatm , $p < 0.01$; Table 3). In fact, during fall, $\Delta p\text{CO}_2$ was significantly positive in the north, which could have led to a CO_2 source for the atmosphere during all years ($p < 0.01$). The opposite situation was evident in the south during fall over all years (with a significantly negative $\Delta p\text{CO}_2$ average of -43.6 ± 39.06 μatm , $p < 0.01$). Therefore, $\Delta p\text{CO}_2$ in the south could have led to a significant sink for atmospheric CO_2 , while the role of the northern peninsula was more complex and depended on the season (Fig. 2d).

Chl *a* and phytoplankton groups

Surface water chl *a* areal average was 1.03 ± 0.25 $\mu\text{g l}^{-1}$ for all years (Table 3). Small interannual differences in chl *a* were observed, with areal aver-

ages of 0.78 ± 0.28 , 1.08 ± 0.25 , and 1.65 ± 0.32 $\mu\text{g l}^{-1}$ for 2002, 2003, and 2004, respectively (Table 3 and Fig. 2f). In the north, chl *a* was insignificantly higher during summer (average of 0.98 ± 0.24 $\mu\text{g l}^{-1}$) than during fall (average of 0.85 ± 0.22 $\mu\text{g l}^{-1}$, $p = 0.31$). In addition, with an average of 1.31 ± 0.32 $\mu\text{g l}^{-1}$, chl *a* was significantly higher in the south during fall than in the north during either summer or fall ($p < 0.01$).

The highest chl *a* concentrations measured in 2002 (between 17.5 and 22.3 $\mu\text{g l}^{-1}$) were found near the coast (at Deception Island, in the Gerlache Strait, and in the north of the peninsula near the Weddell Sea) on 4, 8, and 10 February. In 2003, the highest chl *a* concentrations (between 18.3 and 26.4 $\mu\text{g l}^{-1}$) were measured near the coast in Marguerite Bay on 14 and 15 April. In 2004, the highest chl *a* concentrations (between 12 and 29.4 $\mu\text{g l}^{-1}$) were measured near the coast (at Deception Island and in the northern WAP near the Weddell Sea) on 15 February and 19 and 21 March.

Among the samples analyzed by microscopy, diatoms were the dominant group at the 4 stations with the highest chl *a* concentrations measured (between 8.04 and 22.33 $\mu\text{g l}^{-1}$). Measurements were made at these 4 stations in February 2002 and February 2003, and were found in the northern WAP (i.e. in the Bransfield Strait and near the Weddell Sea). In fact, there was a significant positive relationship between chl *a* and the carbon biomass of diatoms ($r = 0.88$, $p < 0.01$, Fig. 3a). In contrast, no significant relationship was observed between chl *a* and the carbon biomass of phytoflagellates (Fig. 3b). Therefore, the composition of the phytoplankton community influences the chl *a* concentration found in surface waters of the WAP. Of the 20 stations for which phytoplankton composition was analyzed, 12 were dominated by diatoms and the other 8 by phytoflagellates. Therefore, and consistent with the literature (e.g. Garibotti et al. 2003), both

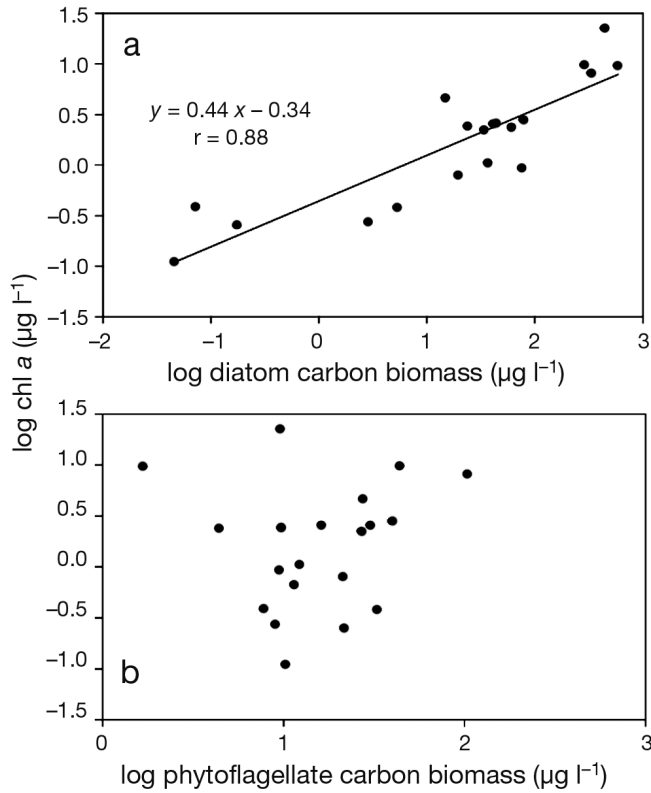


Fig. 3. Chl *a* and carbon biomass of (a) diatoms and (b) phytoflagellates (all log-transformed). A significant ($p < 0.01$) linear regression was found for chl *a* and diatom carbon biomass

phytoplankton groups were important in WAP waters and probably contributed to the observed spatial and temporal differences in the accumulation of chl *a*.

