Answer by authors to reviewer comments for "Ocean-atmosphere exchange of organic carbon and CO2 in the Antarctic Peninsula – physical and biological controls"

Note: Reviewer comments in italics, authors' actions on normal font changes in text between quotations

Mingxi Yang Dec 11, 2013

Review for "Ocean-atmosphere exchange of organic carbon and CO2 in the Antarctic Peninsula – physical and biological controls"

This article describes three sets of air-sea organic carbon and CO2 flux estimates near the Antarctic Peninsula. Both the research topics and the study areas are of importance from a scientific as well as societal perspective. The authors highlighted the need to measure the air/sea concentrations and flux of total gaseous organic compounds, instead of/in addition to the common approach of characterizing individual compounds. The exchangeable dissolved organic carbon (EDOC)- gaseous organic carbon (GOC) extraction method described tries to address this issue operationally.

We thank the reviewer for the appreciation of the work performed and the acknowledgement of the scientific and societal contribution of this article. We have made every effort to address all the issues raised in the revision of the manuscript and the the manuscript is now fit for publication. We appreciate the insightful and constructive comments made by the reviewer. Please find below the responses and a detailed account of the changes made

However, there appear to be some biases in the method as well as in the flux calculation. In ambient air/seawater, solubility of volatile and semi-volatile organic compounds spans over several orders of magnitude. Some compounds emit to the atmosphere from the ocean (e.g. DMS), while others likely deposit from the atmosphere to the ocean (e.g. methanol). Thus the total concentration difference (EDOC – GOC H'), even if measured accurately, is probably different from the sum of the concentration difference of individual compounds. The authors should acknowledge this likely nonlinearity.

We agree with the reviewer that there is a likely nonlinearity arising from the span in H' values of the mixture of compounds measured as EDOC or GOC, and the different nature whether measured in the water phase or in air. We take this opportunity to better describe the nature of our measurements and acknowledge this nonlinearity further. This uncertainty is also the result of the lack of a comprehensive assessment of the many organic chemicals that presumably account for the measured EDOC and GOC concentrations and the associated fluxes.

Further bias lies in the calculation of organic carbon flux. The authors treated the OC ensemble together as being waterside controlled (i.e. sparingly soluble), and used the waterside transfer velocity from Nightingale et al. 2000 in the flux calculation. This probably resulted in an overestimation of OC flux. In reality, a significant portion of the OC should be airside controlled (i.e. highly soluble); the Nightingale k parameterization *is entirely inappropriate for the flux calculation of those compounds. Can the authors provide an estimate for the mean H' to constrain the total gas transfer velocity? If not, OC flux should be presented with a range of assumed H'.*

We agree with the reviewer that the current way of computing OC fluxes across the air-sea interface may lead to an overestimation of the fluxes in case that an important fraction of GOC and EDOC has a low H' value. Just for clarification, we define H as the ratio of vapor pressure over solubility in water. The opposite criteria is used in part of the literature for volatile compounds, but this is how it is defined usually for semivolatile compounds (Schwarzenbach et al. 2003). We have now recalculated the fluxes by: 1) adding the air transfer resistance on the overall air-water mass transfer coefficients and 2) calculating the volatilization and absorption of OC for H' values spanning 3 orders of magnitude, 0.0005, 0.005 and 0.05 or higher (for H' values above 0.05 the contribution of the air-side resistance to the overall mass transfer coefficient is negligible). We hope that this will satisfy the reviewer, as it is one of the major aspects of the review.
Briefly, we now estimate the fluxes by considering the air-water mass transfer coefficient (k_{AW}) as given by,

$$\frac{1}{k_{AW}} = \frac{1}{k_w} + \frac{1}{k_A H'} \qquad [1]$$

Where k_W is the water-side mass transfer coefficient estimated from Nightingale et al. 2000 and scaled by the Schmidt number as previously described, and k_A is the air-side mass transfer coefficient that can be estimated from the k'_A value for water vapor in air (Schwarzenbach et al. 2003) by

