

**C, O and biological
productivity in the
Southern Ocean**

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Carbon, oxygen and biological productivity in the Southern Ocean in and out the Kerguelen plume: CARIOCA drifter results

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Abstract

The Kerguelen Plateau region in the Indian sector of the Southern Ocean supports annually a large-scale phytoplankton bloom which is naturally fertilized with iron. As part of the second Kerguelen Ocean and Plateau compared Study expedition (KEOPS2) in austral spring (October–November 2011), one Carioca buoy was deployed east of the Kerguelen plateau. It drifted eastward downstream in the Kerguelen plume. Hourly surface measurements of $p\text{CO}_2$, O_2 and ancillary observations were collected between 1 November 2011 to 12 February 2012 with the aim of characterizing the spatial and temporal variability of the biological Net Community Production (NCP) downstream the Kerguelen plateau, assess the impact of iron-induced productivity on the biological carbon consumption and consequently on the CO_2 flux exchanged at the air–sea interface.

The trajectory of the buoy until mid-December was within the longitude range, 72–83° E, close to the polar front and then in the polar frontal zone, PFZ, until 97° E. From 17 November to 16 December, the buoy drifted within the Kerguelen plume following a filament carrying dissolved iron, DFe, for a total distance of 700 km.

In the first part of the trajectory, the ocean surface waters are a sink for CO_2 and a source for CO_2 , with fluxes of respective mean values equal to -8 and $+38 \text{ mmol CO}_2 \text{ m}^{-2} \text{ d}^{-1}$. Eastward, as the buoy escapes the iron enriched filament, the fluxes are in opposite direction, with respective mean values of $+5$ and $-48 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$. These numbers clearly indicate the strong impact of biological processes on the biogeochemistry in the surface waters within the Kerguelen plume in November-mid-December, while it is undetectable eastward in the PFZ from mid-December to mid-February.

While the buoy follows the Fe enriched filament, simultaneous observations of dissolved inorganic carbon, DIC, and dissolved oxygen, O_2 , highlight biological events lasting from 2 to 4 days. Stoichiometric ratios, O_2 / C , between 1.1 and 1.4 are observed indicating new and regenerated production regimes. NCP estimates range from

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60 to 140 mmol C m⁻² d⁻¹. Based on the relationship between the time a water parcel has left the plateau and its iron content, we have highlighted that the main control on the value of NCP is the availability of iron in the upper water column, with the largest NCP occurring in waters that have recently left the plateau and presented the highest iron concentrations.

1 Introduction

The Southern Ocean is a key region for the global carbon cycle and the climate system. It accounts for about 25–30 % of the total anthropogenic carbon uptake. The Southern Ocean (south of about 30° S) is found to be a sink area for atmospheric CO₂ in atmospheric or ocean inversion models (Friedlingstein et al., 2006; Gruber et al., 2009) as well as in data based approaches (Metzl et al., 1999; Takahashi et al., 2009). However, it represents a sink for atmospheric CO₂ whose strength and future evolution are debated (Le Quere et al., 2010; Lenton et al., 2013). Despite its importance, the Southern Ocean remains the region where uncertainties regarding the air–sea CO₂ flux and the carbon budget are the highest (e.g., Gruber et al., 2009). This remote part of the global ocean is hardly accessible in winter, leading to a very sparse spatiotemporal coverage of observations, including measurements of surface *p*CO₂. Undersampling biases are aggravated by the high variability which characterizes this oceanic region over a wide range of temporal and spatial scales. Quantification of the impacts of thermodynamics, biology, and physics on the sea surface partial pressure of CO₂ (*p*CO₂) is a necessary step to understand the processes regulating the ocean–atmosphere exchange of CO₂ and help to overcome the unresolved spatio temporal variability effects.

The magnitude of the gradient of *p*CO₂ between the atmosphere and the surface ocean depends on the relative contribution in the ocean mixed layer of the dynamic transport, the thermodynamics and the biological activity. Biological net community production, NCP, decreases sea surface *p*CO₂. In high nutrient-low-chlorophyll (HNLC) regions, including the Southern Ocean, more than two decades of intense research

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have confirmed that increasing iron supply stimulates primary production. (Boyd et al., 2007; Blain et al., 2008). Large and persistent phytoplankton blooms develop annually in the vicinity of sub-Antarctic islands (Blain et al., 2007; Borrione and Schlitzer, 2013; Pollard et al., 2009) due to natural iron supply. The results of field studies in the vicinity of Crozet and Kerguelen islands have clearly highlighted the crucial role of Fe on natural ecosystems and demonstrate the stimulation of the biological carbon pump. In February 2005, the Kerguelen Ocean and Plateau compared Study expedition (KEOPS1) focused on the high productivity area of the Kerguelen Island during the peak and decline of the bloom (Blain et al., 2007). The results emphasized the opportunity of studies on the Kerguelen plateau to investigate the functioning of the biological carbon pump in a naturally iron-fertilized region. The KEOPS2 project in October–November 2011, designed to improve the spatial and temporal coverage of the Kerguelen region, was carried out in austral spring to document the early stages of the bloom and to complement results of KEOPS1.

As part of KEOPS2 a CARIOCA buoy has been launched, drifted eastward close to the polar front then entered the polar frontal zone, PFZ. NCP is deduced from high frequency $p\text{CO}_2$ measurements made in November–December along the trajectory of the drifter. The aim of the present work is to provide a zoom on the extent of the iron seeding downstream the plateau during the end of the spring, its effect on the production of organic carbon and its control of the CO_2 air–sea flux.

2 Data and methods

2.1 Site description

A Carioca buoy was deployed as part of the KEOPS2 expedition that took place from 9 October to 29 November 2011, in the Indian sector of the Southern Ocean in the vicinity of the Kerguelen archipelago. It was deployed on 1 November 2011 over the Kerguelen plateau and drifted eastward downstream within the Kerguelen plume. Until

12 February 2012, its ~ 1800 km long trajectory followed the polar front closely, entering the polar frontal zone on the 16 December 2011 (Fig. 1). The buoy acquired data in the 72–75° E longitude range of the intensive KEOPS 2 field campaign from 1 to 15 November 2011 and then was advected downstream within the Kerguelen plume later in the season.