A significant negative correlation existed between chl *a* and $\Delta p\text{CO}_2$ ($r = -0.66$, $p < 0.01$, Fig. 4a) when all the stations were pooled. Moreover, this relationship held true for stations dominated by diatoms (i.e. defined by Schloss et al. 2007 as stations with more than 50% of the phytoplankton biomass represented by diatoms; $r = -0.68$, $p < 0.01$; Fig. 4b) but not for stations dominated by phytoflagellates (i.e. with more than 50% of the phytoplankton biomass represented by phytoflagellates; Fig. 4c).

A positive relationship existed between chl *a* and $\% \text{O}_2$ saturation ($r = 0.6$, $p < 0.01$, Fig. 4d). The correlation coefficient was greater when considering only stations dominated by diatoms ($r = 0.81$, $p < 0.01$, Fig. 4e), and there was a lack of correlation between chl *a* and $\% \text{O}_2$ saturation for stations dominated by phytoflagellates (Fig. 4f). Therefore, phytoplankton composition plays a crucial role in the relationship between chl *a* and CO_2 and O_2 dynamics in the WAP.

Community metabolism

R was neither correlated with temperature ($p = 0.94$) nor with chl *a* ($p = 0.95$). The average daily R for all studied years was $5.2 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$. Two of

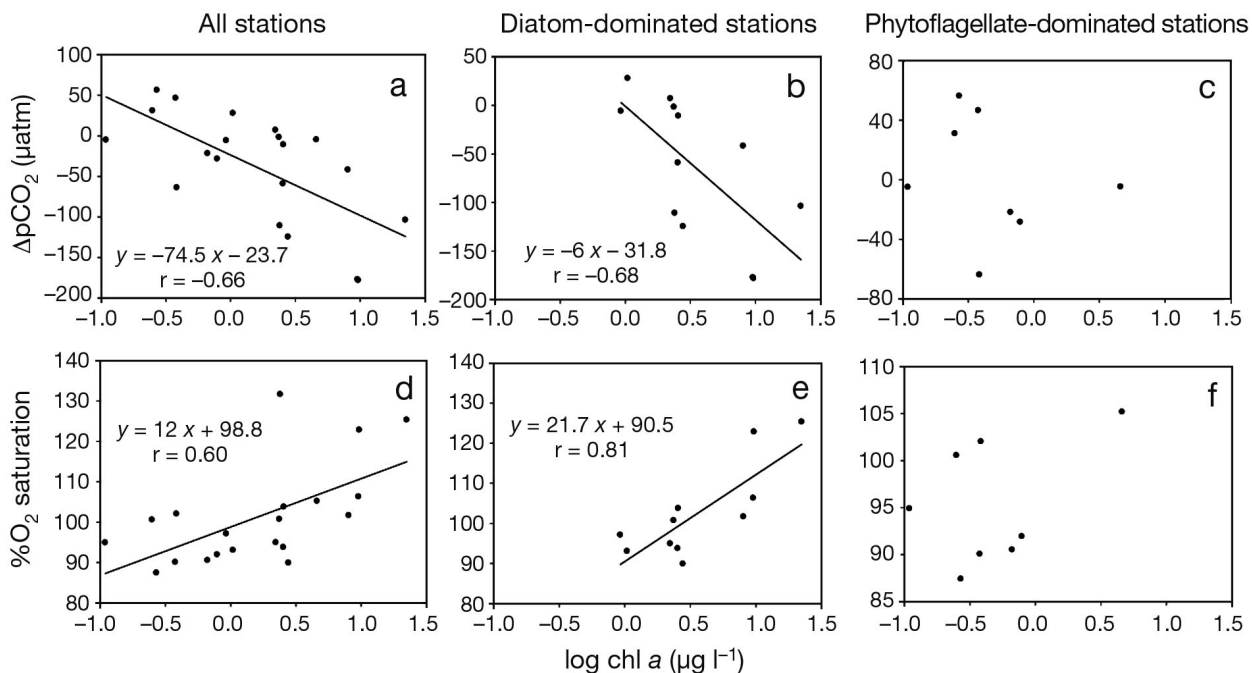


Fig. 4. (a,b,c) $\Delta p\text{CO}_2$ and (d,e,f) $\% \text{O}_2$ saturation plotted against log-transformed chl *a* for all stations, diatom-dominated stations and phytoflagellate-dominated stations. Significant ($p < 0.01$) linear regressions are also plotted

