

*Interactive comment on “Ocean-atmosphere exchange of organic carbon and CO<sub>2</sub> in the Antarctic Peninsula – physical and biological Controls’*

By

*S. Ruiz-Halpern et al.*

NOTE: Reviewers comments are in italics, authors’ response is in regular font, changes to the text are in quotation marks

*Anonymous Referee #3*

*The authors present a novel dataset on exchangeable dissolved organic carbon (EDOC) and gaseous organic carbon (GOC) measured in seawater and in the overlying atmosphere during three different cruises in the Southern Ocean, close to the Antarctic Peninsula. From these results, the authors determine the air-sea flux of organic carbon comparing it with measurements on CO<sub>2</sub> fluxes. For the region studied and the scarcity of measurements on OC fluxes between the ocean and the atmosphere, the article represents a relevant contribution for the understanding of air-sea carbon fluxes of regional and global relevance. The topic is approached with valid scientific methods and the results represent an important contribution to scientific progress within the scope of this journal. In my opinion, the article deserves publication after some aspects have been intensively revised. I hope my comments will help improving the manuscript.*

We thank the anonymous reviewer for the insightful comments that will help improve the quality and reach of our research

*Specifics In general, I would strongly recommend a language check by a native speaker, as many sentences are extremely long and hard to read. Please try to break down the text in smaller sentences easier to follow.*

We agree, after re-reading the manuscript that there was an excessive use of long, wordy sentences. We have done a thorough revision of style and hope that all reviewers (all reviewers expressed the same concern) are happy with the improvement of our essay

*The abstract needs a style revision.*

The abstract has been re-styled

*In the introduction, I would add some references about the ocean as a potential source of CO<sub>2</sub> given by positive feedbacks of microbial metabolism (e.g. Del Giorgio and Duarte, 2002).*

We agree that we missed to mention this feedback in the introduction. We include the reference provided more background on feedback loops of microbial metabolism, especially in light of OC fluxes

*Since the paper is about OC and CO<sub>2</sub> fluxes, I would also add some sentences on biological control of air-sea gas fluxes in the present ocean acidification scenario.*

We agree that it is a burning issue that warrants being included in the introduction. We mention air-sea gas fluxes in a OA scenario and include appropriate references, even though in the case of OC fluxes it has not been assessed yet.

*Moreover, the role of the SML is neglected. Only in the methods and shortly in the discussion the SML is mentioned but it is a burning issue when considering estimates of gas fluxes across the ocean-atmosphere interface. In particular, how was the SML sampled, and which parameters? Consider checking Liss and Duce, 2005 “The Sea-surface and Global Change”.*

We agree, as pointed out by other reviewers, that we have not paid enough attention to the SML, we now provide a methodological description, and its implications for gas fluxes.

*16176 lines 9-13 and 20-23 very long sentence, consider rephrasing*

*16177 lines 2-4 and 20-25 very long sentence, consider rephrasing*

Sentences rephrased, as well as an overall style check on the English writing.

*16177 line 26: Polar ecosystems are characterized...(I would give a reference there as example).*

Reference provided (Clarke et al. 1996)

*16180: Did you filter the samples for DOC? Which depths were considered for EDOC and DOC?*

| DOC samples were not [filtered](#); they were directly transferred from the niskin bottle to the glass ampoules. While the norm is to filter DOC samples up to a depth of aprox. 200 m, we have found that POC generally accounts to less than 5%, normally 1-2%, and it is negligible. The only station where it could pose a problem is where we found high values of Chl-a (bloom conditions). Yet these are only a station or two. We believe this approach to be a better one, since contamination and artefacts (breaking of cells) during filtration may lead to higher errors. We now discuss this in the methods section

*16185: line 5, specify that the fugacity of CO<sub>2</sub> in surface waters is  $f\text{CO}_2\text{-w}$*

Specified

*16186: lines 5-8: what could be an explanation for this observed trend? and lines 9-12,*

*for figure 4 better give the correlation coefficient and p value anyway.*

R<sup>2</sup> and p-value provided

*Figure 5: would that make sense to give a median value instead of showing an additional figure?*

Table 2 provides all the statistics by cruises and basins, these figure provides a global distribution of EDOC and GOC values for all cruises combined. We include the median value in the legend

*16187: lines 5-7, what about the role of the SML in air-sea gas exchange during breaking waves events? (e.g. Upstill-Goddard 2003, 2006)*

We agree that this was not discussed; we include effects of SML on air-sea gas exchange

*16187: line 14 on, at which depths there was no significant correlation of EDOC with other parameters?*

These relationships were only explored for surface (i.e 5m) samples as we did not have enough samples for comparison at other depths.

