**Ocean Science
Discussions**

Absolute Salinity, "Density Salinity" and the Reference-Composition Salinity Scale: present and future use in the seawater standard TEOS-10

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Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper

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**Absolute Salinity,
Density Salinity, and
Reference Salinity**

D. G. Wright et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

|◄ | ►|
◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Absolute Salinity, Density Salinity, and Reference Salinity

D. G. Wright et al.

Abstract

Salinity plays a key role in the determination of the thermodynamic properties of seawater and the new TEOS-10[1] standard provides a consistent and effective approach to dealing with relationships between salinity and these thermodynamic properties. However, there are a number of practical issues that arise in the application of TEOS-10, both in terms of accuracy and scope, including its use in the reduction of field data and in numerical models.

First, in the TEOS-10 formulation for IAPSO Standard Seawater, the Gibbs function takes the Reference Salinity as its salinity argument, denoted S_R, which provides a measure of the mass fraction of dissolved material in solution based on the Reference Composition approximation for Standard Seawater. We discuss uncertainties in both the Reference Composition and the Reference-Composition Salinity Scale on which Reference Salinity is reported. The Reference Composition provides a much-needed fixed benchmark but modified reference states will inevitably be required to improve the representation of Standard Seawater for some studies. The Reference-Composition Salinity Scale should remain unaltered to provide a stable representation of salinity for use with the TEOS-10 Gibbs function and in climate change detection studies.

Second, when composition anomalies are present in seawater, no single salinity variable can fully represent the influence of dissolved material on the thermodynamic properties of seawater. We consider three distinct representations of salinity that have been used in previous studies and discuss the connections and distinctions between them. One of these variables provides the most accurate representation of density possible as well as improvements over Reference Salinity for the determination of other thermodynamic properties. It is referred to as "Density Salinity" and is represented by the symbol S_A^{dens}; it stands out as the most appropriate representation of salinity for use in dynamical physical oceanography. The other two salinity variables provide alternative measures of the mass fraction of dissolved material in seawater. "Solution Salinity",

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[1]TEOS-10: international thermodynamic equation of seawater 2010, http://www.teos-10.org.

D. G. Wright et al.

denoted S_A^{soln}, is the most obvious extension of Reference Salinity to allow for composition anomalies; it provides a direct estimate of the mass fraction of dissolved material in solution. "Added-Mass Salinity", denoted S_A^{add}, is motivated by a method used to re-
5 port laboratory experiments; it represents the component of dissolved material added to Standard Seawater in terms of the mass of material before it enters solution. We also discuss a constructed conservative variable referred to as "Preformed Salinity", denoted S_*, which will be useful in process-oriented numerical modelling studies.

Finally, a conceptual framework for the incorporation of composition anomalies in
10 numerical models is presented that builds from studies in which composition anomalies are simply ignored up to studies in which the influences of composition anomalies are accounted for using the results of biogeochemical models.

1 Introduction

The relationships between the chemical composition, conductivity, salinity, and ther-
15 modynamic properties of IAPSO Standard Seawater, modified only by the addition and removal of pure water through dilution and evaporation (hereafter denoted SSW), are now defined to the best available precision by a linked series of standards. Millero et al. (2008) (hereafter referred to as MFWM) define a fixed Reference Composition (RC) as an estimate of the relative mole fractions of the components of dissolved ma-
20 terial in SSW, and link this to the conductivity/salinity relationship defined by the Practical Salinity Scale 1978 or PSS-78 (UNESCO, 1982). Among other benefits, salinities can now be referenced on an absolute or mass fraction scale, directly related to the dissolved material within seawater. Thermodynamic properties, including density, are consistently linked to salinity by a thermodynamic equation of state for seawater
25 (TEOS-10) represented in terms of a Gibbs function formulation, which itself is based on a comprehensive evaluation of all relevant data (Feistel, 2008, 2010; Feistel et al., 2010a,b; IOC et al., 2010).

Absolute Salinity, Density Salinity, and Reference Salinity

D. G. Wright et al.

However, as discussed here, our direct knowledge of the true chemical composition of SSW has an uncertainty which is equivalent to a mass fraction salinity uncertainty of order $0.05\,\mathrm{g\,kg^{-1}}$, whereas modern conductivity-based measurement techniques can routinely resolve spatial variations of as little as $0.002\,\mathrm{g\,kg^{-1}}$ in salinity. Work done subsequent to MFWM already suggests the presence of small systematic deviations in the relative composition of SSW compared to the RC. Further, even leaving aside the issue of the exact composition of SSW, the composition of real seawater from different parts of the world oceans is known to differ slightly from the composition of SSW, which is derived from North Atlantic surface water. These composition anomalies are in fact the single largest source of errors in estimates of the thermodynamic properties of real seawater when TEOS-10 equations are used under the assumption that composition anomalies are negligible. We are thus led to pose two questions: first, is the fixed composition model and the associated absolute salinity scale an appropriate enduring approach, and second, can we adapt the TEOS-10 formulation to incorporate additional information about these composition variations.

Regarding the Reference Composition defined by MFWM, it is clear that this can serve as a useful benchmark even though the connection with SSW is limited by both data uncertainties and the variability in SSW itself. Further, it is obvious that changes in the definition of the RC would have the potential to cause confusion in the future. Thus, although refinements of the RC will inevitably be required for particular applications (e.g., Pawlowicz, 2010; Pawlowicz et al., 2010), we argue that the set of molar ratios defining the RC should be established as a fixed benchmark.

The use of a fixed absolute salinity scale and the SSW Gibbs function formulation to characterize arbitrary seawaters, affected by biogeochemical processes in the ocean, is less obvious. Although the full ramifications of this choice are not yet definitively known, recent investigations (Millero et al., 2008, 2009; McDougall et al., 2009; Pawlowicz, 2010; Pawlowicz et al., 2010; Feistel et al., 2010a,b; Seitz et al., 2008, 2010a,b) have yielded estimates of the magnitude of the resulting errors in different circumstances, as well as some details of the operational issues that arise. Here we

discuss our present understanding of these issues.

These recent investigations have also highlighted some conceptual difficulties that are not present when discussion is limited to SSW. The term "Absolute Salinity" has been defined for Reference-Composition Seawater (RCSW) and SSW in MFWM and used as a measure of dissolved material in seawater in previous publications (McDougall et al., 2009; Feistel et al., 2010a). In this context, the term "absolute" is taken as implying a true mass fraction measure. This is in contrast to the traditional Practical Salinity, which is defined as a function of conductivity ratio at reference conditions with the function chosen to give a result proportional to Chlorinity, and with the proportionality constant chosen for consistency with past practice, rather than a best estimate of the mass fraction of dissolved material. However, the meaning of "Absolute Salinity" has not yet been precisely defined for seawaters with composition anomalies. Here we consider seawaters with composition anomalies and show that in this case the absolute salinity can be characterized in a number of different ways. A family of salinity variables is defined and a consistent notation introduced to facilitate the discussion of their features and interrelationships.

