

Interactive comment on “The effects of biogeochemical processes on oceanic conductivity/salinity/density relationships and the characterization of real seawater” by R. Pawlowicz et al.

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Reviewer 1 makes a number of technical suggestions that will improve the paper, and I gratefully acknowledge these suggestions, which will be included in the revised version of the manuscript.

The reviewer also has some questions about the inorganic carbon system components used in the reference composition SSW76, from which anomalies are defined. First, there is the issue of pressure-dependent variations and their effect. This is a natural

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question for studies of the ocean, but is sidestepped by the analysis in this paper, which only considers the properties of seawater samples as they would appear in the laboratory (i.e. at atmospheric pressure).

Unfortunately, the effects of pressure dependence are not known well enough to allow for detailed predictions to be made. These effects arise in three ways: changes to the chemical equilibria in the carbon system, changes in the molal volumes of specific ions, and changes in the molar conductivities of specific ions.

Note that the reviewer wonders about pressure-dependent changes in TA and DIC. Since these are conservative quantities, they will not themselves change with pressure. However, the constants (pK) that govern the equilibria between difference constituents of the carbon system (for example, between HCO_3^- and CO_3^{2-}) will change, and hence the actual composition will change as well.

Pressure dependence of the chemical equilibria has been developed theoretically in, e.g., Millero (1995), and these formulas compare well with laboratory measurements. However, there are no in-situ oceanic measurements (for example, a careful study of the differences between in-situ pH measurements and those found later in the lab) that can be used for verification.

Pressure dependence of molal volumes is known experimentally for many of the constituents of seawater. However, the disagreement between different measurements is somewhat large relative to the effects we are considering. Notwithstanding this uncertainty, preliminary estimates have been made using different models, and these are reported in Wright et al. (2011). Although the exact details of pressure-dependence must still be verified as the results are sensitive to model details, the overall magnitude of the changes are small enough that it seems pressure-dependence itself it probably not an important issue for density changes resulting from composition changes.

Finally, the differential effects of composition changes on conductivity at high pressures is at present unknown, although assumed to be the same as at atmospheric pressure.

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The second question has to do with the specification of the reference composition itself. The reference composition SSW76 is used in our paper to define anomalies. The choice for TA in SSW76 follows the choice made in the definition of the Reference Composition (RC; Millero et al., 2008). In recent years TA has become a relatively well-measured variable in Standard Seawater, and although it does vary from batch to batch there seems to be no good reason to use a value different from RC at this time.

On the other hand, the choice for DIC in SSW76 is about 100 $\mu\text{mol kg}^{-1}$ greater than that in RC (2080 rather than 1963 $\mu\text{mol kg}^{-1}$). A comprehensive discussion of factors involved in this choice is given in Pawlowicz (2010), pg. 365-366. In brief, that paper tries to make the case that the value chosen is 'closer' to the real value of 1970s SSW, although it is unlikely that this issue can ever be solved definitively since no new measurements of 1970s SSW are possible (any remaining samples have degraded with age). Measurements of that vintage suggest a higher value (perhaps as high as 2200 $\mu\text{mol kg}^{-1}$, although more recent SSW batches have somewhat lower values), but not necessarily a specific value.

In order to choose a specific value, measurements of North Atlantic surface waters were considered. Actual in-situ measurements do vary over a wide range, as the reviewer correctly points out. Examination of data from a number of (summer) hydrographic datasets in the N. Atlantic shows that near-surface normalized DIC varies from 1938 to 2180 $\mu\text{mol kg}^{-1}$, and winter values may be even higher as temperatures are lower. This is a wide range, but again the midpoint of this range is somewhat higher than the RC value.

However, this issue can be approached another way, by calculating the effects of changes in the reference state on anomaly parameters using the numerical model. Such calculations show that, as long as the change in the reference state is 'small' (which is the case here, as the range of oceanic variation in DIC is much larger than the change we are considering), the multiplicative coefficients in eqns. (51-54) and

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(59-60) do not change significantly. Essentially a decrease in the reference level of DIC is similar in effect to increasing the ΔDIC value used in these formulas.

Thus, using the RC value for DIC a) numerically increases δS_R^{soln} by 5.5 g/kg, b) increases ρ_R by 0.4 g/m³, and c) decreases δS_R^* by 0.8 mg/kg. Effectively this would move all the calculated curves in Figures 7c and 9a upwards by 5.5 units and rightwards by 0.4 units, those in Figures 7d and 9b downwards by 0.8 units and rightwards by 0.4 units, all points in Figure 8 upwards by 0.4 g/m³, all curves in Figure 10a upwards by 5.5 mg/kg and rightwards by 1 ppm, and all curves in Figure 10b upwards by 1 mg/kg and rightwards by 1 ppm.

Calculations related to density itself are therefore relatively insensitive to these changes in DIC as they result in changes of at most 1 ppm and so the choice of reference concentration for such calculations is not too important. However, the changes in Solution Salinity are large. Using RC, δS_R^{soln} for the surface North Atlantic with $\delta\rho_R \approx 0$ is significantly non-zero. By tuning, it was found that setting the DIC reference to 2080 $\mu\text{mol kg}^{-1}$ resulted in $\delta S_R^{\text{soln}} \approx 0$ in these cases.

Additionally, using RC as a reference would move the 'best-fit' relationships of the forms eqn. (55-57) and (62-63) away from the point (0,0) for all the data shown in Figures 7 and 10. That is, some of these equations would have to include a non-zero intercept.

The SSW76 choice for DIC levels then a) better matches the presumed DIC of 1970s SSW, b) leads to simpler interrelationships between the different anomaly variables, and c) results in $S_A^{\text{soln}} \approx S_R (= S_A^{\text{dens}})$ when $\delta\rho_R \approx 0$ in the North Atlantic. In fact, calculations show that this condition holds for hydrographic data from other oceans as well.

Reviewer 2 appreciates the technical results of the paper, but wonders about their practical importance. Of particular concern are the size of errors that might result in neglecting the effects of composition anomalies, and the effects of this neglect on the TEOS-10 parameters such as potential temperature, enthalpy, etc. These are important

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issues, but addressing them properly is beyond the scope of this paper. They are however discussed at length in Wright et al. (2011) in the context of the open ocean, and we recommend reading that paper to learn more about our current understanding of these points.

Briefly, indications are that the NPIW test case represents what is expected to be the “worst case”, with the largest density anomalies. However, it will be difficult to be fully confident of these predictions without more direct density measurements of both SSW and real seawater from different oceans.

In coastal waters the issues are not as clear. Composition anomalies are not as well-understood and other biogeochemical processes may be at work. However, analysis of measurements in the Baltic (Feistel et al., 2010) suggest that in at least that case Absolute Salinity improves the estimation of some parameters, and does not appear to make any worse. Clearly there is still work to be done.

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