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Interactive comment on "Anthropogenic and natural CO$_2$ exchange through the Strait of Gibraltar" *by* I. E. Huertas et al.

I. E. Huertas et al.

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General Comments The manuscript shows interesting and new research. It presents a valuable set of data covering temporal variations in the water exchange through the Strait of Gibraltar. Therewith it gives the bases for improved estimates for the exchange of carbonate system parameters in the Strait, including the fluxes of anthropogenic carbon between the Mediterranean Sea and the Atlantic. The introduction section nicely describes the scientific topic and open questions; it introduces the research area and lists the work that has already be done in this field. The methods are clearly described and the results are detailed. I suggest only some minor corrections for the previously mentioned sections, whereas the discussion part needs some revision and has to be more clearly structured. Overall I recommend the publication of this work after taking into account the comments and suggestions.

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Specific Comments Abstract: In the result and discussion sections new estimates are given for the water mass exchange through the Strait of Gibraltar and for the alkalinity budget in the Mediterranean Sea based on a two-year time series - why not mentioning these results in the abstract?

DONE

"Applying a two-layer model of water mass exchange through the Strait and using a value of -0.85 Sv for the transport of the outflowing Mediterranean water recorded in situ during the considered period"

Page 1025, Line 27: The Strait of Gibraltar behaves as a net sink for alkalinity but not due to carbonate sedimentation. Carbonate sedimentation is a sink for alkalinity in the Mediterranean basin.

CORRECTED

Page 1027, Line 29: For me it is not clear what role a reduced gravity of 0.02 m s-2 plays in this two-layer system. If it is important, please explain it in a further sentence or, if it is extraneous, it might be deleted.

DELETED

Page 1030, Line 5: What data were used for the fresh water balance?

NOW IN THE TEXT AS FOLLOWS:

"From QM and taking into account the fresh water balance in the Mediterranean basin by considering the net annual evaporation mentioned above.."

Page 1031, Line 12: Were there any duplicate samples measured to determine the precision?

We apologize for the misunderstanding. The sentence has been replaced by:

"The accuracy of the AT measurements on CRMs from 3 batches (batch 70, 71 and

76) was ±0.59, 0.72 and 0.79 ±mol kg-1, respectively."

Page 1033, Line 10: In the introduction you mention that Mediterranean waters are supersaturated with respect to calcite and aragonite. Why should there be calcium carbonate dissolution? As proposed by Schneider et al. (2007) the excess alkalinity AT) at depth is caused by the inflow of high alkalinity water from rivers and the Black Sea. Thus, the carbon content would not be changed (unless the rivers and the Black Sea carry exceptional inorganic carbon concentrations). How will the Cant distribution look like without this term?

The work by Schneider et al. (2007) does not consider the $CaCO_3$ dissolution in the Mediterranean whereas our study takes into account the fact that the contribution of biological processes in carbonate utilization within the upper layer can not entirely ruled out along with a certain portion of the buried $CaCO_3$ that can be released back to the water column from the sediment. Our assumption completes the carbon balance presented and it is supported by the mentioned studies. The paragraph regarding $CaCO_3$ dissolution has been rewritten as follows:

"Therefore, if the alkalinity budget for the Mediterranean Sea described in Schneider et al. (2007) is taken into account, which considers a joint alkalinity entrance of 86 kmol s-1 into de basin from the Black Sea and rivers, and the alkalinity export through the Strait of Gibraltar obtained in our work is taken (-44 kmol s-1), 42 kmol s-1 of the alkalinity measured in the Mediterranean do not reach the Atlantic. Using the net export of nitrate through the Strait given by Dafner et al. (2003), a consumption of 4 kmol s-1 of alkalinity is expected to be associated to the remineralization of the organic matter present in the Mediterranean Sea, and the most likely candidate for the loss of the remaining 38 kmol s-1 of alkalinity would be $CaCO_3$ sedimentation. Our results then imply a net carbonate sink of 19 kmol s-1 towards the seafloor. However, an export of -13±0.3 kmol s-1 of $CaCO_3$ is observed to occur through Gibraltar (Table 2 and Fig. 7). This output of carbonate can be attributable to the contribution of the biological $CaCO_3$ pump, which transports downward alkalinity by $CaCO_3$ particulate from the

upper surface layer to deep layer, providing an additional alkalinity gain equivalent to -26 kmol s-1. Although CaCO3 dissolution is not favoured thermodynamically, the increase of alkalinity can be produced in biological mediated environments (Milliman et al., 1999) or released back from the sediment to the water column (Berelson et al., 2006). The combination of all these processes would result in a gross CaCO3 formation of 32 kmol s-1. This budget is coherent with the high downward carbonate fluxes measured recently in the NW Mediterranean (Martin et al., 2006), who reported a mean annual flux of sink of 0.40 mol m-2 y-1 using sediment traps, which matches strongly our gross estimate. According to Schneider et al. (2007), the alkalinity loss via carbonate sedimentation corresponds to a surface calcification rate of 0.38 mol m-2 yr-1, which amounts to 32 kmol s-1 of a net CaCO3 precipitation. These authors, however, neglect carbonate dissolution and consider an alkalinity export through the Strait of -25 kmol s-1. In parallel, the gross CaCO3 formation (32 kmol s-1) in surface waters nearby coastal regions would favour a rise in the oceanic pCO2. Our estimates point to a CO2 outgassing of 21 kmol s-1 to the atmosphere due to settling of CaCO3 particles, assuming that pCO2 is maintained in equilibrium with the atmospheric CO2 levels (Copin-Montégut, 1993)."

