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Biogeosciences Discussions

Interactive comment on "Distributions of the carbonate system properties, anthropogenic CO_2, and acidification during the 2008 BOUM cruise (Mediterranean Sea)" *by* F. Touratier et al.

F. Touratier et al.

touratier@univ-perp.fr

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Comment from Referee #1 : This paper reports on inorganic carbon variables (i.e.DIC and alkalinity) measured during the BOUM cruise in 2008. This is without doubt an important data set since only a very limited number high quality measurement of the carbonate system is available for the Mediterranean Sea, particularly for the western basin. The authors use these data to derive the anthropogenic perturbation to the carbonate system and can thus report on the change in pH and DIC concentrations over time, i.e. "ocean acidification" and anthropogenic carbon (Cant)". A great deal of effort is spent on comparing these results with results obtained by other groups.

The authors frequently report on the acidification of the Mediterranean Sea and that this system is "among the most acidified marine ecosystems". Although, technically speaking, the Delta-pH in the Mediterranean Sea is large as a result of the high Cant concentrations; it is highly miss-leading to talk about "an acidified ecosystem". Fact is that the pH of the Mediterranean Sea is high compared to the world ocean in general; whereas the deep North Atlantic, for instance, has a pH of about 7.7, the pH in the deep Mediterranean Sea is about 7.9, that is roughly 0.2 pH-units higher. The Med is thus a system that has a very high pH compared to the world ocean. It is also misleading to talk about an "acidified" system, since the pH is significantly higher than neutral this is a light basic environment.

Our response: Referee #1 writes that 'it is highly miss-leading to talk about "an acidified ecosystem". For us acidification means a decrease of pH. Referee #1 probably thinks that the term 'acidified' means 'acid'. Of course the Mediterranean Sea is not acid but considering the high levels of anthropogenic CO2 that have been estimated for this marginal sea, we can conclude that it is 'one among the most acidified marine ecosystems'. The comparison of the mean pH values of the Mediterranean Sea (7.9) and the Atlantic Ocean (7.7) given by Referee #1 is meaningless since, for instance, organisms living in a specific area are adapted to a specific mean pH, and this is the mean variation of pH (the level of acidification) that will highly impact the ecosystems.

Comment from Referee #1 : For the deep western Mediterranean Sea, for example, the authors find Cant concentrations in the range of 80 umol/kg. This area is dominated by water types W9 and W10, according to the authors. By doing a calculation on the anthropogenic carbon one could find in a water with those properties as listed in Table 1, one find some re- markable numbers. The difference between the DIC concentrations in thermodynamic equilibrium with the atmospheric CO2 using preindustrial atmospheric CO2 concentrations (280 ppt) and contemporaneous (i.e. in 2008 the pCO2 was 380 ppt) is 70 umol/kg. That is thus the value one could expect in surface waters that are recently ventilated and in equilibrium concentration with the atmosphere. Interestingly is the thermodynamic value about 10 umol/kg lower than the predicted Cant concentration for a deep water (range âĹij1000 – 3000 m) in the Mediterranean Sea. This water is clearly not in equilibrium with the atmosphere, and will have a mean age significantly higher than 0, so that Cant concentrations will by definition have to lower than 70 umol/kg, most likely significantly lower. The situation is similar in the eastern Mediterranean; although the authors present lower Cant concentrations in the deep water (âĹij70 umol/kg), these values are clearly not realistic considering the thermodynamic constrains of the carbonate system.

