Notes on the GSW internal library function gsw_SAAR(p,long,lat)

Notes updated 15th May 2011. These notes apply to version 3.0 of the GSW
Toolbox which looks up version 3 of the global R^δ data base, gsw_data_v3_0.

The thermodynamic properties of seawater are functions of Absolute Salinity S_A (rather than of Practical Salinity S_P). If a seawater sample has Standard Composition (that is, the sample is a sample of Standard Seawater, SSW) then its Absolute Salinity S_A is equal to its Reference Salinity S_R which is proportional to its Practical Salinity S_P according to

$$S_R = \left(\frac{35.165\,04 \text{ g kg}^{-1}}{35} \right) S_P .\qquad(1)$$

When a seawater sample has non-standard composition, the relationship between Practical Salinity and Absolute Salinity is more complicated, and the difference between Absolute Salinity and Reference Salinity (which is given in terms of Practical Salinity by Eqn. (1)) is called the Absolute Salinity Anomaly δS_A , that is,

$$S_A = S_R + \delta S_A .\qquad(2)$$

The most direct way of evaluating δS_A is via measuring the density of a seawater sample, for example, by using a vibrating beam densimeter in the laboratory. Another method of estimating δS_A is via measurements of total alkalinity (TA), dissolved inorganic carbon (DIC), silicate and nitrate, together with a model of seawater properties (such as that of Pawlowicz *et al*. (2011)) to relate these measurements to δS_A .

Due to the relative paucity of these measurements, a method for estimating the Absolute Salinity Anomaly δS_A has been developed based on spatially interpolating a global data base of Absolute Salinity Anomaly Ratio (SAAR), $R^\delta \equiv \delta S_A^{\text{atlas}} \big/ S_R^{\text{atlas}}$, which is stored as a function of longitude, latitude and pressure (McDougall *et al*., 2012). The internal GSW library function **gsw_SAAR**(p,long,lat) does this interpolation. The values of both the Reference Salinity and the Absolute Salinity Anomaly, calculated from the global Gouretski and Koltermann (2004) hydrographic atlas using Eqns. (A.5.2) – (A.5.5) of IOC *et al*. (2010), are used to form the ratio $R^\delta \equiv \delta S_A^{\text{atlas}} \big/ S_R^{\text{atlas}}$ of these atlas values of Absolute Salinity Anomaly and Reference Salinity. These values of R^δ are stored as a function of latitude, longitude and pressure on a $4° \times 4°$ grid in latitude and longitude. These values of R^δ are interpolated onto the latitude, longitude and pressure of an oceanographic observation (the details of the interpolation method can be found in McDougall *et al*., (2012)) and the Absolute Salinity Anomaly of the oceanographic observation is calculated from

$$\delta S_A = R^\delta S_R \quad\text{where}\quad R^\delta \equiv \delta S_A^{\text{atlas}} \big/ S_R^{\text{atlas}} ,\qquad(3)$$

where S_R is the Reference Salinity of the oceanographic observation. For the bulk of the ocean this expression for δS_A is almost the same as simply setting δS_A equal to δS_A^{ref}, (which is how version 2.0 of the GSW code was written) but the use of Eqn. (3) is preferable in situations where the sample's Reference Salinity is small, such as in rivers, in estuaries and after a rain shower at the sea surface in the open ocean. In these situations the influence of the bluewater ocean's biogeochemical processes on δS_A should approach zero and this is achieved by Eqn. (3).

 The **gsw_SA_from_SP**(SP,p,long,lat) function first finds the interpolated Absolute Salinity Anomaly Ratio (R^δ) by calling the present internal GSW library function **gsw_SAAR** to the (p,long,lat) location and then uses this interpolated value of R^δ to calculate Absolute Salinity according to (see appendix A.5 of IOC *et al*. (2010))

$$S_{\mathrm{A}} \;\; = \;\; \frac{35.165\,04\ \mathrm{g\,kg^{-1}}}{35}\ S_{\mathrm{P}}\left(1 + R^{\delta}\right). \qquad\qquad \textit{Non-Baltic} \qquad (4)$$

