

Notes on the GSW function gsw_SA_from_SP

Notes made 29th September 2010

The “raw” physical oceanographic data, as collected from ships and from autonomous platforms (e. g. ARGO), and as stored in national oceanographic data bases, are

- Practical Salinity (S_p , unitless) and
- in situ temperature (t , °C) as functions of
- pressure (p , dbar), at a series of
- longitudes and latitudes.

Under TEOS-10 all the thermodynamic properties are functions of Absolute Salinity S_A (rather than of Practical Salinity), hence the first step in processing oceanographic data is to calculate Absolute Salinity, and this is accomplished by the GSW function gsw_SA_from_SP:- note that it is not possible to calculate either potential temperature θ or Conservative Temperature Θ until Absolute Salinity is first evaluated since θ and Θ are functions of Absolute Salinity (as opposed to being functions of Practical Salinity). Hence this function, gsw_SA_from_SP, is perhaps the most fundamental of the GSW functions as it is the gateway leading from oceanographic measurements to all the thermodynamic properties of seawater under TEOS-10. A call to this function can be avoided only if one is willing to ignore the influence of the spatial variations in the composition of seawater on seawater properties (such as density and specific volume). If this is indeed the intention, then the remaining GSW functions must be called with the salinity argument being Reference Salinity S_R , not Practical Salinity S_p .

The gsw_SA_from_SP(S_p , p , long, lat) function first interpolates the global Absolute Salinity Anomaly (δS_A) data set using the gsw function gsw_delta_SA to the (p , long, lat) location and then uses this interpolated value to calculate Absolute Salinity according to

$$S_A = \frac{35.165\,04\,\text{g kg}^{-1}}{35} S_p + \delta S_A. \quad \text{Non-Baltic} \quad (1)$$

The first part of this expression, $(35.165\,04\,\text{g kg}^{-1}/35) S_p$, is the Reference Salinity S_R , which is the best estimate of Absolute Salinity of a Standard Seawater sample.

Equation (1) is the value of Absolute Salinity returned by gsw_SA_from_SP unless the function detects that the location is in the Baltic Sea (where incidentally the gsw_delta_SA function returns a value of zero). If the observation is from the Baltic Sea, Absolute Salinity Anomaly is calculated according to $S_A - S_R = 0.087\,\text{g kg}^{-1} \times (1 - S_p/35)$ (from Eqn. (A.5.6) of IOC *et al.* (2010), following Feistel *et al.* (2010)), so that Absolute Salinity S_A is given by

$$S_A = \frac{(35.165\,04 - 0.087)\,\text{g kg}^{-1}}{35} S_p + 0.087\,\text{g kg}^{-1}. \quad \text{Baltic Sea} \quad (2)$$

In summary, the gsw_SA_from_SP function returns either Eqn. (1) or Eqn. (2) depending on whether the longitude and latitude of the sample put the observation outside or inside the Baltic Sea. Since Practical Salinity should always be positive but there are sometimes be a few negative values from a CTD, any negative input values of S_p to this function gsw_SA_from_SP are set to zero.

If the latitude and longitude are such as to place the observation well away from the ocean, a flag ‘in_ocean’ is set to zero as a warning, otherwise it is 1. This flag is only set when the observation is well and truly on dry land; often the warning flag is not set until one is several hundred kilometers inland from the coast. When the function detects that the observation is not from the ocean, δS_A is set equal to zero and gsw_SA_from_SP returns $S_A = S_R = (35.165\,04\,\text{g kg}^{-1}/35) S_p$ in accordance with Eqn. (1).

Note that in version 1 of the GSW code which was made available from January 2009, the Absolute Salinity in the Baltic Sea was taken to be related to Practical Salinity by the earlier Millero and Kremling (1976) expression $S_A - S_R = 0.124 \text{ g kg}^{-1} \times (1 - S_p/35)$.

References

- IOC, SCOR and IAPSO, 2010: *The international thermodynamic equation of seawater – 2010: Calculation and use of thermodynamic properties*. Intergovernmental Oceanographic Commission, Manuals and Guides No. 56, UNESCO (English), 196 pp. Available from <http://www.TEOS-10.org>
- Feistel, R., S. Weinreben, H. Wolf, S. Seitz, P. Spitzer, B. Adel, G. Nausch, B. Schneider and D. G. Wright, 2010: Density and Absolute Salinity of the Baltic Sea 2006–2009. *Ocean Science*, **6**, 3–24. <http://www.ocean-sci.net/6/3/2010/os-6-3-2010.pdf>
- Millero, F. J. and K. Kremling, 1976: The densities of Baltic Sea waters. *Deep-Sea Research*, **23**, 1129–1138.

Here follows sections 2.4 and 2.5 and appendices A.4 and A.5 of the TEOS-10 Manual (IOC *et al.* (2010)).

2.4 Reference Composition and the Reference-Composition Salinity Scale

The reference composition of seawater is defined by Millero *et al.* (2008a) as the exact mole fractions given in Table D.3 of appendix D below. This composition was introduced by Millero *et al.* (2008a) as their best estimate of the composition of Standard Seawater, being seawater from the surface waters of a certain region of the North Atlantic. The exact location for the collection of bulk material for the preparation of Standard Seawater is not specified. Ships gathering this bulk material are given guidance notes by the Standard Seawater Service, requesting that water be gathered between longitudes 50°W and 40°W, in deep water, during daylight hours. Reference-Composition Salinity S_R (or Reference Salinity for short) was designed by Millero *et al.* (2008b) to be the best estimate of the mass-fraction Absolute Salinity S_A of Standard Seawater. Independent of accuracy considerations, it provides a precise measure of dissolved material in Standard Seawater and is the correct salinity argument to be used in the TEOS-10 Gibbs function for Standard Seawater.

For the range of salinities where Practical Salinities are defined (that is, in the range $2 < S_p < 42$) Millero *et al.* (2008a) show that

$$S_R \approx u_{PS} S_p \quad \text{where} \quad u_{PS} \equiv (35.165\,04/35) \text{ g kg}^{-1}. \quad (2.4.1)$$

In the range $2 < S_p < 42$, this equation expresses the Reference Salinity of a seawater sample on the Reference-Composition Salinity Scale (Millero *et al.* (2008a)). For practical purposes, this relationship can be taken to be an equality since the approximate nature of this relation only reflects the extent to which Practical Salinity, as determined from measurements of conductivity ratio, temperature and pressure, varies when a seawater sample is heated, cooled or subjected to a change in pressure but without exchange of mass with its surroundings. The Practical Salinity Scale of 1978 was designed to satisfy this property as accurately as possible within the constraints of the polynomial approximations used to determine Chlorinity (and hence Practical Salinity) in terms of the measured conductivity ratio.

