Point-by-Point reply to referee 1

August 24, 2015

We would like to thank the referee for the careful review of our manuscript. Your comments were taken into careful consideration. Here, a point-by-point reply together with the latest changes on the manuscript is presented. We hope that the changes adequately address the reviewer’s comments and that the new version is suitable for publication in Biogeoosciences.

• **Comment 1** – As stated above, I do not know the statistical indicators used by the authors, and these are not used in any biogeochemical modelling studies I am aware of. In addition, from the way they are used here, it appears that they provide only a very coarse qualitative assessment of model performance. Thus, I find these indices of no value here and would suggest to replace them with a Taylor diagram, which is more quantitative and would greatly facilitate the comparison with other modelling studies.

• **Reply to comment 1** – We added the equations and more detail about the statistical indicators (ME, CF and PB). We also added a new figure with a Taylor diagram that is consistent with the Model Efficiency (ME) indicator. This diagram shows a good correlation in the northernmost area (A1), while the areas to the South (A2 and A3) are not correlated with the observations. This may be explained by the higher eddy variability in these areas, as shown in the EKE map (Fig 4a), and thus higher expected pCO2 variability. Another factor may be the limited number of observations in these areas.

Texts changed: 1225-236:

"model efficiency \( ME = 1 - (\Sigma(O - M)^2)/(\Sigma(O - \bar{O})^2) \) (Nash and Sutcliffe, 1970), cost function \( CF = (\Sigma | M - O |)/(n\sigma_o) \) (Oscar et al., 1998) and percentage of bias \( PB =| (\Sigma(O - M).100)/\Sigma O | \) (Allen et al., 2007), where \( M \) stands for modeled \( p\text{CO}_2 \) and \( O \) for observations from SOCAT database, \( n \) is the number of observations and \( \sigma_o \) is the
standard deviation of all observations."

"ME relates model error with observational variability, CF is the ratio of mean absolute error to standard deviation of observations, and PB is the bias normalized by the observations (Dabrowski et al., 2014; Stow et al., 2009). Basically if $ME > 0.5$, $CF < 1$ and $PB < 20$, indicate that the model is "good/reasonable" when comparing to observations. If $ME < 0.2$, $CF > 3$ and $PB > 40$ the model is classified as "poor/bad".""

Texts added: L256-261:

"The Taylor diagram is consistent with the model efficiency (ME) estimate, showing good/reasonable results in A1, with a correlation of 0.8, and poor results in A2 and A3, with negative correlations (Fig.5). Only in A1, the correlation was found to be statistically significant. Aside from greater $pCO_2$ variability in these regions, the poor results found in A2 and A3 could also be due to the paucity of the observational data both in space and time.""

**Comment 2**  – The authors describe several processes lacking in their model, e.g., rivers and tides (p. 7374 bottom to p. 7375 top). While I have no problem accepting this decision, I found the discussion somewhat confusing. On p. 7375, l. 8, it says that the "model results should not be significantly affected ..." but in the next sentence: "These processes will be implemented in future studies." This does not make sense to me: either these processes are (expected to be) important, then the authors should discuss the reasons why they expect that these processes do not strongly affect their present conclusions, or they are not important, then there is no reason to include them in future studies. For example, on p. 73887, l. 10, an expectation is expressed that including tides and rivers could help "diminishing the biases in the southernmost and La Plata regions", which seems to contradict the above statement. This should be resolved in a revised manuscript.

**Reply to comment 2**  – It is known that these processes are locally important in controlling mixing and stratification, with likely impacts on $pCO_2$. But the extent to which regional $pCO_2$ is affected is not established, requiring a separate study, which we leave for the future. Turbulent mixing due to tides is mostly important in the inner shelves of Patagonia. In contrast, the South and Southeastern Brazilian shelves have a micro-tidal
regime. Therefore we expect this process to not significantly effect pCO2 in these regions. Riverine inputs are mostly important in the La Plata region, since it is the major river in our study area, but not elsewhere. Therefore, we expect that the overall large scale pCO2 distribution of the model will not depend substantially on these local processes. These processes should be included in studies with a more regional emphasis. In response, we added some explanation into the text arguing for why these processes are not considered in our study and what the potential implications of this limitation might be.

Texts changed: L105

"Even though some processes as river runoff and tides are locally relevant (i.e., La Plata River, and Patagonia shelf), we are not considering them in the present study (see conclusions section)." ... "These shortcomings may effect the results in some regions, but it is unlikely that they will affect the overall pCO2 results in the wider domain."

Moved paragraph to conclusions section L466:

"Our model does not include river inputs of carbon, which are known to be an important factor regulating pCO2 (Bauer et al., 2013). The lack of tides may adversely affect our model results in the inner shelf of Patagonia, where tidal amplitudes reach up to 12 meters at some points (Kantha et al., 1995; Saraceno et al., 2010) and tidal fronts are known to impact oceanic pCO2 (Bianchi et al., 2005)."

And added: L451:

"In future regional studies focused on the Patagonia shelf, tides and river run-off should be included."

• **Comment 3** – Some minor problems: P. 7374, L 21 "(CESM) climatological model product": a reference should be provided for this product.

On the ocean -> In the ocean (several places)

The axis and tick labels in all figures are much too small and should be increased to the font size of the main text.

• **Reply to comment 3** – Added reference to (CESM) climatological model product "(Moore et al., 2013)". Corrected text to “In the ocean” throughout the manuscript.
Increased axis and tick label in all figures.
Point-by-Point reply to referee 2

August 24, 2015

We would like to thank the referee for the careful review of our manuscript. Your comments were taken into careful consideration. Here, a point-by-point reply together with the latest changes on the manuscript is presented. We hope that the changes adequately address the reviewer’s comments and that the new version is suitable for publication in Biogeosciences.

- **Comment 1** – The title (And abstract) should contain the term seasonal – as longer-term variability is not assessed here, nor could it be due to the experimental design.

- **Reply to comment 1** – Changed title to "Air-sea CO$_2$ fluxes and the controls on ocean surface pCO$_2$ seasonal variability in the coastal and open-ocean southwestern Atlantic Ocean: A modeling study"

- **Comment 2** – P7372: line 11 acting -> acts

- **Reply to comment 2** – corrected “acting” to “acts”.

- **Comment 3** – P7372, line 27: the reference to Takahashi et al (2002) seems to be referencing to coastal ocean, while this ref refers to the open-ocean. This should be rephrased.

- **Reply to comment 3** – Rephrased the reference of Takahashi et al (2002) concerning open-ocean estimates. Changed text to: "In the open-ocean, the South Atlantic is thought to
absorb between 0.3-0.6 PgC/year south of 30°S, while acting as a source to the atmosphere north of 30°S (Takahashi et al., 2002)"

- **Comment 4** - P 7375, line 1-10: this seems better placed in the discussion.

- **Reply to comment 4** - As our discussion section is divided into spatial and temporal analysis, we found it more fitting to move this paragraph (tides and rivers importance) to the conclusions section.

- **Comment 5** - P7379, line 1-19: this evaluation is a bit unclear, the authors need to add a bit more information to the reader about what this means and what are the thresholds. Also please be consistent "reasonable/good" or "good/reasonable".

- **Reply to comment 5** - Added equations and a more detailed explanation of the statistical indicators (ME, CF and PB).

  Texts added: L225-236:
  "model efficiency $ME = 1 - (\Sigma (O - M)^2)/(\Sigma (O - \bar{O})^2)$ (Nash and Sutcliffe, 1970), cost function $CF = (\Sigma | M - O |)/(n \sigma_o)$ (Ospar et al., 1998) and percentage of bias $PB = (\Sigma (O - M)\cdot 100)/\Sigma O$ (Allen et al., 2007), where $M$ stands for modeled $pCO_2$ and $O$ for observations from SOCAT database, $n$ is the number of observations and $\sigma_o$ is the standard deviation of all observations."

  "ME relates model error with observational variability, CF is the ratio of mean absolute error to standard deviation of observations, and PB is the bias normalized by the observations (Dabrowski et al., 2014; Stow et al., 2009). Basically if $ME > 0.5$, $CF < 1$ and $PB < 20$, indicate that the model is "good/reasonable" when comparing to observations. If $ME < 0.2$, $CF > 3$ and $PB > 40$ the model is classified as "poor/bad"."