Equation (4) 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_SAAR** function returns a value of zero). If the observation is from the Baltic Sea, Absolute Salinity Anomaly is calculated according to $S_{\mathrm{A}} - S_{\mathrm{R}} = 0.087\,\mathrm{g\,kg^{-1}} \times \left(1 - S_{\mathrm{P}}/35\right)$ (from Eqn. (A.5.16) of IOC *et al.* (2010), following Feistel *et al.* (2010)), so that Absolute Salinity S_{A} is given by

$$S_{\mathrm{A}} \;\; = \;\; \frac{\left(35.165\,04 \;-\; 0.087\right)\ \mathrm{g\,kg^{-1}}}{35}\ S_{\mathrm{P}} \;+\; 0.087\ \mathrm{g\,kg^{-1}}. \qquad \textit{Baltic Sea} \qquad (2)$$
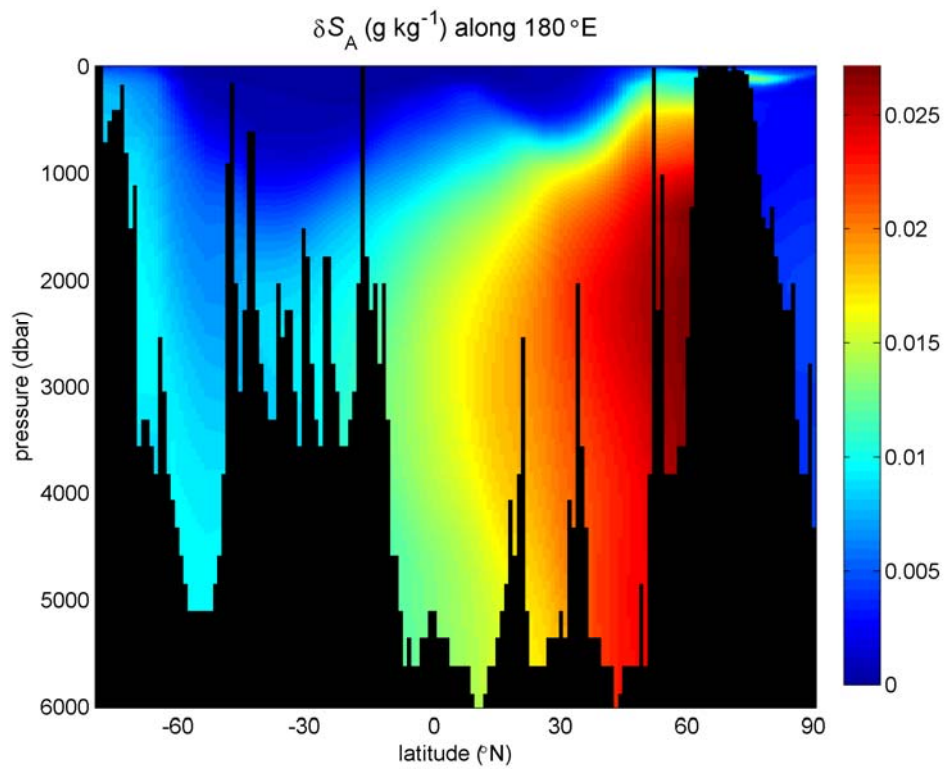
The Absolute Salinity Anomaly of the GSW function **gsw_deltaSA_from_SP** is illustrated in Figure 1 (a) at a pressure of 2000 dbar, and in a vertical section through the Pacific Ocean in Figure 1 (b). As described in appendix A.5 of the TEOS-10 Manual (IOC *et al.* (2010)), the values of Absolute Salinity Anomaly in the global data set underlying the **gsw_delta_SA_from_SP** function have been obtained by correlating densimeter-based measurements of δS_{A} with silicate concentrations in the different ocean basins. Heuristically the dependence of $\delta S_{\mathrm{A}} = S_{\mathrm{A}} - S_{\mathrm{R}}$ 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.

The silicate data which underpins the global data base of R^{δ} in the internal GSW library function **gsw_SAAR** are stored with horizontal resolution of $4° x 4°$ in longitude and latitude, and this has been taken from the Gouretski and Koltermann atlas of hydrographic data by adopting the deepest cast in the Gouretski and Koltermann atlas within $\pm 2°$ of latitude and longitude of the final grid. The resulting $4° x 4°$ global data sets of R^{δ} and $\delta S_{\mathrm{A}}^{\mathrm{atlas}}$ have rather more ocean and less land than does the planet. This has been done to ensure that any sample from the real ocean will definitely be processed by the function. This is illustrated in Figure 2 which indicates how the ocean is allowed to spill over into the continents.

