Interactive comment on "Carbon, oxygen and biological productivity in the Southern Ocean in and out the Kerguelen plume: CARIOCA drifter results" by L. Merlivat et al.

Anonymous Referee #1

Received and published: 24 February 2015

General comments:

The manuscript by Merlivat et al. describes the dynamic of the CO2 system and dissolved O2 during the KEOPS 2 experiment on the Kerguelen plateau, based on high frequency measurements from a lagrangrian buoy. Based on in-situ data, the authors compute the daily DIC consumption and NCP during short periods in the most stable water masses. They then discuss the link between this biological production and the dFe concentrations distribution and hydrodynamic properties in the study region. Their main conclusions are that the approach used to estimate NCP provides conclusive results and that one should be cautious when extrapolating air-sea CO2 fluxes in such dynamics ecosystems as the Kerguelen plateau.

My general opinion is that this study provides interesting insights on the link between biological production/respiration, dFe concentrations and air-sea CO2 and O2 fluxes in fertilised waters. The approach used in the manuscript to compute NCP is not new and has been used by the authors before. In my view, the clarity of the manuscript could be improved (see my specific comments below) and some results highlighted before publication. Each page and line numbers correspond to the printer-friendly version of the manuscript under discussion.

We thank the reviewer #1 for his/her positive feedback and constructive comments. Here below we answer point by point the different comments or remarks he/she raised. Part of them are due to some changes between the submitted manuscript and the one put online in BGD.

Specific comments:

Page16878, line17-19: Please rephrase sentence, where was the sink and where was the source of CO2?
This has been corrected.

Page16879, line25-26: Here and elsewhere in the manuscript, decide if you define a new acronym, for example NCP in brackets (NCP) or between commas, NCP, and do not define twice the same parameter, (for example DIC is redefine in the conclusion!) please homogenise all the manuscript.
This has been corrected

P16881, l25-26: Please provide an estimated accuracy for the computed DIC as this is particularly relevant in the NCP computations.
The accuracy of computed DIC is 10.5 µmol kg^{-1} (Boutin et al., 2008). We indicate it now in the text. However, for the estimation of NCP, it is the relative precision for successive DIC data, expected to be 0.5 µmol kg^{-1}, which is important as its estimation depends on the slope of DIC changes with time.

P16881, l28-29: Indicate accuracies of the O2 measurements (Winkler and Optode).
This has been done. We have written: "During the KEOPS 2 cruise, the optode data were subsequently calibrated against the oxygen Winkler measurements made with an accuracy of 0.2% (D.Lefèvre, personal communication) A constant offset of 13.6 µmol kg^{-1} between the two techniques was found . Johnson [2010] compared the optode measurements recorded at a time series off Monterey Bay, California, with shipboard measurements made using the Winkler method. He found an offset between the two techniques, which remained constant over the 5 months period of his record Therefore, we simply apply an offset of 13.6 µmol kg^{-1}to correct our optode data."

P16884, l3-l5: I think there is a confusion here in the definition of DICmax and O2min, it should read "At night, as a result of respiration and of the mixing between the warm layer and the mixed layer, DIC increases and O2 decreases; they reach maximum (DICmax) and minimum (O2min): : :"
This is right. We have made the change.

P16885, l3: For clarity the paragraph of section 3.4 starting with "Between two consecutive mornings (l13, p16887) and finishing by "we will discuss later the uncertainties related to this choice (l24, p16887) should be moved here in section 2.4.
This has been changed accordingly.

P16886, l12: Replace last sentence by: "In the polar frontal zone, data showed O2 undersaturation".
This has been done

P16886, l23-l25: I do not see this increase of 2 umol/kg.
The exact number is 20 umol/kg. This number was in the original submitted word manuscript. It has been corrected.

P16887, l10: units should be in umol/kg, not 5 and 12 mmol/kg.
This has been corrected.

Section 3.4: As mentioned in the comment above, the description of h/h* should be moved to section 2.4. Here in section 3.4, I would recommend to comment in slightly more details Table 1 and keep the results of NCP from table 2 as described in the current version.
This has been done.

P16889, l24-28: The comparison of NPP versus NCP and how it leads to the underestimation of NCP is confusing, especially the conclusion: "We take into account an underestimation of 33% to compute NCP". Please clarify how this underestimation is taken into account in your final results in tables 1 and 2.
The assumption is that if we consider an MLD equal to 20 meters, we underestimate NPP as ze is equal to 30 meters (Cavagna et al, 2014). We miss part of NPP as shown by the profile of NPP measured by Cavagna et al, 2014. We compute:

$$\mathbf{NCP=1.33\ \rho\ h\ dO_{2bio}}$$

The values of NCP_C and NCP_{O2} in table 2 have been computed in this way.

P16890, l3: Should read 130 mmol m-2 d-1, not 13 mmol m-2 d-1, please correct.
The exact number is 130 mmol m-2 d-1. This number was in the original submitted

word manuscript.

P16890, l15: Replace "Finally" by "further" and do not start on a new line as this is still part of your argument supporting your choice of h, h* and MLD.
This has been corrected.

P16890, l27: Last sentence starting with "Notwithstanding: : :", is unclear and I think should be rephrased as "NCP based on O2 measurements have to be considered with caution when the biological contribution is small: : :"
This has been changed and is much better.

End of section 4.3: After the review of papers on O2/DIC ratios, it would be interesting to discuss the highlight of this study compared to those previous papers.
A sentence has been added to better highlight our results.

First line of section 4.4: This is the first time you discuss Fig. 4, either relocate it or use it earlier in the manuscript to describe the buoy trajectory.
This was an error. It has been relocated in paragraph 2.5 for the first mention.

Last sentence of section 4.4: I think the last conclusion of the last sentence needs to be discussed in more details.
We have changed the sentence and write" 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 160 and 82 mmol m^{-2} d^{-1} assuming a removal constant equal to 0.045 d^{-1}. NCP/NPP ratios are then respectively equal to 0.82 and 0.73.These numbers are close to the f ratio, 0.9, measured by (Cavagna et al.,2014, figure 4) at station F-L on the polar front. The choice of MLD equal to 22 and 25 meters in our estimate of NCP instead of 20 meters would have met this limit but larger values of MLD are not acceptable." We hope that the message is now clearer. The numbers are slightly changed as some calculations have been redone more precisely, but it does not affect the main message which is an upper bound to the value of the MLD.

P16892, l23-24: ": : :as clearly the control by light and nutrients to sustain the biological production of organic matter must be very similar on both sides of the polar front",
Could you provide a reference for this argument?
The sentence has been deleted. The idea was initially to point out, at least for the light, the PAR, that a sudden change could not been expected.

P16893, l25-27: Rephrase sentence, not clear.
The sentence has been rephrased.

P16894, l8-9: Rephrase sentence, not clear.
The sentence has been rephrased.

Figures:
The figures have been modified following the recommendations of the reviewer. The figure caption has been corrected.

Figure: 1: The grey dotes are not visible, please modify, also use an arrow instead of a blue dot to show when the buoy is crossing the front as this is particularly relevant in the discussion.

Figure 2: Why do you use a reverse scale for DIC? In my view, it is better to have the O2 vs DIC signal in opposite directions for scientific purpose.

Figure 3: Increase size of the black line, not clear.

Figure 4: The trajectory of the CARIOCA should be in white, not visible in black.

Figure 5 to 7: The quality of these figures is rather poor. Some axes are difficult to read, colours not visible, etc: : : My advice would be to use thinner lines with no data points and shades of Grey/Black for the plots, and only colour for specific dotes or events you want to illustrate such as on figure 7.

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

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Abstract

Keywords: Biological productivity regime: in situ measurements- Carbon-Oxygen stoichiometry- Natural iron fertilization from the Kerguelen plateau- Iron control on carbon biological production- Phytoplankton blooms extending downstream.

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 (Oct.-Nov. 2011), one Carioca buoy was deployed east of the Kerguelen plateau. It drifted eastward downstream in the Kerguelen plume. Hourly surface measurements of pCO_2, O_2 and ancillary observations were collected between 1st 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°E-83°E, close to the polar front and then in the polar frontal zone, PFZ, until 97° E. From 17

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November to 16 December, the buoy drifted within the Kerguelen plume following a filament carrying dissolved iron, DFe, for a total distance of 700km.