*Which could be possible explanations for this observation? What about the correlation of GOC and SML-EDOC (figure 7)?*

There was no relationship between SML-EDOC and GOC, we include this panel in the graph, however, as there was no relationship between 5m EDOC- and GOC either.

*16188: Discussion. Effects of UV on the SML? (e.g., Lechtenfeld et al. 2013)*

We include this reference and discuss the effects of UV on SML

*16189: lines 27-27 please address a possible explanation why you don't see a relationship between krill and Chl a.*

We now speculate on possible reasons for this lack of relationship

*16189: line 20 "Therefore, at a small scale"*

Changed

*16190: lines 5-6. Do you think there could be a high heterotrophic metabolism supporting a positive feedback to atmospheric CO<sub>2</sub>?*

This is a possibility under non-bloom conditions, and this is the likely reason for the above saturation values of  $fCO_2$  in some areas. We include this in our discussion

*Par. 4.3. for OC fluxes, it would be useful to see the different values according to depth. I would also expect some sentences about microbial remineralization of OC.*

The OC fluxes portrayed here are only air-water. As we do not have enough data except for a few profiles, We have not attempted to calculate downward (or upward, as you point out below) diffusion in the water column, except for the tight coupling between SML and EDOC at 5. Unfortunately the profiles were not always performed at the same depths and descriptive statistics (even based on small sample sizes) cannot be performed. However, we include a new table with all profiles performed with the EDOC concentration and depth and we discuss remineralisation of EDOC by microbes.

16191: line 13, figure 7 (not 8).

Changed

16192: line 22 “This dual source-sink” and “suggests”.

changed

*In the last paragraphs of the discussion (4.3 and 4.4), if I understood right, you discuss the downward flux of EDOC by comparing SML-EDOC and 5m-EDOC as if there is a downward diffusion. Did you consider the upward flux of EDOC coming from the water column in areas where high biological activity is supported, reaching the SML and becoming available to be exchanged with the atmosphere?*

Thank you for pointing this out! We now include this as part of our discussion.

*Conclusions*

*What can be major implication of your findings for future ocean scenarios?*

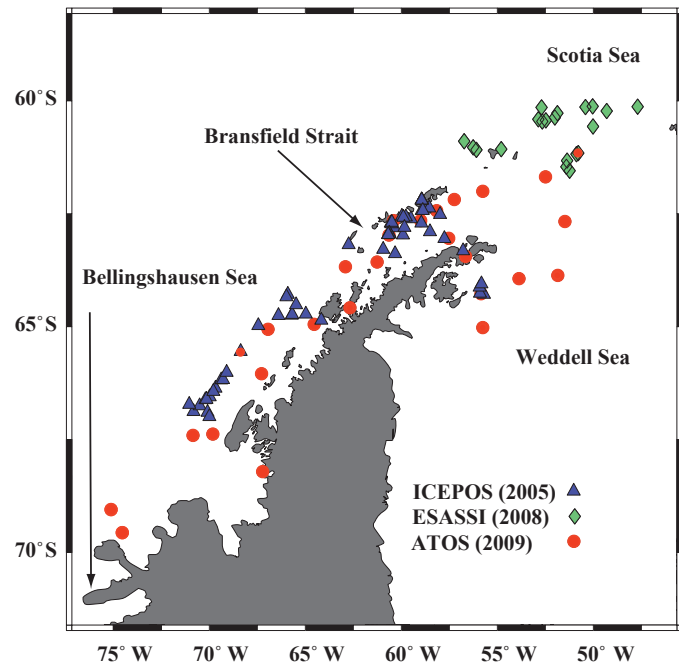
We agree that we have not speculated on the effects on future ocean conditions. We now provide a discussion on the effect of elevated temperatures (decreased solubility, effect on H<sup>+</sup>) ocean acidification (increased  $f\text{CO}_2$  and protonation of volatile compounds) and UV levels (photodegradation of DOC and effect on biota).

We hope that all the changes and improvements made will satisfy the reviewer.