  Also added Taylor diagram as an additional model performance analysis. Now consistently using "good/reasonable" and "poor/bad" to describe the model performance.

- **Comment 6** - P73780 1-3: remove satisfyingly.
• **Reply to comment 6** – removed “satisfyingly”.

• **Comment 7** – P7381, line 16: what is metabolic DIC? Clarify.

• **Reply to comment 7** – Metabolic DIC is the DIC formed by the respiration of CO2.

• **Comment 8** – P7384, line 5 and after: I think it is actually Sea-air fluxes, not air-sea fluxes, please check this.

• **Reply to comment 8** – Both terms “sea-air fluxes” and “air-sea fluxes” can be used. We are using “air-sea fluxes” throughout the text now.

• **Comment 9** – P7385, Section 4.4 This model only deals with seasonal variability, therefore any statements about this site, and what is simulated needs to be tempered with a caveat. Also a reference to Fig 1 is needed in this section.

• **Reply to comment 9** – We agree that our statements and conclusions should be tempered with caveats, since we are working with a climatological analysis. With regards to the OOI site, a more realistic year-specific forcing and boundary conditions would be needed for a appropriate evaluation of the model performance. Here we only discuss the expected climatological behaviour at the OOI site, and use it to relate mixed layer depth with pCO2 and DIC input to the surface ocean. Added a reference to fig 1 a.

• **Comment 10** – Conclusion: in the methods a number or limitations of the modelling approach are highlighted, could the authors please make a comment on how these may modulate the results e.g. riverine input, large phytoplankton etc? Perhaps the implications of only addressing the seasonal variability also need to be considered (particularly as...
part of the paper deals with the Argentina OOI site – see above).

- **Reply to comment 10** – Riverine input and tides are locally important in the inner shelf of Patagonia and in the La Plata region. Therefore these limitations will affect our results only in these areas, while we do not expect a major effect in the overall larger scale study area.

  The fact that we are using a model with only one phytoplankton type is another limitation in this study. Since we are working with a large area, with various biogeochemical characteristics, a single parametrization will inevitably fail in some areas. Nevertheless, experiments were made (not shown) with different biogeochemical parameters more representative of small phytoplankton instead of large phytoplankton (as is the case of the present study, based on Gruber et al 2006). Only minor differences in the ocean surface pCO2 were found, therefore, we decided to keep the parameters as in the previous study.

  We anticipate that we will use more complex, multi-species biogeochemical models in future studies.

  The fixed atmospheric CO2 concentration of 370 uatm also limits a direct comparison between the model results and the sparse data from SOCAT in the region. These limitations do not affect our discussion of the drivers and processes responsible for ocean surface pCO2 variability in our seasonal analysis.

  We agree with the referee that there are implications of only addressing the seasonal variability, but more observations are needed for more detailed model evaluations.

- **Comment 11** – Table 1: If this table is from Gruber (2006), is it needed here?

- **Reply to comment 11** – Removed Table 1 – Only left in citation.

- **Comment 12** – Figure 2-3: consider a diff plot.

- **Reply to comment 12** – A diff plot would not be helpful because we are mostly concerned with the overall behaviour of the ocean surface (In equilibrium, source or sink), rather than
with the absolute values. Furthermore, the only few data available are sparse throughout the years, and most observations are available in only one year, making it challenging to compare with the model climatology.

• **Comment 13** – Figure 4: EKE is shown, but not really used in the text – is this the correct figure to show, given that the analysis does not explicitly deal with eddies?

• **Reply to comment 13** – We show the figure with the EKE map to demonstrate that the areas A2 and A3 are near a maximum of EKE, and therefore present larger variability, which will possibly lead to a decrease in correlation coefficients.

• **Comment 14** – Figure 12: I don’t follow the figure caption, could it be clarified?

• **Reply to comment 14** – Rephrased caption on Fig 12 (Now fig 13) to "Vertical profile at 42°S, 42°W. Upper panels showing monthly mean surface $p$CO$_2$ (solid black line), $p$CO$_2$ anomalies (dashed black line) and the contribution from $T$ and $DIC^*$ (red and blue dashed lines) and the contribution of biology and solubility (green and cyan dashed lines). Lower panels showing vertical profiles of $DIC$ (a), $T$ (b), and chlorophyll a(c), black line represents the mixed layer depth".
Final comment

August 18, 2015

We would like to thank the referees for their careful review of our manuscript. Their comments were taken into careful consideration. A point-by-point reply together with the latest changes on the manuscript is presented separately for each referee. We hope that the changes adequately address the reviewer’s comments and that the new version is suitable for publication in Biogeosciences.

In consideration with the reviewer’s comments and after discussions with the co-authors, additional changes were made in order to clarify and improve our manuscript:

• **L3 - Abstract** – Changed "the region acts as sink" to "the region acts as a sink".

• **L11 - Abstract** – Changed "particularly important on shelf regions" to "particularly important on shelves".

• **L23 - Introduction** – Changed "0.589 PgC/year" to "roughly 0.6 PgC/year".

• **L44 - Introduction** – Removed "characterized as".

• **L49 - Introduction** – Changed "maybe" to "might be".

• **L66 - Introduction** – Changed "spatial and temporal" to "spatially and temporally".
• **L70 - Introduction** – Rephrased sentence to "Our model domain includes the location of the global node mooring that is soon to be deployed as part of the Ocean Observatories Initiative (OOI) at 42°S, 42°W (oceanobservatories.org)."

• **L83 - Material and Methods** – Rephrased sentence to "Our model domain spans from 15°S to 55°S, and from 70°W to 35°W, i.e., covering the southwestern Atlantic from its subtropical to subantarctic latitudes and from the continental shelf all the way out to the open ocean."

• **L94 - Material and Methods** – Added "and the CaCO₃ parameters as in (Hauri et al., 2013)."

• **L103 - Material and Methods** – Added "at the surface" and QuikSCAT reference "Risien and Chelton, 2008)."

• **L106 - Material and Methods** – Added "and without seasonal variations!".

• **L147 - Analysis** – Added "therefore effects from dilution of DIC and ALK through freshwater input are not included in DIC* and ALK* terms.", and rephrased next sentence to "The dilution effect is considered instead in the freshwater component (FW) as it includes the effects of.."

• **L175 - Analysis** – Changed "photosynthetic" to "photosynthetically".

• **L204 - Model Evaluation** – Changed "represents" to "simulates".

• **L216 - Model Evaluation** – Changed "from inner to outer shelf" to "across both inner and outer shelves".
• **L225 - Model Evaluation** – Changed "characterizing these regions as" to "which make these regions".

• **L227 - Model Evaluation** – Added "while".

• **L275 - Model Evaluation** – Rephrased last sentence to "While there is clearly room for improvement, we deem this level of agreement as sufficient for proceeding to the analysis of the processes and parameters affecting pCO₂ variability in this region."

• **L240 - Model Evaluation** – Added reference "Stow et al., 2009".

• **L282 - Results 4.1** – Added "prevailing" and "found".

• **L286 - Results 4.1** – Rephrased sentence to "Even though with a smaller role, ALK’s influence on pCO₂ anomalies presented ..."

• **L296 - Results 4.1** – Rephrased sentence to "We investigate the role of each of these processes in controlling ..."

• **L296 - Results 4.1** – Rephrased sentence to "We investigate the role of each of these processes in controlling ...

• **L328 - Results 4.2** – Changed "appears" to "is relevant"

• **L330-333 Results 4.2** – Rephrased sentence to "This is likely due to our large and heterogeneous domain, which results in much spatial gradients than what is modeled over the seasonal cycle."
• **L389 Results 4.2** – Added "the temporal variability."

• **L419 Results 4.3** – Fixed fluxes estimates on the Patagonia shelf to "\((-1.0 \text{ to } -3.0 \text{ molCm}^{-2}\text{yr}^{-1})\)."

• **L452 Conclusions** – Changed "hydrodynamical model coupled with" to "hydrodynamic model coupled to".

• **L461 Conclusions** – Added "ALK* is a secondarily".