From Eqn. (2.4.1), a seawater sample of Reference Composition whose Practical Salinity S_p is 35 has a Reference Salinity S_R of $35.165\,04 \text{ g kg}^{-1}$. Millero *et al.* (2008a)

estimate that the absolute uncertainty in this value is $\pm 0.007 \text{ g kg}^{-1}$. The difference between the numerical values of Reference and Practical Salinities can be traced back to the original practice of determining salinity by evaporation of water from seawater and weighing the remaining solid material. This process also evaporated some volatile components and most of the $0.16504 \text{ g kg}^{-1}$ salinity difference is due to this effect.

Measurements of the composition of Standard Seawater at a Practical Salinity S_p of 35 using mass spectrometry and/or ion chromatography are underway and may provide updated estimates of both the value of the mass fraction of dissolved material in Standard Seawater and its uncertainty. Any update of this value will not change the Reference-Composition Salinity Scale and so will not affect the calculation of Reference Salinity nor of Absolute Salinity as calculated from Reference Salinity plus the Absolute Salinity Anomaly.

Oceanographic databases label stored, processed or exported parameters with the GF3 code PSAL for Practical Salinity and SSAL for salinity measured before 1978 (IOC, 1987). In order to avoid possible confusion in data bases between different types of salinity it is very strongly recommended that under no circumstances should either Reference Salinity or Absolute Salinity be stored in national data bases.

Detailed information on Reference Composition and Reference Salinity can be found in Millero *et al.* (2008a). For the user's convenience a brief summary of information from Millero *et al.* (2008a), including the precise definition of Reference Salinity is given in appendix A.3 and in Table D3 of appendix D.

2.5 Absolute Salinity

Absolute Salinity is traditionally defined as the mass fraction of dissolved material in seawater. For seawater of Reference Composition, Reference Salinity gives our current best estimate of Absolute Salinity. To deal with composition anomalies in seawater, we need an extension of the Reference-Composition Salinity S_R that provides a useful measure of salinity over the full range of oceanographic conditions and agrees precisely with Reference Salinity when the dissolved material has Reference Composition. When composition anomalies are present, no single measure of dissolved material can fully represent the influences on seawater properties on all thermodynamic properties, so it is clear that either additional information will be required or compromises will have to be made. In addition, we would like to introduce a measure of salinity that is traceable to the SI (Seitz *et al.*, 2010b) and maintains the high accuracy of PSS-78 necessary for oceanographic applications. The introduction of "Density Salinity" S_A^{dens} addresses both of these issues; it is this type of absolute salinity that in TEOS-10 parlance is labeled S_A and called Absolute Salinity. In this section we explain how S_A is defined and evaluated, but first we outline other choices that are available for the definition of absolute salinity in the presence of composition variations in seawater.

The most obvious definition of absolute salinity is "the mass fraction of dissolved non- H_2O material in a seawater sample at its temperature and pressure". This seemingly simple definition is actually far more subtle than it first appears. Notably, there are questions about what constitutes water and what constitutes dissolved material. Perhaps the most obvious example of this issue occurs when CO_2 is dissolved in water to produce a mixture of CO_2 , H_2CO_3 , HCO_3^- , CO_3^{2-} , H^+ , OH^- and H_2O , with the relative proportions depending on dissociation constants that depend on temperature, pressure and pH. Thus, the dissolution of a given mass of CO_2 in pure water essentially transforms some of the water into dissolved material. A change in the temperature and even an adiabatic change in pressure results in a change in absolute salinity defined in this way due to the dependence of chemical equilibria on temperature and pressure. Pawlowicz *et al.* (2010)

and Wright *et al.* (2010b) address this second issue by defining “Solution Absolute Salinity” (usually shortened to “Solution Salinity”), S_A^{soln} , as the mass fraction of dissolved non-H₂O material after a seawater sample is brought to the constant temperature $t = 25^\circ\text{C}$ and the fixed sea pressure 0 dbar (fixed Absolute Pressure of 101 325 Pa).

Another measure of absolute salinity is the “Added-Mass Salinity” S_A^{add} which is S_R plus the mass fraction of material that must be added to Standard Seawater to arrive at the concentrations of all the species in the given seawater sample, after chemical equilibrium has been reached, and after the sample is brought to the constant temperature $t = 25^\circ\text{C}$ and the fixed sea pressure of 0 dbar. The estimation of absolute salinity S_A^{add} is not straightforward for seawater with anomalous composition because while the final equilibrium state is known, one must iteratively determine the mass of anomalous solute prior to any chemical reactions with Reference-Composition seawater. Pawlowicz *et al.* (2010) provide an algorithm to achieve this, at least approximately. This definition of absolute salinity, S_A^{add} , is useful for laboratory studies of artificial seawater and it differs from S_A^{soln} because of the chemical reactions that take place between the several species of the added material and the components of seawater that exist in Standard Seawater. Added-Mass Salinity may be the most appropriate form of salinity for accurately accounting for the mass of salt discharged by rivers and hydrothermal vents into the ocean.

“Preformed Absolute Salinity” (usually shortened to “Preformed Salinity”), S_* , is a different type of absolute salinity which is specifically designed to be as close as possible to being a conservative variable. That is, S_* is designed to be insensitive to biogeochemical processes that affect the other types of salinity to varying degrees. Preformed Salinity S_* is formed by first estimating the contribution of biogeochemical processes to one of the salinity measures S_A , S_A^{soln} , or S_A^{add} , and then subtracting this contribution from the appropriate salinity variable. In this way Preformed Salinity S_* is designed to be a conservative salinity variable which is independent of the effects of the non-conservative biogeochemical processes. S_* will find a prominent role in ocean modeling. The three types of absolute salinity S_A^{soln} , S_A^{add} and S_* are discussed in more detail in appendices A.4 and A.20, where approximate relationships between these variables and $S_A \equiv S_A^{\text{dens}}$ are presented, based on the work of Pawlowicz *et al.* (2010) and Wright *et al.* (2010b). Note that for a sample of Standard Seawater, all of the five salinity variables S_R , S_A , S_A^{soln} , S_A^{add} and S_* and are equal.

There is no simple means to measure either S_A^{soln} or S_A^{add} for the general case of the arbitrary addition of many components to Standard Seawater. Hence a more precise and easily determined measure of the amount of dissolved material in seawater is required and TEOS-10 adopts “Density Salinity” for this purpose. “Density Salinity” S_A^{dens} is defined as the value of the salinity argument of the TEOS-10 expression for density which gives the sample’s actual measured density at the temperature $t = 25^\circ\text{C}$ and at the sea pressure $p = 0$ dbar. When there is no risk of confusion, “Density Salinity” is also called Absolute Salinity with the label S_A , that is $S_A \equiv S_A^{\text{dens}}$. Usually we do not have accurate measurements of density but rather we have measurements of Practical Salinity, temperature and pressure, and in this case, Absolute Salinity may be calculated using Practical Salinity and the computer algorithm of McDougall, Jackett and Millero (2010a) which provides an estimate of $\delta S_A = S_A - S_R$. This computer program was formed as follows.

