# Improved seawater thermodynamics:-
# How should the proposed change in salinity be implemented?

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## Background

The SCOR/IAPSO Working Group 127 on the "Equation of State and Thermodynamics of Seawater" is charged with providing improved algorithms and descriptions of the thermodynamic properties of seawater. The working group has made significant progress on many of its goals, and it is now time to seek the advice of the oceanographic community regarding the best practical ways of adopting these developments into oceanographic practice. The Working Group has met twice to date, once in Warnemünde in 2006, then in Reggio Calabria in 2007. Our next meeting is in Berlin in September 2008.

The working group will soon provide the most accurate algorithms to date for the thermodynamic properties of seawater (such as density, entropy, enthalpy, specific heat capacity, etc). In order to achieve such accuracy it became evident that a salinity variable is required that more accurately represents absolute salinity than does the conductivity-based Practical Salinity. Spatial variations in the composition of seawater upsets the relationship between Practical Salinity $S$ (which is a function of conductivity, temperature and pressure) and Absolute Salinity $S_A$ (defined as the mass of dissolved material per mass of seawater solution). If the thermodynamic properties of seawater are to be written in terms of just one type of salinity, then they are much closer to being functions of $(S_A, t, p)$ than being functions of $(S, t, p)$. Moreover, Absolute Salinity is a conservative property (that is, it is conserved when turbulent mixing occurs) whereas Practical Salinity is not conservative.

## Absolute salinity for seawater of Reference Composition

In order to progress toward evaluating Absolute Salinity our first task was to define the relative concentrations of the constituents of Standard Seawater. This we have done, and this work is published in Millero et al (2008a). The abstract of this paper is as follows.

> Fundamental determinations of the physical properties of seawater have previously been made for Atlantic surface waters, referred to as "Standard Seawater". In this paper a Reference Composition consisting of the major components of Atlantic surface seawater is determined using these earlier analytical measurements. The stoichiometry of sea salt introduced here is thus based on the most accurate prior determination of the composition, adjusted to achieve charge balance and making use of the 2005 atomic weights. Reference Seawater is defined as any seawater that has the Reference Composition and a new Reference-Composition Salinity $S_R$ is defined to provide the best available estimate of the Absolute Salinity of both Reference Seawater and the Standard Seawater that was used in the measurements of the physical properties. From a practical point of view, the value of $S_R$ can be related to the Practical Salinity $S$ by
>
> $$S_R = (35.165\,04 / 35)\ \mathrm{g\ kg^{-1}} \times S\ .$$
>
> Reference Seawater that has been "normalized" to a Practical Salinity of 35 has a Reference-Composition Salinity of exactly $S_R = 35.165\,04\ \mathrm{g\ kg^{-1}}$.
>
> The new independent salinity variable $S_R$ is intended to be used as the concentration variable for future thermodynamic functions of seawater, as an SI-

based extension of Practical Salinity, as a reference for natural seawater composition anomalies, as the currently best estimate for Absolute Salinity of IAPSO Standard Seawater, and as a theoretical model for the electrolyte mixture "seawater".

As described in this abstract, *for seawater of standard composition* we have been able to relate the Absolute Salinity to the Practical Salinity; for example, at a Practical Salinity of 35, seawater of Reference Composition has an Absolute Salinity of 35.165 04 g $kg^{-1}$. We expect shortly to be able to recommend an algorithm that accounts for the variation of seawater composition from the standard composition. That is, we soon expect to be able to recommend an algorithm $S_A = S_A(S_R, , , ,)$ where the extra arguments will be either measured parameters (such as total alkalinity, silicate and nitrate) or more simply the spatial locations longitude, latitude and pressure. Millero and Kremling (1976), Millero (2000) and Millero et al (2008b) are precursor papers to such an algorithm.

**Advantages of Absolute Salinity over Practical Salinity**

Absolute Salinity has the following advantages over Practical Salinity for oceanographic use.