The introduction of new salinity variables that allow for the presence of composition anomalies will increase both the opportunities and the complications involved in quantifying the ocean circulation. It has been common practice to ignore composition anomalies in numerical models and assume perfect conservation of dissolved material to represent the evolution of salinity. The result has then been identified with Practical Salinity to represent the effects of dissolved material on density. Similar approximations have been used in observational studies (Lewis, 1981), but this is no longer the most accurate approximation available. One of the new variables, the "Density Salinity", is proposed as an observational parameter which should provide a measure of absolute salinity with the most general utility for oceanographic research, to be implied by the term "Absolute Salinity". This is because it allows for the most accurate calculations of density. For numerical modelling of ocean circulation, the salinity variable referred to as "Preformed Salinity" will also be very useful since it corresponds to a measure of sea-

Absolute Salinity, Density Salinity, and Reference Salinity

D. G. Wright et al.

water with the influences of biogeochemical processes removed. A hierarchy of possible numerical approaches is outlined that allow for the effects of composition anomalies added to Preformed Salinity. Thus for numerical modelling purposes, Density Salinity is determined as the sum of Preformed Salinity and an appropriately defined anomaly.

In Sect. 2, we briefly review the set of salinity variables that have been used in recent studies and in Sect. 3 we consider issues associated with SSW in the absence of composition anomalies. The accuracy of the Reference-Composition Salinity Scale is reviewed and an argument is presented that future updates of the Reference-Composition Salinity Scale should be avoided in order to provide the required stability of the measurement scale. In Sect. 4 we consider various representations of the dissolved material in seawater that includes composition anomalies. Several representations of the mass fraction of dissolved material in seawater, including the Density Salinity, are defined and approximations used to estimate them are considered. Additional considerations regarding the validity of using Density Salinity as an argument of the Gibbs function are also discussed. A framework for the consideration of the effects of composition anomalies in numerical models is proposed in Sect. 5. Section 6 provides a summary and conclusions.

2 A family of salinity variables

In this article, we refer to seven measures of salinity: Chlorinity Cl, Practical Salinity S_P, Reference Salinity S_R, Density Salinity S_A^{dens}, Solution Salinity S_A^{soln}, Added-Mass Salinity S_A^{add}, and Preformed Salinity S_*. Each of these salinity variables have been discussed in previous publications (Millero et al., 2008, 2009; McDougall et al., 2009; IOC et al., 2010; Pawlowicz, 2010; Pawlowicz et al., 2010), although not necessarily in a consistent or explicit manner. Their definitions will be formalized here. An explanation of the notation used and a figure to illustrate the relations between the various measures of salinity and density is provided in Appendix A.

Chlorinity is the oldest of the salinity measures considered and is still a corner-stone in the study of dissolved material in seawater. Based on the principle of constant relative proportions it provides a measure of the total amount of dissolved material in seawater in terms of the concentration of halides. Practical Salinity has been the internationally accepted standard for the representation of ocean salinity for the past 3 decades; for SSW it is basically a scaled version of Chlorinity estimated via the measurement of conductivity. Reference Salinity is defined by MFWM to provide a measure of the mass fraction of dissolved material in SSW, and incorporates the result of a century of study into the true composition of seawater. The most practical way to estimate Reference Salinity over the Neptunian range of conditions is to determine Practical Salinity and multiply by the fixed scale factor $(35.16504/35)\,\mathrm{g\,kg^{-1}}$. We note however that Reference Salinity provides the best estimate of the mass fraction of solute in a seawater sample only if it has the composition of SSW. The last 4 Salinity Variables have been introduced to more accurately deal with seawater that includes composition anomalies with respect to SSW and are discussed in Sect. 4. Preformed Salinity S_* is constructed to be as conservative as possible; it is designed to be insensitive to biogeochemical processes that affect the other types of salinity to varying degrees. For SSW, five of the Salinity Variables are equal, the exceptions being Chlorinity and Practical Salinity.

As discussed by MFWM and others before them, if the relative proportions of dissolved material in seawater can be assumed constant, then Chlorinity provides a suitable proxy measure of dissolved material in seawater. It is defined as 0.3285234 times the ratio of the mass of pure silver (g) required to precipitate all dissolved halides (chloride, bromide and iodide) in seawater to the mass of seawater (kg). Problems with this measure of salinity are that Chlorinity must be measured by a skilled technician using a precise silver standard, the process is time consuming, and Chlorinity cannot be measured in situ, but only on collected water samples. Also, the approach assumes a fixed (or at least precisely known) composition of dissolved material in order to convert from Chlorinity to a dissolved mass fraction. Finally, the reproducibility of the silver

standard and its traceability to a reliable SI reference is unclear.

Practical Salinity S_P was introduced 30 years ago as a replacement for Chlorinity that addresses the first set of issues, but does not properly account for composition anomalies or allow traceability to the SI (Lewis, 1981). Practical Salinity is relatively easy to measure using now standard equipment, measurements are more precise and less time consuming than measurements of Chlorinity and accurate measurements can even be made in situ. The success of the method relies on the fact that for a fixed composition at specified temperature and pressure, the conductivity is related in a one-to-one manner to the mass ratio of dissolved material in seawater and the conductivity ratio relative to a standard can be precisely measured using robust techniques. Further, reliable standards are routinely available in numbered batches from the Standard Seawater Service (Bacon et al., 2007). In practice, a polynomial relation was empirically determined to calculate Chlorinity Cl from a measured conductivity ratio and the resulting estimate of Chlorinity was converted to Practical Salinity using $S_P = 1.80655$ $Cl/(\text{g kg}^{-1})$, a choice that was made to maintain numerical continuity with historical salinity estimates at $Cl = (35/1.80655)\,\text{g kg}^{-1}$. The strict definition of Practical Salinity requires that measurements be made at a pressure of $P = 101\,325\,\text{Pa}$ and $t = 15\,°\text{C}$ on the IPTS-68[2] temperature scale ($t = 14.996\,°\text{C}$ on the ITS-90[3] scale), but algorithms are available to convert from conductivity measurements at other pressure and temperature values so this is not a serious restriction as long as any composition anomalies present do not corrupt these conversion relations (Feistel and Weinreben, 2008). This is unlikely to be a serious concern in the open ocean given that Pawlowicz (2010) estimates the maximum error in the temperature correction to be of order $0.0004\,\text{g kg}^{-1}$ when converting from $1\,°\text{C}$ to $25\,°\text{C}$ for North Pacific Intermediate Water where composition anomalies are near maximum.

MFWM list several reasons that a revised estimate of salinity is now desirable. Five of these are: 1) to introduce a chemical composition model for SSW which can be used

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[2] IPTS-68: International Practical Temperature Scale 1968

[3] ITS-90: international temperature scale 1990

in defining the Gibbs function for seawater at low salinities; 2) to adjust the numerical value of the standard measure of salinity to be as close as possible, given measurement uncertainties, to the true mass fraction of dissolved material in SSW (i.e., its absolute salinity); 3) to formally allow for arbitrarily large or small values of salinity, 4) to overcome the $T-P$ limitations of PSS-78, and 5) to officially allow mass fraction units for salinity and make oceanographic papers more readable for the wider scientific community. To achieve these goals, they define a stoichiometric composition model for SSW (the Reference Composition or RC), determine a "best estimate" of the mass fraction of dissolved material corresponding to this model at a Practical Salinity of 35, and specify an algorithm to determine a consistent estimate of the mass fraction of dissolved material in a sample of arbitrary salinity with the RC. The resulting measure of salinity is referred to as the Reference-Composition Salinity S_R (or simply Reference Salinity) and the scale on which the Reference Salinity is measured is referred to as the Reference-Composition Salinity Scale (RCSS). By using this approach, the Reference Salinity provides an estimate of the mass fraction of dissolved material in any seawater sample by approximating it with seawater that has the Reference Composition defined by MFWM.

