

REVIEW of Salt et al. (2014): Rapid acidification of mode and intermediate waters in the southwest Atlantic Ocean

This work quantifies the increase of anthropogenic carbon (CANT) and the derived pH decrease in the water column of the southwest Atlantic Ocean using data from two occupations of the WOCE A17 section in 1994 and 2010/11.

Although the CANT increase / pH decrease in the ocean is always a relevant issue, this work suffers from major methodological problems and presents a quite simplistic approach to tackle this question. My first conclusion was rejection, but if several MAJOR IMPROVEMENTS are done, it might be finally accepted in *Biogeosciences*.

#### MAJOR ISSUES

##### 1) Literature references.

Some references are wrongly used (Levine et al., 2011, page 6756, line 21), others are omitted (page 6757, last phrase, e.g., Mikaloff-Flecher et al. (GBC 2011), Lovenduski et al. (GBC 2011)), and on the other hand too many are cited for specific issues. Please read the manuscript again with new eyes.

##### 2) Data.

The data section needs to be reorganized (combine and reorganize current sections 2.1, 2.2 & 2.3). Many details for the 2010/2011 CO<sub>2</sub> data, which is good, but none for the 1994 data (TA was corrected, DIC was measured but also pH, state which CO<sub>2</sub> parameters you used). Not all the 1994 stations shown in Fig 1 were measured for CO<sub>2</sub> data, please show just the stations with CO<sub>2</sub> data used. The legend in Fig 1 is wrong.

Section 2.3. The consistency of CO<sub>2</sub> and ancillary data needs to be compared for both cruises if you are to use an eMLR approach. Why using the whole data set for waters below 400 dbars?. It would be better to choose the data corresponding to the water mass with lower temporal variability maybe CDW. The statements in page 6762 lines 1-3 make me question the rest of the work. When comparing data to find any bias I would look not only at the mean difference but also the standard deviation.

Just using two data sets when there is a well document CO<sub>2</sub> data set in the western AO (Rios et al, 2011) and the new 2013 FICARAM occupation is simplistic and should be justified.

### 3) Methods.

I would separate this section from the one dealing with the Data.

In general, I do not understand / accept why you calculate the CANT increase with the eMLR approach while to calculate the pH decrease you apply the backcalculation technique. It has no sense and it makes me think that something is hidden.

Regarding the eMLR method: clearly state if you use a forward or backward method and why. In Fig 2 the residuals for the 1994 seem to have a rmse (by the way, define this acronym in the text) higher than the 2010/2011 adjustment but in page 6763 lines 7-10, you say 1994 – 6.66 and 2010 – 9.87 umol/kg. The maximum residual in Fig 2 for the 2011 data is higher than 7 umol/kg (page 6763 line 18). In Table 1 what rmse is shown, that for 1994 or 2011?. I think you should give the coefficients for each year and the corresponding rmse and R<sup>2</sup>.

CANT method: no proper references are used for the method use. Although I do not understand why you use it to calculate the pH decrease but not the CANT increase?.

Buffer factors: as commented by the other referee, please check them in Álvarez et al. (Oc. Sc. 2014). Although knowing about the typo in their Table 1, the Egleston et al did not bother to write a correction in GBC, and it took me a few months to get the correct Table. State clearly that the buffer factors related to DIC only consider DIC changes at constant TA, so CO<sub>2</sub> air-sea exchange.

### 4) Results

As they are written now, discussion is also included.

### 5) Discussion

A great deal of the discussion is about the eMLR method in the surface ocean when the title of the work is about intermediate and mode waters.

The part dealing with the buffer factors is obviously questioned.

Fig 6 is just a thermodynamic exercise. In the text there is no explanation for the DIC increase (by the way, either use C<sub>T</sub> or DIC ) calculation for each water mass. It would be more interesting to check with real data (with all the temporal occupations of the W-SAO) how much the buffer factor changed by water masses.

I encourage the authors to answer the questions and improve the paper with the proposed suggestions.

I provide a matlab script to calculate the buffer factors with the matlab version of CO2SYS as I did in the 2014 paper. Just copy the text below and change it accordingly to your data. This option is for DIC and TA input.

```
%[RESULT,HEADERS,NICEHEADERS]=CO2SYS(PAR1,PAR2,PAR1TYPE,PAR2TYPE,...
% ...SAL,TEMPIN,TEMPOUT,PRESIN,PRESOUT,S1,PO4,pHSCALEIN,...
% ...K1K2CONSTANTS,KSO4CONSTANTS)
%

[A,HEADERS,NICEHEADERS]=CO2SYS(TA,DIC,1,2,Sal,25,Tis,0,Pres,SIO2,PO4,1,4,1);

HCO3is=A(:,21); % umol/kg
CO3is=A(:,22); % umol/kg
CO2is=A(:,23); % umol/kg
BAlkis=A(:,24);% umol/kg
OHis=1000*A(:,71)/10.^(A(:,38));% Kw (SWS- Moles/kg)*1000 /10^-pHoutput (SWS) => microMol/kg
OmegaCa=A(:,30);
OmegaAr=A(:,31);
His=10.^(A(:,38)) *1000000; % SWS -- from Moles/Kg to microMoles/kg
KBis=A(:,72)*1000000; % SWS - From Moles/kg to micromol /kg
pHSWSis=A(:,38); % in SWS scale
pCO2is=A(:,19);

% BUFFER FACTORS
S=HCO3is+4*CO3is+[(His.*BAlkis)/(KBis+His)]+His+OHis;
P=HCO3is-[(His.*BAlkis)/(KBis+His)]-His-OHis;
CA=HCO3is+2*CO3is;
% BUFFER FACTORS in umol/kg
GammaDIC=DIC-(CA.^2)./S;
BetaDIC=(DIC.*S-CA.^2)./CA;
OmegaDIC=DIC-(CA.*(2*CO2is+HCO3is))./P;
GammaTA=(CA.^2-DIC.*S)./CA;
BetaTA=((CA.^2)./DIC)-S;
OmegaTA=CA-(DIC.*P)/(2*CO2is+HCO3is);

% Revelle is dimensionless
Revelle=DIC./GammaDIC;
```