In a series of papers (Millero *et al.* (1976a, 1978, 2000, 2008b), McDougall *et al.* (2010a)), accurate measurements of the density of seawater samples, along with the Practical Salinity of those samples, gave estimates of $\delta S_A = S_A - S_R$ from most of the major basins of the world ocean. This was done by first calculating the “Reference Density” from the TEOS-10 equation of state using the sample’s Reference Salinity as the salinity argument

(this calculation essentially assumes that the seawater sample has the composition of Standard Seawater). The difference between the measured density and the “Reference Density” was then used to estimate the Absolute Salinity Anomaly $\delta S_A = S_A - S_R$ (Millero *et al.* (2008a)). The McDougall *et al.* (2010a) algorithm is based on the observed correlation between this $S_A - S_R$ data and the silicate concentration of the seawater samples (Millero *et al.* , 2008a), with the silicate concentration being estimated by interpolation of a global atlas (Gouretski and Koltermann (2004)).

The algorithm for Absolute Salinity takes the form

$$S_A = S_R + \delta S_A = S_A(S_p, \phi, \lambda, p), \quad (2.5.1)$$

Where ϕ is latitude (degrees North), λ is longitude (degrees east, ranging from 0°E to 360°E) while p is sea pressure.

Heuristically the dependence of $\delta S_A = S_A - S_R$ on silicate can be thought of as reflecting the fact that silicate affects the density of a seawater sample without significantly affecting its conductivity or its Practical Salinity. In practice this explains about 60% of the effect and the remainder is due to the correlation of other composition anomalies (such as nitrate) with silicate. In the McDougall *et al.* (2010a) algorithm the Baltic Sea is treated separately, following the work of Millero and Kremling (1976) and Feistel *et al.* (2010c, 2010d), because some rivers flowing into the Baltic are unusually high in calcium carbonate.

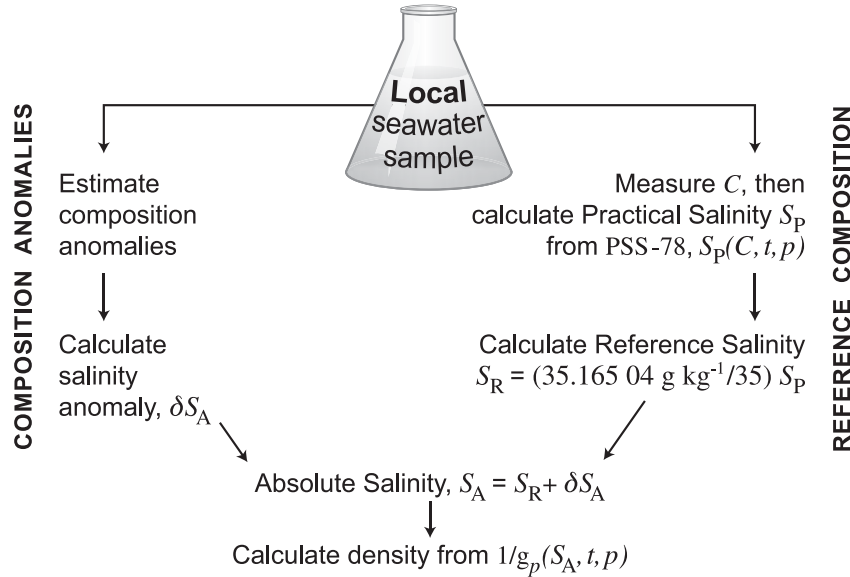


Figure 1. A sketch indicating how thermodynamic quantities such as density are calculated as functions of Absolute Salinity. Absolute Salinity is found by adding an estimate of the Absolute Salinity Anomaly δS_A to the Reference Salinity.

Since the density of seawater is rarely measured, we recommend the approach illustrated in Figure 1 as a practical method to include the effects of composition anomalies on estimates of Absolute Salinity and density. When composition anomalies are not known, the algorithm of McDougall *et al.* (2010a) may be used to estimate Absolute Salinity in terms of Practical Salinity and the spatial location of the measurement in the world oceans.

The difference between Absolute Salinity and Reference Salinity, as estimated by the McDougall *et al.* (2010a) algorithm, is illustrated in Figure 2(a) at a pressure of 2000 dbar, and in a vertical section through the Pacific Ocean in Figure 2 (b).

Of the approximately 800 samples of seawater from the world ocean that have been examined to date for $\delta S_A = S_A - S_R$ the standard error (square root of the mean squared value) of $\delta S_A = S_A - S_R$ is 0.0107 g kg^{-1} . That is, the “typical” value of $\delta S_A = S_A - S_R$ of the 811 samples taken to date is 0.0107 g kg^{-1} . The standard error of the difference between the measured values of $\delta S_A = S_A - S_R$ and the values evaluated from the computer algorithm of McDougall *et al.* (2010a) is 0.0048 g kg^{-1} . The maximum values of $\delta S_A = S_A - S_R$ of approximately 0.025 g kg^{-1} occur in the North Pacific.

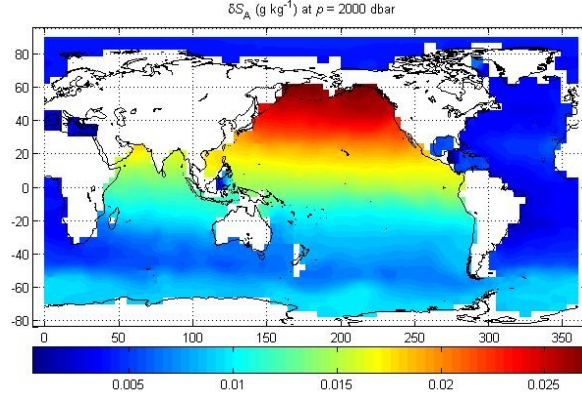


Figure 2 (a). Absolute Salinity Anomaly δS_A at $p = 2000 \text{ dbar}$.

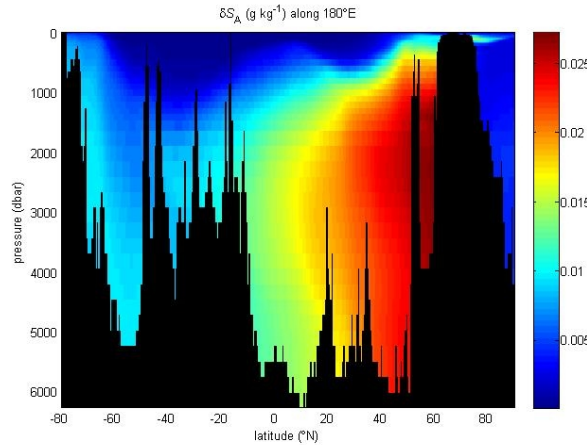


Figure 2 (b). A vertical section of Absolute Salinity Anomaly δS_A along 180°E in the Pacific Ocean.