2.2 Buoy measurements

The Carioca buoy was equipped with a CO₂ sensor (Copin-Montegut et al., 2004; Hood and Merlivat, 2001) and an Anderaa F3835 optode to measure dissolved O₂ (Lefevre and Merlivat, 2012). The partial pressure of CO₂, $p\text{CO}_2$, dissolved oxygen concentration, O₂, sea surface temperature, SST, and sea surface salinity, SSS, were measured at a depth of 2 m on an hourly basis. Atmospheric pressure and wind speed are measured at a height of 2 m, which were subsequently corrected to 10 m height values. Collected data have been transmitted by the buoy in real time via the Advanced Research and Global Observation Satellite (Argos) data network.

Strictly, the CO₂ sensor measures the fugacity of CO₂, $f\text{CO}_2$, which is not identical to $p\text{CO}_2$ owing to the non-ideal nature of the CO₂ gas (Dickson et al., 2007). In the range of SST of our study, the difference between $p\text{CO}_2$ and $f\text{CO}_2$ is close to 1.4 μatm , which is within the instruments 3 μatm absolute error. Accordingly, we will approximate $f\text{CO}_2$ as being equal to $p\text{CO}_2$ within this study.

Alkalinity, Alk ($\mu\text{mol kg}^{-1}$), is computed from SST and sea surface salinity, SSS, using the alkalinity–temperature–salinity relationship proposed by Lee et al. (2006) for the Southern Ocean. Dissolved inorganic carbon, DIC ($\mu\text{mol kg}^{-1}$), is derived from $p\text{CO}_2$, Alk, SST and SSS using the CO₂ dissociation constants of Mehrbach et al. (1973) as refitted by Dickson and Millero (1987) and solubility from Weiss (1974). The relative precision of successive DIC values is expected to be 0.5 $\mu\text{mol kg}^{-1}$ (Boutin et al., 2008; Boutin and Merlivat, 2009; Merlivat et al., 2014).

The oxygen optode measurements were calibrated initially in the laboratory prior to deployment using a zero and 100 % oxygen reference points. They were subse-

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quently calibrated in-situ against Winkler titrations made over the course of the KEOPS 2 cruise. Oxygen saturation, $O_{2\text{sat}}$ (in $\mu\text{mol kg}^{-1}$) is calculated using the equation of Garcia and Gordon (1992). The degree of O_2 saturation (in percent), is given by:

$$\%O_{2\text{sat}} = ([O_2]/[O_2^{\text{sat}}]) \times 100.$$

2.3 Calculation of air–sea fluxes of CO_2 and O_2

The hourly air–sea CO_2 flux (F_{CO_2} , $\text{mmol m}^{-2} \text{d}^{-1}$) is derived from wind speed, the air–sea gradient in $p\text{CO}_2$ and the gas transfer velocity (Boutin et al., 2008; Merlivat et al., 2014), following:

$$F_{\text{CO}_2} = k_{\text{CO}_2} \alpha_{\text{CO}_2} (p\text{CO}_{2\text{sea}} - p\text{CO}_{2\text{atm}}) \quad (1)$$

where α_{CO_2} is the solubility of CO_2 (Weiss, 1974), $p\text{CO}_{2\text{sea}}$ the partial pressure of CO_2 in seawater (μatm), $p\text{CO}_{2\text{atm}}$ the partial pressure of CO_2 in the atmosphere (μatm), and k_{CO_2} (cm h^{-1}) is the gas transfer velocity for CO_2 . $p\text{CO}_{2\text{atm}}$ is computed from the monthly molar fraction $x\text{CO}_2$ at the Macquarie Island atmospheric station (NOAA/ESRL Global Monitoring Division, <http://esrl.noaa.gov/gmd/ccgg/iadv>), the water vapor pressure of Weiss and Price (1980) and the atmospheric pressure recorded on the drifter.

Injection of air bubbles below the air–water interface is neglected for the calculation of the CO_2 flux but this contribution to the flux can be relatively important for oxygen. The equation of the O_2 flux is then given by:

$$F_{\text{O}_2} = k_{\text{O}_2} ([O_2] - [O_{2\text{sat}}]) - F_{\text{bub}} \quad (2)$$

where k_{O_2} is the gas transfer velocity for O_2 and F_{bub} is the contribution of air bubbles using the formula given by Woolf and Thorpe (1991):

$$F_{\text{bub}} = k_{\text{O}_2} 0.01 (U/U_0)^2 [O_{2\text{sat}}] \quad (3)$$

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with U the wind speed at 10 m height in m s^{-1} and U_0 an empirically constant calibrated specifically for O_2 of 9 m s^{-1} . The total oxygen flux becomes:

$$F_{\text{O}_2} = k_{\text{O}_2}([\text{O}_2] - [\text{O}_{2\text{sat}}](1 + 1.2310^{-4}U^2)) \quad (4)$$

It results from this equation that the flux is positive when there is outgassing to the atmosphere.

For both CO_2 and O_2 , the gas transfer velocity is calculated using the formula of Sweeney et al. (2007):

$$k = 0.27U^2(660/Sc)^{0.5} \quad (5)$$

where Sc is the Schmidt number, Sc_{CO_2} , for CO_2 or Sc_{O_2} for O_2 (Wanninkhof, 1992) and U the 10 m wind speed.