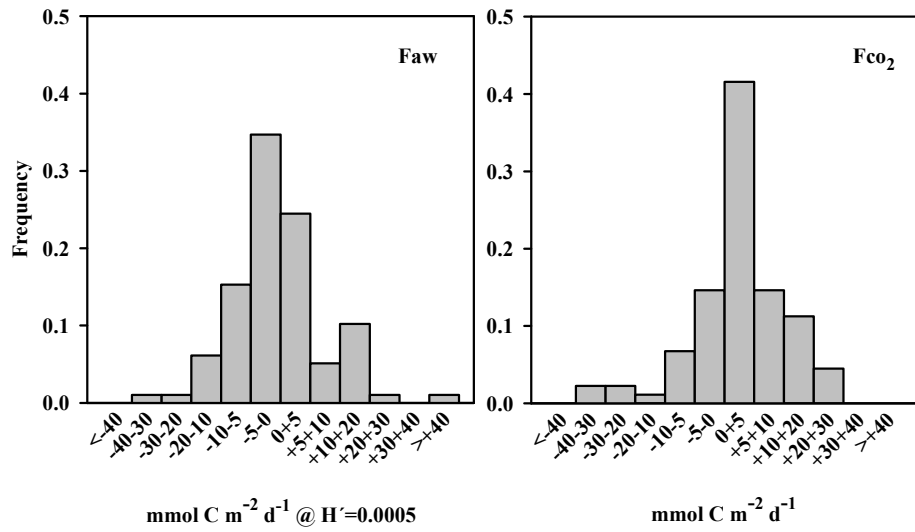
New Table 3. Mean  $\pm$  standard error (s.e), median and ranges for fluxes of organic carbon (Fvol, gross volatilization; Fab, gross absorption; Faw, net OC air-sea water exchange) for three different H' (0.0005, 0.005, 0.05), and CO<sub>2</sub> (F<sub>CO2</sub>) throughout the track of the three cruises, ICEPOS in 2005, ESASSI in 2008, and ATOS-Antarctica in 2009. Data were grouped into cruises and areas. The percentage of stations with undersaturated CO<sub>2</sub>, and OC uptake by the ocean are also shown.

surface	H'	Fvol	Fab	Faw	F <sub>CO2</sub>	CO <sub>2</sub> uptake	OC uptake
cruise		mmol C m <sup>-2</sup> d <sup>-1</sup>	mmol C m <sup>-2</sup> d <sup>-1</sup>	mmol C m <sup>-2</sup> d <sup>-1</sup>	mmol C m <sup>-2</sup> d <sup>-1</sup>	% stations	% stations
<b>ICEPOS</b>	<b>0.0005</b>	11 $\pm$ 2 8[0.3-70]	-10 $\pm$ 1 -8[-28-(-0.6)]	1.4 $\pm$ 2 -1.1[-18-(+60)]			
	<b>0.005</b>	55 $\pm$ 9 37[0.5-395]	-50 $\pm$ 5 -39[-166-(-0.8)]	77 $\pm$ 8 -4.8[-106-(+342)]	1.4 $\pm$ 2 2.3[-39-(+27)]	27	18
	<b>0.05</b>	95 $\pm$ 16 61[0.5-741]	-86 $\pm$ 10 -66[-322-(-0.84)]	14 $\pm$ 15 -6[-207-(+640)]			
<b>ESASSI</b>	<b>0.0005</b>	11 $\pm$ 3 5[0.1-53]	-14 $\pm$ 4 -6[-58-(-2.3)]	-2.5 $\pm$ 2 -0.03[-33-(+12)]			
	<b>0.005</b>	53 $\pm$ 17 25[0.3-285]	-70 $\pm$ 21 -24[-311-(-5)]	-13 $\pm$ 12 -0.07[-170-(+56)]	6.4 $\pm$ 1.7 4.1[-5-(+21)]	10	50
	<b>0.05</b>	87 $\pm$ 31 34[0.5-508]	-118 $\pm$ 37 -33[-553-(-5.5)]	-23 $\pm$ 21 -0.05[-286-(+93)]			
<b>ATOS</b>	<b>0.0005</b>	15 $\pm$ 2 14[0.9-34]	-18 $\pm$ 10 -14[-40-(-3.8)]	-2.6 $\pm$ 1 -2[-21-(+11)]			
	<b>0.005</b>	68 $\pm$ 10 58[3.5-189]	-80 $\pm$ 2 -57[-225-(-16)]	-12 $\pm$ 6 -8[-92-(+43)]	-2 $\pm$ 1.4 0.05[-20-(+13)]	46	88
	<b>0.05</b>	107 $\pm$ 18 84[5-350]	-126 $\pm$ 21 -83[-414-(-23)]	-19 $\pm$ 10 -14[-150-(+60)]			