If the latitude and longitude are found by the **gsw_SAAR** function 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 kilometres inland from the coast.

δS_A (g kg^{-1}) at ρ = 2000 dbar
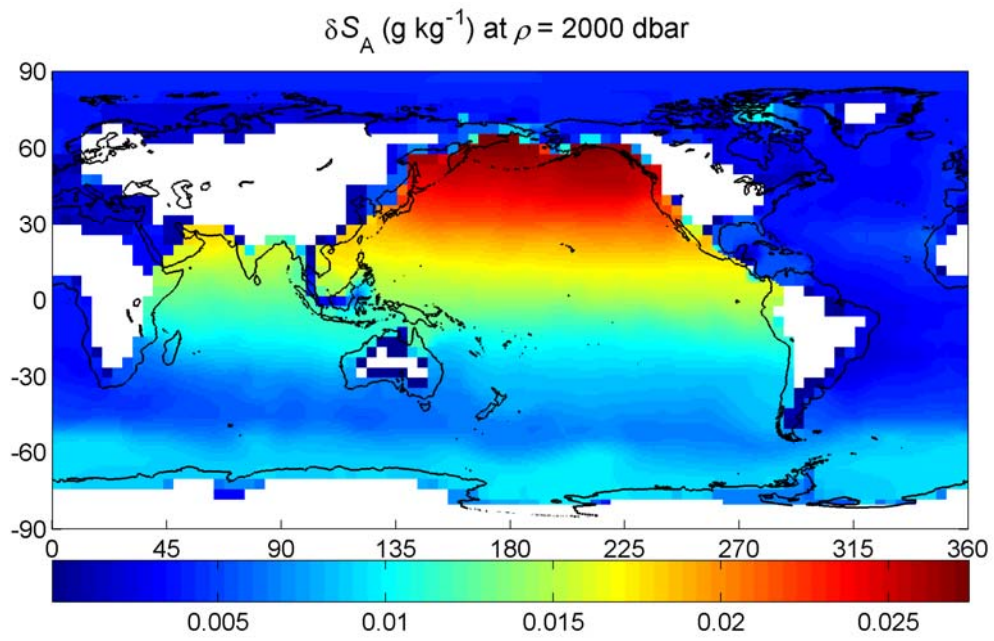
Figure 1 (a). Absolute Salinity Anomaly δS_A at p = 2000 dbar.

δS_A (g kg^{-1}) along 180 °E

Figure 1 (b). A vertical section of Absolute Salinity Anomaly δS_A along 180°E in the Pacific Ocean.
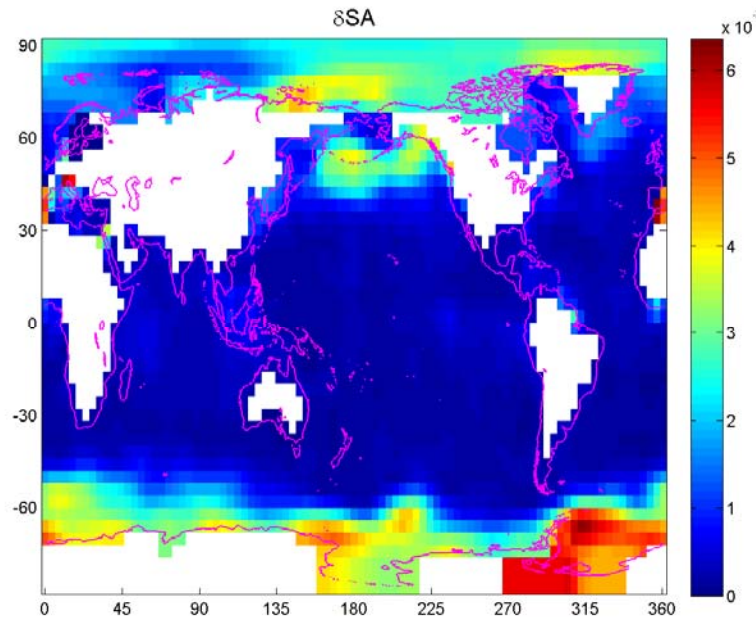
Figure 2. Values of the Absolute Salinity Anomaly ($\mathrm{g\ kg^{-1}}$) of
the $\delta S_{\mathrm{A}}^{\mathrm{atlas}}$ global data set at the sea surface.
The gsw_SAAR function returns the flag 'in_ocean'
as zero in the white regions of this figure, otherwise the
'in_ocean' flag is set to 1.