The thermodynamic description of seawater and of ice Ih as defined in IAPWS-08 and IAPWS-06 has been adopted as the official description of seawater and of ice Ih by the Intergovernmental Oceanographic Commission in June 2009. These thermodynamic descriptions of seawater and ice were endorsed recognizing that the techniques for estimating Absolute Salinity will likely improve over the coming decades. The algorithm for evaluating Absolute Salinity in terms of Practical Salinity, latitude, longitude and pressure, will likely be updated from time to time, after relevant appropriately peer-reviewed publications have appeared, and such an updated algorithm will appear on the www.TEOS-10.org web site. Users of this software should state in their published work which version of the software was used to calculate Absolute Salinity.

The present computer software which evaluates Absolute Salinity S_A given the input variables Practical Salinity S_p , longitude λ , latitude ϕ and pressure is available at www.TEOS-10.org. Absolute Salinity is also available as the inverse function of density

$S_A(T, P, \rho)$ in the SIA library of computer algorithms as the algorithm `sea_sa_si` (see appendix M) and in the GSW software library as the algorithm `gsw_SA_from_density`.

A.4 Absolute Salinity

Millero *et al.* (2008a) list the following six advantages of adopting Reference Salinity S_R and Absolute Salinity S_A in preference to Practical Salinity S_p .

1. The definition of Practical Salinity S_p on the PSS-78 scale is separate from the system of SI units (BIPM (2006)). Reference Salinity can be expressed in the unit (g kg^{-1}) as a measure of Absolute Salinity. Adopting Absolute Salinity and Reference Salinity will 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 $(1 - 0.001 S_p)$. Rather, it is $(1 - 0.001 S_A / (\text{g kg}^{-1}))$, where S_A is the Absolute Salinity, defined as the mass fraction of dissolved material in seawater. The values of $S_A / (\text{g kg}^{-1})$ and S_p are known to differ by about 0.5%. There seems to be no good reason for continuing to ignore this known difference, for example in ocean models.
3. PSS-78 is limited to the range $2 < S_p < 42$. For a smooth crossover on one side to pure water, and on the other side to concentrated brines up to saturation, as for example encountered in sea ice at very low temperatures, salinities beyond these limits need to be defined. While this poses a challenge for S_p , it is trivial for S_R .
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_p .
5. For artificial seawater of Reference Composition, S_R has a fixed relation to Chlorinity, independent of conductivity, salinity, temperature, or pressure.
6. Stoichiometric anomalies can be specified accurately relative to Reference-Composition Seawater with its known composition, but only uncertainly with respect to IAPSO Standard Seawater with its unknown composition. These variations in the composition of seawater cause significant (a few percent) variations in the horizontal density gradient.

Regarding point number 2, Practical Salinity S_p is a dimensionless number of the order of 35 in the open ocean; no units or their multiples are permitted. There is however more freedom in choosing the representation of Absolute Salinity S_A since it is defined as the mass fraction of dissolved material in seawater. For example, all the following quantities are equal (see ISO (1993) and BIPM (2006)),

$$34 \text{ g/kg} = 34 \text{ mg/g} = 0.034 \text{ kg/kg} = 0.034 = 3.4 \% = 34\,000 \text{ ppm} = 34\,000 \text{ mg/kg}.$$

In particular, it is strictly correct to write the freshwater fraction of seawater as either $(1 - 0.001 S_A / (\text{g kg}^{-1}))$ or as $(1 - S_A)$ but it would be incorrect to write it as $(1 - 0.001 S_A)$. Clearly it is essential to consider the units used for Absolute Salinity in any particular application. If this is done, there should be no danger of confusion, but to maintain the numerical value of Absolute Salinity close to that of Practical Salinity S_p we adopt the first option above, namely g kg^{-1} as the preferred unit for S_A , (as in $S_A = 35.165\,04 \text{ g kg}^{-1}$). The Reference Salinity, S_R , is defined to have the same units and follows the same conventions as S_A . Salinity “‰” measured prior to PSS-78 available from the literature

or from databases is usually reported in ‰ or ppt (part per thousand) and is converted to the Reference Salinity, $S_R = u_{PS} S_{‰}$, by the numerical factor u_{PS} from (A.3.3).

Regarding point number 5, Chlorinity Cl is the concentration variable that was used in the laboratory experiments for the fundamental determinations of the equation of state and other properties, but has seldom been measured in the field since the definition of PSS-78 (Millero, 2010). Since the relation $S = 1.80655 Cl$ for Standard Seawater was used in the definition of Practical Salinity this may be taken as an exact relation for Standard Seawater and it is also our best estimate for Reference Composition Seawater. Thus, Chlorinity expressed in ‰ can be converted to Reference-Composition Salinity by the relation, $S_R = u_{Cl} Cl$, with the numerical factor $u_{Cl} = 1.80655 u_{PS}$. These constants are recommended for the conversion of historical (pre 1900) data. The primary source of error in using this relation will be the possible presence of composition anomalies in the historical data relative to Standard Seawater.

Regarding point number 6, the composition of dissolved material in seawater is not constant but varies a little from one ocean basin to another, and the variation is even stronger in estuaries, semi-enclosed or even enclosed seas. Brewer and Bradshaw (1975) and Millero (2000) point out that these spatial variations in the relative composition of seawater impact the relationship between Practical Salinity (which is essentially a measure of the conductivity of seawater at a fixed temperature and pressure) and density. All the thermophysical properties of seawater as well as other multicomponent electrolyte solutions are directly related to the concentrations of the major components, not the salinity determined by conductivity; note that some of the variable nonelectrolytes (e.g., $Si(OH)_4$, CO_2 and dissolved organic material) do not have an appreciable conductivity signal. It is for this reason that the new TEOS-10 thermodynamic description of seawater (Millero *et al.* (2008a), Millero (2010)) has the Gibbs function g of seawater expressed as a function of Absolute Salinity as $g(S_A, t, p)$ rather than as a function of Practical Salinity S_p or of Reference Salinity, S_R . The issue of the spatial variation in the composition of seawater is discussed more fully in appendix A.5.

Regarding point number 2, we note that it is perhaps debatable which of $(1 - 0.001 S_A^{dens} / (g\ kg^{-1}))$, $(1 - 0.001 S_A^{soln} / (g\ kg^{-1}))$, $(1 - 0.001 S_A^{add} / (g\ kg^{-1}))$ or $(1 - 0.001 S_* / (g\ kg^{-1}))$ is the most appropriate measure of the freshwater mass fraction. (These different versions of absolute salinity are defined in section 2.5 and also later in this appendix.) This is a minor point compared with the present use of S_p in this context, and the choice of which of these expressions may depend on the use for the freshwater mass fraction. For example, in the context of ocean modelling, if S_* is the salinity variable that is treated as a conservative variable in an ocean model, then $(1 - 0.001 S_* / (g\ kg^{-1}))$ is probably the most appropriate version of freshwater mass fraction.

