

Interactive comment on

“Ocean-atmosphere exchange of organic carbon and CO₂ in the Antarctic Peninsula – physical and biological controls”

by

S. Ruiz-Halpern et al.

W. Evans (Referee)

Authors: Sergio Ruiz-Halpern et al

NOTE: Reviewer comments are in italics, response to reviewer is in regular font with changes made to the manuscript under quotation marks

Reviewer: Wiley Evans

Ruiz-Halpern et al present a unique and novel data set of exchangeable dissolved organic carbon measurements made in seawater (EDOC) and in the lower atmosphere(GOC) adjacent to the Antarctic Peninsula. They compute sea-air organic carbon fluxes from these data and compare these fluxes to estimates of sea-air CO₂ exchange. There are very few measurements of sea-air OC flux available globally, and for that reason I would recommend this paper for publication following moderate revision. I have described below points I believe will aid the authors in a successful publication.

We thank the reviewer (and referee) for giving us the opportunity to publish our work in Biogeosciences

General Comments:

Given the dynamic nature of the region you have sampled, do you believe the order days of data you have collected well represent the austral summer season as a whole? Did you observe any inter-annual variability? It is hard to follow your discussion of the data because it seems like you are talking about the 3 years collectively. If that is the case, you might consider changing the focus from characterization of the season to specifically to the source/sink nature of the EDOC data. That seems to be the punch line of the paper given these results are very different (i.e. some source regions) from measurements you have made in other regions.

We agree that the Antarctic peninsula is a highly dynamic area, and that a three-four week survey in 3 different years (2005, 2008 and 2009) may not suffice to adequately represent the summer season as a whole. However, getting to Antarctica and working in this harsh environment is not an easy task and we believe that this data set still holds great value in the description of Organic carbon dynamics in the Antarctic peninsula region. We will tone down our seasonal claims and shift our focus towards the source/sink nature of EDOC and its value in redistributing carbon in the environment.

The title of this paper suggests there will be a detailed description of the physical controls on OC and CO₂ fluxes. Other than brief discussion of the winds and its influence on gas exchange, the paper is lacking in the analysis of physical controls and instead focuses on biological controls. Consider revising the title or expanding your discussion

of physical controls.

We agree that not enough discussion on the physical controls is provided. Given the fact that we do not have enough data to provide further insight on the physical aspects, we have removed this claim from the title. The title is now: ““Ocean-atmosphere exchange of organic carbon and CO₂ in the Antarctic Peninsula”. However, we will make our best effort to incorporate a better description of the physical controls (see below)

Specifically, in that regard, how does sea ice melt (and/or glacial melt from the peninsula) impact surface fCO₂ and EDOC concentrations? I understand there might not be data in this set of measurements to resolve sea ice melt contributions, but some discussion should be included. How do fCO₂ and EDOC compare in T/S space? Is there any evidence of upwelling as a driver of fCO₂ and EDOC variability?

We are unable to provide any data on sea ice melt (and or glacial melt) impacts on CO₂ and EDOC, other than what is available in the literature or upwelling controls (for CO₂), but we have plotted CO₂ and EDOC in T/S space to compare and we will provide further discussion. We have added the TS-CO₂ and TS-EDOC as a new figure in the manuscript, which will be discussed in the text.

I found the diel variability very interesting. You should consider comparing fCO₂ diel variability to that of EDOC. How are they related, if at all, and what does this imply of the data collected from broad ship surveys in this region?

We agree that this comparison is warranted, we have included fCO₂ in air and water in the graphs to explore their dynamics and relation to EDOC GOC variability, and its implications for ship surveys

Specific Comments:

“air-sea”, “air-water”, air-seawater”, and “air-sea water” are all used a number of times in this manuscript. Pick one and stick to it throughout.

We agree that this may lead to confusion in the readership, we have fixed this throughout the manuscript

“Indeed” is used a large number of times in the manuscript. Consider trimming the use of this down.

We agree, we will trim down the use of ‘indeed’, as well as majorly revised the style of the manuscript as suggested by all reviewers

Introduction:

Page 16176, Line 26: remove second “neither”

Removed, the text now reads: “...However, there is no inventory of all anthropogenic SOCs neither over the oceanic nor terrestrial atmospheres...”