During the interpolation of the underlying data set, care is taken not to interpolate between different ocean basins in the vicinity of the Panama Canal and the Indonesian Throughflow. Also, if the input data point is deeper than any of the surrounding four vertical atlas profiles, the deepest "bottle" of the four reference profiles is used (that is, the reference profile is effectively extended deeper at the $\delta S_{\mathrm{A}}^{\mathrm{atlas}}$ value of its deepest bottle).

The first version of this function was made available in early 2009, called gsw_deltaSA. The second version of gsw_delta_SA (version 2.0) was released in October 2010. That version called version 2 of the global $\delta S_{\mathrm{A}}^{\mathrm{atlas}}$ data set which is almost identical to the data set of version 1. The changes were that (i) two regions adjacent to the Antarctic continent where there previously was no data have been filled in, (ii) the data set has been formed from the deepest vertical profiles in the Gouretski and Koltermann atlas within $\pm 2°$ of latitude and longitude of the final grid rather than simply sub-sampling to the $4°x4°$ grid, and (iii) the flag 'in_ocean' has been added. The third version of the GSW software contains the internal library function **gsw_SAAR**(p,long,lat) which is part of release 3.0 of the GSW Oceanographic Toolbox. This function calls the data file gsw_data_v3_0.

References

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Below is appendices A.4 and A.5 of the TEOS-10 Manual (IOC *et al*. (2010)) which discusses the spatial variations in seawater composition.

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 $(1 - 0.001\ S_A/(g\ kg^{-1}))$, 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_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)),

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

In particular, it is strictly correct to write the freshwater fraction of seawater as either $(1 - 0.001\ S_A/(g\ kg^{-1}))$ 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 $g\ kg^{-1}$). The Reference Salinity, S_R, is defined to have the same units and follows the same conventions as S_A. Salinity "S‰" 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 $S_P = 1.806\,55\,Cl$ 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 $u_{Cl} = 1.806\,55\,u_{PS}$. 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 TEOS-10 thermodynamic description of seawater 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 debatable which of $(1 - 0.001\ S_A^{dens}/(\mathrm{g\ kg}^{-1}))$, $(1 - 0.001\ S_A^{soln}/(\mathrm{g\ kg}^{-1}))$, $(1 - 0.001\ S_A^{add}/(\mathrm{g\ kg}^{-1}))$ or $(1 - 0.001\ S_*/(\mathrm{g\ kg}^{-1}))$ 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 $(1 - 0.001\ S_P)$ in this context, and the choice of which of the above 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 $(1 - 0.001\ S_*/(\mathrm{g\ kg}^{-1}))$ 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. Under TEOS-10, Absolute Salinity replaces Practical Salinity as the salinity variable in publications, and 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) x 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 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), 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-H2O 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-H2O material in Standard Seawater by Millero *et al.* (2008a). Subsequently, Pawlowicz (2010a) has argued that the DIC content of the Reference Composition is probably about 117 μmol 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.*, 2011) 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.*, 2010). 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.

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$_2$O material in a seawater sample at its temperature and pressure". One drawback of this definition is that because the equilibrium conditions between H$_2$O 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 $t = 25°C$ and the fixed sea pressure 0 dbar, and when this is done, the resulting mass-fraction of non-H$_2$O material is called "Solution Absolute Salinity" (usually shortened to "Solution Salinity"), $S_{\mathrm{A}}^{\mathrm{soln}}$. Another measure of absolute salinity is the "Added-Mass Salinity" $S_{\mathrm{A}}^{\mathrm{add}}$ 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 $t = 25°C$ 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.* (2011) and Wright *et al.* (2011). 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 the 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.