In the first part of the trajectory of the buoy , close to the polar front west of 82°E, the ocean surface waters are a sink for CO_2 and a source for O_2, with fluxes of respective mean values equal to -8 mmol CO_2 $m^{-2}d^{-1}$ and +38 mmol O_2 $m^{-2}d^{-1}$. Eastward, as the buoy escapes the iron enriched filament, the fluxes are in opposite direction, with respective mean values of +5 mmol CO_2 $m^{-2}d^{-1}$ and -48 mmol O_2 $m^{-2}d^{-1}$. 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 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 CO_2 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 CO_2 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 CO_2 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 pCO_2. 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 CO_2 pCO_2 is a necessary step to understand the processes regulating the ocean–atmosphere exchange of CO_2 and help to overcome the unresolved spatio temporal variability effects.

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The magnitude of the gradient of pCO_2 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 pCO_2. In high nutrient-low-chlorophyll HNLC regions, including the Southern Ocean, more than two decades of intense research 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

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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 pCO_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.

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2 Data and methods

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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 1st November 2011 over the Kerguelen plateau and drifted eastward downstream within the Kerguelen plume. Until 12 February 2012, its ~1800 kilometers long trajectory followed the polar front closely, entering the polar frontal zone on the 16 December 2011(figure 1). The buoy acquired data in the 72°E-75°E longitude range of the intensive KEOPS 2 field campaign from 1st 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 CO_2 sensor (Copin-Montegut et al., 2004; Hood and Merlivat,2001) and an Anderaa F3835 optode to measure dissolved O_2 (Lefevre and Merlivat, 2012).The partial pressure of CO_2, pCO_2, dissolved oxygen concentration, O_2, sea surface temperature, SST, and sea surface salinity, SSS, were measured at a depth of 2 meters on an hourly basis. Atmospheric pressure and wind speed are measured at a height of 2 meters, which were subsequently corrected to 10 meters 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 CO_2 sensor measures the fugacity of CO_2, fCO_2, which is not identical to pCO_2 owing to the non-ideal nature of the CO_2 gas (Dickson et al, 2007). In the range of SST of our study, the difference between pCO_2 and fCO_2 is close to 1.4 µatm, which is within the instruments 3µatm absolute error. Accordingly, we will approximate fCO2 as being equal to pCO_2 within this study.

Alkalinity, Alk (µmol 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 (µmol kg^{-1}), is derived from pCO_2, Alk, SST and SSS using the CO_2 dissociation constants of Mehrbach et al. (1973) as refitted by Dickson and Millero (1987) and solubility from Weiss (1974). An accuracy of 10.5 µmol kg^{-1} was estimated, as a result of the combined uncertainties linked to the dissociation constants, the accuracy of pCO2 measurements and the uncertainty of the alkalinity derived from the relationship proposed by Lee et al. 2006 (Boutin et al, 2008).The relative precision of

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successive DIC values is expected to be 0.5µmol kg^{-1} (Boutin et 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. During the KEOPS 2 cruise, the optode data were subsequently calibrated against the oxygen Winkler measurements made with an accuracy of 0.2% (D.Lefèvre, personal communication) A constant offset of 13.6 µmolkg between the two techniques was found . Johnson [2010] compared the optode measurements recorded at a time series off Monterey Bay, California, with shipboard measurements made using the Winkler method. He found an offset between the two techniques, which remained constant over the 5 months period of his record Therefore, we simply apply an offset of 13.6 µmolkg to correct the optode data. Oxygen saturation, O_{2sat} (in µmol kg^{-1}) is calculated using the equation of Garcia and Gordon (1992). The degree of O_2 saturation,(in percent), is given by:

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

2.3 Calculation of air-sea fluxes of CO_2 and O_2

The hourly air-sea CO_2 flux F_{CO2} (mmol m^{-2} d^{-1}), is derived from wind speed, the air-sea gradient in pCO_2 and the gas transfer velocity [Boutin et al., 2008; Merlivat et al, 2014], following:

$$F_{CO2} = k_{CO2}\, \alpha_{CO2}\, (pCO_{2sea} - pCO_{2atm}) \qquad (1)$$

where α_{CO2} is the solubility of CO_2 (Weiss, 1974), pCO_{2sea} the partial pressure of CO_2 in seawater (µatm), pCO_{2atm} the partial pressure of CO_2 in the atmosphere (µatm), and k_{CO2} (cm/h) is the gas transfer velocity for CO_2. pCO_{2atm} is computed from the monthly molar fraction xCO_2 at the Macquarie Island atmospheric station (NOAA/ESRL Global Monitoring

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Supprimé: They were subsequently calibrated in-situ against Winkler titrations made over the course of the KEOPS 2 cruise.

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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:

$$F_{O2} = k_{O2} ([O_2]-[O_{2sat}]) -F_{bub} \qquad (2)$$

where k_{O2} 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):

$$F_{bub} = k_{O2}\ 0.01(U/U_0)^2\ [O_{2sat}] \qquad (3)$$

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

$$F_{O2}=k_{O2} ([O_2]-[O_{2sat}]\ (1+1.23\ 10^{-4}U^2)) \qquad (4)$$

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):

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

where Sc is the Schmidt number, Sc_{CO2} , for CO_2 or Sc_{O2} for O_2 (Wanninkhof, 1992) and U the 10m wind speed .

2.4 Calculation of in-situ Carbon and Oxygen biological production

Net community production, NCP_C, has been previously derived from drifting CARIOCA 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_{O2} (Lefèvre and Merlivat, 2012). The method relies on hourly measurements of SST, SSS, pCO_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 2m 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 effect of photosynthesis and respiration, DIC generally decreases and O_2 generally increases; they reach minimum DICmin and maximum O_2max values at the end of the day. At night, as a result of respiration and of the mixing between the warm layer and the mixed layer, DIC increases and O_2 decreases; they reach maximum DIC max, and minimum, O_2 min values at the end of natural convection. NCP is derived from day-to-day change of DICmax and O_2min, after removing the contribution of the air-sea fluxes. Contribution of biological activity (photosynthesis plus respiration) during daylight is derived from DICmax-DICmin, and O_2min-O_2max after removing the contribution of the air-sea fluxes. Figure 2 shows SST, DIC and O_2 over a 4 days period, 30 November-4 December 2011. The mean increase of SST equal to 0.044°C d^{-1}, superimposed on daily cycles of SST, indicates a stratification of the mixed layer over this 4 days period. No change of salinity is measured (not shown). Thus, the changes in DIC and O_2 observed during the 4 days were only driven by biological processes allowing the computation of NCP. The carbon and oxygen mass balance, either in the daytime interval during the development of the warm layer, h*, or over one day time interval in the mixed layer, h, result in the two following equations:

$$\left(\frac{\Delta DIC}{\Delta t}\right)_{measured} = \left(\frac{\Delta DIC}{\Delta t}\right)_{bio} + \left(\frac{\Delta DIC}{\Delta t}\right)_{air-sea} \quad (6)$$

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$$\left(\frac{\Delta O_2}{\Delta t}\right)_{measured} = \left(\frac{\Delta O_2}{\Delta t}\right)_{bio} + \left(\frac{\Delta O_2}{\Delta t}\right)_{air-sea} \qquad (7)$$

NCP integrated over the mixed layer is given by:

$$NCP_C = \rho h \frac{\Delta DIC_{max}}{\Delta t} + F_{CO_2} \qquad (8)$$

$$NCP_{O_2} = \rho h \frac{\Delta O_{2\,min}}{\Delta t} + F_{O_2} \qquad (9)$$

where F_{CO2} and F_{O2} are the air-sea CO_2 and O_2 flux (mmol m^{-2} d^{-1}), positive when there is outgassing to the atmosphere. h (m) is the depth of the mixed layer, ρ (kg m^{-3}) is the density of seawater and $\Delta DIC_{max}/\Delta t$ and $\Delta O_{2min}/\Delta t$ (µmol.$kg^{-1}d^{-1}$) are the change of DIC (and O_2) between two consecutive maxima (and minima).