Page 16177, Line 11: replace “to” with “with”.

Replaced the span gas

Page 16177, Line 15: Consider citing newest IPCC report.

Point taken, we now cite the newest IPCC report

Methods:

Section 2.3: This section needs more clarification. Atmospheric measurements were made every minute? Or do you mean equilibrated air? What was the sample frequency of the seawater data? Fugacity was calculated from $x\text{CO}_2$ (I'm assuming, maybe add an equation?), so why is partial pressure mentioned? How frequently was a calibration sequence run? State that your zero concentration is N_2 and your span gas is 541 ppm.

We agree that we have not provided an adequate description of the methods. The methods describing CO_2 measurements now reads: "...Seawater surface molar fraction of CO_2 ($x\text{CO}_{2-w}$) was also measured at 1 min intervals, and concurrently with atmospheric measurements by circulating water from a depth of 5 m, depth where the intake of the continuous flow-through system of the vessel is located. Water was pumped through a gas exchange column (1.25 x 9 membrane contactor, Celgard) and a closed-loop gas circuit, where CO_2 equilibrates, fitted with an anhydrous calcium sulfate column circulated through the gas analyzer as above. The continuous flow of water and the small volume of air circulating counter-current through the gas exchange column ensured full and rapid equilibration between water and air (Calleja et al., 2005). CO_2 in water and air corresponds to that in dry air ($x\text{CO}_2$). Fugacity of CO_2 in water ($f\text{CO}_{2-w}$) and air ($f\text{CO}_{2-a}$) are calculated by correcting for a 100% water vapor pressure at 1 atm and by applying the virial equation of state (Weiss, 1974) as per the guide to best practices for ocean CO_2 measurements (Dickson et al. 2007). The analyzer was calibrated daily by using a commercial gas mixture of 541 ppm CO_2 and a pure N_2 as the zero concentration..."

Section 2.5: Did you calibration your echosounder data using net samples? Are the chlorophyll and Krill data presented in this manuscript depth integrated (i.e. what are the data shown in Figure 4?)

The echo sounder was not calibrated with net samples. The data is not depth integrated as they are volumetric units (m^3).

Section 2.7: k_{600} needs to be adjusted to in situ SST and salinity (or at least SST since the salinity correction is usually $\ll 4\%$). It isn't clear how you calculate k_0 . Consider adding an equation here.

We agree that we have not given enough information on the methods to calculate F_{CO_2} , we had done the calculations right but we did not properly explain our steps, we have added the equation to adjust K_{600} to in situ conditions. The text now reads: "...Diffusive air-sea water exchange of CO_2 was estimated by using the wind speed dependence of the mass transfer velocity (k_{600}) from instantaneous wind speeds (U_{10} , m s^{-1}) following the expression $K_{600} = 0.222 U_{10}^2 + 0.333 U_{10}$ (Nightingale et al., 2000). The calculation of air-sea water CO_2 flux (F_{CO_2}) used the expression (eq. 1):

$$(1) F_{\text{CO}_2} = K_w \cdot S \cdot \Delta f\text{CO}_2$$

where $\Delta f\text{CO}_2$ is the difference between CO_2 fugacity in the surface of the ocean and that in the lower atmosphere ($\Delta f\text{CO}_2 = f\text{CO}_{2-w} - f\text{CO}_{2-a}$), K_w , the gas transfer coefficient, was normalized to Schmidt number of 600 ($K_w =$

$K_{600} * (600/S_c)^{0.5}$, and S is the CO₂ solubility term, calculated from sea water temperature and salinity (Weiss, 1974)...”

Am I correct in thinking you averaged 1-min FCO₂ data for +/- 30 minutes about the EDOC and GOC measurements to do your comparison? How you center your hourly averages might affect your comparison.

Yes, this is correct, we have clarified that in the text: “...To characterize the stations sampled and to compare CO₂ and exchangeable organic carbon fluxes, hourly averages of SST, Sal, (U_{10}), and fCO_{2-w} , fCO_{2-a} and F_{CO_2} were calculated centered around (+/- 30 mins) the time EDOC and GOC H⁻¹ estimates were collected.
...”