Since S_* is designed to be a conservative salinity variable, it would appear to also be the best choice for the salinity variable in inverse models. An argument can also be made that S_* should be the salinity variable that is used as an axis of the traditional "$S - \theta$ diagram", which would then become the $S_* - \Theta$ diagram. However, this argument is resisted because potential density contours cannot be drawn on the $S_* - \Theta$ diagram because density is a function of Absolute Salinity, not of Preformed Salinity.

There are no simple methods available 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 $t = 25°C$ 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 $S_A \equiv S_A^{dens}$. There are two clear advantages of $S_A \equiv S_A^{dens}$ 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 $S_A \equiv S_A^{dens}$ yields the best available estimates of the density of seawater. This is important because amongst various thermodynamic properties in the field of physical oceanography, it is density that needs to be known to the highest relative accuracy.

Pawlowicz *et al.* (2011) and Wright *et al.* (2011) 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.* (2011))

$$S_* - S_R \approx -0.35\,\delta S_A, \tag{A.4.1}$$

$$S_A^{dens} - S_R \equiv 1.0\,\delta S_A, \tag{A.4.2}$$

$$S_A^{soln} - S_R \approx 1.75\,\delta S_A, \tag{A.4.3}$$

$$S_A^{add} - S_R \approx 0.78\,\delta S_A. \tag{A.4.4}$$

Eqn. (A.4.2) is simply the definition of the Absolute Salinity Anomaly, $\delta S_A \equiv \delta S_R^{dens} \equiv S_A^{dens} - S_R$. Note that here and in many TEOS-10 publications, the simpler notation δS_A is used for $\delta S_R^{dens} \equiv S_A^{dens} - S_R$, a salinity difference that can now be estimated from a global atlas (McDougall *et al.* (2012)).

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)

$$S_R - S_* \approx 0.35\,\delta S_A, \tag{A.4.5}$$

$$S_A^{dens} - S_* \approx 1.35\,\delta S_A, \tag{A.4.6}$$

$$S_A^{soln} - S_* \approx 2.1\,\delta S_A, \tag{A.4.7}$$

$$S_A^{add} - S_* \approx 1.13\,\delta S_A. \tag{A.4.8}$$

For SSW, all five salinity variables S_R, $S_A \equiv S_A^{\text{dens}}$, S_A^{soln}, S_A^{add} and S_* are equal. The relationships (A.4.1), (A.4.2), (A.4.5) and (A.4.6) are illustrated on the number line of salinity in Figure A.4.1. 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. Eqn. (A.4.6) provides a way by which the effects of anomalous seawater composition may be addressed in ocean models (see appendix A.20).
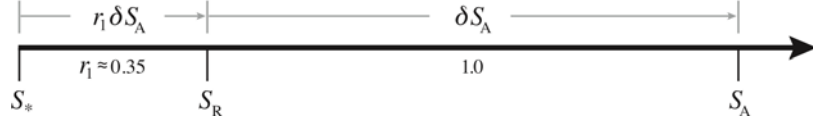
Figure A.4.1. Number line of salinity, illustrating the differences between

Preformed Salinity S_*, Reference Salinity S_R, and Absolute Salinity S_A 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 salinity differences that appear on the left-hand sides of Eqns. (A.4.1) – (A.4.8). Pawlowicz *et al.* (2011) 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.* (2011). 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 (2010a), Pawlowicz *et al.* (2011) and the discussion of this aspect of SSW versus RCSW in Wright *et al.* (2011))).

$$\left(S_* - S_R\right)/(\text{g kg}^{-1}) = \left(-18.1\,\Delta TA - 7.1\,\Delta DIC - 43.0\,NO_3^- + 0.1\,Si(OH)_4\right)\big/(\text{mol kg}^{-1}), \quad (A.4.9)$$

$$\left(S_A^{\text{dens}} - S_R\right)/(\text{g kg}^{-1}) = \left(55.6\,\Delta TA + 4.7\,\Delta DIC + 38.9\,NO_3^- + 50.7\,Si(OH)_4\right)\big/(\text{mol kg}^{-1}), \quad (A.4.10)$$

$$\left(S_A^{\text{soln}} - S_R\right)/(\text{g kg}^{-1}) = \left(7.2\,\Delta TA + 47.0\,\Delta DIC + 36.5\,NO_3^- + 96.0\,Si(OH)_4\right)\big/(\text{mol kg}^{-1}), \quad (A.4.11)$$

$$\left(S_A^{\text{add}} - S_R\right)/(\text{g kg}^{-1}) = \left(25.9\,\Delta TA + 4.9\,\Delta DIC + 16.1\,NO_3^- + 60.2\,Si(OH)_4\right)\big/(\text{mol kg}^{-1}). \quad (A.4.12)$$