2.4 Calculation of in-situ carbon and oxygen biological production

Net community production, NCP_C , has been previously derived from drifting CARICOCA buoys measurements, by looking at day-to-day evolution of DIC at dawn provided that daily cycles of DIC in phase with the ones expected from biological activity are observed (Merlivat et al., 2009; Boutin and Merlivat, 2009; Merlivat et al., 2014). In addition, in case O_2 is measured, it is possible to simultaneously estimate NCP from O_2 day-to-day evolution, NCP_{O_2} . (Lefèvre and Merlivat, 2012). The method relies on hourly measurements of SST, SSS, $p\text{CO}_2$ and O_2 to estimate in-situ biological production from unattended platforms using a non-intrusive method. During the daylight period, photosynthesis, respiration, and air-sea exchange are mechanisms responsible for the change in DIC and O_2 recorded at 2 m depth. If no significant change in salinity is observed, the processes of advection and mixing, and thus DIC and O_2 fluxes through the base of the mixed layer, h , are assumed to be negligible. Depending on atmospheric forcing, a warm diurnal layer, h^* , can form during daylight (Merlivat et al., 2009). In this surface layer, of depth h^* , from sunrise to sunset, due to combined

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kg m^{-3}) is the density of seawater and $\Delta\text{DIC}_{\text{max}}/\Delta t$ and $\Delta\text{O}_{2\text{min}}/\Delta t$, in $\mu\text{mol kg}^{-1} \text{d}^{-1}$ are the change of DIC (and O_2) between two consecutive maxima (and minima).

2.5 Chlorophyll and age distribution of the water parcels over and downstream of the Kerguelen plateau

5 The time and spatial changes of the phytoplankton bloom as revealed by satellite ocean color are shown in Fig. 3 (on which the buoy trajectory is indicated). The strongest bloom is observed from 11 November to 2 December, about two months after bloom initiation, followed by a clear decay early summer in December.

10 The horizontal transport of water parcels eastward of the Kerguelen plateau has been derived from altimetry (d'Ovidio et al., 2014). From this analysis, the time since a water parcel has left the plateau (so called age of the water parcel) could be estimated. The trajectory of the Carioca buoy was placed in this temporal framework using the age map of 25 November. Over the period 1 November to 31 December, the buoy has sampled a large range of water parcels with different ages as shown by the stirring pathways east of the Kerguelen plateau close to the trajectory of the drifter. NCP
15 estimates have been made over the period 18 November–13 December (Tables 1 and 2).

3 Results

3.1 Buoy measurements

20 The variations of SST and SSS observed along the trajectory of the buoy are largely explained by its position relative to the polar front, PF (Fig. 1). From 1 to 12 November, the buoy was drifting in the meander of the PF (Park et al., 2014) with SST $\sim 3^\circ\text{C}$ and SSS ~ 33.83 . From 12 November to 16 December, while the buoy followed closely and sometimes crossed the PF, SST is $\sim 4.2^\circ\text{C}$ and SSS ~ 33.75 . During this time interval,

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simultaneous short time peaks of SST (negative) and SSS (positive) were observed whilst transiting the PF (Figs. 1 and 5a). From 16 December 2011 to 11 February 2012, the buoy drifted in the polar frontal zone, where higher temperature (close to 6 °C) and higher salinity, (in the range 33.8 to 33.9) were measured.

5 A very large variability of $p\text{CO}_2$ values, from ~ 280 to $\sim 400 \mu\text{atm}$, are observed while the buoy is drifting in the meander of the PF (Fig. 5c). Shipboard measurements of $p\text{CO}_2$ made during the KEOPS 2 field campaign show a similar range of variability (Lo Monaco et al., 2014). During periods when the buoy is southward or close to the PF, the surface waters are undersaturated in CO_2 relative to atmospheric CO_2 . After
10 17 December, in the polar frontal zone, the surface waters become supersaturated. Moreover, the surface waters are supersaturated in oxygen until 16 December, with saturation values up to 110 % (Fig. 5d). In the polar frontal zone, an undersaturation is measured.

3.2 Air–sea flux of CO_2 and O_2

15 From 1 November to 17 December surface waters are a source of O_2 (Fig. 6a) for the atmosphere and a sink of CO_2 (Fig. 6b). Conversely, in the polar frontal zone, east of 83° E, we observe an ingassing of O_2 and outgassing of CO_2 . It is worth noting that the absolute values of the fluxes are larger for O_2 than for CO_2 due to the buffer factor of ocean water carbonate chemistry. From 1 November to 16 December, the flux of
20 O_2 and CO_2 are respectively 38 ± 34 and $-8.3 \pm 7.5 \text{ mmol m}^{-2} \text{ d}^{-1}$. After 16 December, they are equal respectively to -48 ± 43 and $5.3 \pm 4.7 \text{ mmol m}^{-2} \text{ d}^{-1}$.

3.3 Dissolved inorganic carbon, DIC, and oxygen

25 A significant reduction in DIC of $\sim 50 \mu\text{mol kg}^{-1}$ is observed from 1 November to 17 December, followed by an increase of approximately $2 \mu\text{mol kg}^{-1}$ when the buoy crossed the PF and starts drifting northward in the polar frontal zone. At the same time, a sharp decrease of the O_2 concentration is measured (Fig. 7). During the first part of the

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trajectory of the buoy close and along the PF, the highly variable distribution of the concentrations of DIC and O_2 are controlled by physical transport processes, lateral advection and vertical mixing, air–sea exchange, and biological processes. Four periods for DIC and O_2 of 3 to 5 days have been identified when only air–sea exchange and biological processes control the change with time of the concentrations of DIC and O_2 , as described by Eqs. (6) and (7) (cf. also Fig. 2). For 7 days during these periods, the amplitude of the difference between the extrema ($|max - min|$) for DIC and O_2 in the warm daily surface layer, h^* , have been measured (Table 1 and Fig. 8).

3.4 Quantification of biological processes

Large amplitudes of the diurnal cycles of DIC and O_2 up to 12 mmol kg^{-1} have been measured, while day-to-day changes peak at 5 mmol kg^{-1} (Fig. 8). These numbers represent the contribution of the biological processes plus the air–sea exchange terms (Eqs. 6 and 7). Their ratio is close to one (Fig. 8). Between two consecutive mornings, at the end of nocturnal convection, $(dDIC/dt)_{\text{air-sea}}$ and $(dO_2/dt)_{\text{air-sea}}$ are equal respectively to F_{CO_2}/h and F_{O_2}/h , (where h is the mixed layer depth). During the daily stratification period, the diurnal mixed layer thickness decreases from h to h^* when DIC is minimum and O_2 is maximum. We make the assumption that it varies linearly from h to h^* in order to compute the hourly values of the air–sea flux contribution, $(F/h)_i$, which then are added over the daily stratification period. We assume that the minimum depth of the diurnal mixed layer, h^* , at the end of the production period is equal to the sampling depth 2 m. A mixed layer depth equal to 20 m has been adopted based on observations made during the KEOPS 2 field campaign under conditions similar to those encountered by the buoy. We will discuss later the uncertainties related to this choice.