Results section:

In each section are you discussing your results from each cruise collectively? There was no inter-annual variability apparent between 2005 and 2009?

Yes, each section presents the results of each cruise and basin collectively. The 2005 and 2009 were similar in their trajectories, the tables show very little variation in SST, Sal, windspeed and chlorophyll, and a slightly more variable CO₂ and EDOC GOH⁻¹, and fluxes. We will incorporate this aspect more explicitly throughout the results and discussion.

Section 3.1: Include some description of the variation in surface ocean solubility with the discussion of temperature and salinity. Move mention of fluorescence and chlorophyll to Section 3.2.

We agree that we have not paid enough attention to salinity and temperature effects on CO₂ solubility. We have now included a description of the effects of salinity and temperature on solubility and moved fluorescence and chlorophyll to section 3.2

Section 3.2: Line 25: insert “times” following 300-fold.

Inserted

Line 28: delete “Surprisingly”.

Deleted

Section 3.3: Line 8: fCO₂ is not partial pressure.

For an ideal gas, the fugacity is the partial pressure in the atmosphere. Since CO₂ is an ideal gas, the partial pressure in the atmosphere in comparison to atmospheric pressure (1 atm) equals the concentration in ppmv, which are the units used usually for CO₂. However, in order to avoid confusion, we have now removed the term partial pressure throughout the manuscript and only use fugacity.

Line 13: replace “than” with “to”.

Replaced

Solubility had no influence on the variation of FCO₂?

Point taken, as part of the physical controls the solubility (affected by temperature and salinity) does influence variations in FCO₂. However, this effect is through the fugacity of CO₂ in water whose variation is now being described in regards to temperature and salinity. We state this clearly through out the manuscript acknowledging the contribution of temperature and salinity affecting the solubility of CO₂ and hence, the fluxes

Line 17: replace “seem to act ”with “acted”.

Replaced

Page 16186, Line 2: I recommend holding to the convention of uptake being negative fluxes.

Agreed. Another reviewer made the same comment. We have fixed this throughout the manuscript for both OC and CO₂ fluxes

Lines 5-8: consider rewriting this sentence using past tense and replacing the word “prevailed”.

Sentence rewritten in past tense, prevailed has been replaced: “...Only in the western sector of the Antarctic Peninsula, was there a dominance in the number of stations showing a net CO₂ uptake, while CO₂ emissions were found in the Weddell Sea sector of the sampled domain and in Bransfield Strait for all the cruises...”

Lines 9-12: were chlorophyll and krill concentrations depth integrated? If not, perhaps doing this integration would improve the fits.

They have not been depth integrated, we will do the depth integration to see if it will improve the fit

Section 3.4: How was the surface micro-layer sampled? This is not in the methods.

We agree, Another reviewer mentioned that as well, we have now included a description of SML sampling in the methods: “...For the surface microlayer, samples were collected on board a small boat drifting away from the research vessel, using a plate ocean microsurface sampler (Carlson 1982). Briefly, two acid-washed perlex blades (50 cm long x 20 cm wide x 0.3 mm wide) were rinses with surface seawater and gently inserted vertically into the water and removed slowly and the microlayer water attached by surface tension was gently squeezed in between two teflon blades. The water was collected onto an acid-washed teflon bottle and the maneuver repeated until 0.5 were collected, typically after 30 min of two persons working in parallel. When wind speed exceed 20 m s⁻¹, this procedure could not be attempted for safety reasons...”

Section 3.5: The diel EDOC data is fascinating. Was a particular water mass tracked during the collection of these samples? If so, how did you ensure you weren't crossing between water masses during the diel sampling?

We agree that the diel variability is interesting and points to the dynamic nature of VOC and SOC. Unfortunately no particular water mass was tracked during the collection of these samples, and we have no way of ensuring we did/did not cross water masses, or when that occurred. We have now plotted CO₂ diel variation as well which may give an indication of different water masses (as well as SST and salinity) since no real diel pattern was observed.

Discussion:

Line 5: delete “an”.

Deleted

Line 18: replace “form” with “from”.