The standard error of the model fits in Eqns. (A.4.9) – (A.4.11) are given by Pawlowicz *et al.* (2011) 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 $S_A^{dens} - S_R$ 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

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

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

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

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

A.5 Spatial variations in seawater composition

When the oceanographic data needed to evaluate Eqn. (A.4.10) for $S_A^{dens} - S_R \equiv S_A - S_R$ is not available, the look-up table method of McDougall *et al.* (2012) is recommended to evaluate $\delta S_A \equiv \delta S_R^{dens} \equiv S_A - S_R$. The following describes how this method was developed.

In a series of papers Millero *et al.* (1976a, 1978, 2000, 2008b) and McDougall *et al.* (2012) have reported on density measurements made in the laboratory on samples collected from around the world's oceans. Each sample 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 $S_A \equiv S_A^{dens}$ by using the equation of state and the equality $\rho^{meas} = \rho\left(S_A^{dens}, 25\,°\text{C}, 0\,\text{dbar}\right)$. The difference $S_A^{dens} - S_R$ 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 δS_A data, based on laboratory measurements of density, was regressed against the silicate concentration of the seawater samples, McDougall *et al.* (2012) found the simple relation

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

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

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.* (2012) 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

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

and the associated standard error is $0.0026 \, \text{g kg}^{-1}$.

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 $\lambda \geq -30°$)

$$\delta S_A \, / (\text{g kg}^{-1}) \;=\; 74.884 \big(1 + 0.3622 [\lambda / 30° + 1] \big) \big(\text{Si(OH)}_4 \, / \, (\text{mol kg}^{-1}) \big), \qquad \textit{Pacific} \;\; (A.5.3)$$

$$\delta S_A \, / (\text{g kg}^{-1}) \;=\; 74.884 \big(1 + 0.3861 [\lambda / 30° + 1] \big) \big(\text{Si(OH)}_4 \, / \, (\text{mol kg}^{-1}) \big), \qquad \textit{Indian} \;\; (A.5.4)$$

$$\delta S_A \, / (\text{g kg}^{-1}) \;=\; 74.884 \big(1 + 1.0028 [\lambda / 30° + 1] \big) \big(\text{Si(OH)}_4 \, / \, (\text{mol kg}^{-1}) \big). \qquad \textit{Atlantic} \;\; (A.5.5)$$

These relationships between the Absolute Salinity Anomaly $\delta S_A = S_A - S_R$ and silicate concentration have been used by McDougall *et al.* (2012) 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.

Version 3.0 of this computer algorithm works as follows. The values of both the Reference Salinity and the Absolute Salinity Anomaly, calculated from the global Gouretski and Koltermann (2004) hydrographic atlas using Eqns. (A.5.2) – (A.5.5), were used to form the ratio $R^\delta \equiv \delta S_A^{\text{atlas}} \big/ S_R^{\text{atlas}}$ of these atlas values of Absolute Salinity Anomaly and Reference Salinity. These values of the Absolute Salinity Anomaly Ratio, R^δ, were stored as a function of latitude, longitude and pressure on a regular $4° \times 4°$ grid in latitude and longitude. These values of R^δ are interpolated onto the latitude, longitude and pressure of an oceanographic observation (the details of the interpolation method can be found in McDougall *et al.* (2012)) and the Absolute Salinity Anomaly δS_A of an oceanographic observation is calculated from

$$\delta S_A \;=\; R^\delta \, S_R \qquad \text{where} \qquad R^\delta \equiv \delta S_A^{\text{atlas}} \big/ S_R^{\text{atlas}}, \qquad\qquad\qquad (A.5.6)$$

where S_R is the Reference Salinity of the oceanographic observation. For the bulk of the ocean this expression for δS_A is almost the same as simply setting δS_A equal to $\delta S_A^{\text{atlas}}$, but the use of Eqn. (A.5.6) is preferable in situations where the sample's Reference Salinity is small, such as in rivers, in estuaries and after a rain shower at the sea surface in the open ocean. In these situations the influence of the ocean's biogeochemical processes on δS_A should approach zero as S_R approaches zero, and this is achieved by Eqn. (A.5.6).