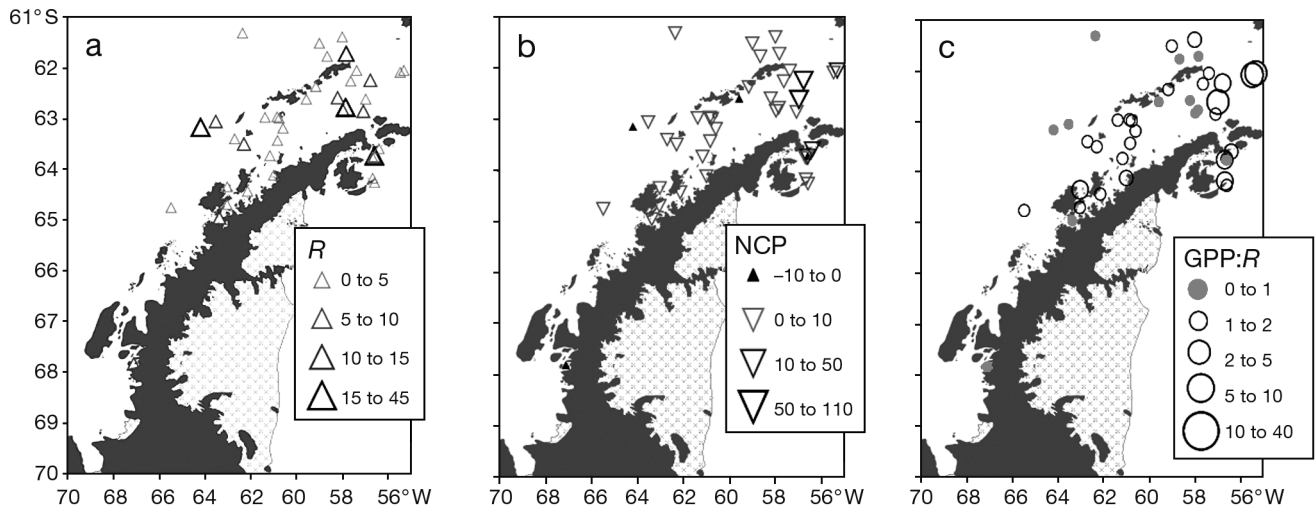


Fig. 5. (a) Community respiration (R , $\text{mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$), (b) net community production (NCP, $\text{mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$), and (c) gross primary production:respiration ratio (GPP:R, dimensionless) measured in incubation experiments in 2002, 2003, and 2004 (combined)

the highest R values (i.e. 22.8 and 42.1 $\text{mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$) were observed in 2002 and were found offshore (on the continental slope, Fig. 5a). Another high R value (16.8 $\text{mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$) was measured in 2004 in the north, in the Bransfield Strait. High R values were rare and were mostly found in the stations located relatively far offshore.

NCP ranged from -3.5 to $103.9 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$. High NCP values (between 15.2 and 103.9 $\text{mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$) were generally found at the northern tip of the peninsula (in the Bransfield Strait and towards the Weddell Sea, Fig. 5b). Negative NCP values were rare and were found in Marguerite Bay, Deception Island, and on the WAP continental slope. NCP was higher than R for 70% of the stations (28/40 stations), showing that, for the majority of stations, plankton communities were potentially net autotrophic. Finally, NCP was significantly correlated with chl a ($r = 0.61$, $p < 0.01$, Fig. 6a) and GPP ($r = 0.86$, $p < 0.01$, Fig. 6b).

As described above, 70% of the stations had a GPP:R > 1 , although this ratio showed a high interannual variability. In 2002 and in 2004, only 57% of the stations had a GPP:R > 1 (12/21 stations for 2002 and 2004), while in 2003, 84% of the stations had a GPP:R > 1 (16/19 stations). No seasonal differences were observed, with 68 and 72% of the stations with a GPP:R > 1 for summer and fall, respectively (15/22 and 13/18 stations, respectively). It also seems that most of the stations with GPP:R > 1 were found close to the coast (Fig. 5c). Finally, there was no difference in nutrient concentration between autotrophic (with averages of 24.4 ± 3.6 , 1.8 ± 0.3 , and $67.9 \pm 9.3 \mu\text{M}$ for nitrate + nitrite, phosphate, and silicate, respectively)

and heterotrophic communities (with averages of 21.6 ± 7.8 , 1.6 ± 0.5 , and $63.4 \pm 17.2 \mu\text{M}$ for nitrate + nitrite, phosphate, and silicate, respectively). However, chl a was usually lower in heterotrophic (average of $1 \pm 0.7 \mu\text{g l}^{-1}$) than in autotrophic communities (average of $2.2 \pm 2.2 \mu\text{g l}^{-1}$). Only 1 station, where the community was net heterotrophic (GPP:R = 0.33), exhibited a high chl a concentration ($18.6 \mu\text{g l}^{-1}$) together with low nitrate + nitrite and phosphate concentrations (3.1 and 0.4 μM , respectively).

Except for 1 station in Marguerite Bay in fall 2002 (not included in the analysis), NCP was negatively correlated with $\Delta p\text{CO}_2$ ($r = -0.42$, $p < 0.01$, Fig. 6c) and positively correlated with % O_2 saturation ($r = 0.59$, $p < 0.01$, Fig. 6d). In contrast, R was neither correlated with $\Delta p\text{CO}_2$ nor with % O_2 saturation (data not shown). Finally, for the 14 incubation stations for which phytoplankton species biomass was determined, GPP and the GPP:R ratio were significantly correlated with diatom biomass ($r = 0.82$, $p < 0.01$ and $r = 0.68$, $p = 0.01$ for GPP and GPP:R, respectively; Fig. 7 a,b) but not with phytoflagellate biomass (data not shown).