A summary of the biological and air–sea flux terms for DIC and O_2 is given in Table 2. Figure 9 shows the simultaneous biological changes of O_2 and DIC observed in the ten selected situations. The DIC measurements are used to calculate carbon NCP

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(Eq. 9 and Table 2). In November, 2 values of NCP respectively equal to 140 ± 7 and $124 \pm 23 \text{ mmol C m}^{-2} \text{ d}^{-1}$ are computed. In December, we have NCP equal to 60 ± 12 and $72 \pm 17 \text{ mmol C m}^{-2} \text{ d}^{-1}$. The SD does not include the uncertainty on the choice of the value of the MLD.

4 Discussion

4.1 Hydrodynamical environment along the trajectory of the buoy

During the 2011 KEOPS2 cruise, Park et al. (2014) determine and validate an up-to-date location of the PF around the Kerguelen Islands over the longitude range, $68\text{--}78^\circ \text{ E}$. The PF, defined as the northern limit of the subsurface minimum of temperature, T_{\min} of 2° C , was validated based on in-situ hydrographic and current measurements made during the cruise, satellite ocean color images, and altimetry-derived surface velocity fields. The PF location rounds the Kerguelen Islands from the south, executing a permanent cyclonic meandering in the off-plateau area immediately east of the Kerguelen Islands until the longitude of 73.5° E , then extends eastward (Fig. 5, Park et al., 2014).

The buoy, after drifting inside the meander, traverses the front many times during which rapid increases of salinity are observed (Figs. 1 and 5). Eastward of 78° E , the comparison of the two routes cannot be so specific as the trajectory of the buoy is compared with a large scale climatological PF (Park et al., 2009, 2011) which certainly does not take into account the highly time-varying frontal circulation of the area. On 16 December, the latitude of the polar front as derived from the buoy measurements (Figs. 1 and 5) is very close to the climatological PF.

4.2 Lagrangian distribution of chlorophyll along the trajectory of the buoy

The sequence of ocean color images on which is superposed the trajectory of the buoy from 11 November to 28 December (Fig. 3) show the rapid development of the bloom

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until 2 December and then its decline. In most cases, the buoy follows the highly time-varying mesoscale meanders observed within satellite chlorophyll images. In their detailed study of the location of the PF during the KEOPS 2 cruise, Park et al. (2014) put forward that the high-resolution chlorophyll concentration images appear as an excellent marker of the fronts and filaments, supporting evidence for the frontal circulation determined from the combined hydrography, altimetry, and drifters tracking data. We then are led to conclude that the biological processes identified during 4 periods along the trajectory of the buoy (Fig. 1 and Table 1) are representative of frontal conditions which favor biological production. Specifically, the data computed between 18 to 28 November, in the longitude domain 76–78° E, seem very tightly linked to the complex structures of the PF (Fig. 1).

4.3 Carbon and oxygen biological production regimes

During the KEOPS 2 expedition, MLD were estimated at 3 stations (TEW-7, TEW-8, F-L) very close to the PF (Park et al., 2014), (Fig. 1). The average MLD at these stations, calculated with the criteria: depth where the potential density = potential density at 10 m + 0.02 kg m⁻³, was equal to 20 m (Park et al., 2014). We elect to use this depth as our MLD definition, as physical (T, S) characteristics at these stations are very similar to CARIOCA measurements (Fig. 5b). Furthermore, the choice of a relatively shallow mixed layer, 20 m, is supported by the work of Taylor and Ferrari (2012) who found, based on numerical simulations, that restratification at fronts can inhibit vertical mixing, triggering high latitude phytoplankton blooms. However, the values of NCP integrated over the depth of the mixed layer may be an underestimate if the depth of the euphotic layer, Z_e , is greater than MLD. During the KEOPS 2 expedition at the station F-L, Cavagna et al. (2014), indicate $Z_e = 30$ m. From the vertical profile of net primary production, NPP, based on the analysis of carbon 13 incubation experiments, the computed value of NPP integrated over 20 m represents about 75 % of NPP integrated over Z_e . NPP at depth greater than Z_e is negligible close to 2%. We take into account an underestimation of 33 % to compute NCP.

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The values of the carbon net community production, which corresponds to DIC transformed into particulate organic carbon, POC and dissolved organic carbon, DOC by biological activity, vary from $13 \text{ mmol m}^{-2} \text{ d}^{-1}$ between 23 and 28 November and then decreases to about $65 \text{ mmol m}^{-2} \text{ d}^{-1}$ at the beginning of December (Table 2). A similar range of values of carbon net community production along fronts in the Southern Ocean have previously been observed (Merlivat et al., 2014).

The biological terms, $\left(\frac{\Delta \text{O}_2}{\Delta t}\right)_{\text{bio}}$ and $-\left(\frac{\Delta \text{DIC}}{\Delta t}\right)_{\text{bio}}$ are represented in Fig. 9 on which the 2 lines with slopes equal to 1.4 and 1.1 indicate the expected oxygen–carbon relationship respectively for a new production regime (photosynthetic quotient, $\text{PQ} = 1.4$) or a regenerated one ($\text{PQ} = 1.1$) (Laws, 1991) Within the uncertainty of the experimental data, it appears that both regimes may have prevailed at different times. This supports the choice of values of h and h^* . With larger values of the MLD, the relative part of the air–sea flux in the DIC and O_2 measurements would have been smaller and make the slope of the oxygen–carbon relationship closer to 1 as in Fig. 8.

Finally, the linear distribution of the data points (Fig. 9) demonstrates that our technique satisfactorily identifies the biological signature during the selected periods that we have considered.