$$k'_A = (0.2U_{10} + 0.3)864 \qquad [2]$$

$$k_A = k'_A \left(\frac{D_A}{D_{A,H2O}}\right)^{0.61} \qquad [3]$$

Where 864 is the conversion factor from cm s^{-1} to m d^{-1}, D_A is the diffusivity of GOC or EDOC in air, and $D_{A,H2O}$ is the diffusivity of water vapour in air. This estimation methodology is widely used for the estimation of the air-water mass transfer coefficients of semivolatile compounds (Scwarzenbach et al. 2003, Dachs et al. 2002). For chemicals with $H'>0.05$, k_{AW} is approximately equal to k_W (assumption done in previous version), but for lower values of H' the two terms in equation [1] are significant, and thus k_{AW} can be significantly lower leading to lower fluxes as pointed out by the reviewer.

We now report all three fluxes in the tables, as they indeed vary greatly (more than 1 order of magnitude) and it is likely to be of importance in Antarctic waters as H' is dependent on temperature, and H' at 0 C is likely to be an order of magnitude lower than at 25 C. Because of the lower H' values in Antarctic waters we use the most conservative fluxes calculated with H'=0.0005 in the graphs and for comparison with CO_2 fluxes. This is also consistent with a very recent study that suggests that semivolatile organic

compounds account for most of the exchangeable OC (Hauser et al. 2013). Find the new fluxes in table 3. The methods section has been rewritten to incorporate these new calculations: the text reads:
"…Likewise, OC net diffusive fluxes (Faw) were estimated as the sum of gross volatilization (Fvol = $k_{aw} \cdot$ EDOC) and absorption (Fab = -$k_{aw} \cdot$ GOC H'^{-1}), where k_{aw} is the gas transfer velocity for exchangeable OC estimated from k_{600} values and Schmidt numbers assuming an average molecular weight (MW) of GOC of 120 g mol^{-1}. The fluxes are estimated by considering the air-water mass transfer coefficient (k_{AW}) as given by,

$$\frac{1}{k_{AW}} = \frac{1}{k_w} + \frac{1}{k_A H\prime} \qquad [1]$$

Where k_W is the water-side mass transfer coefficient estimated from Nightingale et al. 2000 and scaled by the Schmidt number as previously described, and k_A is the air-side mass transfer coefficient that can be estimated from the k'_A value for water vapor in air (Schwarzenbach et al. 2003) by

$$k'_A = (0.2U_{10} + 0.3)864 \qquad [2]$$

$$k_A = k'_A \left(\frac{D_A}{D_{A,H2O}}\right)^{0.61} \qquad [3]$$

Where 864 is the conversion factor from cm s^{-1} to m d^{-1}, D_A is the diffusivity of GOC or EDOC in air, and $D_{A,H2O}$ is the diffusivity of water vapour in air. Details for the associated uncertainties derived from the use of an average MW are given in Ruiz-Halpern et al. (2010), Because there is a wide range of H' in the mix of EDOC and GOC H'^{-1}, the compounds being exchanged from water to air may be regulated by processes in the water, but for highly soluble compounds (i.e methanol) their air-sea exchange is regulated by processes on the air side (Yang et al. 2013). To account for this, we have incorporated an air side transefer term Ka, following Schwartzenbach et al. 2003, and calculated volatilization and absorption fluxes with a range of H' spanning 3 orders of magnitude (0.0005, 0.005, 0.05)"

Another error is apparent in the calculation of CO2 flux, where the authors did not adjust the transfer velocity at Schmidt number of 600 to ambient conditions.These major issues need to be addressed before the article can be considered for publication.