The use of a single absolute salinity variable to represent the material dissolved in a seawater sample is most appropriate for SSW because it has a nearly fixed relative composition. In fact, IAPSO Standard Seawater can be considered as a physical realization of the Reference-Composition Seawater construct. Nevertheless, it should be noted that the composition of SSW from different batch numbers must vary as a consequence of its natural origin, and the exact magnitude of these changes is presently unknown. Even as a conductivity standard there are indications from the intercomparison of field measurements that batch-specific offsets of up to about 0.003 in Practical Salinity occur (Kawano et al., 2006), although the reasons for this have been disputed (Bacon et al., 2007). Seawaters of arbitrary origin may include much larger composition anomalies that will further distinguish them from RCSW. Since these anomalies are of scientific interest it is appropriate to consider them separately.

Absolute Salinity, Density Salinity, and Reference Salinity

D. G. Wright et al.

For a seawater sample of arbitrary composition, a single measure of absolute salinity is too simple to fully describe its properties. This point is most obvious if one considers the dissolution in seawater of a substance that affects density and other properties but does not affect conductivity (silicic acid and sugar provide examples for which this is a reasonable approximation). In such a case, the Practical Salinity S_P and the Reference Salinity S_R, both of which are functions of the conductivity of seawater, each remain almost unchanged even for significant changes to the mass fraction of solute present in the solution. Similarly, Chlorinity is almost unaffected by the addition of typical composition anomalies (real seawater anomalies do not normally include halides but they do slightly modify the mass of solution). Thus, none of these quantities provide a measure of the change in the mass fraction of dissolved material in seawater that allows for general composition anomalies.

In fact, there is still no practical means to actually determine the mass fraction of dissolved material in water for the general case. Hence a precise and easily obtained measure of the amount of dissolved material in seawater is required as an extension of Reference Salinity to allow for composition anomalies. Any extension must agree precisely with the Reference Salinity when the dissolved material has the composition assigned to Standard Seawater. In addition, it is desirable to introduce a measure of salinity that is traceable to the SI (Seitz et al., 2008, 2010a,b; IOC et al., 2010) which is not achieved by the introduction of Reference Salinity (Seitz, 2010b). We shall argue that the introduction of "Density Salinity" S_A^{dens} addresses both of these issues.

It should be noted that MFWM interchangeably used the words "Absolute Salinity" and the symbol S_A for what we now recognize as two different absolute salinity measures, Solution Salinity and Density Salinity. For most of that paper MFWM discuss SSW for which these measures of salinity are equivalent to within measurement uncertainties, but with an implication of Solution Salinity. However, in Sect. 7 of MFWM they consider the influence of composition anomalies and they use the words Absolute Salinity and the symbol S_A for what we now call Density Salinity with the symbol S_A^{dens}.

We now consider uncertainties associated with the definition of the RCSS and the representation of the salinity of SSW. We discuss the effects of composition anomalies in Sect. 4.

3 The Reference-Composition Salinity Scale and the salinity of SSW

The Reference Composition was introduced by MFWM for two primary purposes, to establish a benchmark representation of the composition of SSW and to determine a "best estimate" of the mass fraction of dissolved material in SSW which was then used to determine a scale, the Reference-Composition Salinity Scale. Since all of our salinity estimates except Practical Salinity will be expressed on the RCSS, we first review the definition of this scale and the uncertainties associated with its definition. In this section we deal with the RCSS in the context of SSW. That is, we discuss how accurately the RCSS represents the true absolute salinity of a water sample whose composition precisely matches the SSW that was analyzed in the 1970s, when most of the conductivity and density measurements underlying both EOS-80[4] and TEOS-10 were made. Since the different measures of absolute salinity are defined to be equal for SSW it is appropriate to use the symbol S_A without a superscript in this section.

3.1 Uncertainties in the Reference-Composition Salinity Scale

The Reference Composition includes all important components of seawater having mass fractions greater than about $1\,\mathrm{mg\,kg^{-1}}$ in seawater with a Practical Salinity of 35 that can significantly affect either the conductivity or the density. All mass fractions were defined using the best available information for concentrations and molar masses in 2008, and the RC was carefully adjusted to be in charge balance. The uncertainty in the molar masses alone gives rise to a mass fraction salinity uncertainty of about $1\,\mathrm{mg\,kg^{-1}}$ (Millero et al., 2008), but there are larger sources of uncertainty.

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[4]EOS-80: International equation of state of seawater 1980 (Fofonoff and Millard, 1983)

The most significant ions present in seawater but not included in the RC are Li^+ ($\sim 0.18\,\mathrm{mg\,kg^{-1}}$) and Rb^+ ($\sim 0.12\,\mathrm{mg\,kg^{-1}}$). Dissolved gases N_2 ($\sim 16\,\mathrm{mg\,kg^{-1}}$) and O_2 (up to about $8\,\mathrm{mg\,kg^{-1}}$) are not included since they are highly variable and neither have a significant effect on density or on conductivity. In addition, N_2 remains within a few percent of saturation for the measured temperature in almost all laboratory and in-situ conditions. However, the dissolved gas CO_2 ($\sim 0.7\,\mathrm{mg\,kg^{-1}}$) and the ion OH^- ($\sim 0.08\,\mathrm{mg\,kg^{-1}}$) are included in the RC in spite of their small concentrations because of their important role in the equilibrium dynamics of the carbonate system. Changes in OH^- concentration that are commonly expressed in terms of pH involve conversion of CO_2 to and from other ionic forms and affect conductivity and density. The RC concentrations of the carbonate system components were determined by taking the known total alkalinity, assuming equilibrium with the levels of CO_2 gas in the atmosphere in 1976, and then using known mathematical relationships for the equilibrium chemistry. Concentrations of the major nutrients $Si(OH)_4$, NO_3^-, and PO_4^{3-} are assumed to be negligible in SSW. Dissolved Organic Matter (DOM) is typically present at concentrations of 0.5–$2\,\mathrm{mg\,kg^{-1}}$ in the ocean, but its composition in seawater is complex and poorly known. Although its concentration in SSW is unknown it is likely to be smaller because of the filtration used in the manufacturing procedure. It is not included in the RC.

