REPORTS / RAPPORTS

Progress Report for the SCOR/IAPSO Working Group 127 on "Thermodynamics and Equation of State of Seawater"

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The SCOR/IAPSO Working Group 127 was formed in 2005 with two primary terms of reference:

1) to examine the results of recent research in ocean thermodynamics with a view to recommending a change to the existing internationally-accepted algorithms for evaluating density and related quantities, and to form new expressions for enthalpy, entropy and potential temperature; and

2) to examine the feasibility of using simple functions of three-dimensional space to take account of the influence of composition anomalies on the determination of density in the ocean.

These goals have now been met and exceeded. A brief summary of developments is given here.

The first meeting of WG127 was held in May, 2006. By the end of that meeting, among other things, we had decided that the Gibbs potential function approach was clearly the best method for improving on EOS-80 and systematically representing the thermodynamic properties of seawater; more properties could be considered, more systematically, consistently and accurately. It was also recognized that a new formulation of the Gibbs function must include additional data sets that hadn't been included in earlier versions, and a standard composition model for sea salt was required to determine a unique formulation of the theoretical limiting-law terms of dilute seawater. Over the next 18 months, WG127 formulated the Reference Composition as a benchmark composition model for Standard Seawater (SSW) (Millero et al., 2008) and reformulated the Gibbs potential function for Standard Seawater (Feistel, 2008).

The new salinity formulation is based on the most accurate available chemical composition analyses for SSW (mostly done in the 60s and 70s). It is linked to Practical Salinity and hence also to historical Chlorinity results; it extends the representation of salinity to allow for arbitrarily large or small concentrations; it is precisely electro-neutral and based on the latest values for atomic weights; and it is SI compatible. Seawater with the Reference Composition is now referred to as Reference-Composition Seawater, or simply Reference Seawater, and its salinity is represented by the Reference-Composition Salinity, or Reference Salinity, expressed in g/kg on the Reference-Composition Salinity Scale (RCSS). Over the concentration range where Practical Salinity is defined,

the Reference Salinity can be estimated in terms of Practical Salinity by S_R = (35.16504/35) S_P g/kg. The decision to link Reference Salinity to Practical Salinity recognizes and builds on the important and reliable work done in the 60s and 70s. We also decided that Practical Salinity rather than Reference Salinity must continue to be recorded in national and international data bases to maintain continuity with past practice and reduce the potential for confusion in these central repositories. However, it was agreed that scientific publications should now use salinity on the Reference-Composition Salinity Scale in place of Practical Salinity and that a new representation of dissolved material in seawater was required to deal with composition anomalies – more on this below.

The new Gibbs potential function presented in Feistel (2008) is an empirical formulation that has been carefully verified to reproduce all known reliable data sets on the thermodynamic properties of Standard Seawater within measurement uncertainties. It provides the most accurate representations available to date for density, enthalpy, entropy, heat capacity, sound speed, plus many other thermodynamic quantities. We note in particular that the availability of potential enthalpy (McDougall, 2003) will allow improved representation of "heat" content and transport in the oceans and is expected to be incorporated into the next generation of climate models along with improved representations of salt content and its influence on ocean properties. Importantly, the Gibbs function takes Reference-Composition Salinity expressed on the RCSS as its salinity input. This Salinity Scale must remain fixed over time to ensure the correct representation of dissolved material in the Gibbs function formulation; use of Practical Salinity for this purpose will give incorrect results.