In Table 2 (columns 3 and 5), we note the larger contribution of the air–sea exchange for oxygen (positive) relatively to carbon (negative), with a mean ratio of the absolute values close to 6. In the calculation of NCP, the contribution of CO_2 air–sea exchange is low, and varies between 7 and 25 % of the measured change of DIC. By contrast, for oxygen, air–sea exchange represents 50 to 135 % of the outgassing of O_2 and hence has the ability to have first order control over calculations of NCP. This situation occurs during observations made during the 11–13 December period, when it is not been possible to isolate the oxygen biological signal due to the large air–sea flux.

This is an issue regarding the in-situ estimates of NCP based on dissolved oxygen measurements at the ocean surface (Cassar et al., 2009) in high wind regions when the air–sea flux is large. Notwithstanding that a measurement of the oxygen argon ratio constrain the physical mechanisms of air–sea exchange, NCP based on O_2 mea-

surements have to be considered with caution as long as the biological contribution is a small term relative to the air–sea exchange one.

Simultaneous measurements of oxygen and carbon ratios on oceanographic moorings have been reported in a few situations in tropical or mid-latitudes. Lefèvre and Merlivat (2012), based on data in the tropical Atlantic Ocean on a Pirata mooring equipped with a Carioca $p\text{CO}_2$ sensor and an oxygen optode found an O_2/DIC ratio ranging between -1.0 and -1.3 .

Johnson (2010), using simultaneous measurements of O_2 and DIC, at two moorings M1 and M2 off Monterey Bay, in California, found -0.77 ± 0.02 and $\pm 0.93 \pm 0.03$ respectively for the $\text{O}_2 : \text{TCO}_2$ ratio. He explains these low values by the different impact of gas exchange on DIC and O_2 , the gas exchange for O_2 being 10 times faster than for CO_2 .

Martz et al. (2014) use autonomous oxygen and dissolved inorganic carbon observations to examine the oxygen carbon relationship at an upwelling site in the Southern California Current System. They compute a mean value of O_2/DIC equal to -1.20 ± 0.01 and conclude that it is in good agreement with Redfield ratio, in spite a number different of the theoretical value of the Redfield ratio, 1.30.

4.4 Carbon NCP and dissolved iron

In Fig. 4, the trajectory of the buoy is superposed on a mapping of the age of the water parcels since they have left the plateau where they are loaded with iron (d’Ovidio et, 2014). The rate of change of the horizontal dissolved iron supply, DFe, downstream the plateau is modeled with an exponential decay of the initial on-plateau iron stock in the water column.

The data in Fig. 4 can be interpreted as representative of the changes of the stock of DFe in the ocean upper layer (0–150 m), the largest DFe concentrations in the youngest waters. It is interesting to emphasize, at least qualitatively, the relationship between the distribution of DFe and the signature of the biology on the DIC and O_2 concentrations measured along the trajectory of the buoy. As a first example, when the buoy

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escapes the rich DFe waters on 15–16 November (the cyan square in Fig. 4) large abrupt changes of DIC (an increase) and O₂ (a decrease) are observed (Fig. 7), suggesting the lack of organic matter production in the absence of iron.

A decrease of NCP from ~ 130 to ~ 65 mmol m⁻² d⁻¹ is computed between the 23–28 November and 30 November–13 December periods. During this time interval, the buoy meets water with ages respectively of 35 and 50 days (the cyan dots in Fig. 4). Following the exponential decay of the stock of DFe as a function of the age of the water parcel, a decreasing of DFe concentrations roughly by a factor 2 is calculated (d’Ovidio et al., 2014), indicating that the concentration of DFe control the organic carbon production regime. During the KEOPS 2 expedition, at station F-L, the age of the water is 20 days (d’Ovidio et al., 2014) and NPP is equal to 315 mmol m⁻² d⁻¹ (Cavagna et al., 2014). Assuming that the value of NPP depends only on the stock of DFe, NPP in aged waters, respectively 35 and 50 days old, would be respectively equal to 205 and 91 mmol m⁻² d⁻¹ leading to NCP/NPP ratios respectively equal to 0.63 and 0.71. These values sound reasonable and indirectly support the choice of MLD equal to 20 m.

4.5 Air–sea flux

A striking feature is the abrupt change of the direction of the air–sea CO₂ and O₂ fluxes, from a sink of atmospheric CO₂ at the ocean surface (the opposite for O₂) to a source, on an episodic event on 16 November and on 16 December when the buoy escapes the iron fertilized plume to enter the polar frontal zone (Fig. 5). It illustrates how the carbon biological pump is at first order controlled by the iron availability in the water in the plume, as clearly the control by light and other nutrients to sustain the biological production of organic matter must be very similar on either side of the polar front. These observations highlight the necessity to take into consideration the limits of the different water masses in order to spatially extrapolate field measurements of CO₂ air–sea flux in highly dynamic ocean area like the Southern Ocean. This is reinforced

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in an iron fertilized region, as the distribution of the iron concentration is closely linked to this dynamic environment.

5 Summary and conclusion

Hourly $p\text{CO}_2$ and oxygen measurements have been made along the trajectory of a CARIOCA drifter downstream from the Kerguelen plateau during the austral bloom from 1 November 2011 until 12 February 2012. From 1 November to 12 November, the buoy drifted through a cyclonic meander of the polar front, followed it eastward until 16 December, before heading north and entered the polar frontal zone. The surface water is supersaturated in oxygen until 16 December while $p\text{CO}_2$ ocean is smaller than $p\text{CO}_2$ atmosphere, suggesting that biological production dominates. North of the polar frontal zone, the ocean is a source of CO_2 for the atmosphere and a sink of oxygen.

Using an alkalinity–salinity relationship, dissolved inorganic carbon, DIC, is calculated from $p\text{CO}_2$ and alkalinity. Net community production is calculated from changes of DIC and/or oxygen over short periods of time when biological activity is present and no mixing is encountered. NCP values obtained from 23 November to 13 December decrease from 140 ± 7 to $60 \pm 12 \text{ mmol C m}^{-2} \text{ d}^{-1}$. Concomitant O_2 increases and DIC decreases allow the calculation of the oxygen carbon stoichiometric ratio O_2/C in organic matter (dissolved and particulate) after subtracting the contribution of CO_2 and O_2 air–sea gas exchange. O_2/C values range between 1.1 and 1.4 as expected for new and regenerated biological production regimes.