The Reference-Composition Salinity Scale (RCSS) is defined implicitly in MFWM by an algorithm that is used to specify the Reference Salinity S_R. The Reference Salinity is defined to provide an estimate of the (mass fraction) absolute salinity of seawater with the RC. It is given in terms of two end members, pure water defined as Vienna Standard Mean Ocean Water (VSMOW; IAPWS, 2001) and KCl-normalized Reference-Composition Seawater (RCSW) which is seawater with the Reference Composition at $t = 25\,^\circ$C, $P = 101\,325\,\mathrm{Pa}$ that has been adjusted to a Practical Salinity S_P of 35 (exactly) through the addition or removal of VSMOW. The Reference Salinities of VSMOW and KCl-normalized RCSW are defined to be exactly $0\,\mathrm{g\,kg^{-1}}$ and $35.16504\,\mathrm{g\,kg^{-1}}$, respectively. The Reference Salinity of an arbitrary sample of RCSW is then defined by assuming conservation of dissolved material during the addition or removal of pure wa-

ter to the sample. If a sample with mass m_1 requires the addition or removal of a mass m_2 (>0 for addition and <0 for removal) to bring its Practical Salinity to S_P=35, then its Reference Salinity is $(1+m_2/m_1)\times 35.16504\,\mathrm{g\,kg^{-1}}$. Reference Salinity is not modified by changes in temperature or pressure that are made without mass exchange.

5 Note that in reality, there are small changes in the relative composition of a seawater sample associated with changes in temperature, pressure and concentration. This is because equilibrium chemistry relationships between some of the constituents depend on these factors. Consequently, Reference Salinity is perhaps best thought of as a potential mass fraction salinity that is obtained under the particular reference conditions

10 discussed above.

As noted by MFWM, the value of the Absolute Salinity S_A of RCSW can be related to the atomic weights of the constituents and the Chlorinity of the sample by:

$$S_A = [0.3285234 \times (A_{Ag}/\langle A\rangle) \times (X_{Cl} + X_{Br})]^{-1}Cl, \tag{1}$$

where X_{Cl} and X_{Br} are the mole fractions of chlorine and bromine in the sea salt, A_{Ag}

15 is the atomic weight of silver, $\langle A\rangle$ is the mole-weighted mean atomic weight of solute with the Reference Composition and Cl is the Chlorinity of the sample of RCSW. The mole fractions of dissolved material in RCSW are precisely defined and Eq. (1) is exact for this composition. Thus, for specified Chlorinity the only source of uncertainty in the determination of S_A from Eq. (1) is the uncertainty associated with the atomic weights.

20 For a typical sample with Practical Salinity near 35 (Chlorinity near $19.374\,\mathrm{g\,kg^{-1}}$) the resulting uncertainty in S_A is only about $0.001\,\mathrm{g\,kg^{-1}}$ (Millero et al., 2008).

However, estimates of salinity rely on conductivity measures, so MFWM rewrite Eq. (1) as

$$S_A = u_{PS}S_P, \tag{2}$$

25 where the RCSS scale factor u_{PS} is defined by

$$u_{PS} = [0.3285234 \times SonCl \times (A_{Ag}/\langle A\rangle) \times (X_{Cl} + X_{Br})]^{-1}, \tag{3}$$

Absolute Salinity, Density Salinity, and Reference Salinity

D. G. Wright et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

with the quantity $SonCl$ defined as the ratio of Practical Salinity to Chlorinity for RCSW. MFWM note that the value of $SonCl$ is unknown for RCSW because of practical difficulties associated with the preparation of a solution of RC in the laboratory (Kester et al., 1967; Millero and Lepple, 1973; Millero, 2010), and approximate $SonCl$ by the value 1.80655 $(\text{g kg}^{-1})^{-1}$, which is the value appropriate to SSW (Dauphinee, 1981; Culkin and Smith, 1981). This choice is supported by the fact that the RC was defined as a "best approximation" to the composition of SSW. However, there are uncertainties associated with this value. In particular, any modification of the estimated composition of SSW would imply a difference between its composition and the fixed composition of RCSW, and this could imply a change in the best estimate of $SonCl$ that should be used for the latter in Eq. (1), and thus a deviation of the ratio S_A/S_R from unity for RCSW. The uncertainty associate with $SonCl$ is by far the largest source of uncertainty associated with the determination of the Absolute Salinity of RCSW using Eqs. (2) and (3).

We note however that our interest in Eqs. (1)–(3) is based on the fact that they provide a means to estimate the absolute salinity of SSW rather than a specific interest in the absolute salinity of the theoretical water type referred to as RCSW. Consequently, it is of interest to consider the true uncertainties associated with the use of these equations for this purpose. To investigate this issue, we take a slightly different approach to that presented by MFWM.

Consider a sample of SSW that was used in the determination of PSS-78 and assume that its Practical Salinity has been precisely determined. Since the relation $S_P = 1.80655\, Cl/(\text{g kg}^{-1})$ was used as a definition to convert between Chlorinity measurements and Practical Salinity for this particular vintage of SSW, we can use this relation as an identity here. Thus, given the Practical Salinity of our SSW sample, we know the value of its Chlorinity. Using Eq. (1), we now determine the Absolute Salinity of RCSW that has the same value of Chlorinity and we use this value as an estimate of the absolute salinity of our SSW sample.

Absolute Salinity, Density Salinity, and Reference Salinity

D. G. Wright et al.

There are subtle but important points to note about the modified interpretation given in the previous paragraph. First, the resulting value of Absolute Salinity is recognized as an estimate of the absolute salinity of the SSW sample rather than that of the ideal RCSW sample used in the estimation procedure. Second, the estimate of the absolute salinity of the SSW sample with measured Practical Salinity is given by Eqs. (2) and (3) and is thus exactly the same as the estimate of the absolute salinity of the RCSW sample with the same Practical Salinity. Third, the use of $SonCl = 1.80655\,(\mathrm{g\,kg}^{-1})^{-1}$ for RCSW has been completely eliminated. Consequently, neglecting the small uncertainties associated with the atomic weight estimates, determination of the uncertainty associated with the use of S_R as a measure of the absolute salinity of SSW is reduced to consideration of the accuracy of the RC as a representation of SSW.

We emphasize that use of Eqs. (2) and (3) to estimate the absolute salinity of a sample of RCSW involves uncertainties associated with the use of the value of $SonCl$ for SSW but it does not involve any uncertainties associated with the mole fractions since these are precisely defined for RCSW. On the other hand, use of Eqs. (2) and (3) to directly estimate the absolute salinity of a sample of SSW as described above involves uncertainties associated with the use of RCSW as a model for SSW, but it does not involve any uncertainties associated with the value of $SonCl$ since this value is precisely known for the SSW samples of interest. Since our true interest is in estimating the absolute salinity of SSW, the use of Eqs. (2) and (3) to directly estimate the absolute salinity of a sample of SSW is preferred here and we continue to consider the uncertainties associated with using RCSW as a model for SSW.

Even at the time that the RC was defined it was clear that uncertainty in the true composition of SSW was larger than the scientific requirements for precision in a salinity measure, which are about $0.002\,\mathrm{g\,kg}^{-1}$. Recently, Seitz (2010a and personal communication 2010) have estimated the sulfate (SO_4^{2-}) mass fraction of a sample of KCl-normalized SSW to be $2.702 \pm 0.022\,\mathrm{g\,kg}^{-1}$. This range of values overlaps with the Reference Composition value of $2.71235\,\mathrm{g\,kg}^{-1}$ so it does not suggest any need to revise the RC at this time. However, it also includes a lower bound of $2.68\,\mathrm{g\,kg}^{-1}$ which

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Absolute Salinity, Density Salinity, and Reference Salinity

D. G. Wright et al.

cannot currently be ruled out as a representation of the properties of SSW. If the estimated sulfate mass fraction in SSW were reduced from $2.71235\,\mathrm{g\,kg^{-1}}$ to $2.68\,\mathrm{g\,kg^{-1}}$ (a reduction of $337\,\mathrm{\mu mol\,kg^{-1}}$), then upon using the approach of MFWM in which the sodium (Na^+) concentration is adjusted to achieve charge balance, the estimated absolute salinity of the resulting modified RCSW would be reduced from $35.16504\,\mathrm{g\,kg^{-1}}$ to $35.11114\,\mathrm{g\,kg^{-1}}$. This suggests the possibility that a future change in the estimated absolute salinity of SSW with $S_P=35$ could be as large as $0.054\,\mathrm{g\,kg^{-1}}$, more than an order of magnitude larger than the precision of Practical Salinity measurements and one third of the difference between 35.16504 and 35, i.e., the difference between $S_R/(\mathrm{g\,kg^{-1}})$ and S_P for KCl-normalized RCSW.