• **Throughout the text** – Changed "Patagonian" to "Patagonia"

• **Throughout the text** – Changed "SouthWestern" to "southwestern"

• **Throughout the text** – Changed "annual average" to "annual mean"

• **Throughout the text** – Changed "modelled" to "modeled"

• **Throughout the text** – Changed "surface ocean" to "ocean surface"

• **Throughout the text** – Changed "DIC" and "ALK" to "DIC*" and "ALK*" where appropriate.

• **Throughout the text** – Changed typeset to Roman on "S", "W", "molCm^{-2}\text{yr}^{-1}l", "\mu\text{atm}"; and "CaCO_3".

• **acknowledgements** – Changed project to "the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES Process 23038.004299/2014-53)".
• **Acknowledgements** – Added "Supported by Global Environmental Facilities (GEF) in the frame of PNUD ARG/02/018-GEF BIRF N° 28385-AR, subproject B-B46, and by Servicio de Hidrografía Naval. Additional support was provided by the ARGAU Project, Instituto Antártico Argentino, Institut National de Sciences de l’Univers, Processus Biogéochimiques dans l’Océan et Flux, Université Pierre et Marie Curie."

• **Table 1** – Added columns for Bias, Correlations and number of observations (N). Rephrased caption to "Statistical indicators of model skill for surface ocean $pCO_2$ in the three areas (A1, A2 and A3 - Fig.4). The indicators are: ME (Model Efficiency); CF (Cost Function); and PB (Percentage of Bias). Additionally, showing total bias ($\mu$atm), correlation and total number of observations (N) available on each area. Bold values indicate "good/reasonable" model skill."

• **Figure 1** – Fixed latitudes on fig-b to be the same as fig-a

• **Figure 2 and 3** – Added months for each season:
  "Summer(JFM), Autumn(AMJ), Winter(JAS), Spring(OND)". Changed "First row" and "second row" to "upper row" and "lower row"

• **Figure 4** – Changed boxes and texts to white color in fig-a.

• – All small changes in the text are detailed in the marked-up version of the manuscript.
Air-sea CO\textsubscript{2} fluxes and the controls on ocean surface \( p\text{CO}_2 \) \textit{seasonal} variability in the coastal and open-ocean southwestern Atlantic Ocean: A modeling study

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\textbf{Abstract.} We use an eddy-resolving, regional ocean biogeochemical model to investigate the main variables and processes responsible for the climatological spatio-temporal variability of \( p\text{CO}_2 \) and the air-sea CO\textsubscript{2} fluxes in the southwestern Atlantic Ocean. Overall, the region acts as a sink of atmospheric CO\textsubscript{2} south of 30\textdegree S, and is close to equilibrium with the atmospheric CO\textsubscript{2} to the north. On the shelves, the ocean acts as a weak source of CO\textsubscript{2}, except for the mid/outer shelves of Patagonia, which act as sinks. In contrast, the inner shelves and the low latitude open ocean of the southwestern Atlantic represent source regions. Observed nearshore-to-offshore and meridional \( p\text{CO}_2 \) gradients are well represented by our simulation. A sensitivity analysis shows the importance of the counteracting effects of temperature and dissolved inorganic carbon (\( \text{DIC} \)) in controlling the seasonal variability of \( p\text{CO}_2 \). Biological production and solubility are the main processes regulating \( p\text{CO}_2 \), with biological production being particularly important on the shelf regions/shelves. The role of mixing/stratification in modulating \( \text{DIC} \), and therefore surface \( p\text{CO}_2 \), is shown in a vertical profile at the location of the Ocean Observatories Initiative (OOI) site in the Argentine Basin (42\textdegree S, 42\textdegree W).

\section{Introduction}

Shelf regions are amongst the most biogeochemically dynamical zones of the marine biosphere (Walsh, 1991; Bauer et al., 2013). Even though they comprise only 7 – 10\% of the global ocean
area (Laruelle et al., 2013), continental shelves could contribute to approximately 10 – 15% of the ocean primary production and 40% of the ocean’s carbon sequestration through particulate organic carbon (Muller-Karger et al., 2005). Global discussions about the role of continental margins as a sink of atmospheric CO₂ gained momentum after Tsunogai et al. (1999), who suggested that these shelf regions take up as much as 1 PgC/year of atmospheric CO₂. Recent estimates range from 0.2 PgC/year (Laruelle et al., 2013) to roughly 0.6 PgC/year (Yool and Fasham, 2001), somewhat more modest than initially thought (Gruber, 2015), but still relevant to the global ocean sink estimated around 2.3 PgC/year (Ciais et al., 2014).

Continental shelves tend to act as a sink of carbon at high and medium latitudes (30° – 90°), and as a weak source at low latitudes (0° – 30°) (Chen et al., 2013; Hofmann et al., 2011; Bauer et al., 2013; Laruelle et al., 2014), i.e., they tend to follow similar meridional trends as the open ocean CO₂ fluxes (Landschützer et al., 2014; Takahashi et al., 2009).

However, continental shelves present a higher spatio-temporal variability of air-sea CO₂ fluxes than the adjacent open ocean, with the inner shelf and near coastal regions generally acting as a source of CO₂ to the atmosphere, while the mid/outer shelf and the continental slope generally act as sink as sinks (Cai, 2003). This pattern can be explained by the increased primary production and decreased terrestrial supply towards the outer shelf (Walsh, 1991). Seasonality of the upper ocean (e.g. mixing and stratification) may also be important to the air-sea exchange of carbon. For example, the United States southeast continental shelf acts as a sink of CO₂ in the winter and as a source in the summer (Wang et al., 2005).

In the southwestern Atlantic Ocean, the shelf region presents distinct features. To the south, the Patagonian shelf is one of the world’s largest shelves with an area close to 10⁶ km², broadening to more than 800 km from the coastline (Bianchi et al., 2009). To the north, the Brazilian shelf narrows to around 100-200 km from the coastline. This region is characterized as one of the most energetic regions of the world’s ocean with the confluence of the warm southward-flowing Brazil Current (BC) and the cold Malvinas Current (MC) flowing northward (Piola and Matano, 2001). The extension of the confluence roughly divides the subtropical and subantarctic oceanic gyres in the South Atlantic and might be a hotspot for shelf-open ocean exchange (Guerrero et al., 2014).

This area, In the open-ocean, the South Atlantic is thought to absorb between 0.3-0.6 PgC/year south of 30°S, while acting as a source to the atmosphere north of 30°S (Takahashi et al., 2002). Aside from global open-ocean estimates, only a few local studies were conducted on the continental shelves in this region. The Patagonian Patagonia shelf was characterized as a source of CO₂
to the atmosphere on the inner shelf, and as a sink in the mid-outer shelf (Bianchi et al., 2009). The southeast Brazilian shelf and continental slope were characterized as sources of CO$_2$ to the atmosphere during all seasons (Ito et al., 2005). Such regions are often neglected, or poorly resolved, on relatively coarse global modelling assessments, although they may contribute up to 0.2 PgC/year of global ocean CO$_2$ uptake (Laruelle et al., 2014).

Regional marine biogeochemical models have been used to assess the ocean carbonate system and CO$_2$ fluxes, including the continental margins. For example, along the US east coast, the seasonality of pCO$_2$ was found to be controlled mainly by changes in the solubility of CO$_2$ and biological processes (Fennel and Wilkin, 2009). Along the California coast, biological production, solubility and physical transport (e.g. circulation) were found to be the most influential processes on pCO$_2$ variability, both spatially and temporally (Turi et al., 2014).

In this study we use a regional marine biogeochemical model coupled to a hydrodynamic model to investigate the parameters and processes regulating the variability of ocean surface pCO$_2$ in the southwestern Atlantic Ocean. Our model domain includes the region of the [location of the global node mooring that is soon to be deployed as part of the Ocean Observatories Initiative (OOI) Argentine global node] at 42°S, 42°W (oceanobservatories.org).

We compare modeled surface pCO$_2$ distribution with observations and use the results to investigate the relative importance of the parameters (DIC, temperature, alkalinity and salinity) and processes (biological production, air-sea CO$_2$ flux, CO$_2$ solubility and physical transport) in controlling surface pCO$_2$ distribution and variability on the continental shelf and open ocean in the southwestern Atlantic Ocean.