1. The definition of Practical Salinity $S$ on the PSS-78 scale is separate from the system of SI units. Absolute Salinity can be expressed in the unit (g $kg^{-1}$). Adopting this SI unit for salinity would terminate the ongoing controversies in the oceanographic literature about the use of "psu" or "pss" and make research papers more readable to the outside scientific community and consistent with SI.
2. The freshwater mass fraction of seawater is not $(1 - 0.001\,S)$. Rather, it is $(1 - 0.001\,S_A/(\mathrm{g\,kg^{-1}}))$, where $S_A$ is the Absolute Salinity, defined as the mass fraction of dissolved material in seawater. The values of $S_A$ /(g $kg^{-1}$) and $S$ are known to differ by about 0.5%. There seems to be no good reason for continuing to ignore this known difference, e.g., in ocean models.
3. PSS-78 is limited to the salinity range 2 to 42. For a smooth crossover on one side to pure water, and on the other side to concentrated brines up to saturation, as e.g. encountered in sea ice at very low temperatures, salinities beyond these limits need to be defined. While this poses a challenge for $S$, it is not an issue for $S_A$.
4. The theoretical Debye-Hückel limiting laws of seawater behavior at low salinities, used for example in the determination of the Gibbs function of seawater, can only be computed from a chemical composition model, which is available for $S_R$ but not for $S$.
5. For artificial seawater of Reference Composition, $S_R$ has a fixed relation to Chlorinity, independent of conductivity, salinity, temperature, or pressure.
6. The next largest improvement in the equation of state of seawater will come from incorporating variations in the composition of seawater, that is, from calling the equation of state with Absolute Salinity rather than with Reference Salinity. The determination of Absolute Salinity is facilitated by the introduction of the Reference Composition and Reference Salinity.
7. Absolute Salinity $S_A$ is a conservative variable, whereas, in the presence of compositional variations, Practical Salinity $S$ (which is essentially determined by conductivity alone) is not a conservative variable. All of our oceanographic practice assumes that "salinity" is a conservative variable (e.g. ocean model codes, the practice of mixing along straight lines on salinity-potential temperature diagrams, inverse modelling etc).

Expanding on point 7 above, it seems clear that we presently use Practical Salinity $S$ as though it is a conservative variable, and yet we now know that it is not; for a given Absolute Salinity, Practical Salinity varies by up to 0.02 between different major ocean basins (Millero, 2000). This non-conservative regional variation in Practical Salinity is at least seven times the error with which salinity can be measured by modern instrumentation at sea. This difference of 0.02 in Practical Salinity causes differences in density that are also several times greater than the remaining uncertainty in the best algorithms for the density of seawater. It seems that in our oceanographic practice we intuitively ascribe the conservative properties of Absolute Salinity to our "salinity" variable, which to date has been Practical Salinity. For example, if we were intent on interpreting the salinity of an ocean model as Practical Salinity, then the salt conservation equation should contain a non-conservative source term to take account of the spatial variations in the composition of seawater.

Here we summarize the reasons why Absolute Salinity is the preferred salinity variable for oceanographic research.

- It will be preferred by journals since it is an SI unit.
- It is the natural salinity variable for ocean models since they assume that their salinity variable is conservative, hence it should be used to initialize ocean models at all depths.
- It is the natural variable to use in inverse models, budget studies and on salinity-temperature diagrams because its conservative nature justifies turbulent mixing occurring along straight lines on such a diagram.
- The freshwater fraction and the meridional freshwater flux follow naturally when using Absolute Salinity but not when using Practical Salinity.
- By using Absolute Salinity in the algorithm for the equation of state, the effects of the spatial variations of seawater composition are accounted for, while if Practical Salinity is used in such a call to the equation of state, a density error is incurred.
- It is the common salinity variable used in engineering, natural and geosciences outside oceanography, where Practical Salinity is often unknown or misconstrued.
- It is applicable to low concentrations in brackish lagoons and river mouths, to high concentrations in freezing or desiccating brines, as well as at higher temperatures in desalination plants, whereas Practical Salinity is defined only in the range $2 < S < 42$.
- If necessary for chemical or biological reasons, all partial ion concentrations in a sample are easily available, to which Practical Salinity is unrelated.