In the vicinity of the polar front, within the downstream plateau Kerguelen plume, the absorbed CO_2 air–sea flux is equal to $-8 \text{ mmol m}^{-2} \text{ d}^{-1}$ and the O_2 outgassing equal to $+38 \text{ mmol m}^{-2} \text{ d}^{-1}$. In the polar frontal zone from 16 December 2011 to 12 February 2012, the ocean surface is a source of CO_2 for the atmosphere equal to $+5 \text{ mmol m}^{-2} \text{ d}^{-1}$ and a sink for O_2 equal to $-48 \text{ mmol m}^{-2} \text{ d}^{-1}$. The very abrupt change simultaneously of the sign of the air–sea fluxes of CO_2 and O_2 emphasizes the dominant contribution of biology within the iron fertilized Kerguelen plume. Within the plume,

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a comparison between the biological DIC uptakes localized on a mapping of the modeled stock of dissolved iron, DFe, in the water column shows a coupling between the amount of DFe and the carbon net community production. This highlights that the phytoplankton growth rates appear to increase directly with the level of iron availability.

5 However a patchy distribution of iron within the plume can lead to a patchy organic carbon production and consequently affect unevenly in time and space the uptake of atmospheric CO₂. It is noteworthy to observe the abrupt changes of the air–sea flux of CO₂ and O₂ when the buoy crosses the polar front on 16 December which is likely a frontier for dissolved iron. This study points that care should be taken when extrapolating sparse air–sea flux measurements observations without an understanding of the hydrodynamic features of the upper ocean.

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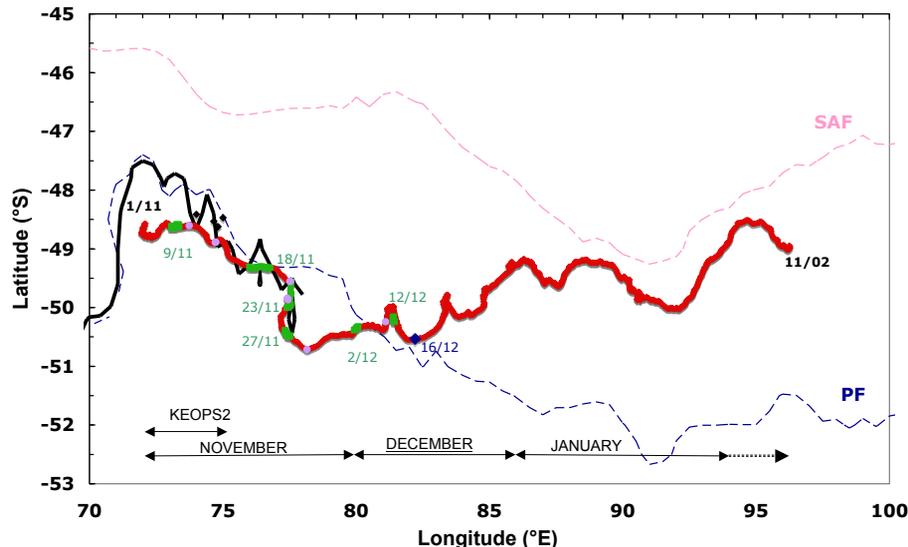


Figure 1. Trajectory followed by the Carioca drifter from 1 November 2011 to 12 February 2012 (red line). The green dots and letters indicate the location and time where the data indicate a large signature of biological effects. The grey dots indicate high isolated salinity anomalies. The buoy enters the polar frontal zone at the location of the blue dot. The pink dotted line represents the location of the subantarctic front, SAF, the blue dashed line shows the location of the polar front (Park et al., 2009, 2011) and the black line, the location of the polar front based on KEOPS 2 observations, PF_Park, (Park et al., 2014). The black dots indicate the location of the KEOPS 2 stations, TEW-7, TEW-8, NPF-L, close to the PF.

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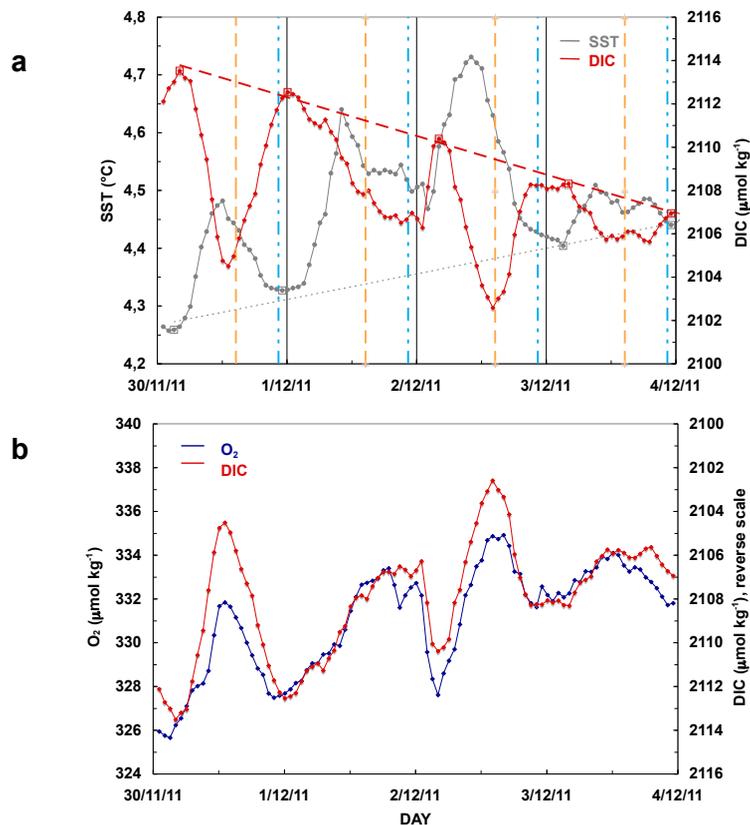


Figure 2. Diurnal cycles of SST, DIC and O₂ from 30 November to 4 December 2011. **(a)** SST (°C) (grey, left vertical axis) and DIC (μmol kg⁻¹) (red, right vertical axis). The vertical dashed lines indicate the time of sunrise (blue) and sunset (orange). **(b)** O₂ (μmol kg⁻¹) (blue, left vertical axis) and DIC (red, right inverse vertical axis).