Between two consecutive mornings, at the end of nocturnal convection, $dDIC/dt_{air-sea}$ and $dO_2/dt_{air-sea}$ are equal respectively to F_{CO2}/h and F_{O2}/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 2m. A mixed layer depth equal to 20m 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.

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

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The time and spatial changes of the phytoplankton bloom as revealed by satellite ocean color are shown in figure 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.

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 25th November.(figure 4).Over the period 1st 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 estimates have been made over the period 18 November-13 December (Tables 1 and 2).

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3 Results

3.1 Buoy measurements

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 (figure 1). From 1st to 12 November, the buoy was drifting in the meander of the PF (Park et al, 2014) with SST~3°C and SSS ~33.83. From 12 November to 16 December, while the buoy followed closely and sometimes crossed the PF, SST is ~4.2°C and SSS ~33.75. During this time interval, simultaneous short time peaks of SST (negative) and SSS (positive) were observed whilst transiting the PF (figures 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.

A very large variability of pCO_2 values, from ~280 µatm to ~400 µatm, are observed while the buoy is drifting in the meander of the PF (figure 5c). Shipboard measurements of pCO_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 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% (figure 5d). In the polar frontal zone, data showed O_2 undersaturation

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3.2 Air-sea flux of CO_2 and O_2

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From 1st November to 17 December surface waters are a source of O_2 (figure 6a) for the atmosphere and a sink of CO_2 (figure 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 1st November to 16 December, the flux of O_2 and CO_2 are respectively 38±34 mmol $m^{-2}d^{-1}$and -8.3±7.5 mmol $m^{-2}d^{-1}$. After 16 December, they are equal respectively to -48±43 mmol $m^{-2}d^{-1}$ and 5.3±4.7 mmol $m^{-2}d^{-1}$.

3.3 Dissolved inorganic carbon, DIC, and oxygen

A significant reduction in DIC of ~ 50µmol kg^{-1} is observed from November 1st to December 17th, followed by an increase of approximately 20µmol 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 (figure 7). During the first part of the 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

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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 equations 6 and 7 (cf. also figure 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 figure 8).

3.4 Quantification of biological processes

Large amplitudes of the diurnal cycles of DIC and O_2 up to 12µmol kg^{-1} have been measured, while day-to-day changes peak at 5µmol kg^{-1} (figure 8). These numbers represent the contribution of the biological processes plus the air-sea exchange terms (equations 6 and 7). Their ratio is close to one (figure 8). In table 1, it is interesting to note the wide range of values of CO_2 and O_2 air-sea fluxes, the O_2 fluxes being up to 6.6 larger than the CO_2 ones.

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 (equation 9 and table 2). In November, 2 values of NCP respectively equal to 140±7 and 124±23 mmol C m^{-2}d^{-1} are computed. In December, we have NCP equal to 60±12 and 72±17 mmol C m^{-2}d^{-1}. The standard deviation 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°E-78°E. The PF, defined as the northern limit of the subsurface minimum of temperature, T_{min} of 2°C, was validated based on

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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 (figure 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 (figures 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 doesn't 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 (figures 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 (figure 3) show the rapid development of the bloom 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 (figure 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°E-78°E, seem very tightly linked to the complex structures of the PF (figure 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), (figure 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 (figure 5b). Furthermore, the choice of a relatively shallow mixed layer, 20 meters, 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, Ze, is greater than MLD. During the KEOPS 2 expedition at the station F-L, Cavagna et al (2014), indicate Ze=30meters. 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 meters represents about 75% of NPP integrated over Ze. NPP at depth greater than Ze is negligible close to 2%. We take into account an underestimation of 33% to compute NCP, as the euphotic layer depth is larger than the MLD which is equal to 20 meters.

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 130 $mmolm^{-2}d^{-1}$ between 23 and 28 November and then decreases to about 65 $mmolm^{-2}d^{-1}$ 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, $\left(\frac{\Delta O_2}{\Delta t}\right)_{bio}$ and $-\left(\frac{\Delta DIC}{\Delta t}\right)_{bio}$ are represented in figure 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, PQ=1.4) or a regenerated one PQ= 1.1 (Laws, 1991) Within the uncertainty of the experimental data, it appears that

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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 figure 8. Further, the linear distribution of the data points (figure 9) demonstrates that our technique satisfactorily identifies the biological signature during the selected periods that we have considered.

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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. NCP based on O_2 measurements have to be considered with caution as long as the biological contribution is a small term relative to the air-sea exchange one.

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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 pCO_2 sensor and an oxygen optode found an O_2/DICratio 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 ±0.93 ± 0.03 respectively for the O_2: 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.

We think that the distribution of the observed simultaneous biological changes of DIC and O_2 (figure 9) exhibit convincingly a spectrum of values ranging from near 100% new production to 100% regenerated production regime.

4.4 Carbon NCP and dissolved iron

In figure 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 el, 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 figure 4 can be interpreted as representative of the changes of the stock of DFe in the ocean upper layer (0-150m), 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 escapes the rich DFe waters on 15-16 November (the cyan square in figure 4) large abrupt changes of DIC (an increase) and O_2 (a decrease) are observed (figure 7), suggesting the lack of organic matter production in the absence of iron.

A decrease of NCP from ~132mmolm^{-2}d^{-1} to ~ 65mmolm^{-2}d^{-1}is computed between the 23-28 November and 30 November- 13December periods. During this time interval, the buoy meets water with ages repectively of 35 and 50 days (the cyan dots in figure 4). Following the exponential decay of the stock of DFe as a function of the age of the water parcel, a

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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 315mmolm^{-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 160 mmol m^{-2}d^{-1} and 82mmol m^{-2}d^{-1} assuming a removal constant equal to 0.045 d^{-1}. NCP/NPP ratios are then respectively equal to 0.82 and 0.73.These numbers are close to the f ratio, 0.9, measured by (Cavagna et al.,2014, figure 4) at station F-L on the polar front. The choice of MLD equal to 22 and 25 meters in our estimate of NCP instead of 20 meters would have met this limit but larger values of MLD are not acceptable.

4.5 Air-sea flux

A striking feature is the abrupt change of the direction of the air-sea CO_2 and O_2 fluxes, from a sink of atmospheric CO_2 at the ocean surface (the opposite for O_2) to a source, on an episodic event on November 16 and on December 16 when the buoy escapes the iron fertilized plume to enter the polar frontal zone (figure 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 CO_2 air-sea flux in highly dynamic ocean area like the Southern Ocean. This is reinforced in an iron fertilized region, as the distribution of the iron concentration is closely linked to this dynamic environment.

5 Summary and Conclusion

Hourly pCO_2 and oxygen measurements have been made along the trajectory of a CARIOCA drifter downstream from the Kerguelen plateau during the austral bloom from 1st November 2011 until 12 February 2012. From 1st November to 12 November, the buoy drifted through a

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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 pCO_2 ocean is smaller than pCO_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, DIC is calculated from p 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 mmol C $m^{-2}d^{-1}$ to 60± 12 mmol C $m^{-2}d^{-1}$. 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 -8mmol$m^{-2}d^{-1}$ and the O_2 outgassing equal to +38mmol$m^{-2}d^{-1}$. 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 +5mmol$m^{-2}d^{-1}$and a sink for O_2 equal to -48mmol$m^{-2}d^{-1}$. The abrupt simultaneous changes of the sign of the air-sea CO_2 and O_2 fluxes when the buoy crosses the polar front show the dominant contribution westward in the iron fertilized Kerguelen plume of biology, which is characterised by an absorption of CO_2 and an outgassing of O_2. Within the plume, 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. 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 CO_2. For instance, this is well illustrated when the buoy crosses the polar front on 16 December .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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Liliane Merlivat 8/4/15 17:32
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Table 1. Difference between the extrema of DIC and O_2 measured in the warm surface layer (columns 4 and 6). In bold, mean values of DIC and O_2 changes over consecutive mornings (columns 5 and 7), CO_2 and O_2 air-sea flux (columns 8 and 9).

