

## Review for “Ocean-atmosphere exchange of organic carbon and CO<sub>2</sub> in the Antarctic Peninsula – physical and biological controls”

This article describes three sets of air-sea organic carbon and CO<sub>2</sub> 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.

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.

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'.

Another error is apparent in the calculation of CO<sub>2</sub> 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.

### 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.

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

66% of total DOC, or non-purgeable DOC

p 16175, break first sentence down to two sentences

p 16176, line 6, over a million types of C10...  
line 24~25, rephrasing

p 16177, line 20~25, rephrasing

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

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

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?

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

What's the blank for GOC H'-1? Is it the same as the blank for EDOC: i.e. bubbling N<sub>2</sub> in mili-Q water?

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?

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  $H'$ ?

p. 16182. Eq (1). This is incorrect. The transfer velocity needs to be adjusted to ambient SST and salinity first. i.e.  $F_{\text{CO}_2} = K_w * S * \Delta f_{\text{CO}_2}$ , where  $K_w = k_{600} * (600/S_c)^{0.5}$ .  $S_c$  is the waterside Schmidt number.

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 CO<sub>2</sub> (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  $K_a$  (airside transfer velocity) is needed for the flux calculation, not  $K_w$  (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  $k_0$  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  $k_0$  following Liss and Slater 1974. For example, if  $k_w = 20$  cm/hr and  $k_a = 5000$  cm/hr, then  $K_w$  (or  $k_0$  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  $k_0$  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.

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

16190, line 6. Instead of assigning the region to be a net sink/source of  $CO_2$ , probably more accurate to just say that the net  $CO_2$  flux is near zero (i.e. neutral).

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

Fig. 4a. Aside from the two high Chla points, the relationship between  $pCO_2$  and Chla seems very weak. Likewise for the  $pCO_2$ -krill relationship. Are they statistically significant?

#### References added

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

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](http://www.pnas.org/cgi/doi/10.1073/pnas.1317840110) 2013