There are smaller uncertainties in the composition of SSW and its absolute salinity associated with uncertainties in carbonate chemistry. Uncertainties associated with the involved equilibrium constants result in uncertainties in the absolute salinity of SSW of order $0.0002\,\mathrm{g\,kg^{-1}}$ or less. Similarly, the estimated amount of boric acid in SSW has recently been revised upwards by $0.0002\,\mathrm{g\,kg^{-1}}$ (Lee et al., 2010). A potentially larger effect arises from uncertainties about the amount of Dissolved Inorganic Carbon (DIC) present in the 1970s SSW. For example, for a KCl-normalized sample, the SSW76 composition used as a representation of SSW by Pawlowicz (2010) has a DIC value that is $117\,\mathrm{\mu mol\,kg^{-1}}$ higher than that associated with the RC. Using Eq. (51) from Pawlowicz et al. (2010), we find that this difference alters the mass fraction absolute salinity by about $0.0055\,\mathrm{g\,kg^{-1}}$. This change is almost an order of magnitude smaller than uncertainties associated with other aspects of the composition (e.g., sulfate), but still larger than the uncertainties associated with Practical Salinity measurements.

The above discussion deals with the accuracy of the RCSS for the determination of the absolute salinity of SSW. That is, it deals with the issue of how accurately the Reference Salinity, determined from conductivity, represents the mass fraction of dissolved material in solution for the ideal case of a sample of 1970s SSW. We have seen that the inaccuracies may be as large as $0.05\,\mathrm{g\,kg^{-1}}$ which is substantially larger than the contributions to the mass fraction of dissolved material from composition anomalies

that we consider in some detail in Sect. 4. However, these offsets will affect all salinity values proportionately and are accounted for in the definition of the Gibbs function for SSW, whereas the composition anomalies discussed in Sect. 4 vary spatially and directly influence horizontal pressure gradients. In the next section, we consider whether the uncertainties in the absolute salinities of SSW and RCSW might result in a need to update the RCSS in the future.

3.2 Will the RCSS need to be updated in the future?

The above discussion emphasizes the uncertainty in the use of the Reference Salinity to estimate the mass fraction of dissolved material in 1970s SSW. It motivates us to ask what should happen if an improved estimate of the composition of this vintage of SSW is determined in the future. At first, it would seem natural to update the Reference Composition and hence the estimate of the mass fraction of dissolved material in SSW. This would in turn change both the RCSS and the uncertainty associated with it. This approach would be necessary if we required the RCSS to always provide the best possible estimate of the mass fraction of the salts dissolved in standard seawater without additional adjustments. Below, we argue that even if at some time in the future an improved estimate for the composition of SSW is definitively determined, it would still be highly undesirable to modify the RC and along with it the RCSS.

There are two primary reasons that updating the RCSS should be avoided. First, we note that changes in Reference Salinity of order $0.002\,\mathrm{g\,kg^{-1}}$ (i.e., changes in Practical Salinity of order 0.002) are detectable in the ocean and salinity changes have been interpreted as indications of climate change (Levitus, 1989; Joyce et al., 1999; Wong et al., 1999; Dickson et al., 2002; Curry et al., 2003). Thus it is highly desirable for climate change studies to use a measure of salinity that will not change by this amount unless there is a true change in the salinity of seawater. Since the *precision* of Reference Salinity estimates is of this order, it provides a suitable measure if the definition of the RCSS remains unchanged. However, the uncertainty of order $0.05\,\mathrm{g\,kg^{-1}}$ as a measure of the mass fraction of dissolved material in seawater introduces the

possibility that the RCSS could be revised several times by amounts considerably in excess of $0.002 \, \text{g} \, \text{kg}^{-1}$ as estimates of the mass fractions in RCSW are improved. Such changes recorded in data bases and in publications could be misinterpreted as signatures of climate change by investigators who are unaware of changes in the mea-

5 surement scale. The potential for confusion is substantial and obviously undesirable. It should be avoided.

The second primary reason to avoid changes in the RCSS relates to the methods used to estimate the parameters in the Gibbs potential function for seawater. The parameters in this function have been determined to provide correct results for SSW for

10 specified values of Absolute Salinity, temperature and pressure with the Absolute Salinity expressed on the current RCSS (recall that Reference Salinity is our best estimate of Absolute Salinity). If this scale were to be changed, then the input salinity argument for the Gibbs function would be changed without any real change in the properties of a sample. Consequently, the Gibbs function would have to be modified to obtain the

15 same thermodynamic properties with a modified salinity input. Although the required change is simple (it can be implemented by changing a single parameter) the possibility that some versions of code used to evaluate the Gibbs function would not be correctly updated is rather large. Even if the updates were somehow made in every existing version of the code, changes in the RCSS over time would require that different

20 parameters be used in the Gibbs function for different time periods. Clearly the chance of introducing confusion through such changes is large.

Based on the above discussion, we conclude that it is desirable to avoid any changes in the definition of the RCSS. Fortunately, such changes should not be necessary. This is because the Reference Salinity is needed first to determine the salinity input to the

25 Gibbs function and second as a measure of the mass fraction of dissolved material in seawater. Measurements on the current scale can serve both purposes very well. As already noted, maintenance of a fixed RCSS is desirable for applications of the Gibbs function to estimate the density and other thermodynamic properties of SSW since the Gibbs function has been constructed to provide correct results with the salinity

specified on the RCSS. So the only concerns are related to use of the RCSS to provide a measure of the true mass fraction of dissolved material in seawater.