2 Materials and Methods

2.1 Model

The physical model used in this study is the Regional Ocean Modeling System (ROMS) (Shchepetkin and McWilliams, 2005). Our model domain spans from 15°S to 55°S, and from 70°W to 35°W, i.e., covering the southwestern Atlantic Ocean. It spans from its subtropical to subantarctic oceanic regions (15°S to 55°S) latitudes and from the continental shelves all the way out to the open ocean (70°W to 35°W). The horizontal grid resolution is 9 km, with 30 vertical levels with increasing resolution towards the surface.
The biogeochemical model is an NPZD type, including the following state variables: phytoplankton, zooplankton, nitrate, ammonium, small and large detritus, and a dynamic chlorophyll to carbon ratio for the phytoplankton (Gruber et al., 2006). A carbon component is also coupled to the model, with the addition of calcium carbonate, $DIC$ and alkalinity to the system of state variables (Gruber et al., 2011; Hauri et al., 2013; Turi et al., 2014). Parameters utilised in the biogeochemical model are listed in Table 2 of Gruber et al. (2006), and the $CaCO_3$ parameters as in Hauri et al. (2013). These parameters represent phytoplankton types with large nutrient requirements and relatively fast growth rates, usually large organisms (Gruber et al., 2006). Since our domain encompasses several ecological provinces (Gonzalez-Silvera et al., 2004), we may not represent all regions equally well with only one phytoplankton functional type.

The initial and boundary conditions used for the physical variables were obtained from a climatology of the Simple Ocean Data Assimilation (SODA) (Carton and Giese, 2008), and for the biogeochemical variables from a Community Earth System Model (CESM) climatological model product (Moore et al., 2013). The model is forced at the surface with climatological winds from QuikSCAT (Risien and Chelton, 2008) and heat and freshwater surface fluxes from the Comprehensive Ocean-Atmosphere Data Set (COADS) (Da Silva et al., 1994). We used a fixed atmospheric $pCO_2$ of 370 $pCO_2$ atm without $CO_2$ incrementation throughout the years and without seasonal variations. Starting from rest we ran the model for 8 years and used a climatology from years 5 through 8 for our analyses.

Since we are mostly concerned with climatological analysis, we chose not to represent processes such as river run off and tides, which can be locally important. Nevertheless, the Even though some processes as river runoff and tides are locally relevant (i.e., la Plata River, and Patagonia shelf), we are not considering them in the present study (see conclusions section). The low salinity waters from the La Plata river are indirectly included as the model nudges to climatological salinity values in the region. However, our model does not include river inputs of carbon, which is known to be an important factor regulating $CO_2$ in the climatological forcing from COADS which are "nudged" into the model. These shortcomings may affect the results in some regions, but it is unlikely that they will affect the overall $pCO_2$ (Bauer et al., 2013). The lack of tides may adversely affect our model results in the inner shelf of Patagonia, where tidal amplitudes reach up to 12 meters at some points (Kantha, 1995; Saraceno et al., 2010) and tidal fronts are known to impact oceanic $pCO_2$ (Bianchi et al., 2005). Despite these local shortcomings our model results should not be significantly affected in the overall climatological estimates of the parameters and processes controlling $pCO_2$ in our domain. These processes will be implemented in future studies results in the wider domain.
2.2 Analysis

Ocean surface $pCO_2$ is the most important variable determining the air-sea $CO_2$ flux. This is because the variability of ocean $pCO_2$ is much greater than that of atmospheric $pCO_2$, and variations in the gas transfer coefficient are usually several times smaller than those of surface ocean surface $pCO_2$ (Takahashi et al., 2002). Seawater $pCO_2$ is regulated by the concentration of dissolved inorganic carbon (DIC), alkalinity (ALK), temperature ($T$) and salinity ($S$). While $T$ and $S$ are controlled solely by physical factors, DIC and ALK are affected both by biological production and physical transport. DIC concentration is also affected by air-sea $CO_2$ fluxes (Sarmiento and Gruber, 2006).

In our model, surface ocean surface $pCO_2$ is calculated through a full model implementation of the seawater inorganic carbon system, i.e., as a function of the state variables $T$, $S$, DIC, and ALK, with the dissociation constants $k_1$ and $k_2$ from Millero (1995). In order to assess the impact of different parameters on $pCO_2$ variability, we decompose $pCO_2$ with respect to $T$, $S$, DIC and ALK, following the approach of Lovenduski et al. (2007); Doney et al. (2009); Turi et al. (2014); Signorini et al. (2013),

$$\Delta pCO_2 = \frac{\partial pCO_2}{\partial DIC} \Delta DIC^* + \frac{\partial pCO_2}{\partial ALK} \Delta ALK^* + \frac{\partial pCO_2}{\partial T} \Delta T + \frac{\partial pCO_2}{\partial FW} \Delta FW$$  \(1\)

where the $\Delta$'s are anomalies, either spatial or temporal, relative to a domain or an annual mean, respectively. $DIC^*$ and $ALK^*$ are the variable concentrations normalized to a domain-averaged surface salinity of 34.66. Therefore, effects from dilution of DIC and ALK through freshwater input are not included in $DIC^*$ and $ALK^*$ terms. The dilution effect is considered instead in the freshwater component (FW) is calculated in order to include the effects of precipitation and evaporation on DIC and ALK concentrations.

The partial derivatives were calculated following Doney et al. (2009). $pCO_2$ was recalculated four times adding a small perturbation to the spatial, or temporal, domain average for each variable ($T$, $S$, DIC, ALK) while maintaining the other 3 variables fixed to the domain averaged surface values.

The perturbation applied here was 0.1% of the domain mean.

In order to investigate the parameters and processes controlling $pCO_2$ on the continental margin, we limited our temporal analysis to three regions with depths shallower than 1000 m: the Southeast Brazilian Shelf (SEBS) in the northern part of the domain, the South Brazilian Shelf (SBS) in the
middle of the domain that encompasses the Uruguayan Shelf, and the Patagonian Patagonia Shelf (PS) to the south of the domain (Fig.1a). We also selected two open ocean regions for comparison with the continental shelves: a subtropical (ST) and a subantarctic (SA) region (Fig.1b). In each of these regions, we estimated the monthly contribution of each parameter to the modeled $p$CO$_2$ variability by spatially averaging the parameters within each region, and using the temporal anomalies (subtracting the annual average) on Eq. 1. For the spatial analysis, we used the whole study area and then calculated in each grid cell the spatial anomalies (subtracting the domain mean of that grid cell), finally applying it to Eq. 1.

In order to identify the main processes responsible for the variability of surface $p$CO$_2$, we used a progressive series of sensitivity experiments as in Turi et al. (2014), focusing on the processes of biological production, CO$_2$ solubility, air-sea CO$_2$ fluxes, and physical transport. To quantify these processes, we made three additional model runs, progressively excluding each process. In the first experiment (E1), we set the CO$_2$ gas exchange flux coefficient between the atmosphere and the ocean to zero, inhibiting gas exchange in the surface layer. In the second experiment (E2), we started from E1 and also turned off the photosynthetic available radiation (PAR), preventing phytoplankton growth. Finally, in experiment E3, the CO$_2$ solubility was set to a constant value, calculated with the domain-averaged surface salinity and temperature of 34.66 and 12.33 $^\circ$C, respectively, while maintaining the changes of E1 and E2. The control run minus E1 represents the impact of gas exchange between ocean and atmosphere, E1 minus E2 represents the impact of biology, E2 minus E3 represents the impact of variable solubility. The last experiment (E3), in which there is no air-sea flux, no biology and constant solubility represents the impact of physical transport (Turi et al., 2014).