We apologize for a wrong methodological description of the calculation of CO_2 fluxes. Transfer velocity was indeed adjusted to a Schmidt number of 600 to ambient conditions. We have improved the methods section to include a detailed description of all CO_2 calculations and necessary equations (see also concerns of other reviewers). 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 (U10, m s-1) following the expression K_{600} = 0.222 U102 + 0.333 U10 (Nightingale et al., 2000). The calculation of air-sea water CO2 flux (FCO2) used the expression (eq. 1):

(1) $FCO_2 = Kw \cdot S \cdot \Delta fCO2$

where ΔfCO_2 is the difference between CO2 fugacity in the surface of the ocean and that in the lower atmosphere ($\Delta fCO2 = fCO2\text{-}w - fCO2\text{-}a$), Kw, the gas transfer coefficient, was normalized to Schmidt number of 600 (Kw = K600*(600/Sc) ^0.5), and S is the CO_2…"

Specifics

A suggestion with regard to writing style, I think it makes for clearer writing to break long, wordy sentences down to multiple short sentences.

We appreciate the thorough reading of the article by the reviewer and have made our best effort to improve our style and broken long sentences to multiple short sentences

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Abstract. what does +/- indicate? Preassembly standard error? Please specify.

Yes, it is standard error; it is now clarified in the abstract (Lines 7&9)

66% of total DOC, or non-purgeable DOC

Good point, it is in fact non purgeable DOC, we have clarified that in the abstract (Line 10)

p 16175, break first sentence down to two sentences

Done: "The ocean and the atmosphere exchange momentum, heat, gas, and materials across an area of 361 million km^2. These interactions play a major role in the dynamics of the Earth's System (Siedler et al., 2001)."

p 16176, line 6, over a million types of C10...

Changed: "Goldstein and Galbally (2007) predicted that over a million types of C_{10} compounds"

line 24~25, rephrasing

Rephrased: "However, there is no inventory of all anthropogenic SOC neither over the oceanic nor terrestrial atmospheres."

p 16177, line 20~25, rephrasing

Rephrased: "Moreover, resolving EDOC is important because it is a component of DOC that is not captured with conventional measurements of DOC (Spyres et al. 2000), which operationally measures non-purgeable organic carbon. Purgeable DOC, equivalent to EDOC, is removed from the pre-acidified sample along with DIC through the bubbling of the sample prior to DOC measurement (Spyres et al., 2000)."

p 16178, line 2~5, references repeated. Phytoplankton was not found to be a source of methanol.

Repeated references removed, and corrected the miss-referenced statement that the ocean is a source of methanol: “low at low temperatures, displacing exchangeable OC to the water phase (Staudinger and Roberts, 2001); (2) polar macroalgae (Laturnus, 2001), and phytoplankton (Sinha et al., 2007) have already been identified as an important source of a wide variety of VOCs, including halogenated VOCs, acetone, acetaldehyde, DMS, and isoprene”

p 16179line 17, how was the microlayer sampled? line 23, "in agreement"?

We agree that we have not given enough information on how the microlayer was sampled. We have now included a paragraph describing the method of microlayer sampling. The text now reads: “Microlayer samples were collected, on board a small boat (Zodiac) drifting away from the research vessel, using a plate ocean microsurface sampler (Carlson 1982). Briefly, two acid-washed perplex blades (50 cm long x 20 cm wide x 0.3 mm wide) were rinsed 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 L were collected, typically after 30 min of two persons working in parallel. When wind speed exceeded 20 m s-1, this procedure could not be attempted for safety reasons.”

p. 16180, line 24, High purity mili-Q water likely still contains some organic carbon. Also, was the mili-Q water kept at the same temperature as SST to account for the temperature-dependence in solubility?

Indeed, high purity miliQ water may still contain traces of carbon, that is why we run blanks, that account for that and other sources of contamination, the claim that miliQ water is “free” of carbon has been removed form the manuscript. MiliQ water was not kept at the same SST as sample water, so slight deviations in temperature may arise from differences between sample water and trap water; However, working on the deck of the boat in Antarctic waters, trap water was close in temperature to the sample water. Since we did not keep track of the temperature of the trap water, so there really isn’t much we can do at this point.

Wouldn't acidifying the water to a pH<2 significantly alter the solubility of some organic compounds? Especially the very polar and ionizing compounds?