Date	Latitude Longitude	SST °C	DIC_{min}-DIC_{max} µmol kg^{-1}	$dDIC_{max}/dt$ µmol kg^{-1}	O_{2max}-O_{2min} µmol kg^{-1}	dO_{2min}/dt µmol kg^{-1}	F_{CO2} mmol m^{-2} d^{-1}	F_{O2} mmol$m^{-2}d^{-1}$
1	2	3	4	5	6	7	8	9
18 Nov	49.3°S76.4°E	4.2	-6.46±1.00		7.19±1.00			
23-25 Nov	**50.1°S77°4E**	**4.3**		**-4.72±0.23**		**3.74±0.54**	**-8.21**	**42.9**
23 Nov			-11.50±1.00		9.77±1.00			
24 Nov			-10.09±1.00		11.41±1.00			
26-28 Nov	**50.4°S77.3°E**	**4.4**		**-4.22±0.85**		**3.90±1.01**	**-5.83**	**38.5**
27 Nov			-9.35±1.00		8.39±1.00			
30Nov4Dec	**50.4°S79.8°E**	**4.5**		**-1.76±0.43**		**1.71±0.32**	**-9.13**	**47.4**
30 Nov			-8.50±1.00		6.17±1.00			
1 Dec			-5.79±1.00		5.73±1.00			
2 Dec			-7.80±1.00		7.25±1.00			
11-13 Dec	**50.2°S81.4°E**	**4.6**		**-2.10±0.65**			**-10.49**	**61.0**

Table 2. Biological changes (columns 2 and 4) and air-sea flux changes (columns 3 and 5) of DIC and O_2. In bold, mean values over consecutive mornings. Calculated values of NCP carbon and NCP oxygen (columns 6 and 7)

Date	$dDIC_{bio}$ µmol kg^{-1}	$dDIC_{air\text{-}sea}$ µmol kg^{-1}	dO_{2bio} µmol kg^{-1}	$dO_{2\ air\text{-}sea}$ µmol kg^{-1}	NCP_C mmol C m^{-2}d^{-1}	NCP_{O2} mmol O_2 m^{-2}d^{-1}
1	2	3	4	5	6	7
18 Nov	-6.79±1.00	-0.32±0.10	10.23±1.35	3.03±0.91		
23-25 Nov	**-5.12±0.26**	**-0.40±0.12**	**5.83±0.83**	**2.09±0.63**	**-140±7**	**160±23**
23 Nov	-12.43±1.04	-0.93±0.28	14.18±1.66	4.41±1.32		
24 Nov	-10.47±1.00	-0.38±0.11	13.88±1.24	2.47±0.74		
26-28 Nov	**-4.50±0.85**	**-0.28±0.09**	**5.78±1.16**	**1.87±0.56**	**-124±23**	**159±31**
27 Nov	-9.74±1.01	-0.39±0.12	10.85±1.24	2.46±0.74		
30Nov4Dec	**-2.20±0.45**	**-0.44±0.13**	**4.02±0.76**	**2.31±0.69**	**-60±12**	**111±20**
30 Nov	-9.07±1.01	-0.58±0.17	8.78±1.27	2.60±0.78		
1 Dec	-6.44±1.02	-0.66±0.20	9.78±1.57	4.05±1.22		
2 Dec	-8.38±1.02	-0.58±0.17	10.88±1.48	3.63±1.09		
11-13 Dec	**-2.61±0.67**	**-0.51±0.15**		**2.96±0.89**	**-72±17**	

FIGURE CAPTIONS

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 diamonds indicate high isolated salinity anomalies. The buoy enters the polar frontal zone at the location of the blue arrow. 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.

Figure 2. Diurnal cycles of SST, DIC and O_2 from 30 November to 4 December 2011. **a** SST (°C) (black, left vertical axis) and DIC (µmol kg^{-1}) (grey, right vertical axis).The vertical dashed lines indicate the time of sunrise (blue) and sunset (orange). **b** O_2 (µmol kg^{-1}) (black, left vertical axis) and DIC (grey, right vertical axis).

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 (d'Ovidio et al, 2015). The white 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).

Figure 5. Buoy data from 1 November 2011 to 12 February 2012. **a** temperature in °C (black, left vertical axis) and salinity (grey, right vertical axis). **b** T-S diagram: 1 to 11 November, black diamonds- 12 November to 16 December, grey diamonds- 17 December to 12 February, black squares. **c** pCO2 measured at a depth of 2 meters in µatm (black) and in the atmosphere in µatm (grey). **d** Dissolved oxygen concentration measured at a depth of 2 meters in µmol kg^{-1}(black, left vertical axis) and oxygen saturation in % (grey, right vertical axis). In figure 5a, the cyan dashed lines indicate the 12 November and 16 December days (see text). In figure 5b,the red dots indicate the data measured at the KEOPS 2 stations, TEW7, TEW8, F-L.

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). **b** CO_2

Figure 7. Distribution of O_2 in µmol kg^{-1} (black, left vertical axis) and DIC in in µmol kg^{-1} (grey, 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).

Figure 8. Measured changes (absolute values) of O_2 (µmol kg^{-1}) as a function of measured changes (absolute values) of DIC (µmol kg^{-1}) between consecutive mornings, (dark blue dots), or during the daylight period (light blue dots). The slope of the black dotted line is 1.

Figure 9. Changes (absolute values) of O_2 (µmol kg^{-1}) attributed to biological activity as a function of changes (absolute values) of DIC (µmol kg^{-1}) attributed to biological activity between consecutive mornings (red dots), or during the daylight period (blue dots). The two dotted lines with a slope of 1.4 and 1.1 respectively characterize the new and regenerated production regime.

Interactive comment on "Carbon, oxygen and biological productivity in the Southern Ocean in and out the Kerguelen plume: CARIOCA drifter results" by L. Merlivat et al.

Anonymous Referee #2

Received and published: 19 March 2015

General comments:

Merlivat et al, present the results of the deployment of the CARIOCA drifter during the Keops 2 over the Kerguelen Plateau experiment (Southern Ocean). The drifter provides some pCO2 values that might be of interest. However, the authors convert the pCO2 values in DIC in order to assess the Net Community Production based on a suite of assumptions. Some of them does not appear very robust to me. So in my mind, a careful assessment of how the uncertainty in the main assumptions (in particular the mixed layer depth) propagates through the series of computation is needed to assess the robustness of the estimates proposed in this study.

We thank the Reviewer for the time invested and the numerous comments that helped to improve our manuscript. Here below we answer point by point the different comments or remarks he/she raised.

We indicate in our manuscript (page 16883, L19-23) the assumptions made in order to compute the biological contribution to the measured DIC (computed from pCO_2 and salinity) and O_2 changes from our hourly measurements of temperature, salinity, pCO2, dissolved oxygen and wind speed made on the Carioca buoy, at 2 meters depth in the water and 2 meters height in the air (equations 6 and 7). We have written: "*During the daylight period, photosynthesis, respiration, and air-sea exchange are mechanisms responsible for the change in DIC and O_2 recorded at 2m 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*" We think that these assumptions are robust. In our study, we have identified 4 situations over a period of 3 to 5 days (tables 1 and 2) for which these assumptions are fulfilled.

The next step is to compute NCP (equations 8 and 9) for which the knowledge of the mixed layer depth, h, is needed. This is a delicate issue as we do not have a direct estimate of h when we measure the DIC and O_2 biological terms. In the manuscript, we discuss the arguments for which we have selected a value of h equal to 20 meters (page 16889,L13-18*):" 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), (figure 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 (figure 5b)."*

Alternatively a comparison with other determination of Net Community Production or Net Primary Production carried out during the same experiment could give confidence in the assessment of NCP derived from the data provided by the CARIOCA drifter.

Cavagna et al (2014) report net primary production at 8 stations visited during KEOPS2 representing the variability encountered over the Kerguelen plateau area and downstream along the polar front. An increase in integrated primary production (up to 8 times) between fertilized Plateau and Polar Front (station F-L) and unfertilized areas (HNLC site) is shown . Cavagna et al write « The production rates reported here for the

Kerguelen plume then fell within the highest rates measured for the Southern Ocean and compare most favorably with the maximum values of 117 and 133 mmolC $m^{-2}d^{-1}$given by Arrigo et al. (2008) for the most productive areas of the Seasonal Ice Zone » The range of NCP values, (necessarily smaller than NPP) along the polar front reported in our study extends from 60 to 140 mmolC $m^{-2}d^{-1}$which sounds reasonable .