Page 1033, Line 18-21: It might be helpful to mention the two different surface AT-S relationships used to calculate the preformed alkalinity.

It would be useful but the explanations would extend the paper too much. References from which both relationships were obtained are given in the text for the readers to check further details.

Page 1034, Line 1-7: This paragraph is not clear, could you maybe explain it in one or two more sentences.

It has been clarified as follows:

"Finally, ΔCDIS represents the disequilibrium term and stands for the air-sea CO2 difference expressed in terms of CT. For the Atlantic water, ΔCDIS on density intervals

of 26.8 (NASW) and 27.1 (NACW) calculated by Lee et al. (2003) in -12 ± 5 μmol kg-1 was used. As for the Mediterranean water,ΔCDIS was obtained using the CFC data given by Rhein and Hinrichsen (1993). From CFC data, the age of the Mediterranean outflow was stabilized in 20 years, which sets ΔCDIS in 0 ± 5 μmol kg-1. DeltaCDIS was obtained for each sample by a mixing analysis using as end members the disequilibrium at the salinity maximum of 38.5, corresponding to the MOW, and those of the Atlantic, NASW and NACW."

Page 1040, Line 25 to Page 1041, Line 17: Taking into account that no carbonate dissolution should take place in the Mediterranean basin because of supersaturation, this paragraph should be revised.

Milliman et al. (1999) proposed carbonate dissolution in supersaturated water and Berelson et al. (2006) suggested an increase of CaCO3 dissolution in deep waters by exchange with sediments. Both processes explain the increase of alkalinity in deep waters and it has been explained in the text.

Page 1041, Line 12-15: The sentence does not make sense to me, because above you said carbonate dissolution exceeds 20 μmol kg-1 in the MOW. Additionally there are no data for the Strait of Gibraltar in Schneider et al.(2007).

CORRECTED. The confusing line has been deleted and the paragraph modified as follows:

"As shown in Fig. 6E, calcium carbonate dissolution in the easternmost part of the Strait ranges from 0 μmol kg-1 in near-surface waters corresponding to NASW to a maximum exceeding 20 μmol kg-1 in the MOW, being affected by the mixing with Atlantic waters inside the AMI upwards in the water column (around 75 m depth, Fig. 6B). The internal hydraulics of the Strait that requires a west-to-east upward slope of the AMI modifies this vertical pattern and thus, lower values can be attained at a same given depth on both sides of the channel (Fig. 6E). As illustrated in Fig. 5C, the spatial distribution of the CaCO3 dissolution along the GIFT leg reaches a maximum in the

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bottom layer where the MOW is detected, with NASW containing a much lower CaCO3 dissolution (Fig. 5C)."

Page 1045, Line 27 to Page 1046, Line 2: The comparison between the values sounds a bit strange. Suggestion: This value lies between the one given by Copin-Montegut (1993), who estimated a net alkalinity flux of -77 kmol s-1 into the Atlantic, that of -60 kmol s-1 provided by Santana- Casiano et al. (2002) and the latest assessment of -25 kmol s-1 reported by Schneider et al. (2007).

Following the reviewer s suggestion the phrase has been rewritten:

"This value lies between the one given by Copin-Montégut (1993), who estimated a net alkalinity flux of -77 kmol s-1 into the Atlantic, that of -60 kmol s-1 provided by Santana-Casiano et al. (2002), and the latest assessment of -25 kmol s-1 reported by Schneider et al. (2007)."

Page 1046, Line 4-5: Copin-Montégut (1993) did not use the water balance described by Béthoux (1979) for the alkalinity outflow estimate through the Strait of Gibraltar. She did an alkalinity balance and compared it to other results using different water flux estimates. I found it hard to read all the rates and fluxes with the unit of kmol s-1, because in most other references they are given in 1012 mol yr-1. Furthermore I noticed some conversion errors, due to that problem (e.g. Page 1046, Line 18 -> 38 and 48 kmol s-1; Page 1047, Line 8 -> 86 kmol s-1; Page 1047, Line 15 -> 30 kmol s-1; Page 1048, Line 8 -> besides I think this should be the reference Copin-Montégut (1993), 87 kmols-1(?)).

CORRECTED. We apologize for the mistakes.

Page 1047, Line 6-26: I cannot reconstruct this alkalinity balance. In my opinion the carbonate dissolution term appears twice and the calcification rate of 16 kmol s-1 is wrong. The paragraph should be structured more clearly and important terms should be emphasised.

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The paragraph has been clarified as indicated above.