Our response: The second point raised by Referee #1 is the level of anthropogenic CO2 (Cant) reached in the deepest layers of the Mediterranean Sea. Based on a very crude calculation, Referee #1 concludes that a value of Ìť80 μmol/kg cannot be reached. Let us examine the data or hypotheses used for this calculation: 1) Input parameters are those from water sources W9 and W10 (Table 1) 2) atmospheric pCO2 for the year 2008 is 380 ppt 3) thermodynamic equilibrium is assumed Using the above data and hypotheses, Referee #1 estimates that the maximum for Cant should be 70 μmol/kg or even lower since the surface sea water is clearly not in equilibrium with the atmosphere. Our responses to the above points are the following: 1) Why Referee #1 used the W9 and W10 properties as input parameters to estimate Cant? W9 and W10 are deep waters whose characteristics (especially CT and AT) have been largely modified by respiration/decomposition and dissolution/formation of CaCO3. To perform such a calculation it would be necessary to know the properties of W9 and W10 when they left the surface at the moment of their formation. 2) The 2008 atmospheric pCO2 value of 380 ppt (let us understand here 380 ppm), used by Referee #1, may not be really representative for the atmosphere above the Mediterranean Sea. Based on atmospheric pCO2 records from the Lampedusa Island, the paper of Chamard et al. (2003; Tellus, 55B, 83-93) shows that this level was already reached during the year 2002. Using the Lampedusa dataset, Chamard et al. also estimated that atmospheric pCO2 increased in average by +1.7 ppmv each year. Based on the latter study, the 2008 atmospheric pCO2 above the Mediterranean Sea can be estimated to 390 ppmv.

3) Most of the time, the thermodynamic equilibrium hypothesis does not hold for the Mediterranean Sea. But contrarily to the opinion of Referee #1, the pCO2 in the surface water of the Mediterranean Sea is often oversaturated. As pointed out by the paper of D'Ortenzio et al. (2008; Deep-Sea Res. I, 55, 405-434), the pCO2 of surface water during the PROSOPE cruise (1999) is $\geq$ 400 μatm. More recently, records from the DYFAMED site (Ligurian Sea) indicates that during the period 2003-2004, the surface pCO2 is in the range 350-500 μatm with a strong seasonal variability. Concerning the eastern Mediterranean Sea, results of the PROSOPE cruise indicates that oversaturation of the surface layer is even larger than in the western basin. The above arguments show that the estimated maximum Cant of Ìť70 μmol/kg given by Referee #1 is far from being realistic and that it cannot be simply derived using such approach.

Comment from Referee #1 : The authors list CT(circ), i.e. the preindustrial CT concentration for that particular mixture of water-types. They do however not list the measured CT in those water masses, but this can be estimated from Figure 5, for the WMED the values of CT in the deep water range from about 2315 to 2330. Reduce the CT(circ) values (2240 – 2250) gives a range of about 75 to 80 umol/kg, i.e. in the same range as the Cant estimates.

Our response: We do not understand the question. Both terms CT(Cir) and CTj(Cir) are clearly defined in the text of the manuscript (p. 2723, from line 18).

Comment from Referee #1 : It seems to me that the calculations in the MIX method don't correctly calculate the CT(bio) correctly. One reason could be that oxygen don't scale linearly with temperature and salinity (which is assumed in the MIX method) and the span in T and S for the very large range of water masses considered in the analysis.

Our response: It seems that Referee #1 does not really understand the MIX approach. Is the term 'linear' synonymous with the term 'conservative'? Clearly, the O2 property is never considered as conservative tracer in the MIX approach. Referee #1 should compare Eq. (3) of the manuscript for conservative tracers (S,Éţ, NO, PO) with Eq. (8)

which is the equation for O2 (this kind of equation is used for non-conservative tracers).

Comment from Referee #1 : In this sense, the MIX and TrOCA methods are conceptually similar; they both use a scheme to compensate for remineralization of organic particles (and calcium carbon- ate). It is not surprising that both methods show similar biases. The authors actually addresses this in the end of the manuscript: "Wherever the TrOCA method has been used, its CANT results provided very similar results compared to those of the MIX approach that requires additional knowledge on the physical properties of the studied ocean area."

Our response: Several other approaches (ΔC^*, ÏŢCT°, CIPSL, Brewer 1978 or Chen and Millero 1979, etc.) used a similar scheme that compensate for respiration/decomposition and CaCO3 dissolution/formation. Consequently, if we refer to Referee #1 point of view, all these approaches should provide similar results. However, numerous published papers show that despite the fact these approaches use this scheme, their results are not similar. To be objective, Referee #1 should also focus on the structural differences that exist between the TrOCA and MIX approaches; these differences are numerous and very important (please read carefully sections 5.1 and 5.2). Clearly, the similarities obtained in the results of the TrOCA and the MIX approaches cannot be explained solely by the argument given by Referee #1.