Given the short model integration times, the vertical gradients in the E3 simulation have not come in to steady-state with the processes. So our physical transport is working on the vertical DIC gradients established by the biological pump. Since the lateral boundary conditions are the same for all experiments, these simulations are therefore only approximations of the impact of each process on $p$CO$_2$. Further, this separation assumes a linear additionality of each process, which is clearly a strong simplification given the non-linear nature of the inorganic carbonate system (Sarmiento and Gruber, 2006). The same spatial and temporal analysis described for the variables (ALK, DIC, T and FW) was also applied for the processes experiments (air-sea CO$_2$ flux, biology, CO$_2$ solubility, physical transport).
3 Model Evaluation and Validation

Model results were evaluated against data from the Surface Ocean CO\textsubscript{2} Atlas (SOCAT) version 2 (Bakker et al., 2013). SOCAT fCO\textsubscript{2} observations were converted into pCO\textsubscript{2} using the set of equations from Körtzinger (1999) and then compared with modeled pCO\textsubscript{2} to assess the overall skill of the model. Due to the paucity of in-situ observations, particularly on the continental shelves, we used monthly climatologies for the comparison. The seasonal model evaluation was made over the whole domain (Fig.1). On the Patagonia Shelf, data from the Argentinian cruises ARGAU and GEF3 were used for a more focused comparison of the model results (Bianchi et al., 2009). For the Brazilian continental shelves no data were found for local comparisons.

Overall, our model represents reasonably well the seasonality of ocean surface pCO\textsubscript{2}, with the latitudinal and cross-shelf gradients represented during all seasons (Fig.2). Since our simulation has a fixed atmospheric pCO\textsubscript{2} of 370 \textmu atm, this value separates the source from the sink regions. In the northernmost oceanic region, between 16°S and 30°S, the observations show pCO\textsubscript{2} close to 370 – 380 \textmu atm. Therefore this region acts as a weak source of CO\textsubscript{2} to the atmosphere. This tendency is well captured by the model, particularly during summer and autumn. From 30°S to 55°S, the whole offshore region acts as a CO\textsubscript{2} sink, with pCO\textsubscript{2} ranging from 250 \textmu atm to 350 \textmu atm during all seasons in the model results. The observations show the same pattern down to 50°S. However in the southernmost region the observed pCO\textsubscript{2} rises to values close to 400 \textmu atm. On the Southeast Brazilian Shelf, there were no data for model evaluation, but the overall behaviour of pCO\textsubscript{2} agrees with previous results from Ito et al. (2005), who suggested that the continental shelf in this region acts as a source to the atmosphere from inner to outer shelf across both inner and outer shelves during all seasons. The southernmost and northernmost regions are where our model has the largest biases, underestimating the ocean surface pCO\textsubscript{2}. These biases could be due to a variety of reasons, including the high variability of the Antarctic Circumpolar Current and/or proximity to the model boundary with potential biases in the lateral boundary conditions used to force the model.

On the Patagonia Shelf the model was evaluated using in-situ observations from Bianchi et al. (2009) during the years 2000 to 2006 (Fig.3). The model agrees very well with the seasonality of the observations of this shelf region, in particular the high pCO\textsubscript{2} values along the inner shelf, characterizing these regions as which make these regions a source of CO\textsubscript{2} during all seasons, but more intense during autumn/winter (Fig.3 b,c,f,g). In the mid-outer shelf the ocean generally acts as a sink, while to the north the ocean is in equilibrium with the atmosphere particularly during winter.

The monthly analysis was restricted to three offshore areas (A1, A2 and A3 in Fig.4a). We compared the spatial monthly mean modeled surface pCO\textsubscript{2} with the monthly average of the SOCAT
$p$CO$_2$ data available in each area. Within these areas, we applied the following statistical indicators used in Dabrowski et al. (2014) in order to quantitatively assess model skill: model efficiency ($ME$), $ME = 1 - (\sum (O - M)^2)/(\sum (O - \bar{O})^2)$ (Nash and Sutcliffe, 1970), cost function ($CF$), $CF = (\sum |M - O|)/(n\sigma_O)$ (Ospar et al., 1998) and percentage of bias ($PB$) ($PB = |(\sum (O - M))/100|/\sum O$) (Allen et al., 2007), where $M$ stands for modeled $p$CO$_2$ and $O$ for observations from SOCAT database, $n$ is the number of observations and $\sigma_O$ is the standard deviation of all observations. These statistics are indicators of the model’s performance and provide complementary information of the model skill (Dabrowski et al., 2014). Basically, ME relates model error with observational variability, CF is the ratio of mean absolute error to standard deviation of observations, and PB is the bias normalized by the observations (Dabrowski et al., 2014; Stow et al., 2009). Basically if $ME > 0.5$, $CF < 1$ and $PB < 20$, indicate that the model is “excellent/good/reasonable” when comparing to observations. If $ME < 0.2$, $CF > 3$ and $PB > 40$ the model is classified as “poor/bad”.

Modeled $p$CO$_2$ results for A1 agree very well with the observations, representing the $p$CO$_2$ evolution throughout the year with maximum values in summer (Fig.4b). All statistical indicators characterized the model with a good/reasonable skill in A1 (Table 1).

A2 is the region with the largest $p$CO$_2$ standard deviation from both model and observations (Fig.4c). This region is near the confluence between the warm Brazil Current and the cold Malvinas Current, generating one of the most energetic regions of the world’s oceans. Moreover, this region comprises the shelfbreak front, with differences in stratification, local dynamics and salinity between shelf waters and Malvinas current waters (Fig.2a). Consequently, ME was estimated as poor/bad in this region, probably due to the high $p$CO$_2$ data variability. But CF and PB were both rated as “good/reasonable/good” (Table 1).

In A3 the model consistently underestimated $p$CO$_2$ (Fig.4d). This bias is seen in the seasonal comparison and in the monthly analysis, where summer is the only season for which modelled/modelled $p$CO$_2$ is within the standard deviation of the observations. ME was estimated as poor/bad in A3, but PB and CF rated our model as reasonable and good, respectively. (Table 1). Both A2 and A3 regions are close to an area of elevated eddy kinetic energy (Fig.4a), which could explain the large standard deviation and biases in these regions.

The Taylor diagram is consistent with the model efficiency (ME) estimate, showing good/reasonable results in A1, with a correlation of 0.8, and poor results in A2 and A3, with negative correlations (Fig.5). Only in A1, the correlation was found to be statistically significant. Aside from greater $p$CO$_2$ variability in these regions, the poor results found in A2 and A3 could also be due to the paucity of
the observational data both in space and time.

Furthermore, in order to validate the baseline of our model, seasonal climatologies of modeled sea surface temperature and chlorophyll-a were compared with climatologies from AVHRR and MODIS-aqua, respectively. Results and a detailed discussion of this validation are shown in the appendix.

In conclusion, our model reproduces satisfyingly the most important north-south and inner-outer shelf gradients seen in the \( p\text{CO}_2 \) observations. We now proceed to estimate the While there is clearly room for improvement, we deem this level of agreement as sufficient for proceeding to the analysis of the processes and parameters affecting \( p\text{CO}_2 \) variability in this region.

4 Results and Discussion

4.1 \( p\text{CO}_2 \) drivers - spatial analysis

Modeled \( p\text{CO}_2 \) spatial anomalies relative to the domain average are shown in Fig.5a, with positive anomalies prevailing on the Brazilian continental shelves, inner-mid Patagonia Shelf and North of \( 32^\circ \)S, while the negative anomalies are found in the open ocean south of \( 32^\circ \)S and in the mid-outer Patagonia Shelf. \( DIC^* \) has the highest impact on the spatial variations, being counteracted by \( ALK^* \) and \( T \). (Fig.5 Fig.6). In contrast, the fresh water flux has a minor influence on the spatial anomalies of \( p\text{CO}_2 \), agreeing with Turi et al. (2014) and Doney et al. (2009). After \( T \) and \( DIC^* \), \( ALK \) has the larger Even though with a smaller role, \( ALK^* \) influence on \( p\text{CO}_2 \) anomalies with presented absolute values higher (\(-100\) to \(100 \mu\text{atm}\)) than previous studies in other regions (Lovenduski et al., 2007; Turi et al., 2014). The higher contribution of both \( DIC \) and \( ALK \) to the spatial variations in \( p\text{CO}_2 \) could be explained by the more heterogeneous domain that encompasses several distinct surface water masses and frontal zones. Also, the elevated contribution of \( ALK \) \( ALK^* \) could be due to our relatively high \( Ca\text{CO}_3 \) to biological production ratio of \(0.07\).