It should be noted that the quantity S_A appearing as an argument of the function $g(S_A, t, p)$ is the Absolute Salinity (the “Density Salinity” $S_A \equiv S_A^{dens}$) measured on the Reference-Composition Salinity Scale. This is important since the Gibbs function has been fitted to laboratory and field measurements with the Absolute Salinity values expressed on this scale. Thus, for example, it is possible that sometime in the future it will be determined that an improved estimate of the mass fraction of dissolved material in Standard Seawater can be obtained by multiplying S_R by a factor slightly different from 1 (uncertainties permit values in the range 1 ± 0.002). We emphasize that since the Gibbs function is expressed in terms of the Absolute Salinity expressed on the Reference-Composition Salinity Scale, use of any other scale (even one that gives more accurate estimates of the true mass fraction of dissolved substances in Standard Seawater) will reduce the accuracy of the thermodynamic properties determined from the Gibbs function. In part for this reason, we recommend that the Reference-Composition Salinity continue to be measured on the scale defined by Millero *et al.* (2008a) even if new results

indicate that improved estimates of the true mass fraction can be obtained using a modified scale. That is, we recommend that the value of u_{ps} used in (A.3.3) not be updated. If a more accurate mass fraction estimate is required for some purpose in the future, such a revised estimate should definitely not be used as an argument of the TEOS-10 Gibbs function.

Finally, we note a second reason for recommending that the value assigned to u_{ps} not be modified without very careful consideration. Working Group 127 is recommending that the practice of expressing salinity as Practical Salinity in publications be phased out in favour of using Absolute Salinity for this purpose. It is critically important that this new measure of salinity remain stable into the future. In particular, we note that any change in the value of u_{ps} used in the determination of Reference Salinity would result in a change in reported salinity values that would be unrelated to any real physical change. For example, a change in u_{ps} from 35.16504/35 to $(35.16504/35) \times 1.001$ for example, would result in changes of the reported salinity values of order 0.035 g kg^{-1} which is more than ten times larger than the precision of modern salinometers. Thus changes associated with a series of improved estimates of u_{ps} (as a measure of the mass fraction of dissolved salts in Standard Seawater) could cause very serious confusion for researchers who monitor salinity as an indicator of climate change. Based on this concern and the fact that the Gibbs function is expressed as a function of Absolute Salinity measured on the Reference-Composition Salinity Scale as defined by Millero *et al.* (2008a), we strongly recommend that the Reference-Composition Salinity continue to be expressed on this scale; no changes in the value of u_{ps} should be introduced.

For seawater of Reference Composition, Reference Salinity S_{R} is the best available estimate of the mass-fraction of non- H_2O material in seawater. As discussed in sections 2.4 and 2.5, under TEOS-10 S_{R} was determined to provide the best available estimate of the mass-fraction of non- H_2O material in Standard Seawater by Millero *et al.* (2008a). Subsequently, Pawlowicz (2010) has argued that the DIC content of the Reference Composition is probably about $117 \mu\text{mol kg}^{-1}$ low for SSW and also for the North Atlantic surface water from which it was prepared. This difference in DIC causes a negligible effect on both conductivity and density, and hence on Reference Salinity and Density Salinity. The influence on Solution Salinity is nearly a factor of 10 larger (Pawlowicz *et al.*, 2010) but at 0.0055 g kg^{-1} it is still just below the uncertainty of 0.007 g kg^{-1} assigned to the estimated Absolute Salinity by Millero *et al.* (2008a). In fact, the largest uncertainties in Reference Salinity as a measure of the Absolute Salinity of SSW are associated with uncertainties in the mass fractions of other constituents such as sulphate, which may be as large as 0.05 g kg^{-1} (Seitz *et al.*, 2010a). Nevertheless, it seems that the sulphate value of Reference-Composition Seawater lies within the 95% uncertainty range of the best laboratory-determined estimates of SSW's sulphate concentration, so there is no justification for an update of the Reference Composition at this time.

When the composition of seawater differs from that of Standard Seawater, there are several possible definitions of the absolute salinity of a seawater sample, as discussed in section 2.5. Conceptually the simplest definition is “the mass fraction of dissolved non- H_2O material in a seawater sample at its temperature and pressure”. One drawback of this definition is that because the equilibrium conditions between H_2O and several carbon compounds depends on temperature and pressure, this mass-fraction would change as the temperature and pressure of the sample is changed, even without the addition or loss of any material from the sample. This drawback can be overcome by first bringing the sample to the constant temperature $t = 25^\circ\text{C}$ and the fixed sea pressure 0 dbar, and when this is done, the resulting mass-fraction of non- H_2O material is called “Solution Absolute Salinity” (usually shortened to “Solution Salinity”), $S_{\text{A}}^{\text{soln}}$. Another measure of absolute salinity is the “Added-Mass Salinity” $S_{\text{A}}^{\text{add}}$ which is S_{R} plus the mass fraction of material

that must be added to Standard Seawater to arrive at the concentrations of all the species in the given seawater sample, after chemical equilibrium has been reached, and after the sample has been brought to $t = 25^\circ\text{C}$ and $p = 0$ dbar.

Another form of absolute salinity, “Preformed Absolute Salinity” (usually shortened to “Preformed Salinity”), S_* , has been defined by Pawlowicz *et al.* (2010) and Wright *et al.* (2010b). Preformed Salinity S_* is designed to be as close as possible to being a conservative variable. That is, S_* is designed to be insensitive to biogeochemical processes that affect the other types of salinity to varying degrees. S_* is formed by first estimating the contribution of biogeochemical processes to one of the salinity measures S_A , S_A^{soln} , or S_A^{add} , and then subtracting this contribution from the appropriate salinity variable. Because it is designed to be a conservative oceanographic variable, S_* will find a prominent role in ocean modeling.

There is still no simple means to measure either S_A^{soln} or S_A^{add} for the general case of the arbitrary addition of many components to Standard Seawater. Hence a more precise and easily determined measure of the amount of dissolved material in seawater is required and TEOS-10 adopts “Density Salinity” S_A^{dens} for this purpose. “Density Salinity” S_A^{dens} is defined as the value of the salinity argument of the TEOS-10 expression for density which gives the sample’s actual measured density at the temperature $t = 25^\circ\text{C}$ and at the sea pressure $p = 0$ dbar. When there is no risk of confusion, “Density Salinity” is also called Absolute Salinity with the label S_A , that is $S_A \equiv S_A^{\text{dens}}$. There are two clear advantages of $S_A \equiv S_A^{\text{dens}}$ over both S_A^{soln} and S_A^{add} . First, it is possible to measure the density of a seawater sample very accurately and in an SI-traceable manner, and second, the use of $S_A \equiv S_A^{\text{dens}}$ yields the best available estimates of the density of seawater. This is important because in the field of physical oceanography, it is density that needs to be known to the highest relative accuracy.