Replaced

Section 4.2: Sea ice melt plays a large role in shaping surface ocean pCO₂ distributions in this region. Based on Figure 4, it looks like this and other physical-chemical alterations to the carbon system are driving variability well beyond the biological forcings as indicated by chlorophyll and krill concentrations. Please comment on this.

We agree that sea ice melt plays a role in shaping CO₂ distributions that we have somehow neglected. We now comment on the effect of sea ice melt on CO₂ in Antarctic waters

Page 16190, Line 1-2: You could test this by comparing your 1-min (?) data to the hourly average data. You should do this to rule out any possibility that the hourly averages are not capturing short-term large CO₂ fluxes.

We agree, we have now compared the 1-min data to our hourly data and discussed the implications. Further analysis will be run to explore such relationships

“...The range in fluxes when no hourly averaging is performed is widened (Figure3, panel C). There is a maximum emission to the atmosphere of 63.5 mmol m⁻² d⁻¹, a maximum uptake of -151.6 mmol m⁻² d⁻¹ and a mean of -0.3 mmol m⁻² d⁻¹.

As it stands the comparison of OC flux data to CO₂ fluxes is a bit apples-to-oranges given that the methods were not clearly described (how is k₀ calculated?), and have issues (k600), as well as the possibility of temporal mismatch (is your hourly average centered about the EDOC measurements?).

Please refer to the comments to MingXi Yang. We have properly explained our calculations of CO₂ fluxes (we had done the calculations right, just omitted some details and used wrong expressions), and recalculated the OC fluxes based on an air side transfer coefficient, and on 3 different H', to reassess the magnitude of the fluxes and its variation with H'. The hourly FCO₂ data was centered around the EDOC measurements.

Section 4.4: How does the diel variability of EDOC compare to that of fCO₂? Please comment on how this variability could corrupt your interpretation of the source/sink nature of a region depending on when sampling was conducted.

We agree that we have not explored $f\text{CO}_2$ diel variability. We have incorporated this in the plots and discuss the implications in the source/sink nature depending on time of sampling

Conclusions:

Lines 15-16: Delete “as 57% of the stations indicated an OC flux from the atmosphere toward the ocean” as this is redundant.

Deleted

Line 22: insert slash between “source” and “sink”.

Done

Line 23: replace “other” with “others”.

Done

Page 16193, Line 17: delete “to”.

Deleted

Page 16194, Line 11: replace “on” with “about”.

Replaced

Figures and Tables:

Table 1: Are these hourly average data? So the ranges are hourly averages for each cruise and area?

Yes, we selected the physical data of the water column about the EDOC-GOC measurements, the same way we selected the $f\text{CO}_2$ data, except Chl-a, which comes from grab samples collected at the stations. We make this clear on the table's legend

Figure 1: Consider color-coding station locations. Even with different symbols, overlapping stations are hard to discern.

We agree that the black and white figure does not allow to properly distinguishing between cruises. We have now colour coded the station locations to provide clarity and the figure has much improved

Figure 2: Which cruise are these data from? All? Consider changing projection and reducing white area.

Figure 3: Which cruise are these data from? All? Consider changing projection and reducing white area.

Both of these figures present the data for all three cruises, we clarify this in the figures' legend. However, I have tried several projections (Orthographic oblique and south polar, mollweide and Mercator) and they do not improve (sometimes it is even worse) the reduction in white area. For clarity and to compare with Figure 1, I

have let the figures as they are. If you feel there is a way to improve the figures I would gladly work on them further

Figure 4: Are chlorophyll and krill concentrations depth integrated?

Neither Chl-a nor krill concentrations are depth integrated. The units are m^{-3} , we clarify that in the figure's legend

Figure 6: Flux distributions peak near zero, so maybe it would be good to show refine the binning to show this better? You could stack the plots vertically, increase the binning and change the aspect ratio to highlight the large positive and negative Faw data.