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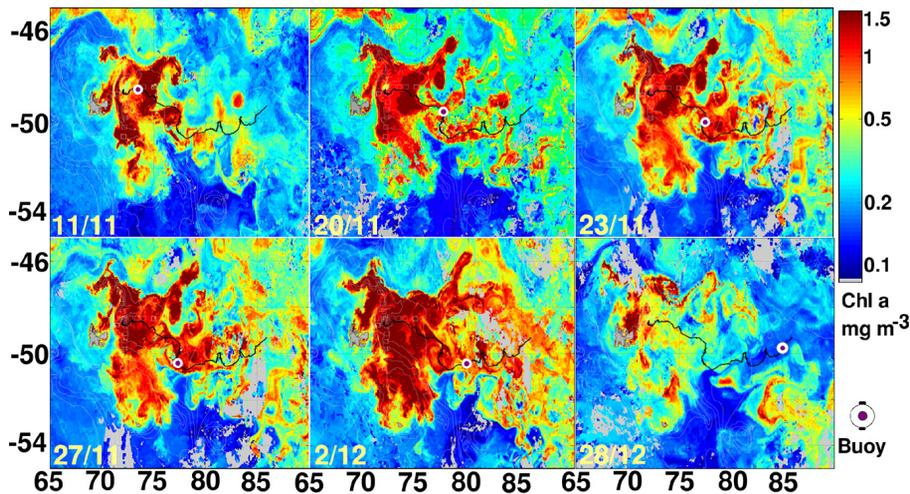


Figure 3. Spatial extent of phytoplankton blooms over and downstream from the Kerguelen plateau as revealed by satellite ocean color on 6 selected days, from 11 November to 28 December 2011. The trajectory followed by the CARIOCA drifter is superposed on the chlorophyll patches (black line). The circles indicate the location of the buoy the same days.

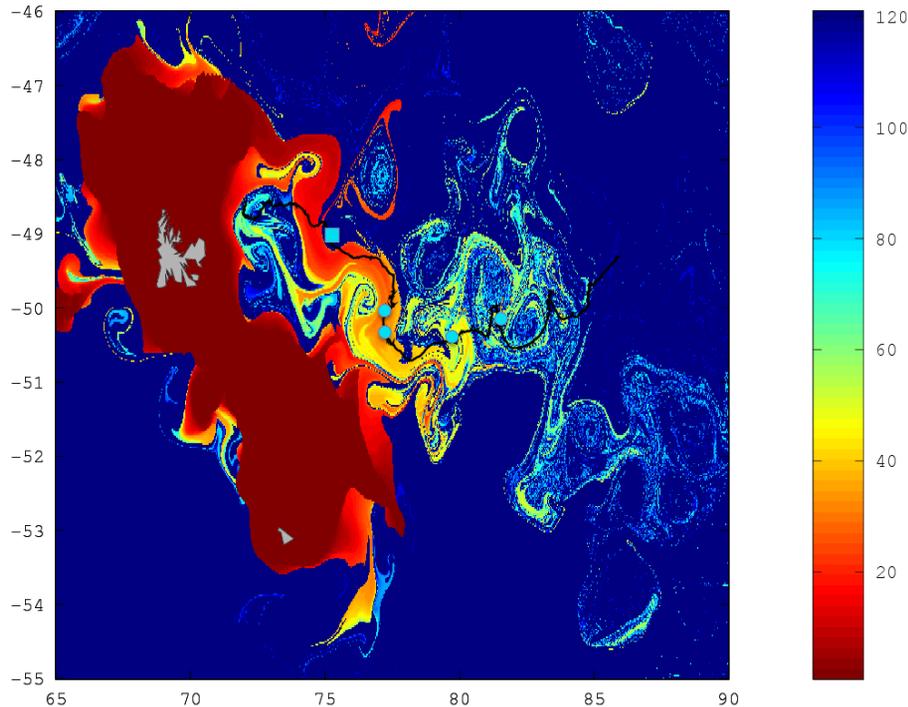


Figure 4. Lagrangian perspectives on large scale natural iron fertilization on the Kerguelen plateau and in the downstream plume: a snapshot on 25 November 2011. The color code indicates the time in days since leaving the plateau for each water parcel. The black line indicates the trajectory of the Carioca drifter from 1 November to 31 December 2011. The cyan dots indicate the locations where carbon NCP estimates are calculated. The cyan square is the position of the buoy on 16 November (see text).

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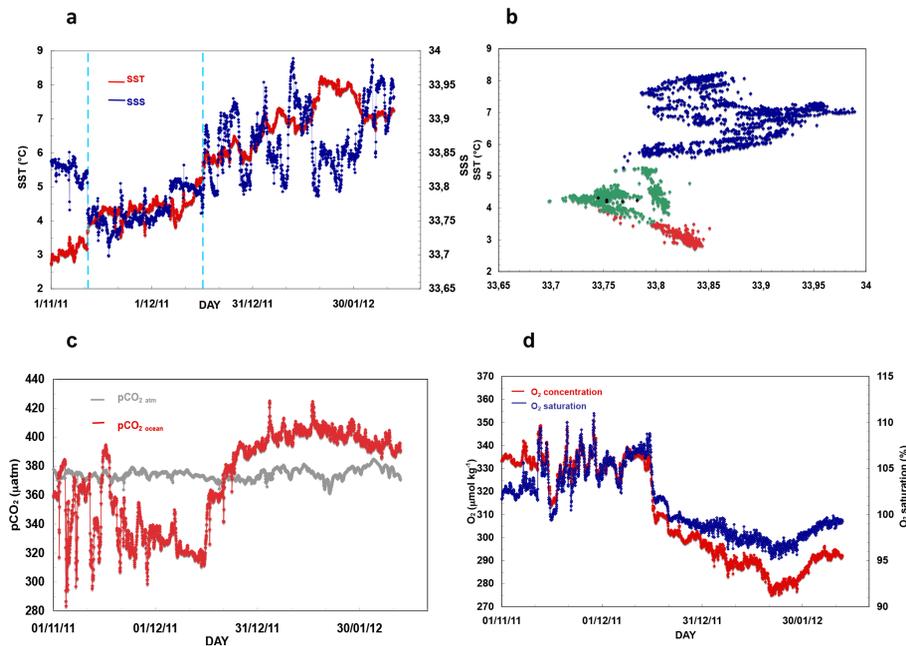