Pawlowicz *et al.* (2010) and Wright *et al.* (2010b) found that while the nature of the ocean’s composition variations changes from one ocean basin to another, the five different salinity measures S_R , S_A^{dens} , S_A^{soln} , S_A^{add} and S_* are approximately related by the following simple linear relationships, (obtained by combining equations (55) – (57) and (62) of Pawlowicz *et al.* (2010))

$$S_* - S_R \approx -0.35 \delta S_R^{\text{dens}}, \quad (\text{A.4.1})$$

$$S_A^{\text{dens}} - S_R \equiv 1.0 \delta S_R^{\text{dens}}, \quad (\text{A.4.2})$$

$$S_A^{\text{soln}} - S_R \approx 1.75 \delta S_R^{\text{dens}}, \quad (\text{A.4.3})$$

$$S_A^{\text{add}} - S_R \approx 0.78 \delta S_R^{\text{dens}}. \quad (\text{A.4.4})$$

Eqn. (A.4.2) is simply the definition of the Absolute Salinity Anomaly, $\delta S_A \equiv \delta S_R^{\text{dens}} \equiv S_A^{\text{dens}} - S_R$. Note that in many TEOS-10 publications, the simpler notation δS_A is used for $\delta S_R^{\text{dens}} \equiv S_A^{\text{dens}} - S_R$, a salinity difference for which a global atlas is available (McDougall *et al.* (2010a)). In the context of ocean modelling, it is more convenient to cast these salinity differences with respect to the Preformed Salinity S_* as follows (using the above equations)

$$S_R - S_* \approx 0.35 \delta S_R^{\text{dens}}, \quad (\text{A.4.5})$$

$$S_A^{\text{dens}} - S_* \approx 1.35 \delta S_R^{\text{dens}}, \quad (\text{A.4.6})$$

$$S_A^{\text{soln}} - S_* \approx 2.1 \delta S_R^{\text{dens}}, \quad (\text{A.4.7})$$

$$S_A^{\text{add}} - S_* \approx 1.13 \delta S_R^{\text{dens}}. \quad (\text{A.4.8})$$

These relationships are illustrated on the number line of salinity in Figure A.4.1. For SSW, all five salinity variables S_R , S_A^{dens} , S_A^{soln} , S_A^{add} and S_* are equal. It should be noted that

the simple relationships of Eqns. (A.4.1) – (A.4.8) are derived from simple linear fits to model calculations that show more complex variations. However, the variation about these relationships is not larger than the typical uncertainty of ocean measurements. These linear relationships provide a way by which the effects of anomalous seawater composition may be addressed in ocean models (see appendix A.20).

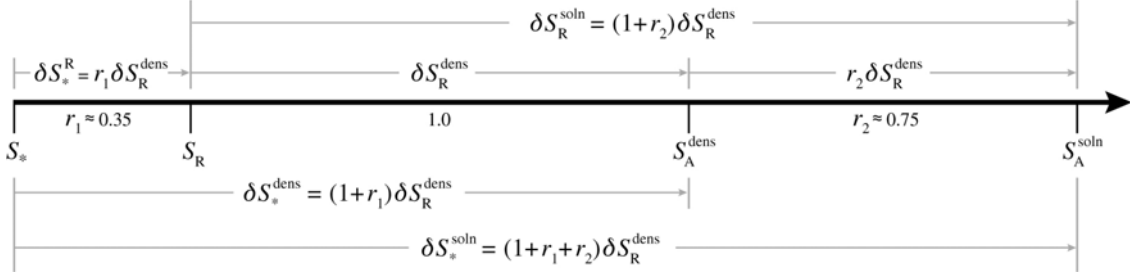


Figure A.4.1. Number line of salinity, illustrating the differences between various forms of salinity for seawater whose composition differs from that of Standard Seawater.

If measurements are available of the Total Alkalinity, Dissolved Inorganic Carbon, and the nitrate and silicate concentrations, but not of density anomalies, then alternative formulae are available for the four salinity differences that appear on the left-hand sides of Eqns. (A.4.1) – (A.4.8). Pawlowicz *et al.* (2010) have used a chemical model of conductivity and density to estimate how the many salinity differences introduced above depend on the measured properties of seawater. The following equations correspond to Eqns. (A.4.1) – (A.4.4) above, and come from equations (51) – (54) and (59) of Pawlowicz *et al.* (2010). These equations are written in terms of the values of the nitrate and silicate concentrations in the seawater sample (measured in mol kg^{-1}), the difference between the Total Alkalinity (TA) and Dissolved Inorganic Carbon (DIC) of the sample and the corresponding values of our best estimates of TA and DIC in Standard Seawater, ΔTA and ΔDIC , both measured in mol kg^{-1} . For Standard Seawater our best estimates of TA and DIC are $0.0023 (S_p/35) \text{ mol kg}^{-1}$ and $0.00208 (S_p/35) \text{ mol kg}^{-1}$ respectively (see Pawlowicz (2010), Pawlowicz *et al.* (2010) and the discussion of this aspect of SSW versus RCSW in Wright *et al.* (2010b)).

$$(S_* - S_R) / (\text{g kg}^{-1}) = (-18.1 \Delta\text{TA} - 7.1 \Delta\text{DIC} - 43.0 \text{NO}_3^- + 0.1 \text{Si(OH)}_4) / (\text{mol kg}^{-1}), \quad (\text{A.4.9})$$

$$(S_A^{\text{dens}} - S_R) / (\text{g kg}^{-1}) = (55.6 \Delta\text{TA} + 4.7 \Delta\text{DIC} + 38.9 \text{NO}_3^- + 50.7 \text{Si(OH)}_4) / (\text{mol kg}^{-1}), \quad (\text{A.4.10})$$

$$(S_A^{\text{soln}} - S_R) / (\text{g kg}^{-1}) = (7.2 \Delta\text{TA} + 47.0 \Delta\text{DIC} + 36.5 \text{NO}_3^- + 96.0 \text{Si(OH)}_4) / (\text{mol kg}^{-1}), \quad (\text{A.4.11})$$

$$(S_A^{\text{add}} - S_R) / (\text{g kg}^{-1}) = (25.9 \Delta\text{TA} + 4.9 \Delta\text{DIC} + 16.1 \text{NO}_3^- + 60.2 \text{Si(OH)}_4) / (\text{mol kg}^{-1}). \quad (\text{A.4.12})$$