DISCUSSION

Over the 3 consecutive years studied (2002, 2003, and 2004) $\Delta p\text{CO}_2$ was significantly negative during the summer to fall period (areal average of $-20.46 \pm 44.3 \mu\text{atm}$), which could have led to a significant CO_2 sink in the WAP. However, during summer, $\Delta p\text{CO}_2$ was significantly negative in the north of the peninsula in 2002 only, while during fall, it was significantly positive in the north and significantly negative

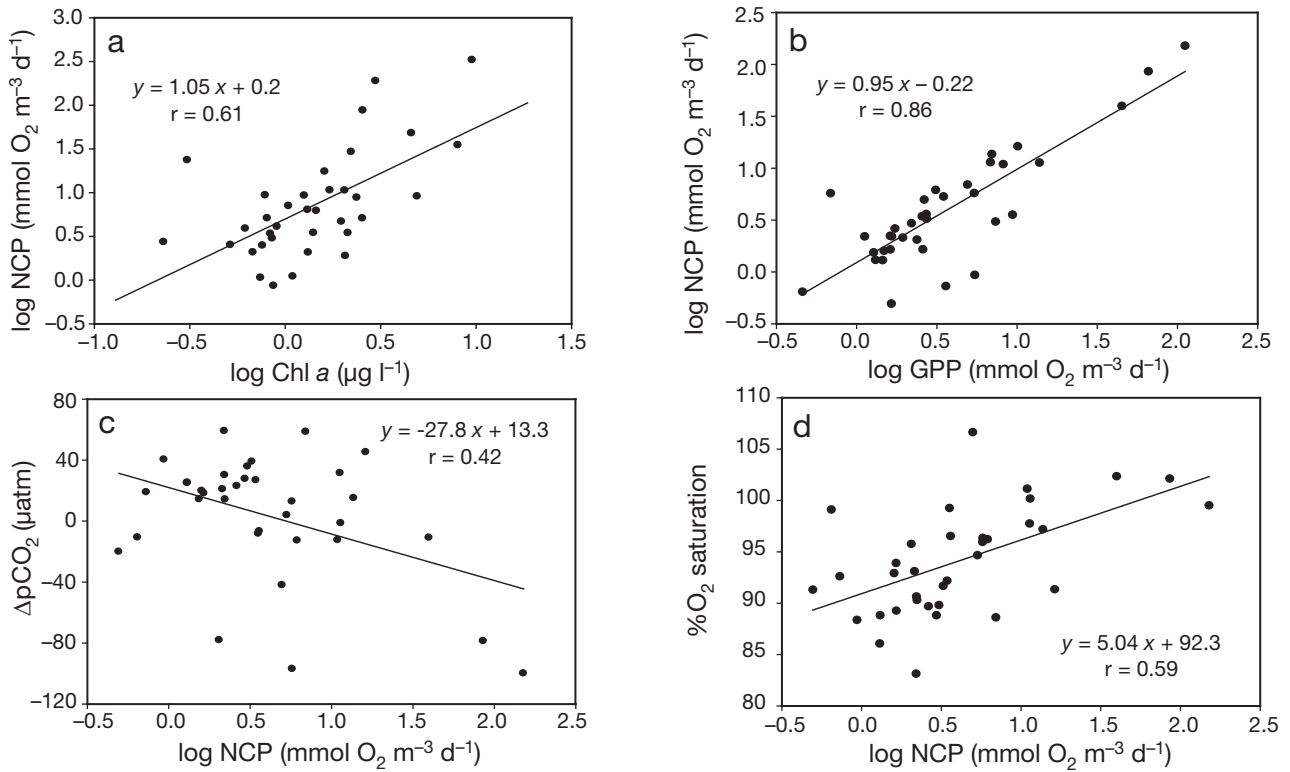


Fig. 6. Net community production (NCP) and (a) chl *a* and (b) gross primary production (GPP) (all log-transformed). (c) $\Delta p\text{CO}_2$ and (d) $\% \text{O}_2$ saturation and NCP (log-transformed). Significant ($p < 0.01$) linear regressions are also plotted

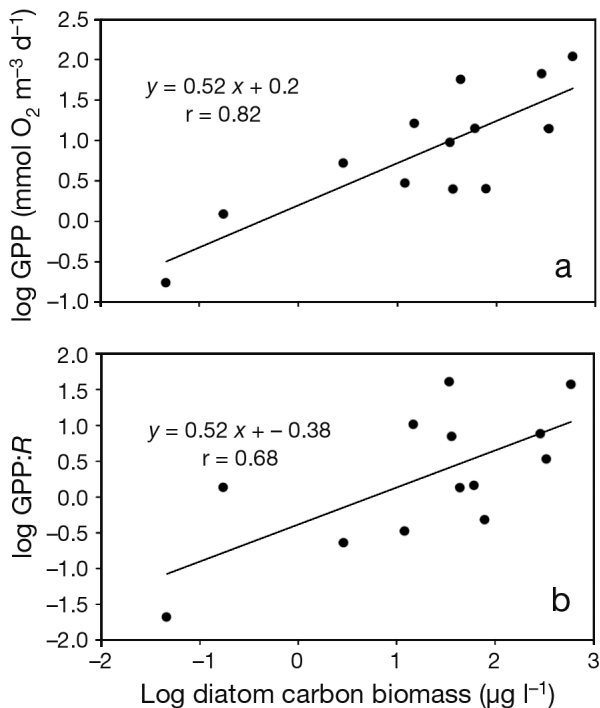


Fig. 7. Diatom carbon biomass and (a) gross primary production (GPP) and (b) GPP:respiration (*R*) ratio (all log-transformed). Significant ($p < 0.01$ and $p = 0.01$ for panels a and b, respectively) linear regressions are also plotted

in the south, possibly leading to, respectively, CO_2 sources and sinks (Fig. 2d and Table 3). These findings are coherent with the literature, which suggests that the southern coastal WAP is a CO_2 sink during summer (Carrillo et al. 2004). These results are also consistent with the results of Carrillo & Karl (1999) and Álvarez et al. (2002) which suggest that CO_2 sinks and sources show a complex distribution in the northern WAP, but they are not entirely consistent with the suggestion of Agustí et al. (2004) that the northern WAP is a net CO_2 sink during summer because it is mainly autotrophic. The differences observed between the north and the south are reported here for the first time, and some of the possible mechanisms controlling $\Delta p\text{CO}_2$, such as community composition, community metabolism (i.e. primary production and respiration), and sea surface temperature, are discussed below.