There is the possibility of a small change in the best estimate of mass fraction absolute salinity of SSW at some time in the future. For rare applications in which the error incurred by using the current scale to estimate the mass fraction might be significant, a correction could be made. This could be achieved by multiplying the Reference Salinity determined on the current scale by the ratio of the revised estimate of the absolute salinity of KCl-normalized SSW (from the 1970s) to the current estimate of $35.16504\,\mathrm{g\,kg^{-1}}$. Note that by avoiding repeated updates over time, a single correction factor will be applicable to all archived measurements. One of the very firm recommendations of the Intergovernmental Oceanographic Commission (IOC), the Scientific Committee on Ocean Research (SCOR) and the International Association for the Physical Sciences of the Oceans (IAPSO) in endorsing the use of TEOS-10 was that Practical Salinity should continue to be archived in national data bases (see IOC et al., 2010). This practice of storing results for a measured quantity but publishing results based on another related quantity is analogous to the present practice of archiving in situ temperature even though potential temperature is used for most analyses. This recommendation of IOC et al. (2010) is primarily intended to avoid confusion in data bases but it also means that the influence of any modifications of our best mass fraction estimates will be easily and consistently applied to both future data and past data that whas been archived since Practical Salinity was defined 3 decades ago. In fact, since Practical Salinity is related to Chlorinity by the simple relation $S_\mathrm{P}=1.80655\,Cl$, any improvement in mass fraction estimates will also be easily applied to all of the Chlorinity data collected during the century before the introduction of Practical Salinity.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

4 The characterization of seawaters of arbitrary composition

4.1 Salinity variables for the representation of arbitrary seawater

The differences between the compositions of SSW and RCSW are important in accurately determining the true absolute salinity of SSW, and would therefore be important
in (e.g.) determining the best possible estimate of the total salt content of the oceans.
On the other hand, the Gibbs function has been defined based on salinity measurements represented on the RCSS so the thermodynamic properties of SSW determined
from the Gibbs function will be accurate even if the RCSS provides a slightly incorrect
estimate of the mass fraction of dissolved material in SSW. However, as seawater circulates within the world oceans, its composition undergoes additional changes due
to biogeochemical processes. The magnitudes of these changes are generally smaller
than our uncertainty in the absolute salinity of SSW, but these anomalies are systematic
and measurable, and their neglect results in errors in the representation of geographic
changes in the thermodynamic properties of seawater. In contrast to any inaccuracies
associated with the RCSS, these anomalies cannot be accounted for in the determination of the Gibbs function for SSW and they cannot be corrected for through a uniform
scale factor applied to salinity estimates. In particular, their neglect results in systematic errors in basin-scale density gradients, and thus in inferred basin-scale transports.
Consequently, it is important to consider how these anomalies can be characterized.
In this section, we discuss how the composition of seawater changes, and different
methods of incorporating these changes in measures of salinity that can be used to
describe arbitrary seawaters.

We limit consideration to changes that will affect salinities at amounts larger than
about $0.001\,\mathrm{g\,kg^{-1}}$. Anomalies associated with the carbonate system (positive and
negative) tend to be largest due to the influences of air–sea exchange and biological
cycling (Brewer and Bradshaw, 1975; Pawlowicz, 2010). Their effects on the components of the RC can be adequately parameterized using just the total alkalinity (TA)
and dissolved inorganic carbon (DIC) contributions, although they typically result in

changes to the relative concentrations of all components of the carbonate system. In addition, there may be anomalies for species that are not present in the RC. These include nutrients, of which the most significant are silicic acid and nitrate. Fortunately, TA, DIC, $Si(OH)_4$ and NO_3^- are all routinely measured in hydrographic programs. Fi-
5 nally, the actual composition anomaly must involve parameters that are not routinely measured, since arbitrary changes in TA and NO_3^- must be compensated in some way to preserve charge balance. The most important process contributing to changes in TA in the deep ocean is likely the dissolution of $CaCO_3$ (Sarmiento and Gruber, 2006), although other processes (e.g., sulfate reduction; Chen, 2002) may be at work, par-
10 ticularly in coastal and marginal seas. Pawlowicz (2010) chooses to balance charge in his model through the addition or removal of Ca^{2+} with the caveat that other processes are recognized to be important at least under some conditions. Comparison with observations reveals that the resulting estimates of Ca^{2+} are accurate to within about $0.8\,\mathrm{mg\,kg^{-1}}$.

15 Pawlowicz et al. (2010) use the above approach in a model study; they represent the major contributions to composition anomalies relative to SSW by specifying the anomalies in four components: TA, DIC, NO_3^- and $Si(OH)_4$, with anomalies in Ca^{2+} estimated from the requirements of charge balance. The largest anomalies occur in the North Pacific. To motivate the following discussion we refer to Tables 1a and b
20 where numerical values for the different salinity variables that we are about to discuss are provided for a North Pacific scenario. A full description of this table will be provided below, but it is useful to note at this stage that the differences between the different salinity variables are of order $0.01\,\mathrm{g\,kg^{-1}}$, significantly larger than the precision with which Practical Salinity is measured ($0.002\,\mathrm{g\,kg^{-1}}$).

25 We assume throughout our discussion that the dissolved material in a seawater sample consists of a component with the composition of SSW plus anomalies from this composition as discussed above. To be more specific, we must specify a representation of SSW from which composition anomalies can be determined. The RC was defined as a representation of SSW and it would thus seem reasonable to determine

Absolute Salinity, Density Salinity, and Reference Salinity

D. G. Wright et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Title Page

Abstract   Introduction

Conclusions   References

Tables   Figures

◄◄   ►►

◄   ►

Back   Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

composition anomalies from this reference. However, as more information becomes available about the composition of SSW, better approximations for SSW will be obtained. Thus although there is no need to update the RCSS (and indeed important reasons not to do so, as discussed in Sect. 3.2), anomalies should be determined relative to the best available estimate of SSW composition rather than from the RC. We follow Pawlowicz (2010) and Pawlowicz et al. (2010) and represent SSW by the reference state referred to as SSW76 for the purpose of dealing with anomalies.

The considerations leading to the definition of SSW76 are discussed in detail by Pawlowicz (2010) and Pawlowicz et al. (2010). Briefly, both the RC and SSW76 are based primarily on analyses of SSW done in the 1970s. However, the borate and carbonate components represent significant contributions to the composition of SSW that were not systematically investigated and MFWM and Pawlowicz (2010) adopt different choices for these components. MFWM estimate these components under the assumption of equilibrium with atmospheric conditions at 25 °C whereas Pawlowicz (2010) sets the DIC content of SSW76 to force the density to match that of in situ North Atlantic surface water, and (scanty) information about the true DIC content of SSW. The result is that the DIC specified by Pawlowicz (2010) is 2080 µmol kg^{-1}, significantly higher than the RC value of 1963 µmol kg^{-1}. Correspondingly, the estimated mass fraction of dissolved material in KCl-normalized seawater is increased from 35.16504 g kg^{-1} to 35.17124 g kg^{-1}. In this context, it is noteworthy that Brewer and Bradshaw (1975) determined the DIC content of SSW batch P61 to be 2238 µmol kg^{-1} and Millero et al. (1976b, 1978) report a value of 2226 µmol kg^{-1} in SSW used to determine the equation of state. Although there is significant uncertainty associated with the carbonate components of SSW, it is very likely that the value of DIC corresponding to SSW76 is more representative of the analysed batches of SSW than the value corresponding to the RC; this choice also simplifies the equations used to model interrelationships between the different salinity variables by avoiding the need to introduce offsets in the relations presented in Tables 1a and b below.