Comment from Referee #1 : The authors frequently refer to the the TrOCA method as "robust and accurate", for instance page 2718, line 6. They have, however, no evidence for that, other than some studies that found similar (but not identical) inventories of Cant for the TrOCA method and other methods. It should be noted that in several of those papers there are signifi- cant differences in the distribution of Cant compared to other models. That means that it may be coincidental that the inventories are similar, the concentrations are mostly not. There is no evidence in any of the papers cited by the authors that the TrOCA method should be the "accurate" one.

Our response: One possible definition for the robustness of a model is 'the ability of its

results to remain realistic when applied to a large panel of environmental conditions'. In this sense, all our previous publications that use the TrOCA approach show that this model is robust. We agree with Referee #1 that the term 'accurate' is not adapted here and we propose to replace it by the word 'precise'. We never wrote that the TrOCA approach is the ''accurate' one.

Comment from Referee #1 : On the contrary, in a very careful analysis of the TrOCA method, Yool et al., (2010) compares the TrOCA method to other observational methods applied to the GLODAP data set. Using the formulation by Touratier and Goyet (2004) they find global inventories more than twice that of any other method, and they find unlikely distributions of Cant, such as the highest column inventories of Cant in the poorly ventilated eastern tropical Pacific. The authors deny this comparison made by Yool et al. (2010), page 2730, line 28. The paper by Yool et al., (2010) uses a model to, very carefully, point out the reasons for the bias in the TrOCA method. They even suggest improvements to the TrOCA method (regional determination of constants) by which the can reduce the global bias to about 50% (which is still a lot).

Our response: Referee #1 describes the Yool et al. paper as a 'careful analysis of the TrOCA approach'. In the manuscript we objectively state that it is not correct to conclude that the TrOCA approach provides unrealistic inventories (more than twice!) and unlikely distributions. All inventories that have been computed with TrOCA are very similar to those computed with other approaches (see the papers of Touratier and Goyet 2004; Vazquez-Rodriguez et al., 2009). It must be remembered here that the inventories published in these papers were computed using measurements of several properties (like O2, CT, AT, S, Éţ, etc.) So, why Yool et al. (2010) find that the TrOCA approach largely overestimates the inventories? The reason is clear: it is because Yool et al. feed the TrOCA approach with outputs of their 3D model instead of using real data. In other words they use a mix of 1) model values (to compute TrOCA) and 2) a mix of real data and model values (to compute TrOCA°). Consequently, we conclude that the large differences that exists between the data-based inventories and the 3D model-based inventories, both generated using the TrOCA approach, is only due to the 3D model used by Yool et al. that provides unrealistic results. This is not a surprise since there is a lack of a real validation of their 3D-OCCAM model.

Comment from Referee #1 : Touratier et al. are representing the findings of various comparison studies very subjectively, apparently with the objective to convince the reader that TrOCA is accurate, and that other methods are flawed.

Our response: One of the tasks of scientists is to compare their results with those of other published studies. Since other approaches have provided estimates of Cant in the Mediterranean Sea, it is our duty to compare these results. Otherwise the reviewer could rightly point out that we were not aware of our colleagues'work..

Comment from Referee #1 : The authors rightfully point out some difficulties applying the TTD method in the Mediterranean Sea, as done recently (Schneider et al., 2010). They are, however, not correct in that "the determination of the seawater age remains very doubtful". A large amount of tracer data from, particularly the eastern Med, is available, and con- strains the age of the water relatively well, within some error ranges. The mean age of the interior Mediterranean is likely between 50 and 120 years, i.e. neither the EMT nor the WMT did (far from) completely exchange the deep waters, as the authors here seems to suggest.