Figure 5. Buoy data from 1 November 2011 to 12 February 2012. **(a)** Temperature in °C (red, left vertical axis) and salinity (blue, right vertical axis). **(b)** T – S diagram: 1 to 11 November, red – 12 November to 16 December, green – 17 December to 12 February, blue. **(c)** $p\text{CO}_2$ measured at a depth of 2 m in μatm (red) and in the atmosphere in μatm (grey). **(d)** Dissolved oxygen concentration measured at a depth of 2 m in $\mu\text{mol kg}^{-1}$ (red, left vertical axis) and oxygen saturation in % (blue, right vertical axis). In Fig. 5a, the cyan dashed lines indicate the 12 November and 16 December days (see text). In Fig. 5b, the black dots indicate the data measured at the KEOPS 2 stations, TEW7, TEW8, F-L.

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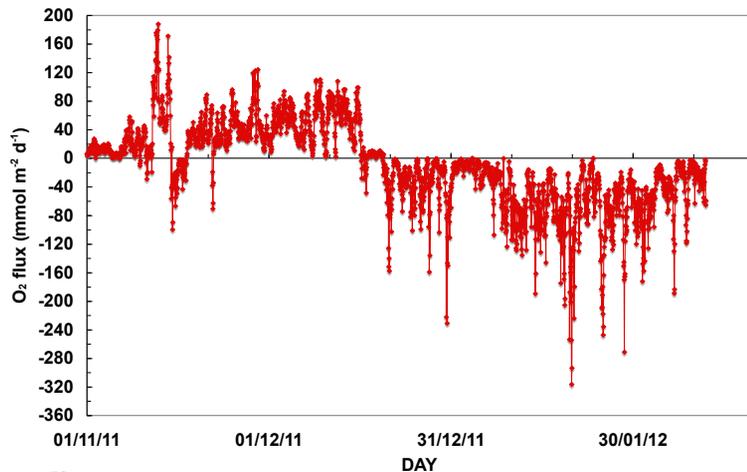
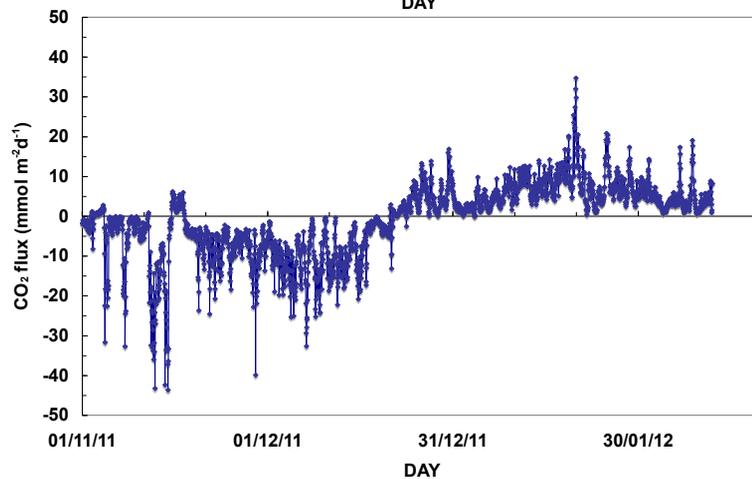
a**b**

Figure 6. Air–sea flux from 1 November 2011 to 12 February 2012 in mmol m⁻² d⁻¹ (positive for outgassing). **(a)** O_2 (red). **(b)** CO_2 (blue).

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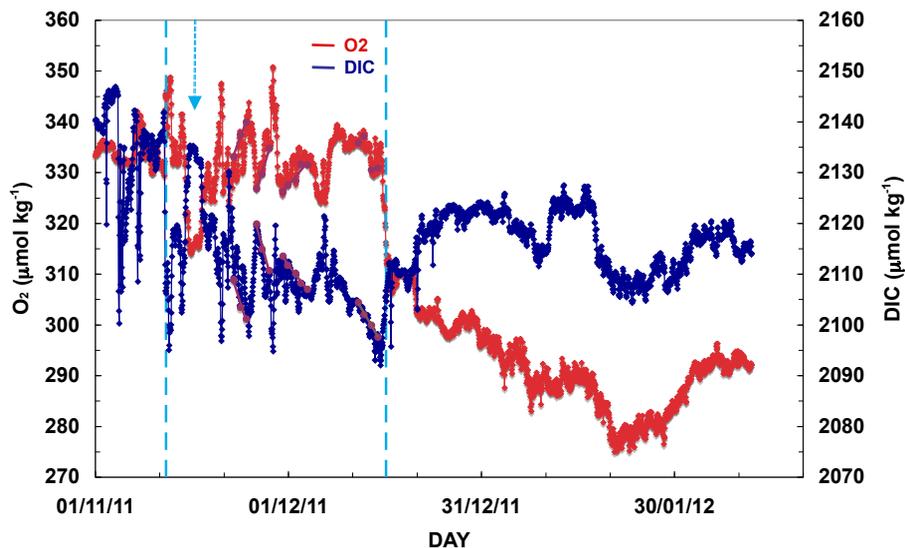


Figure 7. Distribution of O_2 in $\mu\text{mol kg}^{-1}$ (red, left vertical axis) and DIC in $\mu\text{mol kg}^{-1}$ (blue, right vertical axis) between 1 November 2011 and 12 February 2012. The purple dots and lines indicate the periods when NCP estimates have been made. The cyan dashed lines indicates the 12 November and 16 December days and the cyan arrow the 16 November (see text).

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