The changes in the state variables affecting \( p\text{CO}_2 \) are ultimately being driven by physical and biogeochemical processes, we thus investigate which of these processes control. We investigate the role of each of these processes in controlling the changes in surface \( p\text{CO}_2 \) from our sensitivity experiments (E1, E2, E3). The most important processes affecting the spatial distribution of \( p\text{CO}_2 \) spatial distribution are biological production (E1 - E2) and physical transport (E3) (Fig.6.7). When physical transport (vertical and horizontal) is the only process altering \( p\text{CO}_2 \), we observe an increase in \( p\text{CO}_2 \) of up to \(800 \mu\text{atm} \) on the continental shelves, due to the upwelling and vertical mixing
of DIC-rich subsurface waters. At the same time, the effect of biological production on the uptake of DIC and changes in ALK due to nitrate uptake and production/dissolution of \( \text{CaCO}_3 \) accounts for a decrease of up to \(-600\mu\text{atm} \) on the continental shelves. Solubility effects (E2 - E3) are responsible for a decrease in \( p\text{CO}_2 \) south of \( 45^\circ\text{S} \) and an increase in \( p\text{CO}_2 \) to the north, ranging from \(-50\mu\text{atm} \) to \( 50\mu\text{atm} \). Finally, air-sea \( p\text{CO}_2 \) fluxes (Control - E1) have little impact on regulating the ocean surface \( p\text{CO}_2 \). The effect of both biological production and physical transport is maximal on the continental shelves, with the balance between these processes largely controlling \( p\text{CO}_2 \). In the open ocean, physical transport largely controls \( p\text{CO}_2 \), again being counteracted by biological production. North of \( 45^\circ\text{S} \), biological production is being counteracted by physical transport and solubility, whereas to the south of \( 45^\circ\text{S} \) physical transport is being counteracted by biological production and solubility.

The strong effect of biological production on the shelf region is a result of the elevated nutrient supply and high primary production found in these regions, with increasing contribution towards the inner shelves. Physical transport presents a higher contribution on the continental shelves, where the mixed layer often spans the entire water column, showing the importance of vertical mixing in bringing metabolic DIC as well as nutrients to the surface waters, therefore increasing \( p\text{CO}_2 \). These results are in agreement with previous studies (c.f. Turi et al. (2014)), showing the importance of the biological net community production and advection of ALK and DIC (physical transport) in controlling ocean surface \( p\text{CO}_2 \). This suggests a major role of net community production in reducing ocean \( p\text{CO}_2 \) in the region.

### 4.2 \( p\text{CO}_2 \) drivers - temporal analysis

In order to identify the seasonal variability of the contribution of each parameter, we used local grid temporal anomalies over the seasonal cycle (Fig. 7, 8). DIC* and \( T \) are still the most influential parameters, with increasing importance on the continental shelves. The contribution by ALK* appears is relevant only on continental shelves south of \( 32^\circ\text{S} \), and FW have a minor influence (not shown). It is important to highlight that the magnitude of the signals seen in this analysis is one order of magnitude smaller than the previous spatial analysis. Thus, the high absolute contributions found in the spatial analysis are This is likely due to our large and heterogeneous domain, which results in much spatial gradients than what is modeled over the seasonal cycle.

The contribution of the state variables in each continental shelf region (Fig. 8, 9) shows that these three regions have distinct characteristics, with different contributions from each parameter. In all three regions, DIC* and \( T \) are the most important parameters affecting \( p\text{CO}_2 \) anomalies, albeit with opposing and seasonally varying contributions. While in summer the \( T \) contribution increases...
$pCO_2$, that of $DIC^{*}$ acts to diminish $pCO_2$. The opposite occurs in winter. The Southeast Brazilian Shelf (SEBS) is the region with the least variability in $pCO_2$ anomalies, with the contributions of both $DIC^{*}$ and $T$ in this region ranging from $-10 \mu atm$ to $10 \mu atm$ to $10 \mu atm$.

The South Brazilian Shelf (SBS) is the region with the largest variability in $pCO_2$ anomalies, with $ALK^{*}$ having the most prominent impact on $pCO_2$ when compared to the other regions - up to $15 \mu atm$ in spring. $DIC^{*}$ is the most important parameter in this area, with a contribution of up to $70 \mu atm$, followed by temperature, with a contribution of up to $60 \mu atm$ in the winter. On the Patagonia Shelf (PS) and South Brazilian Shelf (SBS), although the amplitude of the contributions by $DIC^{*}$ and $T$ are large, the tendency of these two terms to cancel each other out results in smaller $pCO_2$ anomalies. In both SBS and PS, $pCO_2$ is predominately controlled by $T$ and $DIC^{*}$, with small contributions from ALK and FW.

Seasonal warming/cooling is largely controlling $pCO_2$ anomalies signals throughout the continental shelves, only being dampened by $DIC^{*}$, and also by $ALK^{*}$ in the case of the South Brazilian Shelf (SBS). This pattern of seasonal variation of the parameters on continental shelves agrees with the results from Signorini et al. (2013); Turi et al. (2014), although with different absolute values. Also the The pattern of diminishing variability towards subtropical continental shelves is also shown by Signorini et al. (2013).

This pattern of opposing contributions of $T$ and $DIC$ was also found along the North American east coast by Signorini et al. (2013), who attributed winter mixing and the spring-summer biological drawdown as the processes responsible for $pCO_2$ and $DIC$ variability. In the offshore subtropical region (ST) the $pCO_2$ anomalies have higher amplitude than in the adjacent continental shelf (SEBS), and are driven mainly by Temperature, with the other variables having minor contributions (Fig. 10, 11). In the offshore southern region (SA), $DIC^{*}$ controls $pCO_2$ variability, with $T$ and $ALK-T$ and $ALK^{*}$ dampening $pCO_2$ anomalies (Fig. 9, 10), similar to the adjacent shelf (PS).

The analysis of the processes underlying this seasonal variability using our progressive sensitivity simulations shows that on all shelf regions, biological production and $CO_2$ solubility mostly control $pCO_2$ variability (Fig. 9, 10). Physical transport, although weaker than biological production, acts to diminish the $pCO_2$ variability by counteracting the effects of biology and increasing $DIC$ concentrations. In our case, physical transport controls $pCO_2$ spatially, but the temporal effects of physical transport are much weaker than in Turi et al. (2014) along the California coast. This is probably because the much stronger upwelling in that region acts to dampen the effects of biology by bringing $DIC$ rich waters to the surface. Along western boundaries, upwelling is weaker and
more localized. Physical transport is therefore more related to processes that modulate vertical mixing and stratification, thereby controlling the seasonal enrichment of surface waters, and horizontal advection due to the presence of two major western boundary currents. Finally, air-sea CO₂ fluxes are only a minor contribution to the $pCO_2$ anomalies.

In conclusion, on the Patagonia Shelf (PS), the biological production is the most important contributor to $pCO_2$ variability, with a peak summer contribution of $-80\mu atm$ and a maximum in the winter of $70\mu atm$. On the South Brazilian Shelf (SBS), solubility is the most influential process (up to $90\mu atm$), followed by biological production and physical transport, during all seasons. On the Southeast Brazilian Shelf (SEBS), the pattern is the same as in the SBS, although with a smaller magnitude and variability. Physical transport, although large in absolute contributions in the spatial analysis, has a lower contribution to $pCO_2$ variability in the temporal analysis.

In the subtropical region, processes that control $pCO_2$ variability of $pCO_2$ on the shelf and offshore are different. In the open ocean (ST) (Fig.10) $pCO_2$ is mainly controlled by solubility, with the biological production having the least effect on $pCO_2$. This contrasts with the importance of biology on mid/low latitude continental shelves (SEBS). In the subantarctic region, the processes controlling $pCO_2$ are similar for both the offshore region (SA) and the adjacent continental shelf (PS) (Fig.9). In this case biological production is the most important process being countered mainly by solubility, although with a smaller magnitude in the offshore region.