This figure has been redone to incorporate the recalculation of the OC flux data, and we have increased the binning, but with the new calculation Faw are not as large, so there is no real need for vertical stacking to highlight the large Faw data

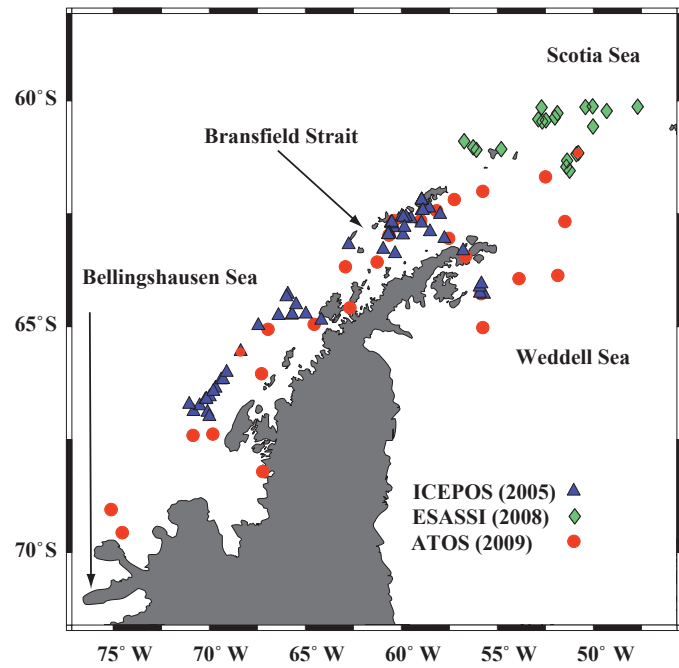
Figure 9: Why is there no solar radiation data for 3-5 February in top panel?

Unfortunately, On 3-5 February there was no solar radiation data because of equipment failure; However, we still believe that, regardless of cloud cover, the other dates give a clear indication of the photoperiod, as it will not change too much over a period of less than a month

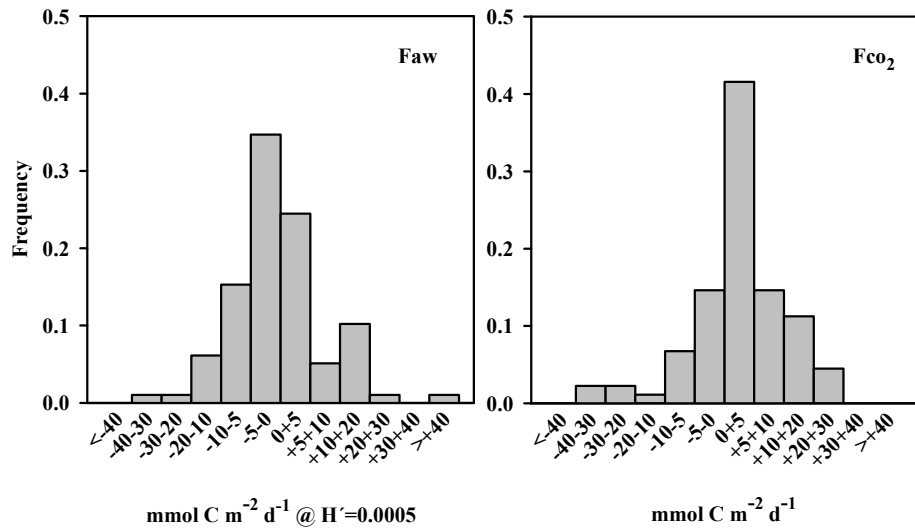
New Table 3. Mean \pm standard error (s.e), median and ranges for fluxes of organic carbon (Fvol, gross volatilization; Fab, gross absorption; Faw, net OC air-sea water exchange) for three different H' (0.0005, 0.005, 0.05), and CO₂ (F_{CO2}) throughout the track of the three cruises, ICEPOS in 2005,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