Influence of community composition on the WAP CO_2 dynamics

A significant negative correlation existed between chl *a*, as a proxy of primary producers, and $\Delta p\text{CO}_2$, and a positive relationship existed between chl *a* and

%O₂ saturation (Fig. 4), suggesting that the dynamics of these 2 gases in the WAP were influenced by primary producers. Moreover, and consistent with the findings of Schloss et al. (2007) at the Patagonian shelf off Argentina, the 2 relationships between chl *a* and ΔpCO₂ and %O₂ saturation only held true for stations dominated by diatoms. Chl *a* concentration was itself influenced by the composition of the phytoplankton community, with high and low chl *a* concentrations found for diatom- and phytoflagellate-dominated communities, respectively. In fact, in the majority of samples analyzed, diatom cells were significantly larger than phytoflagellates. This is consistent with previous findings in the literature (e.g. Montes-Hugo et al. 2008, Olguín & Alder 2011) which showed that, in the WAP, high and low chl *a* concentration are usually associated with the presence of large and small cells, respectively. One may therefore extrapolate and argue that large- and small-cell-dominated phytoplankton communities may lead to negative and positive ΔpCO₂ and therefore to CO₂ sinks and sources, respectively.

It has been hypothesized that the community composition of the WAP is shifting from diatom- to cryptophyte-dominated waters because of regional warming (Moline et al. 2004) and in relation to temporal changes in sea-ice dynamics (Garibotti et al. 2005a) which were observed in the WAP during the last decades (Stammerjohn et al. 2008). More specifically, Montes-Hugo et al. (2008) showed that the phytoplankton shifts from large to small cells that have taken place in the northern WAP in the last decade were probably related to changes in sea-ice anomalies. In another study, Montes-Hugo et al. (2009) showed that, because of regional warming, chl *a* concentration has decreased by 12% in the whole WAP during the summer (December to February) over the last 30 yr. In contrast, Montes-Hugo et al. (2008) found higher chl *a* and larger cells in the southern part of the peninsula. Moreover, and contrasting with observations in the north, Montes-Hugo et al. (2009) observed increases in surface chl *a* in the southern WAP. These authors hypothesized that the WAP was undergoing a southward displacement of species of all trophic levels, from phytoplankton to top predators, with likely greater contributions of diatoms and large cells in the south and the opposite trend in the north. This is consistent with our observations of higher chl *a* concentrations in the southern WAP (Table 3), and can potentially explain the lower ΔpCO₂ values observed in the south in this study.

Other than a direct impact on total phytoplankton biomass, a shift in phytoplankton composition and

cell size might also have other implications on carbon fluxes. Indeed, small cells, such as cryptophytes or other phytoflagellates, are believed to be responsible for less carbon export than diatoms. Large diatoms are the base of multivore and herbivore food webs which are responsible for a high export of carbon from the euphotic zone to deep waters through direct sedimentation of phytoplankton cells or the sinking of zooplankton fecal pellets (Legendre & Rassoulzadegan 1995, Armbrust 2009). In contrast, small phytoplankton cells are the base of microbial food webs for which most of the carbon is expected to be consumed within the euphotic layer (Legendre & Rassoulzadegan 1996). For example, several authors measured higher sinking rates for waters dominated by large diatoms than for waters dominated by small phytoplankton (Serret et al. 2001, Anadón et al. 2002).

Community metabolism and CO₂ dynamics

First, it should be considered that most of the incubation experiments presented here (95%) were performed in the northern WAP (north of Anvers Island, Fig. 5). The average daily respiration rate for all studied years was low (present summer to fall data of 5.2 mmol O₂ m⁻³ d⁻¹) which is consistent with average respiration rates of 2.65 and 6.95 mmol O₂ m⁻³ d⁻¹ reported by Agustí et al. (2004) for the Bransfield and Gerlache Straits, respectively. High respiration rates were rare and were mostly found far from the coast and mostly during summer. In contrast, the net community production was high (ranging from -3.5 to 103.9 mmol O₂ m⁻³ d⁻¹) over all studied years when compared to previously reported estimates of NCP in the WAP, with NCP ranging from -6.29 to 35.4 mmol O₂ m⁻³ d⁻¹ in the study of Agustí et al. (2004). In addition, NCP was correlated to chl *a* and to GPP (Fig. 6a,b), showing that NCP in the WAP was mainly driven by primary production rather than by respiration. This is consistent with the findings of other studies which described an uncoupling between phytoplankton production and heterotrophic respiration in Antarctic waters (Morán et al. 2002, Agustí et al. 2004, Pearce et al. 2007).