The SCOR/IAPSO Working Group 127 regards these as compelling reasons for adopting Absolute Salinity as the new preferred salinity variable in the analysis of oceanographic data. Accordingly we are formulating new algorithms for density, enthalpy, entropy, potential temperature, sound speed, etc in terms of Absolute Salinity, temperature and pressure (Feistel (2008)). The extended validity range of the new formulas in temperature and salinity precludes using Practical Salinity as the independent variable of these thermodynamic quantities. For example, in situ density will have the functional form $\rho(S_A, t, p)$ and potential temperature will have the functional form $\theta(S_A, t, p, p_r)$. Absolute Salinity $S_A$ will be defined as

$$S_A = S_R + \delta S_A$$

where Reference salinity $S_R$ is simply proportional to Practical Salinity $S$ as described in Millero et al (2008), namely by

$$S_R = (35.165\,04 / 35)\ \mathrm{g\ kg^{-1}} \times S\,,$$

and $\delta S_A$ is the difference between Absolute and Reference Salinities. $\delta S_A$ will be available as a look up table as a function of latitude, longitude and pressure and also as an alternative linear relationship of nutrient and silicate concentrations, or for example, as a Calcium excess estimate from the river discharge into estuaries. We expect to have algorithms available before the end of 2008.

**How to adopt Absolute Salinity?**

Having made the case that Absolute Salinity possesses many advantages over Practical Salinity, how should present oceanographic practice adapt to incorporate these advantages?

The obvious thing to do would be to decide on a date on which the whole community ceases to use Practical Salinity and switches to using Absolute Salinity. However the algorithm to convert Reference Salinity to Absolute Salinity is less mature and will probably remain a "work in progress" for several years. Moreover, data that is stored in archives should have a very close connection to a measurement (like temperature or conductivity) rather than being the result of an algorithm that is likely to change with time. Hence one cannot really imagine storing Absolute Salinity in data bases. Rather, the closest thing to do in this vein is to store Reference Salinity

Storing Reference Salinity in data centres would have the advantage that it is an SI unit. However before the equation of state (or other thermodynamic quantities) can be evaluated using the new software, the Reference Salinity data needs to be converted to Absolute Salinity using the most up-to-date version of this software. Moreover, the community cannot completely abandon Practical Salinity since it will remain as the salinity variable in the archives for cruises undertaken before the change over date. By changing the salinity variable that is reported from cruises to data bases from Practical Salinity to Reference Salinity the possibility of contamination of the data archives arises as salinity of one type is incorrectly labeled and stored as the other type of salinity.

Hence the best route is not clear in order to avail ourselves of the benefits of using Absolute Salinity in preference to Practical Salinity. In the long run, as with many other historical non-SI units like torr, cal or dyn, it would seem to be an advantage to use only Reference Salinity and abandon the use of Practical Salinity completely. If Reference Salinity were the salinity variable to be used in all of the revised thermodynamic algorithms, the argument for "biting the bullet" and abandoning Practical Salinity as much as possible would seem to be the correct path. But it is Absolute Salinity that we seek, and Reference Salinity is only part way towards the evaluation of Absolute Salinity. Given this, is it worthwhile changing the present archiving practice in favour of a variable (Reference Salinity) that is still not the final salinity that we will use (Absolute Salinity)?

Any choice of action inherently involves compromises, and the best course of action is not obvious to the Working Group. Accordingly we now seek input from the oceanographic community on how to gain the advantages of adopting Absolute Salinity in our oceanographic research work. The key issue seems to revolve around which type of salinity is required to be reported to and archived by oceanographic data centres. We encourage frank responses and promise that each response will be thoughtfully considered by the Working Group. Please email your comments to trevor.mcdougall@csiro.au with the words "Comment for WG127 on how to adopt Absolute Salinity" as the message title. As a conversation starter, we outline two possible routes for adopting the advantages of Absolute Salinity, labeled Option 1 and Option 2. These are just two of many options; please do not feel constrained in your comments to these options.

**Option 1**

- Change from reporting Practical Salinity to reporting Reference Salinity to national and international data bases. This implies that the data bases store Practical Salinity from the old cruises and store Reference Salinity from new cruises (from say 1st January 2010).
- Provide software (for example, of the form $S_A(S_R, x, y, p)$) to produce the best available estimate of Absolute Salinity from Reference Salinity (using additional information on position or water properties).
- Have all the thermodynamic software in the form $\rho(S_A, t, p)$.

*Discussion of Option 1*

The main advantage of Option 1 is that the community eventually ceases to use the non-SI unit Practical Salinity, and instead uses the two SI salinity measures, Reference Salinity and Absolute Salinity.

A drawback of Option 1 is that there will be cases of contamination of the data bases where cruise salinity is labeled and stored as Reference salinity whereas in fact it is Practical Salinity data, and vice versa. This kind of error presently contaminates the temperature, oxygen and pressure/depth data bases.