Otherwise the assessment of NCP should be removed.

If we acknowledge that the absolute values of NCP rely on an indirect debatable estimation of the MLD, we think that three other messages were highlighted:

- the control of biology by the availability of iron in the plume along the trajectory of the buoy (table 2 and figure 4).

-the control of the air-sea CO_2 and O_2 flux by the biological carbon pump as it changes of sign as the buoy escapes the iron enriched filament (figure 6).

-the biological oxygen–carbon change ratio, between 1.1 and 1.4, as expected for new and regenerated regimes, but with very few experimental determination in the field.

Major comment:

CARIOCA drifters are good tools for survey of pCO2 and related parameters. However, for determination of Net Community Production, it is necessary to make several assumptions. Among them, one of the most critical is the Mixed Layer Depth (MLD). In this study, MLD is set to 20m for all the estimates of Net Community Production (NCP) according to the study of Park et al. 2014. However, I did not find the information about the MLD in the paper of Park et al. 2014, so that it is difficult to assess how robust is this assumption, and what is the variability of the MLD, since this variability will affect the accuracy of the determination of NCP.

The MLD have been computed by Park starting from the CTD casts made during the KEOPS 2 cruise. The values for each cast are listed in table 4 in the paper of Trull et al (Biogeosciences, 12, 1029–1056, 2015 2014). It is clear that it is a very variable quantity with values ranging from 17 to 163 m depending on the bathymetry and the physical and dynamical regime prevailing in the upper layers in the KEOPS 2 field study.The reference to Trull, 2014 has been added

In my mind, as the drifter is moving along the polar front, and possibly meanders or eddies, and then crossing the polar front towards the Subantarctic Zone, there is very little chance that the MLD remain constant. In line, in the study from Cavagna et al. in the same issue, it is stated that "Except for the HNLC reference station, the euphotic layer depth is relatively constant between stations while mixed layer depth varies significantly. The latter is generally deeper, more variable and extends more significantly below the euphotic layer over the Kerguelen plateau and at the HNLC reference station". Indeed in this study, the MLD range from 35 m to 120 m. In the same way, Jouandet et al assessed the MLD to be around 70m with an uncertainty of at least 15m. I acknowledge that the last study has been carried out south of the area covered by the Carioca drifter, and that the criteria for determination of the mixed layer depth are different. But still, to me, the assumption of a constant mixed layer depth is not supported by reports in this area, and 20 m may be an underestimate. This call for a careful assessment of the variability of the mixed layer depth in the area covered by the CARIOCA drifter, and how this uncertainty propagates in further computation and ultimately in NCP computations. An alternate way to provide the reader with some clues about the robustness of the computation of NCP could be a careful comparison (a table with the number of both studies at similar sites) with other assessment of the NPP as the estimates provided by

Cavagna et al. 2014 during the same experiment. This latter is potentially robust and implied less assumptions than in the current study. I acknowledge that Cavagna et al. 2014 address NPP, but still, in such pelagic environment, I do not expect so much differences. Comparison with other studies like the one of Jouandet et al. 2008, could have also been proposed to the reader.

As previously stated, the 4 situations for which we have estimated NCP using a MLD value equal to 20 meters are all located in the close vicinity of the polar front (figure 1). It is questionable to compare the reported values of NCP, between 60 and 140mmol C m^{-2} d^{-1} ,owing to the very large spatial and temporal variability of data previously reported in the KEOPS region. The variability of NPP measured by Cavagna et al (2014) in the KEOPS 2 area illustrates nicely this argument. During the KEOPS 1 expedition in 2005, Lefevre et al (2008) and Jouandet et al (2008) measured NCP at 2 stations south of the polar front .At the same locations, NCP measured at a five days interval varies between 105 and 43 mmol C m^{-2} d^{-1}.This illustrates that as long as the spatial and temporal variability of processes which control NCP are not understood, a comparison between different results is difficult to assess.
A sentence has been added in the paragraph 4.3

The manuscript reads "With larger values of the MLD, the relative part of the air–sea flux in the DIC and O2 measurements would have been smaller and make the slope of the oxygen–carbon relationship closer to 1". I agree, but the point is that the MLD is subject to change, and probably to increase. How this affects the discussion/conclusion related to the status of production (new vs regenerated) issued from PQ computed from fig 8 ?
The ten data points on figures 8 and 9 correspond to the four periods for which we have computed the biological and air-sea contribution to the observed changes of DIC and O_2 either during daytime or from dawn to dawn (equations 6 and 7 and table 2). Only the air-sea term depends on the MLD, being smaller for a larger MLD. The minimum of the slope of the oxygen-carbon relationship is equal to the ratio of the observed quantities if the air-sea flux is zero, i.e , equal to one in our case (figure 8) . The slope increases if MLD decreases as the air-sea flux term becomes larger. The maximum slope shown on figure 9, equal to 1.4 ,has been computed with MLD equal to 20m. It is unexpected that MLD could be smaller.

Finally, if the changes in DIC over one day time corresponds to the NCP, I'm not sure what the evolution of DIC/O2 during the daytime interval corresponds to. For me this latter correspond to something between Net and Gross primary production. Hence, at first sight, I would not mixed them up, and I would refer only to the changes in DIC from dawn to dawn.

During daytime, DIC and O_2 variations represent GCP-R/2 (GCP, Gross Community Production, R, Respiration) if we assume the respiration rate constant over a day. From dawn to dawn, it corresponds to GCP-R. So, it is correct that the daytime and the dawn to dawn ratio must be different. The difference is smaller when R is small compare to GCP (autotrophy, high f ratio). On figure 9 within the errors bars we can't estimate the difference. A sentence has been added in paragrah 4.3

Minor comments

P16878, L18. It not clear to me what the "mean" of fluxes correspond to. I would have

indicated the range of fluxes.
The sentence has been modified.

P16881 L25. Even, I do not expect large shift in total alkalinity, what is the impact of change in TA on the assessment on DIC. What is the overall accuracy of the estimation of DIC ?
The accuracy of computed DIC is 10.5 µmol kg^{-1} (Boutin et al., 2008). We indicate it now in the text. However, for the estimation of NCP, it is the relative precision for successive DIC data, expected to be 0.5 µmol kg^{-1}, which is important as its estimation depends on the slope of DIC changes with time.

P16883 L7. Is there particular reasons to choose the formulation of Sweeney et al. 2007, instead of a widely used formulation like the formulation from Wanninkhof (1992), or a formulation that has been specifically developed for the Southern Ocean (Ho et al. 2007)
Sweeney has rerun the formulation of Wanninkhof (1992) with different wind fields and updated ^{14}C.The Sweeney parameterization shows agreement within 15% with the other parameterizations derived from local gas exchange tracer studies (Ho et al., 2006, Nightingale et al., 2000). This is shown in Boutin et al. (2009) and Wanninkhof et al. (2013)

P16886, L17 "It is worth noting that the absolute values of the fluxes are larger for O2 than for CO2 due to the buffer factor of ocean water carbonate chemistry." I think that the differences in the Schmidt number for CO2, and O2 should also play a role in the differences in the fluxes, together
The Schmidt number for O_2 and CO_2 are respectively equal to 1048 and 1433 at 5°C and S=35.This means that the ratio of the gas transfer velocity, kO_2/kCO_2= 1.17 (equation 5), a number which is a relatively small term compare to the range of values, between a factor 5 and 9, of the ratio of the air-sea fluxes of O_2 and CO_2.

P16890, L 15 "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." So far I understand, an error in the MLD depth should affect DIC and O2 in a similar way, so that this does not provide so much information about the potential errors on the NCP. The dot should just moved along a line with a slope of 1.
If it is exact that an error on MLD should not affect the data points shown on Fig.8 , this is not true for Fig.9 as the contribution of air-sea change depends on the value of MLD as previously explained.