surface	H'	Fvol	Fab	Faw	F _{CO2}	CO ₂ uptake	OC uptake
cruise		mmol C m ⁻² d ⁻¹	mmol C m ⁻² d ⁻¹	mmol C m ⁻² d ⁻¹	mmol C m ⁻² d ⁻¹	% stations	% stations
ICEPOS	0.0005	11 \pm 2 8[0.3-70]	-10 \pm 1 -8[-28-(-0.6)]	1.4 \pm 2 -1.1[-18-(+60)]			
	0.005	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
	0.05	95 \pm 16 61[0.5-741]	-86 \pm 10 -66[-322-(-0.84)]	14 \pm 15 -6[-207-(+640)]			
ESASSI	0.0005	11 \pm 3 5[0.1-53]	-14 \pm 4 -6[-58-(-2.3)]	-2.5 \pm 2 -0.03[-33-(+12)]			
	0.005	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
	0.05	87 \pm 31 34[0.5-508]	-118 \pm 37 -33[-553-(-5.5)]	-23 \pm 21 -0.05[-286-(+93)]			
ATOS	0.0005	15 \pm 2 14[0.9-34]	-18 \pm 10 -14[-40-(-3.8)]	-2.6 \pm 1 -2[-21-(+11)]			
	0.005	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
	0.05	107 \pm 18 84[5-350]	-126 \pm 21 -83[-414-(-23)]	-19 \pm 10 -14[-150-(+60)]			

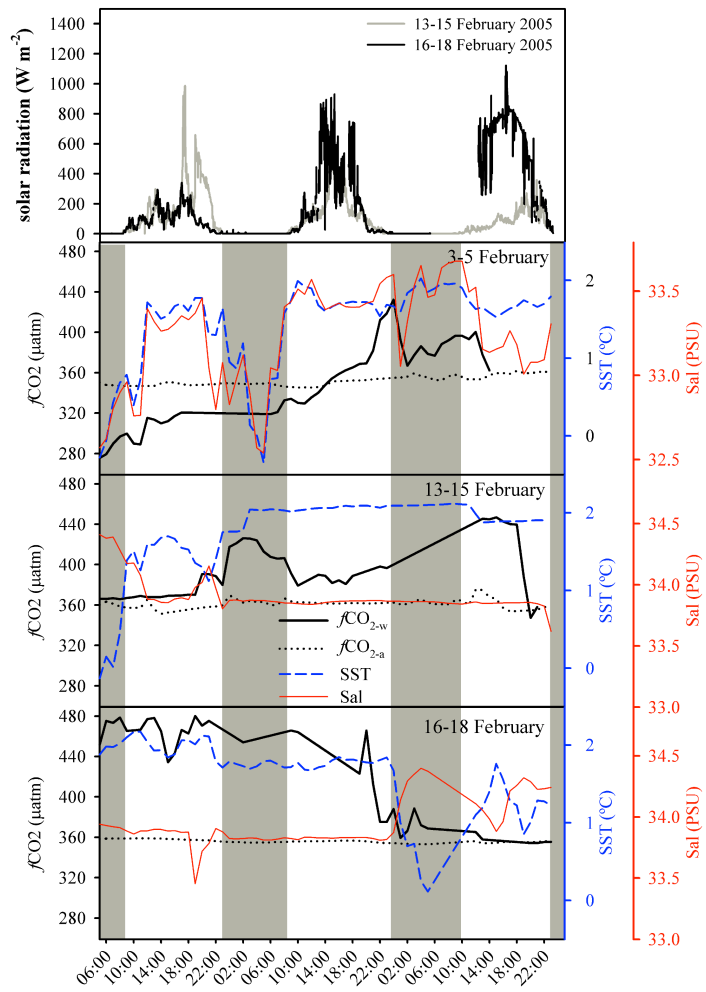
Basin							
Weddell sea	0.0005	15 ± 3 9[0.1-70]	-14 ± 3 -8[-58-(-2.3)]	1.5 ± 3 0.5[-34-(+60)]			
	0.005	73 ± 17 44[0.4-396]	-68 ± 15 -39[-311-(-5)]	9 ± 17 2.2[-170-(+343)]	-2.1 ± 3 [-39-(+21)]	38	41
	0.05	1234 ± 32 68[0.5-740]	-114 ± 26 -68[-553-(-6)]	17 ± 30 3.3[-286-(+640)]			
Bransfield strait	0.0005	12 ± 1.2 10[0.4-34]	-14 ± 1.3 -13[-40-(-0.6)]	-2.3 ± 1 -1.8[-18-(+14)]			
	0.005	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
	0.05	100 ± 14 79[0.5 399]	-121 ± 14 -102[-414-(-0.84)]	-17 ± 9.7 -11[-207-(+196)]			
Bellingshausen sea	0.0005	10 ± 2 6.5[1.1-28]	-9 ± 1 -7[-37-(-1.3)]	0.9 ± 2 -1[-19(+18)]			
	0.005	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
	0.05	64 ± 12 40[4.6-268]	+62 ± 12 -45[-352-(-4)]	4.2 ± 11 -4[-150-(+140)]			
Total Mean ± s.e	0.0005	12 ± 1	-13 ± 1	-0.3 ± 1			
	0.005	58 ± 6	-61 ± 6	-1.1 ± 6	1.6 ± 1.2	27	58
	0.05	96 ± 12	-102 ± 10	-1.5 ± 10			