Indeed, changing the pH would change the condition of some compounds, especially polar and ionizing ones. However, acidification is performed to the MiliQ trap water, not the sample water, so that any effect on the solubility would happen in the water trap not the sample water, and the purging with N_2 happens to unmodified conditions in the sample. While we acknowledge that changes in solubility might be an issue, we consider this a fair tradeoff to drive off DIC. Regarding polar and ionizing compounds, that become protonated, it may actually render them insoluble and stabilizing them in the water trap until analysis.

What's the blank for GOC H'^{-1}? Is it the same as the blank for EDOC: i.e. bubbling N2 in mili-Q water?

Yes, We used the same blank for both. GOC values tend to be more robust, because they are not subject to the artifact of N2 bubbling, still we felt it provided a more conservative estimate of GOC.

p. 16181, line 3, line 5, etc. "as with" instead of "as for"For the measurement of EDOC, was the seawater filtered? If not, would there be a risk of breaking cells and releasing organic compounds?

“as with” changed instead of “as for”.

The seaweter was unfiltered and gently siphoned from the niskin bottle with minimum bubbling and exposure to air to prevent unwanted purging and contamination. Indeed filtering the seawater could potentially damage the cells and release DOC both as non-purgeable and volatile. Furthermore, the filtering procedure generally involves a certain degree of turbulence in the water, and vacuum conditions, that could drive some of the volatile compounds away. This is now made clear in the methods: “EDOC measurements were obtained by bubbling 1 L of sampled unfiltered seawater with high-grade (free of carbon) N_2 for 8 minutes, which we determined to suffice to reach equilibrium. The stream of gas with the evolved EDOC is re-dissolved in 50 mL of acidified, Mili-Q water as with GOC H'^{-1}. The unfiltered seawater was gently siphoned from a niskin bottle to a 1 L pre-combusted (4.5 h, 500ºC) glass bottle to avoid turbulence of the sample water and minimum contact with the atmosphere”

Line 15. Can the solubility of organic compounds, which spans several orders of magnitude, be described by a single effective number (H')? Can you provide an estimate for this ensemble averaged H’? Or better, a distribution of H’?

We agree that this is a difficult task, we have now provided an air side transfer coefficient to improve the flux estimates and calculated the fluxes based don 3 different H’ spanning 3 orders of magnitude (0.0005, 0.005, 0.05)

p. 16182. Eq (1). This is incorrect. The transfer velocity needs to be adjusted to ambient SST and salinity first. i.e. FCO2 = Kw * S * ΔfCO2, where Kw = k600*(600/Sc)^0.5. Sc is the waterside Schmidt number.

Again, we apologize for a wrong description of the methods and provide the necessary information to properly assess the validity of our CO_2 fluxes. The CO_2 flux calculation section in the methods 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_{CO2}) used the expression (eq. 1):

(2) $F_{CO2} = K_w \cdot S \cdot \Delta fCO_2$

where ΔfCO_2 is the difference between CO_2 fugacity in the surface of the ocean and that in the lower atmosphere ($\Delta fCO_2 = fCO_{2\text{-w}} - fCO_{2\text{-a}}$), K_w, the gas transfer coefficient, was normalized to Schmidt number of 600 ($K_w = K_{600}$*(600/Sc) ^0.5), and S is the CO_2 solubility term, calculated from sea water temperature and salinity (Weiss, 1974)."

p. 16183, line 5. Again, the solubility of organic gases spans a range of several orders of magnitude. Some gases are sparingly soluble (e.g. isoprene) . Their air-sea exchange is regulated by processes on the waterside, just like CO2 (i.e. the Nightingale et al 2000 parameterization may be appropriate). Other gases are highly soluble (e.g. methanol). Their air-sea exchange is regulated by processes on the airside (Yang et al. 2013). For those gases Ka (airside transfer velocity) is needed for the flux calculation, not Kw (e.g. Nightingale et al. 2000). Then there are gases with intermediate solubility (e.g. acetone,

acetaldehyde), which are subject to both airside and waterside control (see two layer equation from Liss and Slater 1974). Clearly using a single waterside k0 will lead to large biases. A better approach would be to incorporate a distribution of H'.