Following the approach used for the RC, we represent SSW76 by exact mole fractions at the reference conditions of atmospheric pressure and 25 °C. For SSW76, we include the 16 main non-zero sea salt constituents listed in Table 3 of Pawlowicz (2010), $x_a^{76} > 0$, $a = 1, 2, \ldots, 16$. Let $m_a > 0$ represent the molality (moles/(kg solvent)) of species a in a sample of SSW76. Since chloride is an approximately conserved constituent, we choose to use it as a measure of the component of dissolved material associated with SSW. If x_{Cl}^{76} represents the mole fraction of chloride in SSW76 and m_{Cl} represents the chloride molality of the particular solution under consideration, then the molality of component a associated with SSW76 is given by $m_{Cl} \times x_a^{76} / x_{Cl}^{76}$ and the molal composition anomaly for species a is $\delta m_a = m_a - m_{Cl} \times x_a^{76} / x_{Cl}^{76}$. In addition, there may be anomalies for species such as nutrients that are not present in SSW76, for which $\delta m_a = m_a$, $a > 16$.

Although we use SSW76 to estimate the magnitude of anomalies from Standard Seawater, we note that the salinity argument of the Gibbs function must be expressed on the RCSS which was determined using the RC. In practice, salinity will be determined from Reference Salinity plus anomalies in observational studies. Reference Salinity is defined using Eq. (8) so it is automatically expressed on the RCSS. Strictly speaking, the salinity anomalies determined by the formulae of Pawlowicz et al. (2010) should be multiplied by the factor 35.16504/35.17124 to express them on the RCSS, but this adjustment is entirely negligible for the small anomalies that occur in the open ocean.

To proceed further, we must carefully define what is meant by terms like "Absolute Salinity" when composition anomalies are present; this has not been done rigorously in previous publications.

The approach of Millero and co-workers has been to argue that changes in the mass fraction of dissolved material in seawater relative to S_R are adequately approximated by $(\rho - \rho_R)/(\beta_R \, \rho_R)$ where β_R and ρ_R are the haline contraction coefficient and density at $S = S_R$ determined from EOS-80 or TEOS-10 (the differences are negligible in this context). This approximation for the mass fraction of dissolved material is now referred to as Density Salinity, and denoted by S_A^{dens}. The approach is supported by previous

Absolute Salinity, Density Salinity, and Reference Salinity

D. G. Wright et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

work (Millero, 1975; Chen and Millero, 1986) indicating that density changes of natural waters are affected primarily by the mass of added material, with the relative composition providing only a secondary effect. This definition naturally reverts to the existing definition of Reference Salinity as anomalies from SSW tend to zero since the density
5 varies smoothly as composition anomalies tend to zero.

However, the limitations and biases of this approach are not well understood for seawater that includes anomalies from SSW. Previous verification has not systematically considered the range of composition variations that occur in the ocean and since the physical/chemical characteristics of different solutes can vary greatly, it is not really
10 clear how Density Salinity is related to the mass fraction of dissolved material in seawater with arbitrary composition. Nor were changes in conductivity considered, which would affect Practical and Reference Salinity. In fact, we will see below that the difference between Density Salinity and Reference Salinity does not necessarily provide a good approximation for the anomalies in the mass fraction of dissolved material in
15 seawater. Thus, although it will be argued that Density Salinity is well-suited to most physical oceanographic applications, an alternative measure of salinity is required to provide a precise measure of the mass fraction of material dissolved in seawater.

To develop a more rigorous definition of mass fraction salinity that will apply in the presence of composition anomalies and agree with the definition established in MFWM
20 when no anomalies are present, we first re-examine the procedure followed by MFWM for SSW. The basic principles used to determine the Absolute Salinity of SSW are

1. addition or removal of pure water (i.e. dilution or evaporation) until $S_P = 35.000$ (or equivalently $Cl = 19.374 \, \text{g kg}^{-1}$),

2. adjustment of the sample to chemical equilibrium at the reference conditions,
25 $t = 25\,°C$ and $P = 101\,325\,\text{Pa}$, without exchange of mass, under which conditions the Absolute Salinity of the sample can be determined from Eqs. (2) and (3), and

3. determination of the Absolute Salinity of the original sample as the mass of

dissolved material in the adjusted sample divided by the total mass of the original sample.

The obvious first steps in any definition of Absolute Salinity for anomalous compositions are then to standardize the concentration and adjust to equilibrium conditions at $t=25\,°C$ and $P=101\,325\,Pa$. Unfortunately a precise adjustment to the conditions used for SSW is not possible because the chemical equilibria in the solution will inevitably be affected to some degree by the anomalous solute. However, operationally effective definitions are possible. Below, we discuss a conceptual approach followed by operationally practical approaches.

A crude standardization could be achieved simply by adjusting the Chlorinity of the solution to $19.374\,g\,kg^{-1}$. In this case S_P would not in general be equal to 35.000 as it would for SSW because of the influence of composition anomalies on conductivity. Also, the total mass of solution, and hence the Chlorinity, is influenced by the presence of anomalous material so this approach to standardization is imprecise and will be inaccurate for large anomalies. A normalization approach that is less affected by composition anomalies can be achieved (at least conceptually or in numerical calculations) by adjusting the chloride molality, the total number of moles of chloride per kg of solvent, instead of Chlorinity. Unlike Chlorinity, the chloride molality is not influenced by the addition of anomalous solute that does not react with water; there is a weak influence if the added solutes react with water since they reduce the amount of water by a small amount.

It should be noted here that the separation between what is pure water and what is dissolved material is not totally clear, but this is not a serious issue at the level of accuracy that we currently require ($\sim$1 ppm in density and salinity). In particular, one might question whether H_3O^+ (the form that H^+ actually takes in water) and OH^- are solute or solvent but it makes little difference at this level of accuracy. We have already noted that OH^- is included as solute in the RC, but its mass fraction is just $0.08\,mg\,kg^{-1}$ so its contributions to density and salinity are negligible. Given this estimate for OH^-, an order of magnitude estimate for H_3O^+ is easily determined. Since the dissociation constant

of water is of order 10^{-14} (IAPWS, 2007), we have $[H_3O^+][OH^-]=K_w\approx10^{-14}$ $(mol/l)^2$ and with a pH of order 8 (changes of order 0.1 associated with the choice of pH scale don't influence our order of magnitude estimate), it follows that pOH $(=14-pH)$ is near 6. Thus, the concentration of H_3O^+ is roughly two orders of magnitude less than that of

5　OH^-. Hence although H_3O^+ is considered as solute, it is not explicitly included in the RC because its contributions to density and salinity are far below the level of current concern.

　　For consistency with the normalization used in the definition of Reference Salinity, we normalize to the chloride molality of SSW76 that has a Chlorinity of 19.374. This

10　choice gives a chloride molality of $0.556642\,mol\,kg^{-1}$ ($=19.734631\,g$ chloride per kg H_2O). Thus for consistency with the definition of Absolute Salinity in the absence of composition anomalies, we add or subtract mass m_2 of pure water to adjust the original seawater sample of mass m_1 to a chloride molality of $0.556642\,mol\,kg^{-1}$. We refer to this adjustment as chloride-normalization. We now divide the dissolved material

15　(all material not in the pure water component of the solution) into two components. The first component includes the chloride component plus each of the other components of SSW76 in the same mole ratios as defined for SSW76. The mass of solute in a chloride-normalized solution of SSW76 is $36.45335\,g/(kg\,H_2O)$ ((35.17124 g solute)/(1000 g solution-35.17124 g solute)). The second component includes all re-

20　maining dissolved material. Note that negative contributions from the chemical species in SSW are permitted in this second part although the total concentration of any species is non-negative. We now assume that the total mass of solute in this normalized solution can be determined and is m_{solute}. The mass of solvent in the normalized solution is then $m_{solvent}=m_1+m_2-m_{solute}$. The total mass of the first component of so-

25　lute is $m_3=0.03645335\times m_{solvent}=0.03645335\times(m_1+m_2-m_{solute})$ and that of the second component is $m_4=m_{solute}-0.03645335\,m_{solvent}=1.03645335\,m_{solute}-0.03645335$ (m_1+m_2). In principle m_4 may be negative (e.g., when some of a species in SSW is removed from solution).