The standard error of the model fits in Eqns. (A.4.9) – (A.4.11) are given by Pawlowicz *et al.* (2010) at less than $10^{-4} \text{ kg m}^{-3}$ (in terms of density) which is equivalent to a factor of 20 smaller than the accuracy to which Practical Salinity can be measured at sea. It is clear that if measurements of TA, DIC, nitrate and silicate are available (and recognizing that these measurements will come with their own error bars), these expressions will likely give more accurate estimates of the salinity differences than the approximate linear expressions presented in Eqns. (A.4.1) – (A.4.8). The coefficients in Eqn. (A.4.10) are reasonably similar to the corresponding expression of Brewer and Bradshaw (1975) (as corrected by Millero *et al.* (1976a)):- when expressed as the salinity anomaly $S_A^{\text{dens}} - S_R$

rather than as the corresponding density anomaly $\rho - \rho_R$, their expression corresponding to Eqn. (A.4.10) had the coefficients 71.4, -12.8, 31.9 and 59.9 compared with the coefficients 55.6, 4.7, 38.9 and 50.7 respectively in Eqn. (A.4.10).

The salinity differences expressed with respect to Preformed Salinity S_* which correspond to Eqns. (A.4.5) – (A.4.8) can be found by linear combinations of Eqns. (A.4.9) – (A.4.12) as follows

$$(S_R - S_*) / (\text{g kg}^{-1}) = (18.1 \Delta \text{TA} + 7.1 \Delta \text{DIC} + 43.0 \text{NO}_3^- - 0.1 \text{Si(OH)}_4) / (\text{mol kg}^{-1}), \quad (\text{A.4.13})$$

$$(S_A^{\text{dens}} - S_*) / (\text{g kg}^{-1}) = (73.7 \Delta \text{TA} + 11.8 \Delta \text{DIC} + 81.9 \text{NO}_3^- + 50.6 \text{Si(OH)}_4) / (\text{mol kg}^{-1}), \quad (\text{A.4.14})$$

$$(S_A^{\text{soln}} - S_*) / (\text{g kg}^{-1}) = (25.3 \Delta \text{TA} + 54.1 \Delta \text{DIC} + 79.5 \text{NO}_3^- + 95.9 \text{Si(OH)}_4) / (\text{mol kg}^{-1}), \quad (\text{A.4.15})$$

$$(S_A^{\text{add}} - S_*) / (\text{g kg}^{-1}) = (44.0 \Delta \text{TA} + 12.0 \Delta \text{DIC} + 59.1 \text{NO}_3^- + 60.1 \text{Si(OH)}_4) / (\text{mol kg}^{-1}). \quad (\text{A.4.16})$$

A.5 Spatial variations in seawater composition

When the oceanographic data needed to evaluate Eqn. (A.4.10) for $S_A^{\text{dens}} - S_R$ is not available, the look-up table method of McDougall *et al.* (2010a) is recommended to evaluate $\delta S_A \equiv \delta S_R^{\text{dens}} \equiv S_A^{\text{dens}} - S_R$. The following paragraphs describe how this method was developed.

In a series of papers Millero *et al.* (1976a, 1978, 2000, 2008b) and McDougall *et al.* (2010a) have reported on density measurements made in the laboratory on samples collected from around the world's oceans. Each sample has had its Practical Salinity measured in the laboratory as well as its density (measured with a vibrating tube densimeter at 25 °C and atmospheric pressure). The Practical Salinity yields a Reference Salinity S_R according to Eqn. (A.3.3), while the density measurement ρ^{meas} implies an Absolute Salinity $S_A \equiv S_A^{\text{dens}}$ by using the equation of state and the equality $\rho^{\text{meas}} = \rho(S_A^{\text{dens}}, 25 \text{ °C}, 0 \text{ dbar})$. The difference $S_A^{\text{dens}} - S_R$ between these two salinity measures is taken to be due to the composition of the sample being different to that of Standard Seawater. In these papers Millero established that the salinity difference $S_A - S_R$ could be estimated approximately from knowledge of just the silicate concentration of the fluid sample. The reason for the explaining power of silicate alone is thought to be that (a) it is itself substantially correlated with other relevant variables (e.g. total alkalinity, nitrate concentration, DIC [often called total carbon dioxide]), (b) it accounts for a substantial fraction (about 0.6) of the typical variations in concentrations (g kg^{-1}) of the above species and (c) being essentially non-ionic; its presence has little effect on conductivity while having a direct effect on density.

When the existing data on δS_A , based on laboratory measurements of density, was regressed against the silicate concentration of the seawater samples, McDougall *et al.* (2010a) found the simple relation

$$\delta S_A / (\text{g kg}^{-1}) = (S_A - S_R) / (\text{g kg}^{-1}) = 98.24 (\text{Si(OH)}_4 / (\text{mol kg}^{-1})). \quad \text{Global (A.5.1)}$$

This regression was done over all available density measurements from the world ocean, and the standard error in the fit was 0.0054 g kg^{-1} .

The dependence of δS_A on silicate concentration is observed to be different in each ocean basin, and this aspect was exploited by McDougall *et al.* (2010a) to obtain a more accurate dependence of δS_A on location in space. For data in the Southern Ocean south of 30°S the best simple fit was found to be

$$\delta S_A / (\text{g kg}^{-1}) = 74.884 \left(\text{Si(OH)}_4 / (\text{mol kg}^{-1}) \right), \quad \text{Southern Ocean (A.5.2)}$$

and the associated standard error is 0.0026 g kg^{-1} .

The data north of 30°S in each of the Pacific, Indian and Atlantic Oceans was treated separately. In each of these three regions the fit was constrained to match (A.5.2) at 30°S and the slope of the fit was allowed to vary linearly with latitude. The resulting fits were (for latitudes north of 30°S , that is for $\lambda \geq -30^\circ$)

$$\delta S_A / (\text{g kg}^{-1}) = 74.884 (1 + 0.3622 [\lambda / 30^\circ + 1]) \left(\text{Si(OH)}_4 / (\text{mol kg}^{-1}) \right), \quad \text{Pacific (A.5.3)}$$

$$\delta S_A / (\text{g kg}^{-1}) = 74.884 (1 + 0.3861 [\lambda / 30^\circ + 1]) \left(\text{Si(OH)}_4 / (\text{mol kg}^{-1}) \right), \quad \text{Indian (A.5.4)}$$

$$\delta S_A / (\text{g kg}^{-1}) = 74.884 (1 + 1.0028 [\lambda / 30^\circ + 1]) \left(\text{Si(OH)}_4 / (\text{mol kg}^{-1}) \right). \quad \text{Atlantic (A.5.5)}$$

These relationships between the Absolute Salinity Anomaly $\delta S_A = S_A - S_R$ and silicate concentration have been used by McDougall, Jackett and Millero (2010a) in a computer algorithm that uses an existing global data base of silicate (Gouretski and Koltermann (2004)) and provides an estimate of Absolute Salinity when given a seawater sample's Practical Salinity as well as its spatial location in the world ocean. This computer algorithm accounts for the latest understanding of Absolute Salinity in the Baltic Sea, but it is silent on the influence of compositional variations in other marginal seas. The Absolute Salinity Anomaly in the Baltic Sea has been quite variable over the past few decades of observation (Feistel *et al.* (2010c)). The computer algorithm of McDougall *et al.* (2010a) uses the relationship found by Feistel *et al.* (2010c) that applies in the years 2006-2009, namely

$$S_A - S_R = 0.087 \text{ g kg}^{-1} \times (1 - S_R / S_{SO}), \quad (\text{A.5.6})$$

where $S_{SO} = 35.165 \text{ 04 g kg}^{-1}$ is the standard-ocean Reference Salinity that corresponds to the Practical Salinity of 35.