An inadequate approach that's still better than the current one would be to use a mean solubility H' to calculate a mean k0 following Liss and Slater 1974. For example, if kw = 20 cm/hr and ka = 5000 cm/hr, then Kw (or k0 per your definition) = 0.95 cm/hr, 6.7 cm/hr, 16.7 cm/hr for H' of 0.002, 0.002, 0.02, respectively. My guess is that k0 computed this way will be significantly lower than what's given by the Nightingale et al 2000 parameterization. i.e. the current OC fluxes are likely overestimated.

We thank you for your insight and comments on the flux calculations of OC. We have now incorporated an air side transfer term and a range of H'. Indeed, for a H' of 0.0005 (likely in cold environments such as the Antarctic) fluxes are an order of magnitude lower than our previous estimates. However, the net exchange, regardless of H', remains fairly similar (Faw=-2 mmoml m^{-2} d^{-1}, compared to -0.3, -1.1 and -1.5 mmol m^{-2} d^{-1} with the incorporation of Ka and a range of H'). Please Refer to our previous comments for the description of the new estimated fluxes, we hope that including an air side transfer coefficient and a range of H' is a valid re-assessment of our flux calculations.

p. 16186, line 2, Recommend the use of a minus sign to differentiate between emission and uptake fluxes

Agreed, al uptake or absorption fluxes are now preceded by a (-) sign

16190, line 6. Instead of assigning the region to be a net sink/source of CO2, probably more accurate to just say that the net CO2 flux is near zero (i.e. neutral).

Good point! The text now reads: ". Overall, the region was found to be in near balance (i.e neutral) with a net flux close to 0."

16193, line 1, "could potentially be" instead of "expected to be" changed

Fig. 4a. Aside from the two high Chla points, the relationship between pCO2 and Chla seems very weak. Likewise for the pCO2-krill relationship. Are they statistically significant?

They actually are, mostly by the high number of data points, however, the R^2 where low, so we decided to just graphically show the tendencies. The third reviewer has asked to provide p values and R^2, so all this information is now presented. Please see new figure 4

References added

Dachs, J., R. Lohmann, W.A. Ockenden, L. Mejanelle, S.J. Eisenreich, K.C. Jones. Oceanic biogeochemical controls on global dynamics of persistent organic pollutants. Environ. Sci. Technol 36, 4229-4237, 2002.

Hauser, E.J., R.M. Dickhut, R. Falconer, A.S. Wosniak. Improved method for quantifying the air-sea flux of volatile and semi-volatile organic carbon. Limnol. Oceanogr. Methods 11, 287-297, 2013.

Liss, P. S., and Slater, P. G.: Flux of gases across the air - sea interface, Nature, 247, 181–184, doi:10.1038/247181a0, 1974.

Schwarzenbach, R.P., P.M. Gschwend, D.M. Imboden. Environmental Organic Chemistry. 2nd edition, Willey-Interscience, 2003.

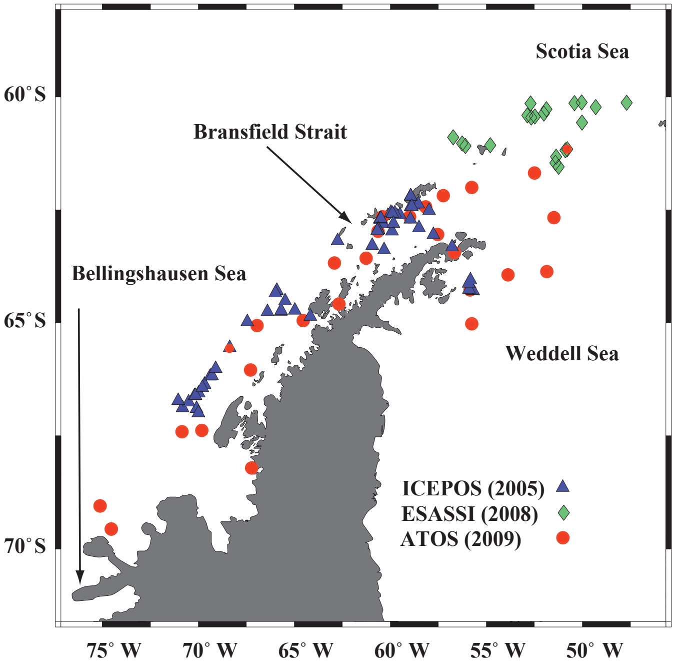
Yang, M., Nightingale, D., Beale, R., Liss, P., Blomquist, B., Fairall, F.: Atmospheric deposition of methanol over the Atlantic Ocean, www.pnas.org/cgi/doi/10.1073/pnas.1317840110 2013