### 4.3 Air-sea CO₂ fluxes

On the continental margins, we investigate monthly averaged air-sea CO₂ fluxes on the inner shelf (0-100 meters depth), mid-outer shelf (100-200 meters depth) and shelf break-slope (200-1000 meters depth). As shown in the previous sections, the inner shelves have a potential to act as a source of CO₂, while the mid/outer shelves tend to act as a sink of CO₂. On the Brazilian shelves (SBS and SEBS) the flux density of CO₂ in the inner shelves is around $0 - 0.5\text{molCm}^{-2}\text{yr}^{-1}$, thus characterizing this region as a weak source. On the mid/outer shelf these regions shift to sinks of CO₂, with a flux density of $1 - 0.5\text{molCm}^{-2}\text{yr}^{-1}$ on the Southeast Brazilian shelf (SEBS). On the mid/outer South Brazilian Shelf (SBS) the sink is slightly stronger with an average flux between $-1.5$ and $-0.5\text{molCm}^{-2}\text{yr}^{-1}$ (Figs. 11a and 11b). The Patagonia Shelf (PS) acts on average as a sink of CO₂, with fluxes larger than on the Brazilian shelves. CO₂ absorption on PS intensifies from the inner shelf ($-1.0 / -0.5\text{molCm}^{-2}\text{yr}^{-1}$) to the outer shelf and continental slope ($-2.0 / -4.0\text{molCm}^{-2}\text{yr}^{-1}$) (Fig. 11c).

Although, PS acts on average as a sink throughout the whole continental shelf, there are some coastal
regions that act as a source of CO₂, which agrees with the observations of Bianchi et al. (2009).

Annual averaged mean modeled air-sea CO₂ fluxes agreed reasonably well with global climatologies in the oceanic regions (not shown) (Takahashi et al., 2002; Landschützer et al., 2014).

South of 30°S, the open ocean acts on average as a sink of atmospheric CO₂, absorbing up to 4 mol C m⁻² yr⁻¹, and the Brazilian shelves act as a weak source of CO₂ (0 to 1 mol C m⁻² yr⁻¹). Nevertheless, we found variability on each continental shelf, with regions on the inner Patagonia Shelf acting as a sink of CO₂ (−1.0 to −1.0 mol C m⁻² yr⁻¹), and regions on the outer Brazilian shelves acting as a sink of CO₂.

4.4 Vertical Structure - Case Study at Argentine OOI Site

Seasonal variations in mixing and stratification control the evolution of the mixed layer depth and consequently the vertical structure of the state variables of the carbonate system. Diapycnal fluxes of DIC and DIC sinks from primary production are important processes regulating ocean surface pCO₂ (Rippeth et al., 2014). Therefore, the mixed layer depth is linked with the surface pCO₂ variability.

In order to understand the seasonal evolution of the upper ocean vertical distribution of the state variables in the region and how it affects surface pCO₂, we chose the location of the Ocean Observatory Initiative (OOI) site in the Argentine Basin at 42°S, 42°W (Fig. 1a), as it will soon become a test-bed for the validation of biogeochemical models globally and regionally. We extracted modeled climatological vertical profiles of DIC concentration, temperature and chlorophyll-a, and compared with the modeled surface pCO₂ and mixed layer depth (Fig. 12). During the entire year, this location acts in our model as a sink for atmospheric CO₂, with modeled surface pCO₂ ranging from 280 μatm to 320 μatm. The contribution of DIC* and T are again driving surface pCO₂ anomalies. In this case DIC* is controlling the anomalies signal, being dampened by temperature. The main processes affecting pCO₂ in this location is biological production and solubility. Minimum pCO₂ in summer coincides with strong stratification and elevated subsurface biological production, respectively, with the opposing contribution of DIC* and T leading to pCO₂ anomalies near zero. Maximum pCO₂ occurs when the mixed layer depth deepens, during fall and winter, when vertical mixing cause an increase in
the concentration of DIC in the surface waters. This affects $pCO_2$ much more than the decrease in temperature, resulting in positive $pCO_2$ anomalies. After winter, this excess of DIC is consumed by biological fixation during spring and summer, thus reducing surface $pCO_2$.

5 Conclusions

In this study, we used a regional hydrodynamical model coupled with a biogeochemical model to investigate, in a climatological sense, the main parameters and processes that control ocean surface $pCO_2$ and air-sea $CO_2$ fluxes in the southwestern Atlantic Ocean. Modeled ocean surface $pCO_2$ compared well with the available in-situ data, reproducing the expected meridional and cross-shelf gradients of $pCO_2$, with elevated $pCO_2$ in the inner shelves and at lower latitudes. Our results highlight that the most important variables controlling the spatio-temporal variability of $pCO_2$ are $T$ and DIC. These two variables have opposing effects on $pCO_2$ and have been shown to be the main drivers of $pCO_2$ both in global (Sarmiento and Gruber, 2006; Doney et al., 2009) and in other regional studies (Turi et al., 2014; Signorini et al., 2013; Lovenduski et al., 2007). Following DIC and $T$, we found that $ALK$ is a secondarily important spatial regulator of $pCO_2$, with increasing importance on the South brazilian Shelf (SBS) and in the southern open ocean region (SA).

The most important processes underlying changes on the state variables and thus on $pCO_2$ are biological production and $CO_2$ solubility. Biological production is particularly important on the continental shelves, with higher contribution in shelf regions at high latitudes. In the open ocean, $CO_2$ solubility is the main process driving $pCO_2$ variations in the subtropics, while in the subantarctic both $CO_2$ solubility and biological production are important drivers of $pCO_2$ variability.

The southwestern Atlantic Ocean acts, on average, as a sink of atmospheric $CO_2$ south of 30°S, and is close to equilibrium to the north. In the inner continental shelves the ocean acts either as a weak source or is in equilibrium with the atmosphere. To the outer shelf the ocean shifts changes to a sink of $CO_2$. The entire Patagonian shelf acts, on average, as a sink, but there are some particular regions in the inner shelf that acts as a source of $CO_2$. The total integrated flux agrees well with Laruelle et al. (2014), particularly on the Brazilian Shelves (SEBS and SBS). However, in the Patagonia Shelf (PS), we found a slightly stronger sink on the mid/outer Patagonian Shelf (−1.0 to −3.0 molCm$^{-2}$yr$^{-1}$) and more variability towards the inner shelf.

Modelling studies. Our model does not include river inputs of carbon, which are known to be an important factor regulating $pCO_2$ (Bauer et al., 2013). The lack of tides may adversely affect
our model results in the inner shelf of Patagonia, where tidal amplitudes reach up to 12 meters at some points (Kantha, 1995; Saraceno et al., 2010) and tidal fronts are known to impact oceanic pCO₂ (Bianchi et al., 2005). In future regional studies focused on the Patagonia shelf, tides and river run-off should be included.

Modeling studies such as this one depend heavily on in-situ observations, the lack of which hampers our ability to properly refine our model. This will certainly be improved by future efforts of data assimilation of vertical profiles of biogeochemical and physical variables from the OOI site at the Argentine basin. In future studies we will also add tides and river run-off to the model, hopefully diminishing the biases in the southernmost and La Plata regions. However, this study is a first step in understanding the processes controlling surface pCO₂ in an undersampled, yet highly important, region of the world’s ocean. Improved understanding of the processes controlling the surface distribution of pCO₂ on continental shelves and in the open ocean is fundamental for quantifying the ocean’s response to and its feedback on climate change.

Appendix A: Model Validation (SST and Chlorophyll-a)

Seasonal climatologies of 4 years of modeled sea surface temperature and chlorophyll-a concentration were compared with climatologies from the sensors AVHRR (1985-2002) and Modis-aqua (2003-2013), respectively (Figs. 13 and 14 and 15). Modeled sea surface temperature compared well with AVHRR (Fig. 13 and 14) representing both subantarctic and subtropical oceanic regions during all seasons.

Modeled chlorophyll-a concentration reproduces the general pattern from MODIS-aqua (Fig. 14 and 15), with low concentrations in the oceanic regions and higher concentrations on the continental shelves. However, modeled chlorophyll-a concentrations are overestimated in the oceanic open ocean regions (0.5 mgChla-am⁻³/mgChla-am⁻³), especially in the spring season (up to 1 mgChla-am⁻³/mgChla-am⁻³). In the coastal regions, we underestimate chlorophyll-a on the Patagonia Shelf during spring and summer seasons. Expectedly, there was an underestimation in the La Plata region, since we are not modeling the nutrient and organic loads from the river. Finally, on the Brazilian shelf our model overestimates chlorophyll-a, particularly during summer and spring seasons. These biases may be due to our application of a relatively simple ecosystem model with only one phytoplankton functional type in such a wide region, which encompasses several ecological provinces. Nevertheless, the general pattern is well reproduced in this first effort in modeling the biogeochemistry of the southwestern Atlantic Ocean, and the biases may not significantly compromise our analysis of
drivers and processes of $p$CO$_2$ variability.