Where the nutrient and carbon chemistry data are available to evaluate Eqn. (A.4.10), the results obtained are similar although not identical to those obtained from Eqn. (A.5.6) using the McDougall *et al.* (2012) algorithm.

The relationships between the three salinity variables $S_A, \, S_*$ and S_R are found as follows. First we note the relationships between these salinities (from Eqns. (A.4.2), (A.4.1) and (A.4.6))

$$S_A \;=\; S_R + \delta S_A, \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (A.5.7)$$

$$S_* \;=\; S_R - r_1 \delta S_A, \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (A.5.8)$$

$$S_A \;=\; S_* + \left(1 + r_1 \right) \delta S_A. \qquad\qquad\qquad\qquad\qquad\qquad\qquad (A.5.9)$$

Substituting Eqn. (A.5.6) into these equations gives the following simple linear relationships between the three different salinities,

$$S_A = S_R \left(1 + R^\delta\right), \tag{A.5.10}$$

$$S_* = S_R \left(1 - r_1 R^\delta\right), \tag{A.5.11}$$

$$S_A = S_* \frac{\left(1 + R^\delta\right)}{\left(1 - r_1 R^\delta\right)} = S_* \left(1 + F^\delta\right) \quad \text{where} \quad F^\delta = \frac{[1 + r_1] R^\delta}{\left(1 - r_1 R^\delta\right)} . \tag{A.5.12}$$

These three equations are used in the six functions in the GSW Oceanographic Toolbox that relate one salinity variable to another, where r_1 is taken to be 0.35 while R^δ is obtained from the look-up table of McDougall *et al.* (2012).

This approach has so far assumed that the Absolute Salinity Anomaly in fresh water is zero. This is usually a good assumption for rainwater, but is often not true of water in rivers. For example, the river water flowing into the Baltic has an absolute Salinity Anomaly of approximately 0.087 g kg^{-1}. When one has knowledge of the Absolute Salinity Anomaly due to river water inflow, this can be incorporated as follows

$$\delta S_A = R^\delta S_R + \delta S_A^{river}, \tag{A.5.13}$$

leading to (using Eqn. (A.5.7))

$$S_A = S_R \left(1 + R^\delta\right) + \delta S_A^{river}. \tag{A.5.14}$$

In turn, an estimate for δS_A^{river} might be constructed in the vicinity of a particular river from prior knowledge of the Absolute Salinity Anomaly at the river mouth $\delta S_A^{river\_mouth}$ (this is actually the Absolute Salinity Anomaly appropriate for river water extrapolated to $S_R = 0$) by a formula such as (drawing inspiration from the formula for the Baltic, see below)

$$\delta S_A^{river} = \delta S_A^{river\_mouth} \left(1 - S_R / S_R^{atlas}\right). \tag{A.5.15}$$

The computer algorithm of McDougall *et al.* (2012) 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.* (2012) uses the relationship found by Feistel *et al.* (2010c) that applies in the years 2006-2009, namely

$$S_A - S_R = \delta S_A = 0.087 \text{ g kg}^{-1} \times \left(1 - S_R / S_{SO}\right), \qquad \textit{Baltic} \tag{A.5.16}$$

where S_{SO} = 35.165 04 g kg^{-1} is the standard-ocean Reference Salinity that corresponds to the Practical Salinity of 35. The Absolute Salinity Anomaly in the Baltic Sea is not due to biogeochemical activity, but rather is due to the rivers bringing material of anomalous composition into the Baltic. Hence Absolute Salinity in the Baltic is a conservative variable and Preformed Salinity is defined to be equal to Absolute Salinity in the Baltic. That is, in the Baltic $S_* = S_A$, implying that $r_1 = -1$ and $F^\delta = 0$ (see Eqns. (A.5.7) − (A.5.9) and (A.5.12)).