We have added Yang et al. 2013.The approach we used was extracted from Schwartzenbach et al. 2003 that summarizes and updates the work of Liss and Slater and others.

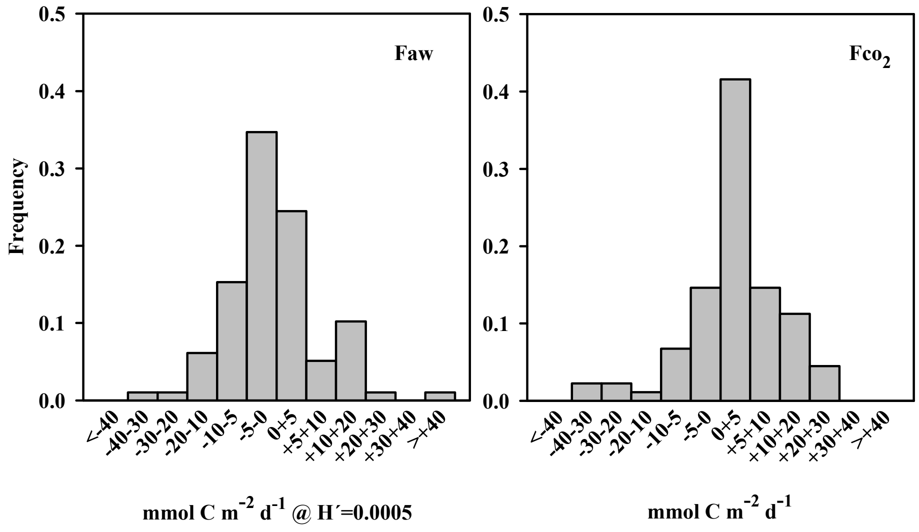
New Table 3. Mean ± standard error (s.e), median and ranges for fluxes of organic carbon (Fvol, gross volatilization; Fab, gross absorption; Faw, net OC air-sea water exchange) for three different H’ (0.0005, 0.005, 0.05), and CO_2 (F_{CO2}) throughout the track of the three cruises, ICEPOS in 2005, ESASSI in 2008, and ATOS-Antarctica in 2009. Data were grouped into cruises and areas. The percentage of stations with undersaturated CO_2, 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 ± 2 8[0.3-70]	-10 ± 1 -8[-28-(-0.6)]	1.4 ± 2 -1.1[-18-(+60)]	1.4 ± 2 2.3[-39-(+27)]	27	18
	0.005	55 ± 9 37[0.5-395]	-50 ± 5 -39[-166-(-0.8)]	77 ± 8 -4.8[-106-(+342)]			
	0.05	95 ± 16 61[0.5-741]	-86 ± 10 -66[-322-(-0.84)]	14 ± 15 -6[-207-(+640)]			
ESASSI	**0.0005**	11 ± 3 5[0.1-53]	-14 ± 4 -6[-58-(-2.3)]	-2.5 ± 2 -0.03[-33-(+12)]	6.4 ± 1.7 4.1[-5-(+21)]	10	50
	0.005	53 ± 17 25[0.3-285]	-70 ± 21 -24[-311-(-5)]	-13 ± 12 -0.07[-170-(+56)]			
	0.05	87 ± 31 34[0.5-508]	-118 ± 37 -33[-553-(-5.5)]	-23 ± 21 -0.05[-286-(+93)]			
ATOS	**0.0005**	15 ± 2 14[0.9-34]	-18 ± 10 -14[-40-(-3.8)]	-2.6 ± 1 -2[-21-(+11)]	-2 ± 1.4 0.05[-20-(+13)]	46	88
	0.005	68 ± 10 58[3.5-189]	-80 ± 2 -57[-225-(-16)]	-12 ± 6 -8[-92-(+43)]			
	0.05	107 ± 18 84[5-350]	-126 ± 21 -83[-414-(-23)]	-19 ± 10 -14[-150-(+60)]			