Our response: Schneider et al. (2010) does not discuss the uncertainties associated with the calculation of the seawater water age estimates; this is one of the reasons we think that these estimates are doubtful. The CFC data, used to estimate the age of a water mass, are far from being a common property for the Mediterranean Sea (this is also true for other anthropogenic tracers like tritium). In fact, we only know two cruises that have provide CFC and tritium data (1987 and 2001 METEOR cruises). In support of his point of view, Referee #1 should indicate 1) the names of all other cruises from which tracers data are available, and 2) the error ranges of age estimates for the study of Schneider et al. (2010). In our paper, we never suggest that the age

of the WMDW is close to zero or that it is completely exchanged. We simply say that the deep water formation in the Mediterranean Sea can be a very rapid and intense process that significantly affects the properties of the deep waters.

Comment from Referee #1 : The authors discuss the relation between CFC concentrations and Cant concentrations. They are correct in that there is no simple linear relationship between these components; the salinity and temperature has very different effect on the "solubility" of CFCs and Cant, so that they are decoupled. The TTD method however, does take all of this into account. Firstly, the TTD method deals with the partial pressure of CFCs, in which, obviously, the effect of varying S and T are compensated for. Secondly, the buffer capacity of seawater of varying S and T are also taken into account by the TTd method (Waugh et al., 2006). It is true that the formulation of (Thomas and England, 2002) did not do this to the same extent as the TTD method, and the differences between the TTD method and the method suggested by Thomas and England are well documented (Waugh et al., 2006), the TTD method giving lower values. The authors of the present study don't seem to be aware of how the TTD method actually works. The statement that "Only carbon based approaches such as the MIX or TrOCA method can appropriately deal with the specificities of each particular ocean basin and provide meaningful estimates of CANT" (page 2733, line 6), is unbalanced and is apparently based on the author's lack of understanding for the tracer based methods.

Our response: We fully agree with the fact that TTD approach takes into account the effect of temperature and salinity when the solubility of CFC is calculated. However, the problem comes essentially from the way by which Cant is estimated from the CFCs. As mentioned by Referee #1, CFC and Cant are totally decoupled (this is also clearly shown by the relationship between CFC and Δ14C, Fig. 13). How is modeled such a decoupling in the TTD approach? No clear argument is given in the papers of Schneider et al. (2011) and Waugh et al. (2006) that could explain the influence of the decoupling on the CFC derived Cant estimates. Unfortunately, this uncertainty is particularly relevant when the objective is to estimate Cant for the Mediterranean Sea because this region is characterized by huge longitudinal gradients for both the temperature and the salinity. This should have been clearly discussed in the light of the published TTD Cant estimates. Carbon based approach like MIX or TrOCA do not have to face such a problem of decoupling since tracers like CFCs are not used to derive Cant. With these two approaches (MIX and TrOCA), the distribution of anthropogenic CO2 is directly computed using carbon data.

Comment from Referee #1 : In summary, this is, unfortunately, a manuscript that in an unbalanced way is trying to discredit some observational methods to calculate Cant, and is trying to suppress criticism to the particular methods to calculate Cant that the authors favor. This is unfortunate since there are only very limited numbers of observations of Cant in the Mediterranean, and I think we know that there are significant amounts of Cant in the interior of the Mediterranean. The Med is thus an important sink for atmospheric Cant that it is important to accurately quantify. The authors present a potentially interesting data set of carbonate parameters, but the interpretation into Cant and "acidification" is biased if favor to two methods that are known to be biased. By doing so the authors go to great length so miss-credit other approaches that doubtless provides some insight on the very difficult problem – to accurately determine the Cant concentration of the world's oceans.

Our response: The above Referee #1 point of view is very subjective. We never try to 'discredit' or 'suppress criticisms', and we could return exactly the same arguments to Referee #1. All critics on either the TrOCA or the MIX approach are welcomed if they remain objectives and non-partisan. MIX and TrOCA are two very different approaches, and they provide very close estimates of Cant. This is very encouraging since it shows that probably the underlying reasoning behind each approach may be realistic. We do not understand why Referee #1 simply affirms that these two approaches are 'biased'; where is the scientific proof that leads to this conclusion?

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