With the Reference Salinity defined and the new Gibbs function formulated and verified, the next major consideration was the proper accounting for the influence of composition anomalies; this has been one of the most challenging aspects of the work of WG127. Previously, under the principle of constant proportions, the composition anomalies had simply been neglected, but now they were the single largest factor limiting the accurate determination of the thermodynamic properties of seawater, particularly the density. It was decided that direct measurements of density provide the most reliable approach to represent the most important effects of composition anomalies and a program was initiated to collect direct measurements of density along with Practical Salinity
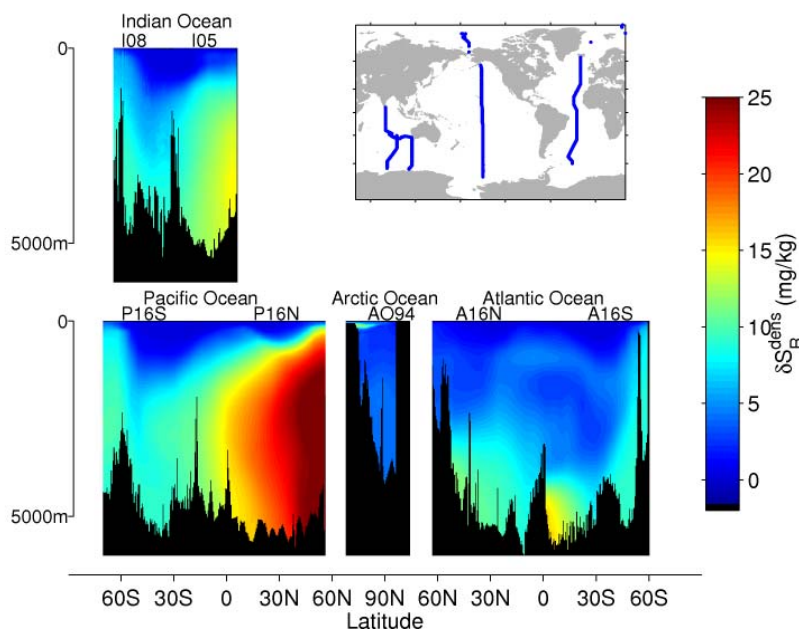
Figure 1: Salinity anomalies predicted using the algorithm of McDougall et al., (2009) along some recent trans-oceanic sections.

and various measures of biogeochemical material dissolved in seawater. The density data were converted to salinity based on an inversion of the expression for density in terms of the Gibbs potential. (At the time, this measure of salinity was simply referred to as Absolute Salinity, but as discussed below, it is more precisely referred to as Density Salinity to distinguish it from other measures of dissolved material in seawater when composition anomalies are present). Based on a small but unprecedented data set consisting of less than a thousand points scattered around the globe, empirical relations between Density Salinity and various measures of biological material in seawater were considered. It was found that anomalies in Density Salinity relative to Reference Salinity could be rather accurately represented using a simple linear regression on the anomalies in silicate relative to the Reference Composition, with different linear relations in each of the ocean basins but all convergent to the same values at the intersection with the Southern Ocean at 30 °S (McDougall *et al.*, 2009). Since global silicate concentrations can be estimated by interpolation of the global hydrographic atlas of Gouretski and Koltermann (2004), this provided the first global correction of density for the effects of composition anomalies. Figure 1 provides examples of salinity anomalies estimated using this approach.

Accounting for the influence of composition anomalies on the properties of seawater opens exciting new areas of research but also introduces new complications. Indeed, the scariest aspect of the new formulation for the properties of seawater, for both its developers and its users, is probably the addition of new salinity variables that are required to account for these effects. There are now six different salinity variables that we feel oceanographers should be aware of. The first three of these are used to represent the properties of SSW and will be

readily accepted within current oceanographic practice:

1) Chlorinity is the historical cornerstone for measures of salinity based on the principle of constant proportions. Simply put, the halide content of seawater is used as a measure of all dissolved material in seawater.

2) Practical Salinity has been the international standard for the representation of dissolved material in seawater for the past three decades. It is based on estimating Chlorinity using conductivity measurements and then scaling the result to give a "salinity" consistent with Knudsen's formula which was based on the relation between Chlorinity and the mass fraction of dissolved material in seawater determined by evaporation experiments. Although Knudsen's formula was known to be inaccurate by about 0.5% even at the time that Practical Salinity was formulated, it was decided to maintain historical continuity by specifying the numerical value of Practical Salinity to agree with Knudsen's salinity at the value of Chlorinity corresponding to 35 ppt. Practical Salinity was, however, defined as a unitless quantity, possibly influenced by this known inconsistency with the true mass fraction of dissolved material in seawater.

3) Reference Salinity has been discussed above. It is expressed as a mass fraction on the RCSS which was determined by Millero et al. (2008) based on the best available estimates of the composition of SSW. For most oceanographic applications Reference Salinity can be thought of as a scaled version of Practical Salinity expressed in units of g/kg, i.e., S_R = (35.16504/35) S_P g/kg. Compared to Practical Salinity, it provides a much improved estimate of the mass fraction of dissolved material in Standard Seawater.