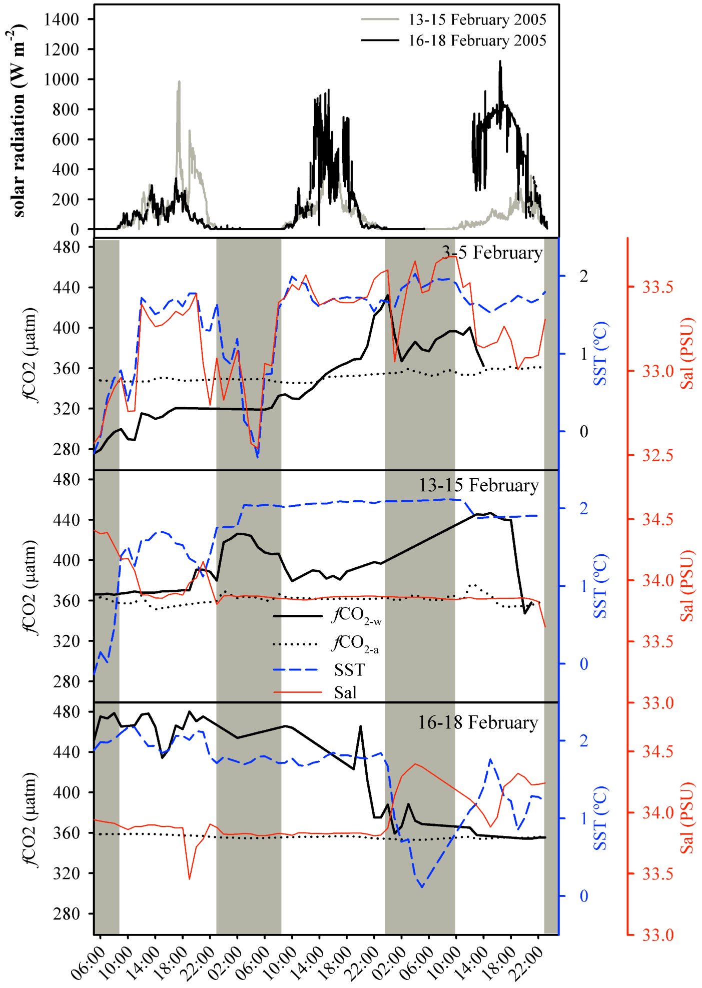
Basin							
Weddell sea	**0.0005**	15 ± 3 9[0.1-70]	-14 ±3 -8[-58-(-2.3)]	1.5 ± 3 0.5[-34-(+60)]	-2.1 ± 3 [-39-(+21)]	38	41
	0.005	73 ± 17 44[0.4-396]	-68 ± 15 -39[-311-(-5)]	9 ± 17 2.2[-170-(+343)]			
	0.05	1234 ± 32 68[0.5-740]	-114 ± 26 -68[-553-(-6)]	17 ± 30 3.3[-286-(+640)]			
Bransfield strait	**0.0005**	12 ± 1.2 10[0.4-34]	-14 ± 1.3 -13[-40-(-0.6)]	-2.3 ± 1 -1.8[-18-(+14)]	6.9±1.22 4.2.3(0-23)	0	71
	0.005	58 ± 7.4 52[0.5-190]	-71 ± 7.4 -57[-224-(-0.8)]	-11 ± 5.2 -7[-106-(+91)]			
	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)]	-1.5±0.78 -1.7[-9-(+6)]	56	55
	0.005	42 ± 7 26[3.6-150]	-39 ± 7 -31[-197-(-3.4)]	3.4 ± 7 -3.3[-92-(+86)]			
	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** **0.005** **0.05**	12 ± 1 58 ± 6 96 ± 12	-13 ± 1 -61 ± 6 -102 ± 10	-0.3 ± 1 -1.1 ± 6 -1.5 ± 10	1.6 ± 1.2	27	58