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References


Moore, J. K., Lindsay, K., Doney, S. C., Long, M. C., and Misumi, K.: Marine ecosystem dynamics and biogeochemical cycling in the Community Earth System Model (CESM1 (BGC)): Comparison of the 1990s with the 2090s under the RCP4.5 and RCP8.5 scenarios, Journal of Climate, 26, 9291–9312, 2013.


Parameters of the biogeochemical model as in Gruber et al. (2006) Parameter Value units

Seawater light attenuation 0.04 m⁻¹ Chl-a light attenuation 0.024 m⁻¹ (mgChl[m⁻³])⁻¹ Carbon to Nitrogen ratio 0.625

Ratio of CaCO₃ to Cₐ₄ formation 0.07 Dissolution of CaCO₃ 0.0057 day⁻¹ Phytoplankton Half-sat. for nitrate uptake 0.75 mmolm⁻³ Phytoplankton Half-sat. for ammonium uptake 0.50 mmolm⁻³ Phytoplankton linear mortality rate 0.024 day⁻¹ max chlorophyll/carbon ratio 0.0535 mgChla/mgC

Zoo. Grazing rate 0.6 day⁻¹ Zoo. Assimilation efficiency 0.75 Grazing half-sat. for Phytoplankton 1.0 mmolNmmZoo. Mortality rate 0.1 day⁻¹ (mmolm⁻³)⁻¹ Zoo. Basal metab. rate 0.1 day⁻¹ Zoo. Mortality alloc. fract. 0.33 Zoo. Egestion alloc. fract. 0.33 Particle coagulation rate 0.005 day⁻¹ Nitrification rate 0.05 day⁻¹ Nitrification inhibition threshold 0.0095 Wm⁻² Nitrification inhibition half dose 0.036 Wm⁻² Remin. ratio of small detritus 0.05 day⁻¹ Remin. ratio of large detritus 0.01 day⁻¹ Phytoplankton sinking velocity 0.5 mday⁻¹ Small detritus sinking velocity 1.0 mday⁻¹ Large detritus sinking velocity 10 mday⁻¹

Table 1. Statistical indicators of the model skill for surface ocean pCO₂ in the three areas (A1, A2 and A3 - Fig.4). The indicators are: ME (Model Efficiency); CF (Cost Function); and PB (Percentage of Bias). Additionally, showing total bias (µatm), correlation and total number of observations (N) available on each area. Bold values indicate “good/excellent reasonable” model skill when comparing to the SOCAT database.

<table>
<thead>
<tr>
<th>Area</th>
<th>ME</th>
<th>CF</th>
<th>PB</th>
<th>Bias</th>
<th>Correlation</th>
<th>N</th>
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</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.23</td>
<td>0.52</td>
<td>2.88</td>
<td>30.26</td>
<td>0.80</td>
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</tr>
<tr>
<td>A2</td>
<td>-0.18</td>
<td>0.61</td>
<td>4.23</td>
<td>15.0</td>
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<tr>
<td>A3</td>
<td>-4.70</td>
<td>1.83</td>
<td>11.59</td>
<td>40.4</td>
<td>-0.13</td>
<td>40</td>
</tr>
</tbody>
</table>
Figure 1. Areas utilised for the temporal analysis, (a) show the 3 continental shelves (SEBS, SBS and PS) analysed in a map with annual mean ocean surface $pCO_2$. The green circle represents the location of the vertical profile at the OOI site. (b) show the two oceanic regions (ST and SA) in a map with bathymetry.
Figure 2. Seasonal climatology of modeled surface ocean surface pCO$_2$ (first upper row) and observations of pCO$_2$ from the SOCAT database (second lower row). The white separation between red and blue is set to 370 µatm which is the atmospheric pCO$_2$ used in this study. Blue represents a sink of atmospheric CO$_2$ and red a source.
Figure 3. Model evaluation on the Patagonia Shelf (PS) (zoom in from model domain in Fig. 2a). Seasonal climatology of modeled ocean surface $p$CO$_2$ (upper row) and $p$CO$_2$ observations from ARGAU and GEF3 cruises (second lower row) (Bianchi et al., 2009). The white separation between red and blue is set to 370 µatm which is the atmospheric $p$CO$_2$ used in this study. Blue represents a sink of atmospheric CO$_2$ and red a source.
Figure 4. Location of the three areas used for the monthly comparison with SOCAT database (a) in a map with annual averaged mean eddy kinetic energy. In figures (b), (c) and (d), green lines are the modeled monthly mean $p$CO$_2$ and black lines are the monthly mean $p$CO$_2$ from SOCAT. Error bars are two standard deviations.
Figure 5. Taylor Diagram showing the three areas used for comparison with SOCAT observational data. A1 is the only area with statistically significant correlation.
Figure 6. $pCO_2$ spatial anomalies - difference between annual mean and domain mean (a) and the contribution of the main drivers: $ALK^*$ (b), FW (c), $T$ (d) and $DIC^*$ (e). Computed using spatial anomalies for $\Delta$. 
Figure 7. Processes driving the annual mean surface $pCO_2$. Contribution of Air-sea flux of CO$_2$ [Control - E1] (a), CO$_2$ solubility [E2 - E3] (b), physical transport [E3] (c) and biological production [E1 - E2] (d).

Figure 8. Sensitivity of $pCO_2$ computed with grid point anomalies in time to local annual means. Annual average contribution of the main drivers: $ALK^*$ (a), $T$ (b) and $DIC^*$ (c).
Figure 9. Temporal evolution of $pCO_2$ anomalies and their drivers in each continental shelf (right hand side of Eq. 1 using temporal anomalies), red line represents the effects of Temperature, blue line the effects of $DIC^*$, green line FW, and yellow line $ALK^*$. 
Figure 10. Temporal evolution of the monthly anomalies of each process in regulating $pCO_2$ anomalies, green line represents the biological production, red line the physical transport, light blue line the air-sea $CO_2$ fluxes and dark blue line the solubility. Black lines represent the temporal $pCO_2$ anomalies.
Figure 11. Figures (a) and (b) show the temporal evolution of $pCO_2$ anomalies and its drivers in each oceanic regions (ST and SA) (right hand side of Eq. 1 using temporal anomalies), red line represents the effects of $T$, blue line the effects of $DIC$, green line the FW and yellow line $ALK$. Figures (c), and (e) show the temporal evolution of the monthly anomalies of each process in regulating temporal $pCO_2$ anomalies, green line represents the biological production, red line the physical transport, light blue line the air-sea $CO_2$ fluxes and dark blue line the solubility. Black lines represent the temporal $pCO_2$ anomalies.
Figure 12. Figure (a) is the annual average of air-sea CO$_2$ fluxes. Figures (b), (c) and (d) show the monthly average of surface CO$_2$ fluxes constrained to bathymetry levels of 100m, 200m and 1000m.
Figure 13. Vertical profile at 42°S, 42°W: Upper panels showing monthly mean surface $pCO_2$ (solid black line), $pCO_2$ anomalies (dashed black line) and the contribution from the main drivers (Fig. (a) $T$ and $DIC^*$ (red and blue dashed lines)) and the main processes contribution of biology and solubility (Fig. (b) green and cyan dashed lines). Lower panels showing vertical profiles of $DIC$ (a), $T$ (b) and chlorophyll concentration.
Figure 14. Seasonal climatology of modeled sea surface temperature \( ^{\circ}C \) - 4 years average (first upper row), and climatology from AVHRR sensor - from 1985 to 2002 (second lower row).
Figure 15. Seasonal climatology of modeled chlorophyll-a concentration $\text{mg Chl-a m}^{-3}$ - 4 years average (first-upper row), and climatology from Aqua-Modis sensor - from 2003 to 2013 (second-lower row).