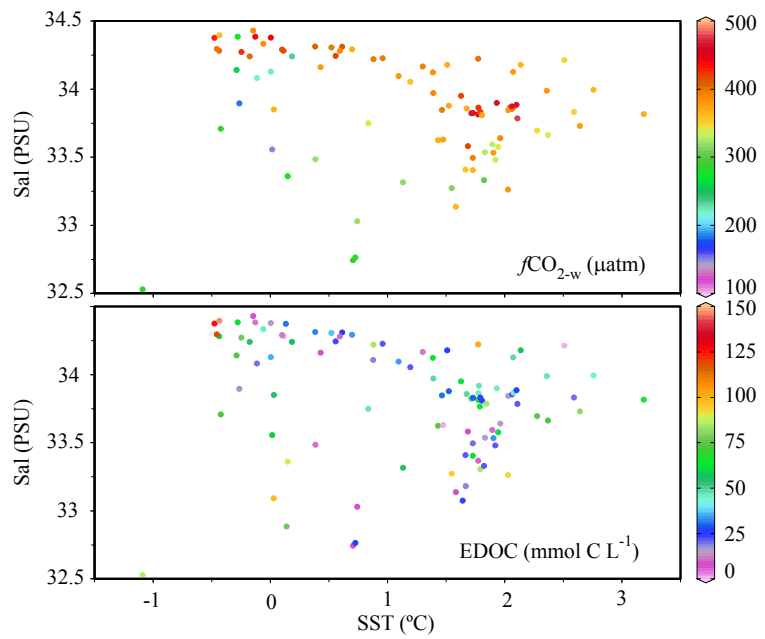
New figure 1. With color coded symbols of the different cruises



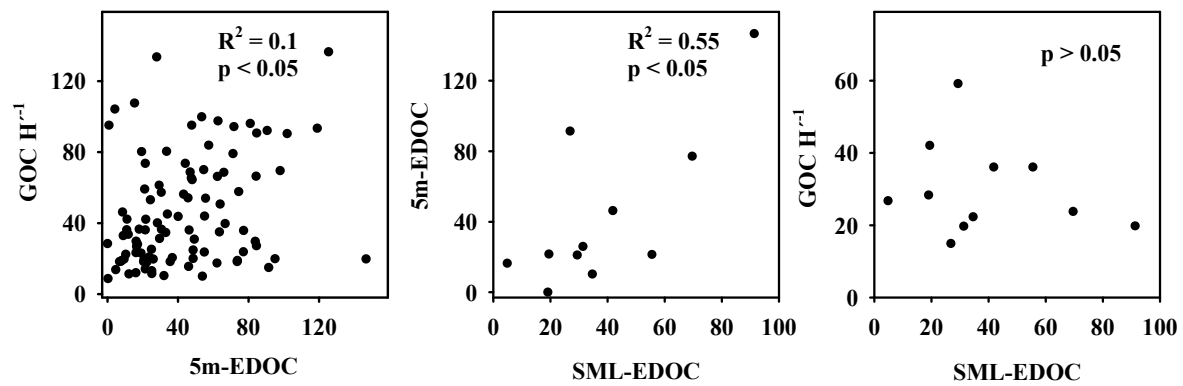
New figure 6 With increased binning and recalculated OC fluxes base don a H'=0.0005



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⁻¹