Basin							
<b>Weddell sea</b>	<b>0.0005</b>	15 ± 3 9[0.1-70]	-14 ± 3 -8[-58-(-2.3)]	1.5 ± 3 0.5[-34-(+60)]			
	<b>0.005</b>	73 ± 17 44[0.4-396]	-68 ± 15 -39[-311-(-5)]	9 ± 17 2.2[-170-(+343)]	-2.1 ± 3 [-39-(+21)]	38	41
	<b>0.05</b>	1234 ± 32 68[0.5-740]	-114 ± 26 -68[-553-(-6)]	17 ± 30 3.3[-286-(+640)]			
<b>Bransfield strait</b>	<b>0.0005</b>	12 ± 1.2 10[0.4-34]	-14 ± 1.3 -13[-40-(-0.6)]	-2.3 ± 1 -1.8[-18-(+14)]			
	<b>0.005</b>	58 ± 7.4 52[0.5-190]	-71 ± 7.4 -57[-224-(-0.8)]	-11 ± 5.2 -7[-106-(+91)]	6.9±1.22 4.2.3(0-23)	0	71
	<b>0.05</b>	100 ± 14 79[0.5 399]	-121 ± 14 -102[-414-(-0.84)]	-17 ± 9.7 -11[-207-(+196)]			
<b>Bellingshausen sea</b>	<b>0.0005</b>	10 ± 2 6.5[1.1-28]	-9 ± 1 -7[-37-(-1.3)]	0.9 ± 2 -1[-19(+18)]			
	<b>0.005</b>	42 ± 7 26[3.6-150]	-39 ± 7 -31[-197-(-3.4)]	3.4 ± 7 -3.3[-92-(+86)]	-1.5±0.78 -1.7[-9-(+6)]	56	55
	<b>0.05</b>	64 ± 12 40[4.6-268]	+62 ± 12 -45[-352-(-4)]	4.2 ± 11 -4[-150-(+140)]			
<b>Total Mean ± s.e</b>	<b>0.0005</b>	12 ± 1	-13 ± 1	-0.3 ± 1			
	<b>0.005</b>	58 ± 6	-61 ± 6	-1.1 ± 6	1.6 ± 1.2	27	58
	<b>0.05</b>	96 ± 12	-102 ± 10	-1.5 ± 10			