P16890, L 26. "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." That the reason why Cassar et al. 2009 are using O2:Ar ratio. By measuring Ar they can somehow compensate the effect of physical processes (i.e. air-sea exchange, bubble injection...).
We should have written L26 "based on dissolved oxygen argon ratio measurements" instead of "dissolved oxygen measurements." This has been corrected. Our point is that if the air-sea gas exchange term represents for instance 90% of the total measured signal, the error on the biological contribution will be very large.

P 16892, L12 "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 91mmol 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 20m." This is not a very robust assessment of what could be the NPP production. Also, what support the statement that the difference is reasonable. You might cite some other comparison found in the literature. I would have expected closer agreement.

We have changed the sentence and write" 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 160 and 82 mmol m^{-2} d^{-1} assuming a removal constant equal to 0.045 d^{-1}. NCP/NPP ratios are then respectively equal to 0.82 and 0.73.These numbers are close to the f ratio, 0.9, measured by (Cavagna et al.,2014, figure 4) at station F-L on the polar front. The choice of MLD equal to 22 and 25 meters in our estimate of NCP instead of 20 meters would have met this limit but larger values of MLD are not acceptable." We hope that the message is now clearer.The numbers are slightly changed as some calculations have been redone more precisely, but it does not affect the main message which is an upper bound to the value of the MLD.

Figures must be reordered according to the text. For instance in the text, the Figure 5 come first, then figure 1, then figure 3.

We have checked this point .We have noticed some errors which we hope are now corrected.

Figure 4. I think that the figure caption must refer to the original paper of d'Ovidio et al. 2014. It it stated in the text, but this information should also appear in the figure caption of the figure

This has been done

Figure 7. I found difficult to see the purple dots and lines superimposed to a red curve. You may consider to choose another color.

The figure has been modified.

The figure caption has been corrected.

Figure 8 & 9. At first sight, I would not mix day to day estimates with estimates over daytime, since the estimates over daytime does not correspond to NCP in my mind.

We have explained earlier why we think it is worthwhile to keep both sets of data points not withstanding that they do not represent exactly the same quantities. A sentence has been added in the text.

Typo P16880 L7, "KErguelen" should be changed in "Kerguelen"

It is written "KErguelen" as the letters KE are used in the KEOPS acronym.

P16881 L8, "Hood and Merlivat,2001" should be changed in "Hood and Merlivat, 2001"

This has been corrected.

P16886 L22. In the subtitle, you should to write either DIssolved Inorganic Carbon, or DIC

This has been corrected.

P16892 L9. replace decreasing by decrease

This has been corrected

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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

Keywords: Biological productivity regime: in situ measurements- Carbon-Oxygen stoichiometry- Natural iron fertilization from the Kerguelen plateau- Iron control on carbon biological production- Phytoplankton blooms extending downstream.

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 (Oct.-Nov. 2011), one Carioca buoy was deployed east of the Kerguelen plateau. It drifted eastward downstream in the Kerguelen plume. Hourly surface measurements of pCO_2, O_2 and ancillary observations were collected between 1st 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°E-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 700km.

In the first part of the trajectory, within the iron plume, the ocean surface waters are always a sink for CO_2 and a source for O_2, with fluxes of respective mean values equal to -8 mmol CO_2 $m^{-2}d^{-1}$ and +38 mmol O_2 $m^{-2}d^{-1}$. Eastward, as the buoy escapes the iron enriched filament, the fluxes are in opposite direction, with respective mean values of +5 mmol CO_2 $m^{-2}d^{-1}$ and -48 mmol O_2 $m^{-2}d^{-1}$. 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 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 CO_2 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 CO_2 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 CO_2 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 pCO_2. 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 CO_2 (pCO_2) is a necessary step to understand the processes regulating the ocean–atmosphere exchange of CO_2 and help to overcome the unresolved spatio temporal variability effects.

The magnitude of the gradient of pCO_2 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 pCO_2. In high nutrient-low-chlorophyll (HNLC) regions, including the Southern Ocean, more than two decades of intense research 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 pCO_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 1st November 2011 over the Kerguelen plateau and drifted eastward downstream within the Kerguelen plume. Until 12 February 2012, its ~1800 kilometers long trajectory followed the polar front closely, entering the polar frontal zone on the 16 December 2011(figure 1). The buoy acquired data in the 72°E-75°E longitude range of the intensive KEOPS 2 field campaign from 1st 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 CO_2 sensor (Copin-Montegut et al., 2004; Hood and Merlivat, 2001) and an Anderaa F3835 optode to measure dissolved O_2 (Lefevre and Merlivat, 2012).The partial pressure of CO_2, pCO_2, dissolved oxygen concentration, O_2, sea surface temperature, SST, and sea surface salinity, SSS, were measured at a depth of 2 meters on an hourly basis. Atmospheric pressure and wind speed are measured at a height of 2 meters, which were subsequently corrected to 10 meters 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 CO_2 sensor measures the fugacity of CO_2, fCO_2, which is not identical to pCO_2 owing to the non-ideal nature of the CO_2 gas (Dickson et al, 2007). In the range of SST of our study, the difference between pCO_2 and fCO_2 is close to 1.4 μatm, which is within the instruments 3μatm absolute error. Accordingly, we will approximate fCO2 as being equal to pCO_2 within this study.

Alkalinity, Alk (μmol 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 (μmol kg^{-1}), is derived from pCO_2, Alk, SST and SSS using the CO_2 dissociation constants of Mehrbach et al. (1973) as refitted by Dickson and Millero (1987) and solubility from Weiss (1974). An accuracy of 10.5 μmol kg^{-1} was estimated, as a result of the combined uncertainties linked to the dissociation constants, the accuracy of pCO2 measurements and the uncertainty of the alkalinity derived from the relationship proposed by Lee et al. 2006 (Boutin et al, 2008). The relative precision of

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successive DIC values is expected to be 0.5µmol kg^{-1} (Boutin et al, 2008, Boutin et 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 subsequently calibrated in-situ against Winkler titrations made over the course of the KEOPS 2 cruise. Oxygen saturation, O_{2sat} (in µmol kg^{-1}) is calculated using the equation of Garcia and Gordon (1992). The degree of O_2 saturation,(in percent), is given by:

$$\% \; O_2 \; sat = ([O_2] / [O_2^{sat}]) \; x100$$

2.3 Calculation of air-sea fluxes of CO_2 and O_2

The hourly air-sea CO_2 flux (F_{CO2}, mmol m^{-2} d^{-1}) is derived from wind speed, the air-sea gradient in pCO_2 and the gas transfer velocity [Boutin et al., 2008; Merlivat et al, 2014], following:

$$F_{CO2} = k_{CO2} \, \alpha_{CO2} \, (pCO_{2sea}\text{-}pCO_{2atm}) \qquad (1)$$

where α_{CO2} is the solubility of CO_2 (Weiss, 1974), pCO_{2sea} the partial pressure of CO_2 in seawater (µatm), pCO_{2atm} the partial pressure of CO_2 in the atmosphere (µatm), and k_{CO2} (cm/h) is the gas transfer velocity for CO_2. pCO_{2atm} is computed from the monthly molar fraction xCO_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:

$$F_{O2} = k_{O2} \, ([O_2]\text{-}[O_{2sat}]) \, \text{-}F_{bub} \qquad (2)$$

where k_{O2} 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):

$$F_{bub} = k_{O2}\, 0.01(U/U_0)^2\, [O_{2sat}] \qquad (3)$$

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

$$F_{O2}=k_{O2}\, ([O_2]-[O_{2sat}]\, (1+1.23\ 10^{-4}U^2)) \qquad (4)$$

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):

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

where Sc is the Schmidt number, Sc_{CO2} , for CO_2 or Sc_{O2} for O_2 (Wanninkhof, 1992) and U the 10m wind speed .