As a consequence, the northern WAP waters were mainly autotrophic, and the GPP:R ratio exceeded 1 at 70% of the stations, very similar to the results of Agustí et al. (2004), who found that 73% of the stations they analyzed in the northern WAP during the summer were autotrophic. In addition, there was no strong difference in the proportion of stations with a

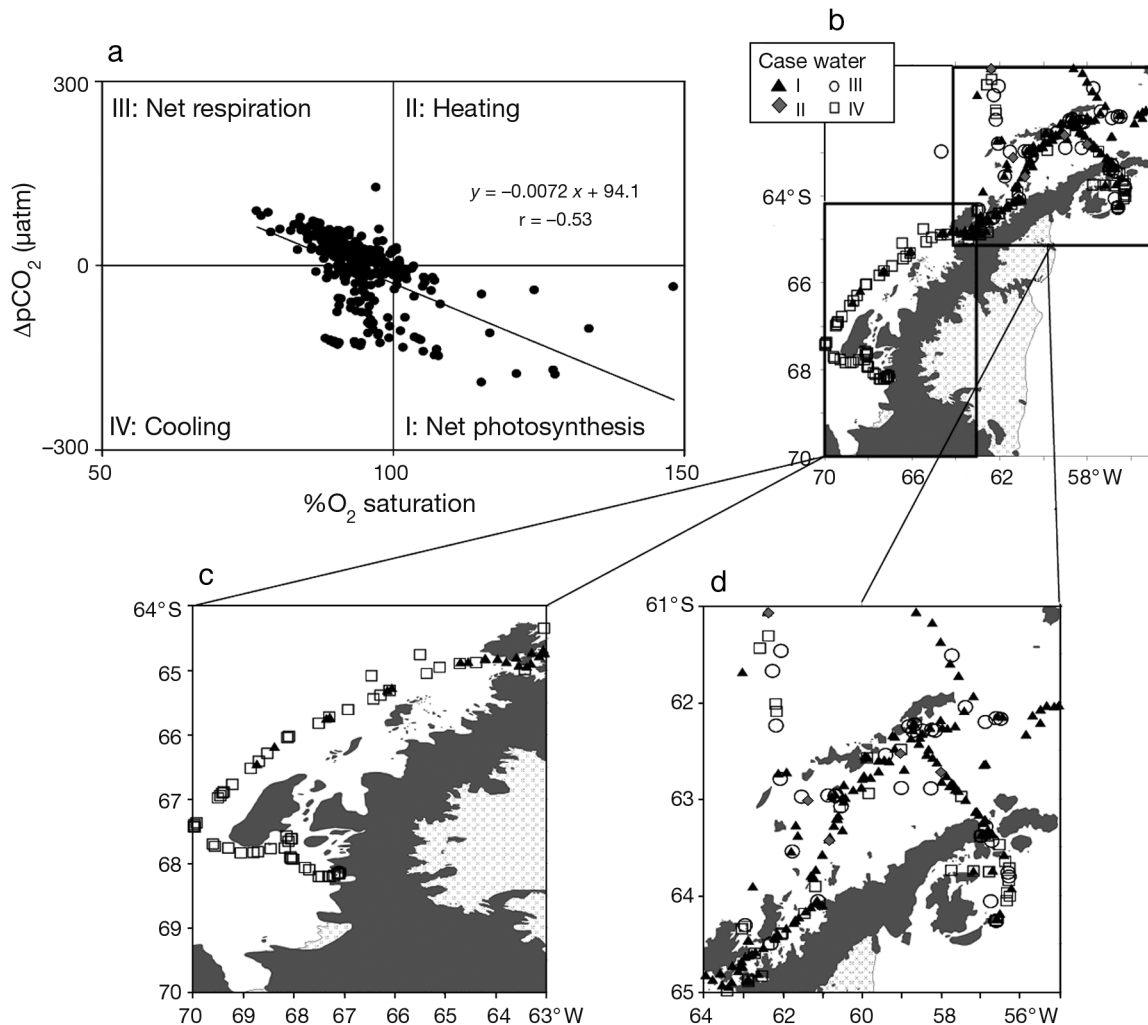


Fig. 8. (a) $\Delta p\text{CO}_2$ and $\% \text{O}_2$ saturation. The plot is divided into 4 quadrants. The significance of these quadrants is explained in the 'Discussion'. (b) Geographical distribution of Case I, II, III, and IV waters described in (a). (c) Geographical distribution of Case I, II, III, and IV waters within the southern portion of the western Antarctic Peninsula (WAP) and (d) geographical distribution of Case I, II, III, and IV waters within the northern WAP

GPP: $R > 1$ between summer and fall (with 68 and 72 % of the stations, respectively). Because the northern WAP is mainly autotrophic, and because respiration seems to be uncoupled to primary production (i.e. R was not correlated with chl a , NCP, or GPP), one would expect the northern WAP to behave as a significant CO_2 sink. Indeed, NCP correlated negatively with $\Delta p\text{CO}_2$ and positively with the $\% \text{O}_2$ saturation (Fig. 6c,d), while R was neither correlated to $\Delta p\text{CO}_2$ nor to the $\% \text{O}_2$ saturation. According to the linear regression between $\Delta p\text{CO}_2$ and NCP presented in Fig. 6c, the minimum NCP value required to yield negative $\Delta p\text{CO}_2$ was $3.02 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$. This value was achieved in 36% and 11% of the incubation experiments performed during the summer and fall, respectively. This is consistent with the lower and higher $\Delta p\text{CO}_2$ values observed in the

northern WAP during the summer and fall, respectively (Table 3). However, this is not consistent with the proportion of autotrophic stations sampled in the northern WAP (70%). Therefore, NCP, and more particularly primary production, seems to play a significant role in CO_2 and O_2 dynamics in the WAP, although autotrophy does not necessarily lead to negative $\Delta p\text{CO}_2$ values in the northern WAP.

