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.

Anonymous Referee #1

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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.

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 remarkable 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 $\sim 1000 - 3000$ 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 ($\sim$70 umol/kg), these values are clearly not realistic considering the thermodynamic constrains of the carbonate system. 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. 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. 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 carbonate). 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."

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 significant 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. 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). 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.

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 constrains 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.

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.

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.

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