2.4 Calculation of in-situ Carbon and Oxygen biological production

Net community production, NCP_C, has been previously derived from drifting CARIOCA 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, $NCP_{O2.}$ (Lefèvre and Merlivat, 2012). The method relies on hourly measurements of SST, SSS, pCO_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 2m 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 effect of photosynthesis and respiration, DIC generally decreases and O_2 generally increases; they reach minimum (DICmin) and maximum (O_2max) values at the end of the day. At night, as a result of respiration and of the mixing between the warm layer and the mixed layer, DIC increases and O_2 decreases; they reach minimum (DICmin) and maximum (O_2max) values at the end of natural convection. NCP is derived from day-to-day change of DICmax and O_2min, after removing the contribution of the air-sea fluxes. Contribution of biological activity (photosynthesis plus respiration) during daylight is derived from DICmax-DICmin, and O_2min-O_2max after removing the contribution of the air-sea fluxes. Figure 2 shows SST, DIC and O_2 over a 4 days period, 30 November-4 December 2011. The mean increase of SST equal to 0.044°C d^{-1}, superimposed on daily cycles of SST, indicates a stratification of the mixed layer over this 4 days period. No change of salinity is measured (not shown). Thus, the changes in DIC and O_2 observed during the 4 days were only driven by biological processes allowing the computation of NCP. The carbon and oxygen mass balance, either in the daytime interval during the development of the warm layer, h*, or over one day time interval in the mixed layer, h, result in the two following equations:

$$\left(\frac{\Delta DIC}{\Delta t}\right)_{measured} = \left(\frac{\Delta DIC}{\Delta t}\right)_{bio} + \left(\frac{\Delta DIC}{\Delta t}\right)_{air-sea} \tag{6}$$

$$\left(\frac{\Delta O_2}{\Delta t}\right)_{measured} = \left(\frac{\Delta O_2}{\Delta t}\right)_{bio} + \left(\frac{\Delta O_2}{\Delta t}\right)_{air-sea} \tag{7}$$

NCP integrated over the mixed layer is given by:

$$NCP_C = \rho h \frac{\Delta DIC_{max}}{\Delta t} + F_{CO_2} \tag{8}$$

$$NCP_{O_2} = \rho h \frac{\Delta O_{2min}}{\Delta t} + F_{O_2} \qquad (9)$$

where F_{CO2} and F_{O2} are the air-sea CO_2 and O_2 flux (mmol m^{-2} d^{-1}), positive when there is outgassing to the atmosphere. h (in m) is the depth of the mixed layer, ρ (in kg m^{-3}) is the density of seawater and $\Delta DIC_{max}/\Delta t$ and $\Delta O_{2min}/\Delta t$, in µmol.$kg^{-1}d^{-1}$ 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

The time and spatial changes of the phytoplankton bloom as revealed by satellite ocean color are shown in figure 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.

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 25th November.(figure 4). Over the period 1st 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 estimates have been made over the period 18 November-13 December (Tables 1 and 2).

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3 Results

3.1 Buoy measurements

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 (figure 1). From 1st to 12 November, the buoy was drifting in the meander of the PF (Park et al, 2014) with SST~3°C and SSS ~33.83. From 12 November to 16 December, while the buoy followed closely and sometimes crossed the PF, SST is ~4.2°C and SSS ~33.75. During this time interval, simultaneous short time peaks of SST (negative) and SSS (positive) were observed whilst transiting the PF (figures 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.

A very large variability of pCO_2 values, from ~280 μatm to ~400 μatm, are observed while the buoy is drifting in the meander of the PF (figure 5c). Shipboard measurements of pCO_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 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% (figure 5d). In the polar frontal zone, an undersaturation is measured.

3.2 Air-sea flux of CO_2 and O_2

From 1st November to 17 December surface waters are a source of O_2 (figure 6a) for the atmosphere and a sink of CO_2 (figure 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 1st November to 16 December, the flux of O_2 and CO_2 are respectively 38±34 mmol $m^{-2}d^{-1}$and -8.3±7.5 mmol $m^{-2}d^{-1}$. After 16 December, they are equal respectively to -48±43 mmol $m^{-2}d^{-1}$ and 5.3±4.7 mmol $m^{-2}d^{-1}$.

3.3 DIssolved Inorganic Carbon, DIC, and oxygen

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A significant reduction in DIC of ~ 50µmol kg^{-1} is observed from November 1st to December 17th, followed by an increase of approximately 20µmol 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 (figure 7). During the first part of the 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 equations 6 and 7 (cf. also figure 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 figure 8).

3.4 Quantification of biological processes

Large amplitudes of the diurnal cycles of DIC and O_2 up to 12mmol kg^{-1} have been measured, while day-to-day changes peak at 5mmol kg^{-1} (figure 8). These numbers represent the contribution of the biological processes plus the air-sea exchange terms (equations 6 and 7). Their ratio is close to one (figure 8). Between two consecutive mornings, at the end of nocturnal convection, $(dDIC/dt)_{air\text{-}sea}$ and $(dO_2/dt)_{air\text{-}sea}$ are equal respectively to F_{CO2}/h and F_{O2}/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 2m. A mixed layer depth equal to 20m 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 (equation 9 and table 2). In November, 2 values of NCP respectively equal to 140±7 and 124±23 mmol C $m^{-2}d^{-1}$ are computed. In December, we have NCP equal to 60±12 and 72±17 mmol C $m^{-2}d^{-1}$. The standard deviation 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°E-78°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 (figure 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 (figures 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 doesn't 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 (figures 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 (figure 3) show the rapid development of the bloom 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 (figure 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°E-78°E, seem very tightly linked to the complex structures of the PF (figure 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), (figure 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, Trull et al., 2015)). We elect to use this depth as our MLD definition, as physical (T, S) characteristics at these stations are very similar to CARIOCA measurements (figure 5b). Furthermore, the choice of a relatively shallow mixed layer, 20 meters, 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, Ze, is greater than MLD. During the KEOPS 2 expedition at the station F-L, Cavagna et al (2014), indicate Ze=30meters. 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 meters represents about 75% of NPP integrated over Ze. NPP at depth greater than Ze is negligible close to 2%. We take into account an underestimation of 33% to compute NCP.

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 140 mmolm^{-2}d^{-1} between 23 and 28 November and then decreases to about 60 mmolm^{-2}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). During the KEOPS 1 expedition in 2005, Lefevre et al (2008) and Jouandet et al (2008) measured NCP at 2 stations south of the polar front .At the same locations, NCP measured at a five days interval varies between 105 and 43 mmol C m^{-2} d^{-1}.This illustrates the large spatial and temporal variability of processes which control NCP, depending on the bathymetry and the physical and dynamical regime prevailing in the upper layers in the KEOPS 2 field study.

The biological terms, $\left(\frac{\Delta O_2}{\Delta t}\right)_{bio}$ and $-\left(\frac{\Delta DIC}{\Delta t}\right)_{bio}$ are represented on figure 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, PQ=1.4) or a regenerated one (PQ= 1.1) (Laws, 1991) . During daytime, DIC and O_2 variations represent GCP-R/2 (GCP, Gross Community Production, R, Respiration) if we assume the respiration rate

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constant over a day. From dawn to dawn, it corresponds to GCP-R. As a result, the daytime and the dawn to dawn ratio should be different, the difference being smaller when R is small compare to GCP (autotrophy, high f ratio). On figure 9 within the errors bars, we can't estimate the difference. Nevertheless, 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 figure 8.

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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 argon 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 measurements 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 pCO_2 sensor and an oxygen optode found an O_2/DICratio 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 ±0.93 ± 0.03 respectively for the O_2: 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 figure 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 el, 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 figure 4 can be interpreted as representative of the changes of the stock of DFe in the ocean upper layer (0-150m), 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 escapes the rich DFe waters on 15-16 November (the cyan square in figure 4) large abrupt changes of DIC (an increase) and O_2 (a decrease) are observed (figure 7), suggesting the lack of organic matter production in the absence of iron.

A decrease of NCP from ~130mmol$m^{-2}d^{-1}$ to ~ 65mmol$m^{-2}d^{-1}$is computed between the 23-28 November and 30 November- 13December periods. During this time interval, the buoy meets water with ages repectively of 35 and 50 days (the cyan dots in figure 4). Following the exponential decay of the stock of DFe as a function of the age of the water parcel, a decrease

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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 315mmolm^{-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 160 µmol m^{-2}d^{-1} and 82 µmol m^{-2}d^{-1} assuming a removal constant equal to 0.045 d^{-1}. NCP/NPP ratios are then respectively equal to 0.82 and 0.73.These numbers are close to the f ratio, 0.9, measured by (Cavagna et al.,2014, figure 4) at station F-L on the polar front. The choice of MLD equal to 22 and 25 meters in our estimate of NCP instead of 20 meters would have met this limit but larger values of MLD are not acceptable.