Since both $S$ and $S_R$ are simply measures of conductivity, and since they are simply proportional to each other, will it be seen that we are taking a course of action that has potential for confusion for only academic benefit?

Recall that scientific work and papers are mostly done with potential temperature $\theta$ rather than in situ temperature $t$ so the first thing that one usually does with the $S$, $t$, $p$ data from a data centre is to form $\theta$. Similarly, scientific work and papers should be done with Absolute Salinity rather than Reference Salinity so the first thing that one needs to do under Option 1 with the $S_R$, $t$, $p$ data from a cruise or from a data centre is to form not only $\theta$ but also $S_A$. This analogy with what we already do with storing the measured variable $t$ but using the derived variable $\theta$ is very close.

Under Option 1 we cannot imagine that the community can altogether forget about Practical Salinity however, as the data from older cruises (e.g. all of WOCE) is stored in data centres in terms of Practical Salinity. This data will need converting first to Reference Salinity and then to Absolute Salinity before the thermodynamic routines such as potential temperature, density, potential enthalpy etc, can be called by oceanographic researchers.

There will be some instances when the new software is called with the salinity data being $S$ and in those instances an error will be made. This type of error is an undesirable consequence of both Options 1 and 2.

Option 1 requires manufacturers (such as Seabird) to change what they presently do. The instruments will need to output their salinity in terms of Reference Salinity. Also the ampoules of standard seawater will need to quote their salinity in terms of Reference Salinity. The transition date of say 1st January 2010 has to be handled very carefully in these respects. Further, anyone wanting to make use of older ampoules will have to be aware of the transition and how to deal with it.

**Option 2**

- Continue to report Practical Salinity *S* from cruises and to have only Practical Salinity *S* stored at national and international data centres.
- Provide software (for example, of the form $S_A(S, x, y, p)$) to produce the best available estimate of Absolute Salinity from Practical Salinity (using additional information on position or water properties).
- Have all the thermodynamic software in the form $\rho(S_A, t, p)$

*Discussion of Option 2*

By reporting only *S* in data bases we would expect to greatly reduce the possibility of salinity data being mislabeled in data bases.

Since both *S* and $S_R$ are simply measures of conductivity, option 2 is consistent with the argument that there is little value in replacing one measure of conductivity (namely Practical Salinity) with another (namely Reference Salinity) in data bases. Rather, under Option 2 data centres store *S* and *S* alone.

As mentioned above, scientific work and papers are mostly done with potential temperature $\theta$ rather than in situ temperature *t* so the first thing that one usually does with the *S, t, p* data from a data centre is to form $\theta$. Similarly, scientific work and papers will be mostly done with Absolute Salinity rather than Practical Salinity so the first thing that one needs to do under Option 2 with the *S, t, p* data from a cruise or from a data centre is to form not only $\theta$ but also $S_A$. This analogy with what we already do with storing the measured variable *t* but using the derived variable $\theta$ suggests that storing *S* but using $S_A$ will not cause oceanographers any serious difficulties.

There will be some instances when the new software is called with the salinity data being *S* and in those instances an error will be made. This type of error is an undesirable consequence of both Options 1 and 2. However this error will affect the results and the publications arising out of those who make this error, but this error will not contaminate an archived data set.

Option 2 does not require manufacturers (such a Seabird and the Standard Seawater Service) to change what they presently do. Rather, Option 2 puts the responsibility for the changes in the hands of practicing research oceanographers.

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**Membership of SCOR/IAPSO Working Group 127 on**
"Thermodynamics and the Equation of State of Seawater"

Trevor J. McDougall, *Chair,* E-mail: Trevor.McDougall@csiro.au

Chen-Tung Arthur Chen, E-mail: ctchen@mail.nsysu.edu.tw

Rainer Feistel, E-mail: rainer.feistel@io-warnemuende.de

Valentina N. Gramm-Osipova, E-mail: levgo@poi.dvo.ru

David R. Jackett, E-mail: David.Jackett@csiro.au

Brian A. King, E-mail: bak@noc.soton.ac.uk

Giles M. Marion, E-mail: Giles.Marion@dri.edu

Frank J. Millero, E-mail: fmillero@rsmas.miami.edu

Petra Spitzer, E-mail: petra.spitzer@ptb.de

Dan Wright, E-mail: wrightdan@mar.dfo-mpo.gc.ca

*Associate Member*
Peter Tremaine, Email: tremaine@uoguelph.ca