In order to gauge the importance of the spatial variation of seawater composition, the northward gradient of density at constant pressure is shown in Fig. A.5.1 for the data in a world ocean hydrographic atlas deeper than 1000m. The vertical axis in this figure is the magnitude of the difference between the northward density gradient at constant pressure when the TEOS-10 algorithm for density is called with $S_A \equiv S_A^{\text{dens}}$ (as it should be) compared with calling the same TEOS-10 density algorithm with S_R as the salinity argument. Figure A.5.1 shows that the “thermal wind” is misestimated by more than 2% for 58% of the data in the world ocean below a depth of 1000m if the effects of the variable seawater composition are ignored.

The importance of the spatial variations in seawater composition illustrated in Fig. A.5.1 can be compared with the corresponding improvement achieved by the TEOS-10 Gibbs function for Standard Seawater compared with using EOS-80. This is done by ignoring spatial variations in seawater composition in both the evaluation of TEOS-10 and in EOS80 by calling TEOS-10 with S_R and EOS-80 with S_p . Figure A.5.2 shows the magnitude of the improvement in the “thermal wind” in the part of the ocean that is deeper than 1000m through the adoption of TEOS-10 but ignoring the influence of compositional variations. By comparing Figs. A.5.1 and A.5.2 it is seen that the main benefit that TEOS-10 delivers to the evaluation of the “thermal wind” is through the incorporation of spatial variations in seawater composition; the greater accuracy of TEOS-10 over EOS-80 for Standard Seawater is only 18% as large as the improvement gained by the incorporation of compositional variations into TEOS-10 (i. e. the rms value of the vertical axis in Fig. A.5.2 is 18% of that of the vertical axis of Fig. A.5.1). If the Atlantic were excluded from this comparison, the relative importance of compositional variations would be even larger.

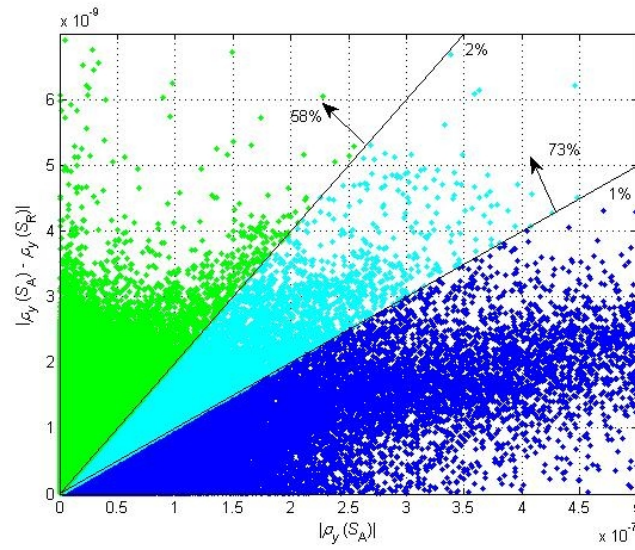


Figure A.5.1. The northward density gradient at constant pressure (the horizontal axis) for data in the global ocean atlas of Gouretski and Koltermann (2004) for $p > 1000$ dbar. The vertical axis is the magnitude of the difference between evaluating the density gradient using S_A versus S_R as the salinity argument in the TEOS-10 expression for density.

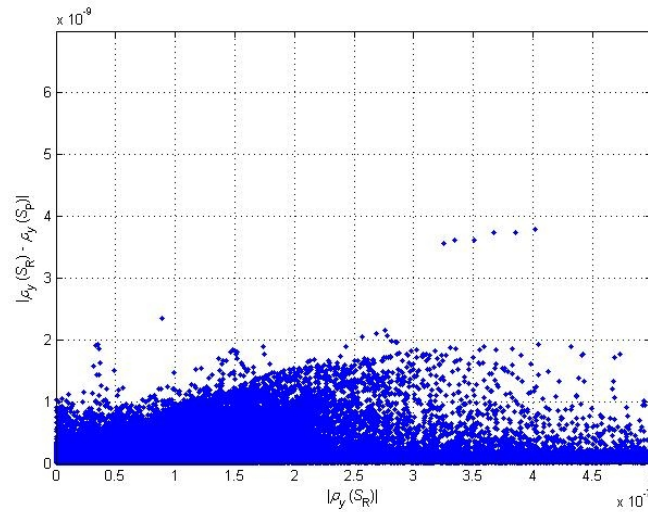


Figure A.5.2. The northward density gradient at constant pressure (the horizontal axis) for data in the global ocean atlas of Gouretski and Koltermann (2004) for $p > 1000$ dbar. The vertical axis is the magnitude of the difference between evaluating the density gradient using S_R as the salinity argument in the TEOS-10 expression for density compared with using S_p in the EOS-80 algorithm for density.

The thermodynamic description of seawater and of ice Ih as defined in IAPWS-08 and IAPWS-06 has been adopted as the official description of seawater and of ice Ih by the Intergovernmental Oceanographic Commission in June 2009. The adoption of TEOS-10 has recognized that this technique of estimating Absolute Salinity from readily measured quantities is perhaps the least mature aspect of the TEOS-10 thermodynamic description of

seawater. The present computer software, in both FORTRAN and MATLAB, which evaluates Absolute Salinity S_A given the input variables Practical Salinity S_p , longitude λ , latitude ϕ and sea pressure p is available at www.TEOS-10.org. It is expected, as new data (particularly density data) become available, that the determination of Absolute Salinity will improve over the coming decades, and the algorithm for evaluating Absolute Salinity in terms of Practical Salinity, latitude, longitude and pressure, will be updated from time to time, after relevant appropriately peer-reviewed publications have appeared, and such an updated algorithm will appear on the www.TEOS-10.org web site. Users of this software should state in their published work which version of the software was used to calculate Absolute Salinity.