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4.5 Air-sea flux

A striking feature is the abrupt change of the direction of the air-sea CO_2 and O_2 fluxes, from a sink of atmospheric CO_2 at the ocean surface (the opposite for O_2) to a source, on an episodic event on November 16 and on December 16 when the buoy escapes the iron fertilized plume to enter the polar frontal zone (figure 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 CO_2 air-sea flux in highly dynamic ocean area like the Southern Ocean. This is reinforced in an iron fertilized region, as the distribution of the iron concentration is closely linked to this dynamic environment.

5 Summary and Conclusion

Hourly pCO_2 and oxygen measurements have been made along the trajectory of a CARIOCA drifter downstream from the Kerguelen plateau during the austral bloom from 1st November

2011 until 12 February 2012. From 1st 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 pCO_2 ocean is smaller than pCO_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 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 mmol C $m^{-2}d^{-1}$ to 60± 12 mmol C $m^{-2}d^{-1}$. 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 -8mmol$m^{-2}d^{-1}$ and the O_2 outgassing equal to +38mmol$m^{-2}d^{-1}$. 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 +5mmol$m^{-2}d^{-1}$and a sink for O_2 equal to -48mmol$m^{-2}d^{-1}$.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, 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. 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 CO_2. It is noteworthy to observe the abrupt changes of the air-sea flux of CO_2 and O_2 when the buoy crosses the polar front on 16 December which is likely is 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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We are grateful to N. Martin from LOCEAN for software development and to L. Beaumont from DT-INSU, who supervised the CARIOCA preparation. We thank S. Blain, project leader, and B. Quéguiner, chief scientist, as well as the captain and crew of R.R.V. Marion Dufresne and the staff at the French Polar Institute (IPEV) who provided logistic support. Special thanks to Claire Lo Monaco for access to pCO_2 results and Dominique Lefèvre for access to O_2results. We thank Y.Park for having provided the data files for correctly positioning the polar front. We also enjoyed the stimulating discussions with N.Cassar during his stay at LOCEAN and the comments of S.Blain in the course of the preparation of the manuscript.

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Table 1. Difference between the extrema of DIC and O_2 measured in the warm surface layer (columns 4 and 6). In bold, mean values of DIC and O_2 changes over consecutive mornings (columns 5 and 7), CO_2 and O_2 air-sea flux (columns 8 and 9).

Date	Latitude Longitude	SST °C	DIC_{min}-DIC_{max} µmol kg^{-1}	$dDIC_{max}/dt$ µmol kg^{-1}	O_{2max}-O_{2min} µmol kg^{-1}	dO_{2min}/dt µmol kg^{-1}	F_{CO2} mmol m^{-2} d^{-1}	F_{O2} mmolm^{-2}d^{-1}
1	2	3	4	5	6	7	8	9
18 Nov	49.3°S76.4°E	4.2	-6.46±1.00		7.19±1.00			
23-25 Nov	**50.1°S77°4E**	**4.3**		**-4.72±0.23**		**3.74±0.54**	**-8.21**	**42.9**
23 Nov			-11.50±1.00		9.77±1.00			
24 Nov			-10.09±1.00		11.41±1.00			
26-28 Nov	**50.4°S77.3°E**	**4.4**		**-4.22±0.85**		**3.90±1.01**	**-5.83**	**38.5**
27 Nov			-9.35±1.00		8.39±1.00			
30Nov4Dec	**50.4°S79.8°E**	**4.5**		**-1.76±0.43**		**1.71±0.32**	**-9.13**	**47.4**
30 Nov			-8.50±1.00		6.17±1.00			
1 Dec			-5.79±1.00		5.73±1.00			
2 Dec			-7.80±1.00		7.25±1.00			
11-13 Dec	**50.2°S81.4°E**	**4.6**		**-2.10±0.65**			**-10.49**	**61.0**

Table 2. Biological changes (columns 2 and 4) and air-sea flux changes (columns 3 and 5) of DIC and O_2. In bold, mean values over consecutive mornings. Calculated values of NCP carbon and NCP oxygen (columns 6 and 7)

Date	$dDIC_{bio}$	$dDIC_{air\text{-}sea}$	dO_{2bio}	$dO_{2\ air\text{-}sea}$	NCP_C	NCP_{O2}
	μmol kg^{-1}	μmol kg^{-1}	μmol kg^{-1}	μmol kg^{-1}	mmol C m^{-2}d^{-1}	mmol O_2 m^{-2}d^{-1}
1	2	3	4	5	6	7
18 Nov	-6.79±1.00	-0.32±0.10	10.23±1.35	3.03±0.91		
23-25 Nov	**-5.12±0.26**	**-0.40±0.12**	**5.83±0.83**	**2.09±0.63**	**-140±7**	**120±23**
23 Nov	-12.43±1.04	-0.93±0.28	14.18±1.66	4.41±1.32		
24 Nov	-10.47±1.00	-0.38±0.11	13.88±1.24	2.47±0.74		
26-28 Nov	**-4.50±0.85**	**-0.28±0.09**	**5.78±1.16**	**1.87±0.56**	**-124±23**	**159±31**
27 Nov	-9.74±1.01	-0.39±0.12	10.85±1.24	2.46±0.74		
30Nov4Dec	**-2.20±0.45**	**-0.44±0.13**	**4.02±0.76**	**2.31±0.69**	**-60±12**	**111±20**
30 Nov	-9.07±1.01	-0.58±0.17	8.78±1.27	2.60±0.78		
1 Dec	-6.44±1.02	-0.66±0.20	9.78±1.57	4.05±1.22		
2 Dec	-8.38±1.02	-0.58±0.17	10.88±1.48	3.63±1.09		
11-13 Dec	**-2.61±0.67**	**-0.51±0.15**		**2.96±0.89**	**-72±17**	

FIGURE CAPTIONS

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 diamonds indicate high isolated salinity anomalies. The buoy enters the polar frontal zone at the location of the blue arrow. 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.

Figure 2. Diurnal cycles of SST, DIC and O_2 from 30 November to 4 December 2011. **a** SST (°C) (black, left vertical axis) and DIC (μmol kg^{-1}) (grey, right vertical axis).The vertical dashed lines indicate the time of sunrise (blue) and sunset (orange). **b** O_2 (μmol kg^{-1}) (black, left vertical axis) and DIC (grey, right vertical axis).

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 (d'Ovidio et al, 2015). The white 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).

Figure 5. Buoy data from 1 November 2011 to 12 February 2012. **a** temperature in °C (black, left vertical axis) and salinity (grey, right vertical axis). **b** T-S diagram: 1 to 11 November, black diamonds- 12 November to 16 December, grey diamonds- 17 December to 12 February, black squares. **c** pCO2 measured at a depth of 2 meters in µatm (black) and in the atmosphere in µatm (grey). **d** Dissolved oxygen concentration measured at a depth of 2 meters in µmol kg^{-1}(black, left vertical axis) and oxygen saturation in % (grey, right vertical axis). In figure 5a, the cyan dashed lines indicate the 12 November and 16 December days (see text). In figure 5b,the red dots indicate the data measured at the KEOPS 2 stations, TEW7, TEW8, F-L.

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). **b** CO_2

Figure 7. Distribution of O_2 in µmol kg^{-1} (black, left vertical axis) and DIC in in µmol kg^{-1} (grey, 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).

Figure 8. Measured changes (absolute values) of O_2 (µmol kg^{-1}) as a function of measured changes (absolute values) of DIC (µmol kg^{-1}) between consecutive mornings, (dark blue dots), or during the daylight period (light blue dots). The slope of the black dotted line is 1.

Figure 9. Changes (absolute values) of O_2 (µmol kg^{-1}) attributed to biological activity as a function of changes (absolute values) of DIC (µmol kg^{-1}) attributed to biological activity between consecutive mornings (red dots), or during the daylight period (blue dots). The two dotted lines with a slope of 1.4 and 1.1 respectively characterize the new and regenerated production regime