Page 1048, Line 10-21: Again, this section seems not clearly written to me. Which data are used for the column inventory or how is the increase of 0.7 μmol kg-1 yr-1 calculated? Furthermore, I am not sure if the method used for calculating the Cant storage (with the MPD) is appropriate for the Mediterranean Sea, because we find relatively young waters in the deep basins (and therewith relatively high in Cant).

In order to calculate the CANT storage in the Mediterranean Sea, we have assumed that the MPD is equivalent to the average depth of the basin. This is due to the discrepancy existing in the literature with respect to the residence time of the Mediterranean waters since some authors using tracers obtain 20 years whereas others report a residence time as high as 170 years. Therefore, considering this assumption, the increase of 0.7 μmol kg-1 yr-1 is obtained.

Are there shown any data from the stations 1-5 or where they used to do any of the calculations? If yes, it would be good to know, (because I only find data from the GIFT section) and if not, for simplification they could be left out in the method section and in Fig.1.

Data from stations 1 to 5 have been used throughout the study to perform several calculations. In fact, such data are explicitly shown in the three plots included in Figure 4, being also considered to obtain the AT-S relationship, as stated in the text. In addition, station 3 shares location with station 7 so in each campaign this site was sampled twice while completing both sections, the one perpendicular to the main axis of the Strait and the GIFT leg that goes longitudinal to the channel. Consequently, data from station 3 have been also employed to represent the section plots (Figs. 3 and 5). In the Material and Method section, it is indicated that both sites possess identical coordinates.

Figures: I think Fig. 6 does not show more details than Fig. 3a,b and Fig. 5 a-d. One of the two representations (profile or section plot) would be enough.

Figure 6 can not be deleted because it shows the data obtained on both sides of the Strait (stations 6 and 8), which are used subsequently to calculate the fluxes indicated in Table 2.

Fig.1: Diamond for station 7 is missing.

Stations 3 and 7 have the same geographical coordinates

Fig.2, caption: If one looks at the figure it is clear which one shall be the solid line, but actually they are both solid. The plotted transport data are daily means? That should be in caption.

The figure caption has been rewritten as follows:

"Figure 2. Time series of the Mediterranean water transport (QM) measured in ES section from May 2005 to July 2007. The plotted transport data correspond to daily means during the monitoring period. Solid and horizontal line marks the average value of all data, equivalent to -0.85 Sv."

Fig.5a and b: For better comparison the colorbars should be scaled equally. DONE

Technical Corrections Page 1022, Line 17: It might be easier to use the same unit (25 Tg C yr-1) as in line19 (or vice versa) (same on Page 1051, Line 6-7). DONE

Page 1023, Line 3: remain large uncertainties CORRECTED

Page 1025, Line 2: human pressure they (?) suffer. CORRECTED

Page 1025, Line 27: A recent study has pointed; CORRECTED

Page 1027, Line 5: Water exchange through; CORRECTED

Page 1027, Line 5-8: The sentence sounds a bit random: strongly influenced ;wide variety;diverse frequency of variability;

The sentence has been modified in the text

"Water exchange through the Strait is subjected to the influence of different mechanisms that present diverse frequency of variability, from daily to seasonal or interannual scale, such as tidal currents, winds or atmospheric pressure variations (García-Lafuente et al., 2002; Vargas et al., 2006). "

Page 1029, Line 3: In this study, ES station; CORRECTED

Page 1029, Line 5: at this particular station;

The sentence is aimed at explaining a phenomenon that takes place in a particular place of the channel so the word section or station has been changed by place, as this term describes better the process.

Page 1029, Line 6: subinertial flow needs to be explained here (happens later on line 16) CORRECTED

Page 1029, Line 27:through the Strait; CORRECTED

Page 1031, Line 3: Kind is not in the equation above. CORRECTED

Page 1032, Line 19: Niskin bottles CORRECTED

Page 1033, Line 16: I think I should be: frac12; (DeltaAT+AOU/RN), because later on line 17 you talk of AT. CORRECTED

Page 1038, Line 13: There are direct measurements of dissolved inorganic carbon available at CDIAC database from Meteor cruise M51/2)

We apologize for the omission. In order to avoid misunderstandings the paragraph has been rewritten as:

"Nonetheless, CT concentrations reported by Pérez et al. (1986) for the western Mediterranean, Frankignoulle et al. (1990) for the LIW, Copin-Montégut and Begovic (2002) for DYFAMED, all based on indirect computations by using pH and AT measurements, and the satellite-based computations summarized in Dacute;Ortenzio et

al. (2008) for the whole Mediterranean are in good agreement to the values obtained in our study."

Page 1040, Line 28: (Fig. 5 c+d) CORRECTED

Page 1040, Line 29: (Figs. 5 c and 6e) CORRECTED

Page 1041, Line 5: (Figs. 5 c+d) CORRECTED

Page 1046, Line 13-15: In this sentence the word is must be replaced. DONE

Page 1048, Line 20: the last value has no unit.

Units have been added

Page 1050, Line 15: 8216; a concentration of 27 $\pm$ kmol s-1 ; -> this is not a concentration.

Units of kmol s-1 have been replaced by μmol kg-1 in the text. We apologize for the mistake and kindly acknowledge the reviewer s advice.

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