To allow for composition anomalies, three other representations of the dissolved material in seawater have been introduced, each fulfilling a different purpose:

1) Density Salinity, also referred to as Absolute Salinity type 1, is designed to be used with the Gibbs function formulation to provide the best estimate of the density of seawater whether or not it includes composition anomalies. Since it also provides estimates of Conservative Temperature and heat capacity that are accurate to within measurement uncertainties, it is ideally suited for use in numerical modeling studies. An additional advantage of Density Salinity is that it provides a means to establish SI traceability.

2) Solution Salinity, also referred to as Absolute Salinity type 2, is defined as the mass fraction of material in solution and is the most natural extension of Reference Salinity to account for composition anomalies. However, it is not necessarily the most useful measure of salinity since Density Salinity provides more accurate estimates of density which is considered to be the most important thermodynamic quantity to determine precisely.

3) Preformed Salinity is basically the salinity of clean Standard Seawater to which anomalies are added by biogeochemical processes. It is the most relevant representation of salinity if one wishes to model the processes that result in Absolute Salinity anomalies. In particular, although it is natural to consider anomalies from Reference Salinity for field measurements, it is more natural to consider anomalies from Preformed Salinity for theoretical work and in ocean models.

It is important to realize that connections exist between the various forms of salinity discussed above. In particular, the results of Pawlowicz (2010) and Pawlowicz et al. (2010) have contributed both improved understanding and practical formulas for the relations between all of these different salinity variables based on theoretical models of conductivity/salinity/density variations in seawater that result from composition anomalies relative to SSW (as represented by Reference-Composition Seawater).

How might the proliferation of salinities affect the working lives of oceanographers? **DON'T PANIC!** We note that for studies where the influences of composition anomalies are negligible, the only changes necessary compared to past practice will be to replace Practical Salinity by Reference Salinity, $S_R = (35.16504/35) \, S_P$, and to use the new library routines discussed below to calculate the required properties of seawater. Even this simple adjustment will provide more accurate seawater properties as a result of using the new Gibbs function formulation. However, TEOS-10 opens the doors to new research opportunities for those interested in pursuing them. The uses of the different salinity variables may be succinctly summarized as follows: Chlorinity is a historical measure, Practical Salinity is well-known to oceanographers and will continue to be measured by oceanographic instruments and stored in data bases (just as we store in situ temperature, not potential temperature), either Reference Salinity or Density Salinity (obtained via Reference Salinity plus an anomaly salinity when the highest precision is required) will be used to calculate all thermodynamic quantities under TEOS-10, and Preformed Salinity will prove very useful in ocean modeling studies. Solution Salinity (and yet another salinity called Added-Mass Salinity) will likely only be used by those oceanographers specifically studying the variable composition of seawater.

Finally, we note that WG127 has developed software libraries that are available via the World Wide Web to assist the community in using the new formulation for the thermodynamic properties of seawater. Three sets of library routines have been developed for this purpose. The most comprehensive set of routines is available from the Sea-Ice-Air (SIA) library (Feistel et al., 2010; Wright et al. 2010). This library includes a broad range of routines dealing with the thermodynamic properties of pure water (liquid, vapour and solid), seawater, and humid or dry air. Properties of both individual components and equilibria between them are considered. The second set of routines focusses on the properties of seawater and is referred to as the Gibbs SeaWater (GSW) library. It is less comprehensive than the

SIA library, but is more computationally efficient and inputs and outputs are expressed in terms more familiar to oceanographers. Finally, an ultra-efficient set of routines based on the approach taken in Jackett et al. (2006) has recently been developed to deal specifically with the special needs of numerical modelers (McDougall et al., 2010). Initially the SIA library is being made available in Visual Basic and FORTRAN while the GSW library is available mainly in MATLAB. All of these routines will be made available from the TEOS-10 web site (http://www.TEOS-10.org).

The formulation discussed above is referred to as the International Thermodynamic Equation of Seawater - 2010 (TEOS-10). In September 2008 the seawater Gibbs function of Feistel (2008) was endorsed as a release (IAPWS, 2008) of the International Association for the Properties of Water and Steam, so establishing TEOS-10 as the world-wide standard for seawater in the engineering profession. In June 2009, it was approved by the International Oceanographic Commission as the official replacement for the previous international standard known as EOS-80. A major compendium of information on the thermodynamic properties of seawater, including the background and details of TEOS-10, is being published by the IOC as IOC *et al.* (2010). This manual is available from the TEOS-10 web site.

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