Spatial variability of CO_2 and O_2 dynamics in the WAP

In order to explain the observed discrepancies between community metabolism and the distribution of negative and positive $\Delta p\text{CO}_2$ values and the possible mechanisms responsible for their distribution, we

studied the distribution of both $\Delta p\text{CO}_2$ and $\% \text{O}_2$ saturation (Fig. 8). Fig. 8a shows a scatter diagram of $\Delta p\text{CO}_2$ as a function of $\% \text{O}_2$ saturation. A significant negative correlation existed between these 2 variables ($r = -0.53$, $p < 0.01$), confirming the hypothesis of Agustí et al. (2004) and Álvarez et al. (2002) that photosynthesis and respiration, rather than other physical processes, are the driving processes in O_2 and CO_2 dynamics in the WAP. This figure was inspired and modified from the work of Carrillo et al. (2004), who studied the relationship between $\% \text{O}_2$ saturation and the surface seawater fugacity of CO_2 (which is similar to $p\text{CO}_2$) relative to the atmosphere ($f\text{CO}_2$) in the southern WAP waters. In Fig. 8a, the graph was divided into 4 quadrants: Quadrant I (simultaneous positive $\Delta p\text{CO}_2$ and O_2 undersaturation) implies respiration as the process controlling seawater $p\text{CO}_2$ and $\% \text{O}_2$ undersaturation, Quadrant II (simultaneous positive $\Delta p\text{CO}_2$ and O_2 supersaturation) implies heating as the process controlling seawater $p\text{CO}_2$ and $\% \text{O}_2$ supersaturation; Quadrant III (simultaneous negative $\Delta p\text{CO}_2$ and O_2 supersaturation) implies photosynthesis as the main process controlling seawater $p\text{CO}_2$ and $\% \text{O}_2$ supersaturation; and Quadrant IV (simultaneous negative $\Delta p\text{CO}_2$ and O_2 undersaturation) implies cooling as a the process controlling seawater $p\text{CO}_2$ and $\% \text{O}_2$ undersaturation.

From this figure, a clear demarcation appeared between the north and the south (i.e. north and south of Anvers Island; Fig. 8b), with southern waters mainly represented by case IV waters and northern waters represented by case I, III, and IV waters. Indeed, $\Delta p\text{CO}_2$ was negative in 91 % of the stations in the southern peninsula, consistent with the findings of Carrillo et al. (2004), who showed that most of the coastal southern WAP was represented by case III and case IV waters (i.e. with negative $\Delta p\text{CO}_2$). However, and although $\Delta p\text{CO}_2$ was negative in 91 % of the stations in the south, the $\% \text{O}_2$ saturation was above 100% in only 1.5% of the stations (Fig. 8a). Because primary production plays a significant role in CO_2 dynamics in WAP waters, one would expect southern WAP waters to be supersaturated with respect to O_2 . However, as described previously, surface water was particularly cold in the south, a fact that may have increased oxygen solubility and would explain the oxygen undersaturation found in these waters. The $\% \text{O}_2$ saturation was positively correlated with sea surface temperature ($r = 0.45$, $p < 0.01$, data not shown). Moreover, the relatively high chl *a* concentration found in the south (Fig. 2f, Table 3) may indicate that primary production was strong even

though incubation experiments were not performed in this part of the peninsula. Therefore, even though most of the southern WAP waters were undersaturated with respect to O_2 , primary production may still have been the main driver for the significant negative $\Delta p\text{CO}_2$ values observed.

North of Anvers Island, only 35% of the stations showed negative $\Delta p\text{CO}_2$ values (Fig. 8d). Of these, 52% were supersaturated with respect to O_2 (quadrant III) and the other 48% were undersaturated with respect to O_2 (quadrant IV). There was no clear distribution pattern of any of the 4 quadrant types in the northern WAP (Fig. 8d). Moreover, $\Delta p\text{CO}_2$ was mainly positive in the northern WAP as shown by the dominance (65%) of quadrant I waters, possibly leading to a significant CO_2 source in the northern WAP. Therefore, the role of the northern WAP with regards to CO_2 was much more complex than and not as strong as the southern WAP waters, consistent with the results presented in Table 3 and with the results of Carrillo & Karl (1999) and Álvarez et al. (2002), who described a complex distribution of CO_2 sinks and sources in the northern WAP.

Fig. 9 describes the possible influence of community metabolism (represented by the GPP:R ratio) on the distribution of $\Delta p\text{CO}_2$ and $\% \text{O}_2$ saturation in the northern WAP, which will ultimately contribute to the distribution of CO_2 sinks and sources. Unexpectedly, there was no clear distribution pattern in GPP:R from *in vitro* measurements regarding $\Delta p\text{CO}_2$ and $\% \text{O}_2$ saturation. In fact, autotrophic and heterotrophic