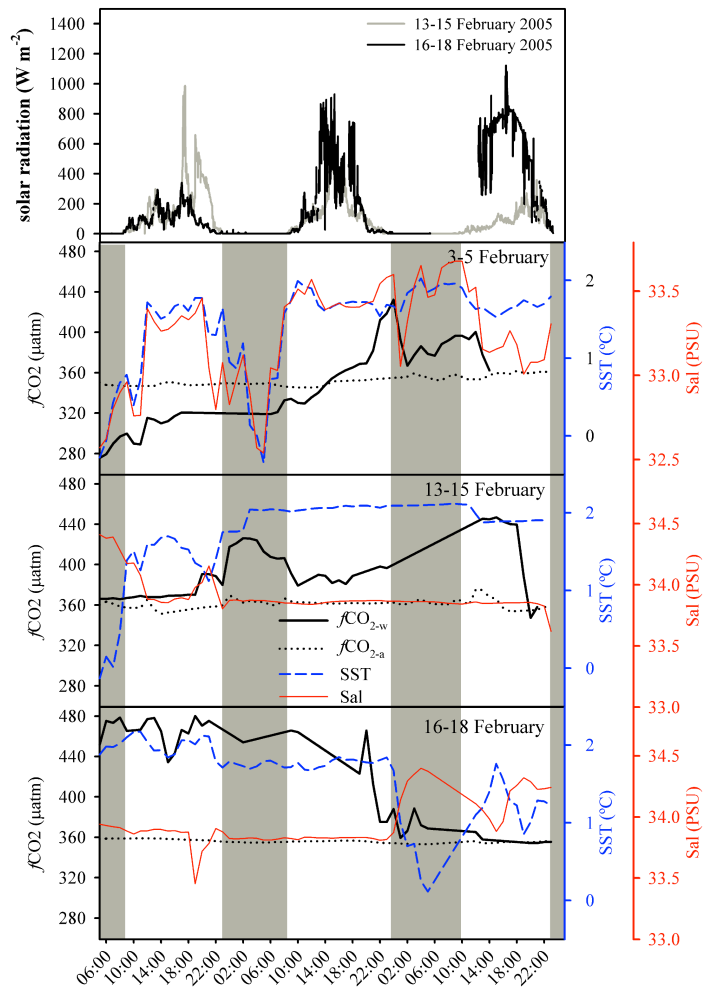


New figure 1. With color coded symbols of the different cruises

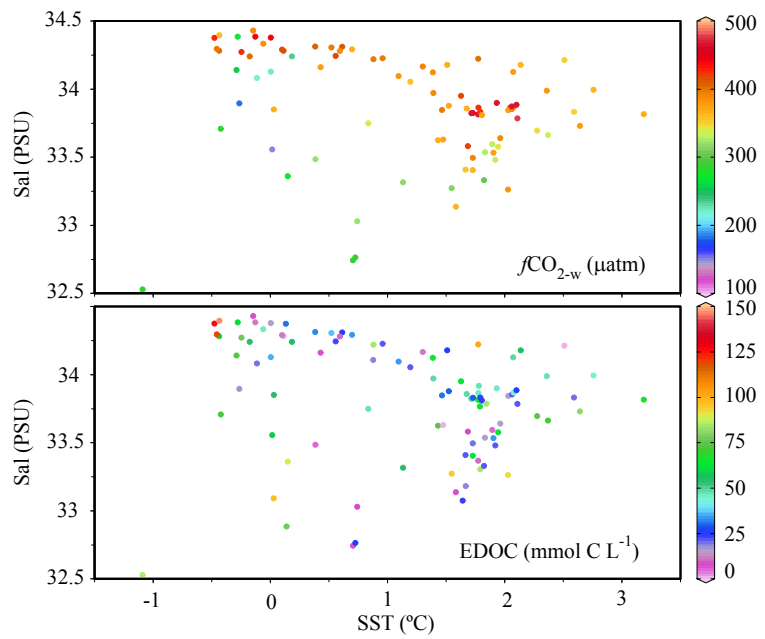


New figure 6 With increased binning and recalculated OC fluxes base don a H'=0.0005

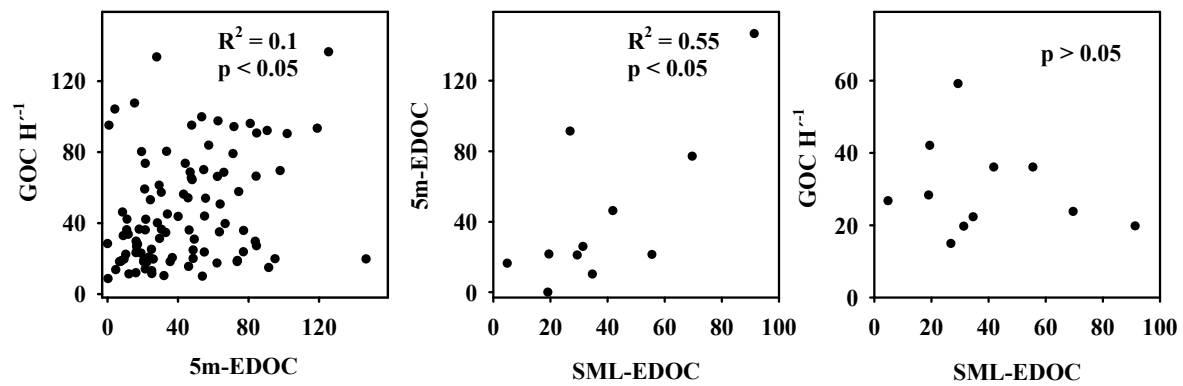




New panel for figure 9 showing diel variability of  $fCO_2$  in water and air as well as salinity and temperature



New figure comparing EDOC and  $f\text{CO}_{2-w}$  ins the T-S space



New figure 7 with extra panel showing the relationship between SML-EDOC and GOC H<sup>-1</sup>