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 $S_A \equiv S_A^{dens}$ (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. When this same comparison is done for only the North Pacific, it is found that 60% of the data deeper than 1000m has "thermal wind" misestimated by more than 10% if S_R is used in place of S_A.
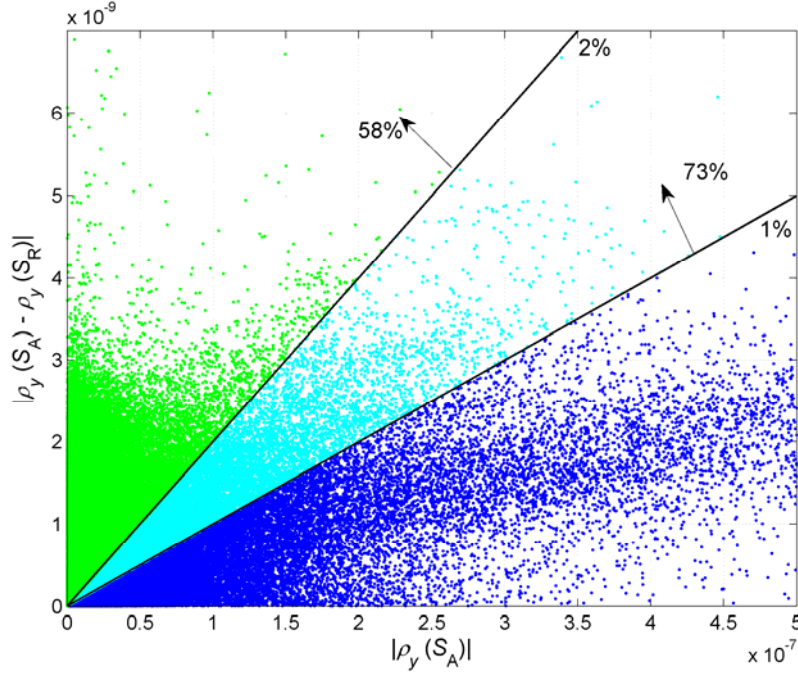
Figure A.5.1. The northward density gradient at constant pressure (the horizontal axis) for data in the global ocean atlas of Gouretski and Koltermann (2004) for $p > 1000$ dbar. The vertical axis is the magnitude of the difference between evaluating the density gradient using S_A versus S_R as the salinity argument in the TEOS-10 expression for density.

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 1000 m 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 17% 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 17% of that of the vertical axis of Fig. A.5.1). If the North Atlantic were excluded from this comparison, the relative importance of compositional variations would be even larger.
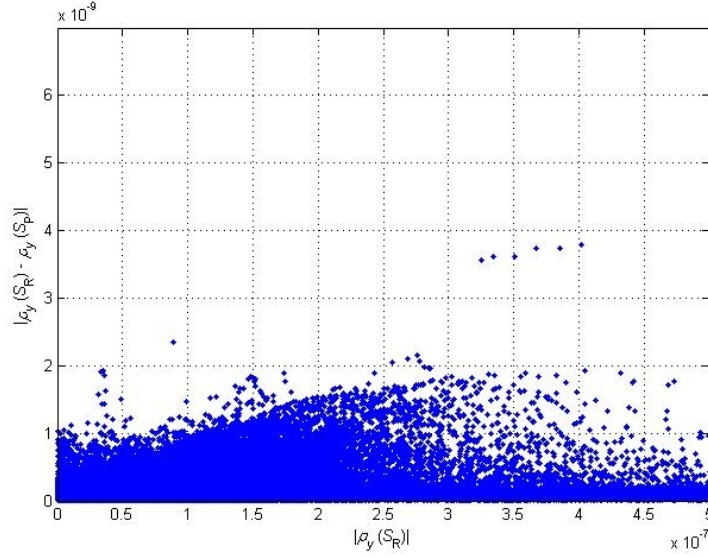
Figure A.5.2. The northward density gradient at constant pressure (the horizontal axis) for data in the global ocean atlas of Gouretski and Koltermann (2004) for $p > 1000$ dbar . The vertical axis is the magnitude of the difference between evaluating the density gradient using S_{R} as the salinity 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.