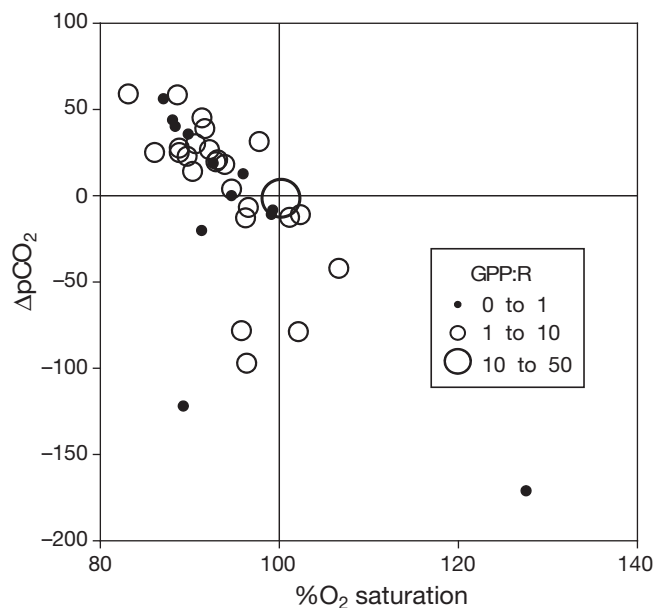


Fig. 9. Distribution of the gross primary production:respiration (GPP:R) ratio in relation to $\Delta p\text{CO}_2$ and $\% \text{O}_2$ saturation

communities (with GPP:*R* ratios > 1 and < 1 , respectively) were both found in Quadrants I, III, and IV with no clear pattern. Therefore, the community metabolism balance, represented by the GPP:*R* ratio, cannot explain by itself the distribution of negative $\Delta p\text{CO}_2$ values in the northern WAP and suggests that the relationship between community metabolism and $\Delta p\text{CO}_2$ and % O_2 saturation in the WAP is more complex than previously thought (Fig. 9).

In the WAP, mixing is believed to play a major role in primary production (Mitchell & Holm-Hansen 1991). In fact, surface water salinities measured in the northern WAP were much higher than in the south (Fig. 2b and Table 2), suggesting that mixing was more important in the north, therefore limiting primary production and the drawdown of CO_2 from the atmosphere. Schloss et al. (2002) showed that King George Island phytoplankton communities were potentially very productive, although they rarely met the adequate growth conditions *in situ*. In a mesocosm experiment, it took 12 d before the exponential growth of phytoplankton started and finally reached levels of chl *a* as high as $36 \mu\text{g l}^{-1}$ with complete nutrient exhaustion (Schloss et al. 2002), showing the strong primary production potential of WAP waters. Mixing is caused by winds which can be very intense in the WAP (Smith et al. 2008). Moreover, associated with regional warming, there has been a 15 to 20% increase in the strength of westerly winds in the WAP since the 1960s (Orr et al. 2004), which may have limited the biological uptake of CO_2 (Le Quéré et al. 2010). This strengthening of winds over the last decades in the WAP may explain the complex distribution of $\Delta p\text{CO}_2$ observed in the north in this study.

In addition, nutrient limitation may have explained the discrepancies found between the community metabolism balance (i.e. GPP:*R* ratio) and the distribution of $\Delta p\text{CO}_2$ and % O_2 saturation in the WAP. For example, 1 station sampled for an *in vitro* experiment showed a high chl *a* concentration ($18.6 \mu\text{g l}^{-1}$) together with low nitrate + nitrite and phosphate concentrations (3.1 and $0.4 \mu\text{M}$, respectively) and low $\Delta p\text{CO}_2$ ($-171 \mu\text{atm}$). However, this community had a low NCP ($-3.5 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$) and a fairly high *R* value ($8.8 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$) together with a GPP:*R* of 0.33, representative of a heterotrophic community. It is probable that this station was sampled after a phytoplankton bloom took place, which consumed nitrite, nitrate, and phosphate present in the water column. The high respiration rate measured probably reflects the consumption of organic matter by heterotrophs (i.e. bacteria and micro- and mesozoo-

plankton). However, this particular scenario was only found once, and nutrient concentrations were high in the remaining incubation experiments, suggesting that physical factors (e.g. water column mixing) limited *in situ* primary production rather than nutrient concentrations.

As pointed out by Schloss et al. (2007), metabolic activities such as respiration and primary production rely on different time and spatial scales than CO_2 and O_2 exchanges between the atmosphere and the ocean. Indeed, gas exchanges between the ocean and the atmosphere are processes occurring over weeks, whereas incubation experiments reflect short-term metabolic activities. In addition, recent studies have shown that incubation experiments performed in bottles may underestimate NCP and GPP when compared to non-incubation methods (e.g. Quay et al. 2010), although the authors did not conclude which method gives the more realistic results. This possible limitation needs to be considered for the present study, and simultaneous incubation and non-incubation estimations should be done simultaneously in order to solve this question. Therefore, more studies are needed to determine the relationship between CO_2 and O_2 exchanges between the atmosphere and the ocean and the community metabolism in WAP waters.

Finally, although the role of the WAP and its community composition in CO_2 and O_2 dynamics was determined, these results only concerned summer and fall. However, due to the increasing disappearance of sea ice along with regional warming (Stammerjohn et al. 2008), the seasonal rectification hypothesis of Yager et al. (1995) may require reconsideration. Some recent studies performed during winter to spring in the WAP (e.g. Wang et al. 2009) additionally point towards a weak CO_2 source during winter but a moderate sink during spring. Ideally, as described by Montes-Hugo et al. (2010), the study of CO_2 dynamics in relation to sea-ice dynamics over periods of several years is needed to be able to adequately assess the role of WAP waters in CO_2 dynamics.

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