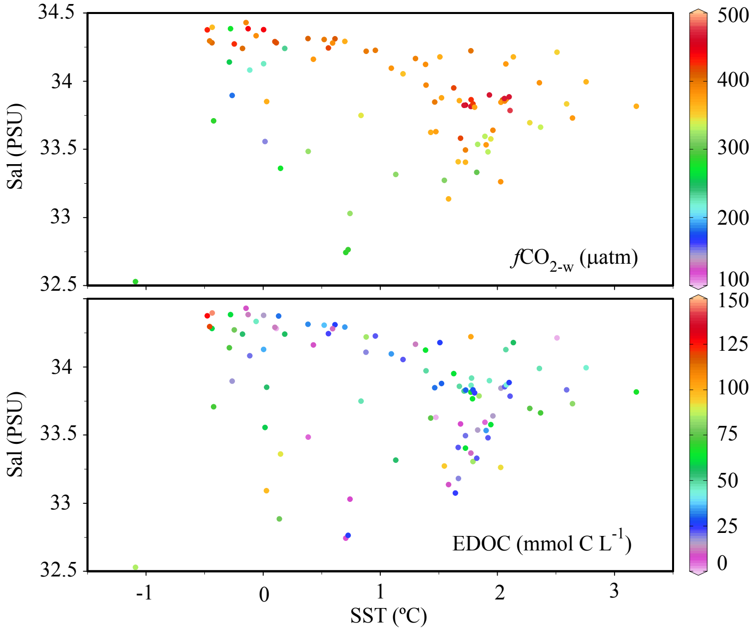
New figure 1. With color coded symbols of the different cruises



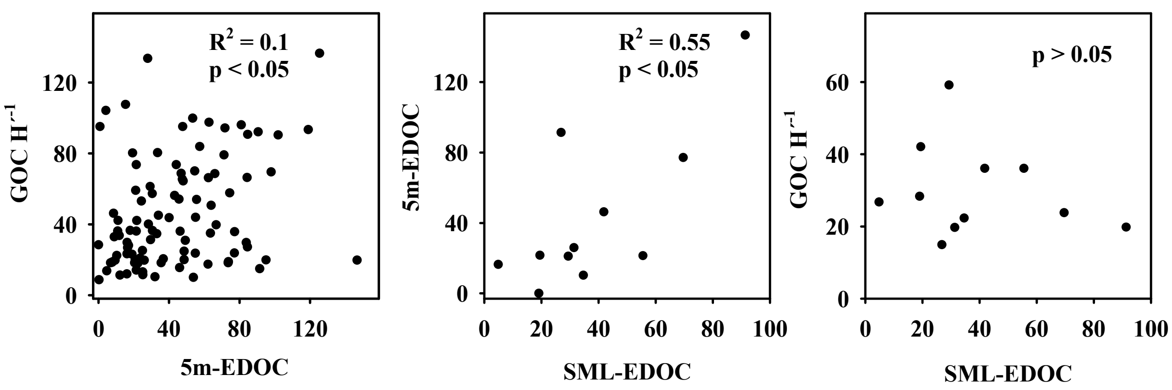
New figure 6 With increased binning and recalculated OC fluxes base don a H’=0.0005



New panel for figure 9 showing diel variabiility of *f*CO2 in water and air as well as salinity and temperature



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



New figure 7 with extra panel shwoing the relationship between SML-EDOC and GOC H'^{-1}