Given the above information, the mass fraction definition of Absolute Salinity used by Millero et al. (2008) can be extended to include composition anomalies in a (conceptually) very straightforward manner. The absolute salinity of the chloride-normalized solution can then be simply defined as the mass of material dissolved in the solution divided by the total mass of the solution $m_{\text{solute}}/(m_1+m_2)$. The mass fraction of dissolved material in the original solution is then determined as before under the assumption of salt conservation during the addition or removal of pure water and is given by $(1+m_2/m_1) \times m_{\text{solute}}/(m_1+m_2) = m_{\text{solute}}/m_1$ or $(m_3+m_4)/m_1$. We refer to this as the Solution Salinity, and denote it as S_A^{soln}, where "soln" refers to the fact that the mass of dissolved material is determined after it reaches equilibrium in solution. This definition is consistent with the definition of Absolute Salinity given by MFWM (see Sect. 3 above) for SSW and uses the same basic approach to extend the definition to allow for composition anomalies.

The separation of solute into the two components introduced above is of interest in its own right. Since chloride does not take part in biogeochemical cycling and so is essentially a conservative variable, the component associated with the Reference Composition will be quasi-conservative following the ocean general circulation, analogous to other similarly constructed quasi-conservative tracers like N^* and NO^* (Sarmiento and Gruber, 2006). It has mass fraction absolute salinity $S_* = m_3/m_1$ and will be referred to as the Preformed Salinity. S_* is modified by exchanges of water at the ocean surface and by mixing in the ocean interior, but the effects of biogeochemical processes on it are deliberately excluded. It is thus an ideal baseline to which material is added by biogeochemical processes. The remainder of the solute is referred to as the anomalous part. Again, we note that it is possible for the "remainder" to be negative as in the case when some of a SSW species is removed from solution.

We emphasize that S_A^{soln} deals with a solution in equilibrium and treats all non-water components of seawater as dissolved material. Consequently, when new material is added to solution, the change in mass of the dissolved material may deviate from the added mass. Perhaps the most obvious example 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. Similar situations occur for other dissolved materials; some may also release water upon dissolution, such as certain calcium minerals.

In contrast to the case for Solution Salinity, it is sometimes useful to deal with the anomalous mass added to SSW directly. This is particularly true in laboratory experiments. If a mass m_{add} of anomalous solute is added to a sample of KCl-normalized (or equivalently chloride-normalized) SSW of mass m_{ssw} then a mass fraction absolute salinity may be defined as $(0.03517124\,m_{ssw}+m_{add})/(m_{ssw}+m_{add})$, where $0.03517124\,m_{ssw}$ is the mass of dissolved material in the original sample of SSW, m_{add} is the added mass of anomalous material and $m_{ssw}+m_{add}$ is the total mass of the final solution. We refer to this as Added-Mass Salinity, and denote it as S_A^{add}. For Standard Seawater S_A^{add} is also consistent with the definition of Absolute Salinity for SSW given by MFWM since no mass is added in that case, but for seawater of anomalous composition the mass of anomalous solute is determined before it is added to the solution rather than after equilibrium conditions have been established for the new solution, as would be required for the Solution Salinity. Any chemical reactions of the added solute with the SSW solution are therefore not considered for Added-Mass Salinity. That is, neither precipitation of species nor redistributions between solvent and solute have any effect on Added-Mass Salinity. It is therefore conceptually very different from Solution Salinity and we will see below that it is also substantially different in practice.

Although the Added-Mass Salinity may be useful in the laboratory, it is not straightforward to estimate for seawater with anomalous composition that is sampled from the ocean. Even if we assume that the composition of the final equilibrium state is known, one must still estimate the mass of anomalous solute prior to any chemical reactions with SSW. Since equilibrium states are independent of their history, any combination of chemical species that irreversibly evolve to the given sample composition is a potential

candidate for the computation of Added-Mass Salinity, which therefore is highly ambiguous for a given final solution. Additional information must therefore be provided to resolve this ambiguity if Added-Mass Salinity is to be determined for ocean seawater. Pawlowicz et al. (2010) provide an algorithm to achieve this estimate, at least approximately, once some assumptions about ocean biogeochemical processes are made. The details are substantially more complicated than those required for Solution Salinity and will not be reproduced here. The main point that we wish to emphasize is that the difference between Solution Salinity and Added-Mass Salinity lies in the treatment of the anomalous contributions and that (as illustrated in Tables 1a and b) these differences are important at the level of precision being considered here. In either case, the Preformed Salinity S_* can be uniquely determined from the chloride molality. However, the numerical values of the salinity anomalies $\delta S_*^{\mathrm{soln}}$ and $\delta S_*^{\mathrm{add}}$ which are added to Preformed Salinity S_* to determine S_A^{soln} and S_A^{add} may differ significantly.

To illustrate the magnitude and range of the numerical variations between different measures of salinity, we consider an extreme example. Deepwater composition anomalies from SSW in the open ocean are largest at depth in the North Pacific. For KCl-normalized seawater, TA is increased relative to SSW values by about $150\,\mu\mathrm{mol\,kg}^{-1}$, and DIC by $300\,\mu\mathrm{mol\,kg}^{-1}$. NO_3^- concentrations are as high as $40\,\mu\mathrm{mol\,kg}^{-1}$, and $Si(OH)_4$ concentrations are as large as $170\,\mu\mathrm{mol\,kg}^{-1}$. The corresponding increase in Ca^{2+} is inferred to be $95\,\mu\mathrm{mol\,kg}^{-1}$ to balance charge. Maximum density anomalies relative to densities calculated using S_R and the TEOS-10 equation of state in this region are estimated to be about $0.015\,\mathrm{kg\,m}^{-3}$, both from direct measurements and using the model calculations of Pawlowicz et al. (2010). The approximate magnitude of the corrections to determine salinities of the different types defined above can be derived from this density anomaly using equations proposed by Pawlowicz et al. (2010). The corrections and the numerical values of the different salinities are shown in Tables 1a and b. Table 1a shows the changes to the various salinity variables with respect to the Reference Salinity, while Table 1b shows the same salinity perturbations with respect to the Preformed Salinity. The salinity perturbations in Table 1a are

appropriate for the estimation of various measures of absolute salinity when the Practical Salinity (and hence Reference Salinity) is available as a measured quantity (using, for example the lookup table of McDougall et al. (2009) to determine the corrections) while Table 1b is relevant to the consideration of biogeochemical effects.

Importantly, the model study of Pawlowicz et al. (2010) shows that, for the anomalies arising from ocean biogeochemical processes, correlations between the anomalies of different constituents are strong enough in all ocean basins that the linear relations given in column 2 apply for all deep-ocean sites within an uncertainty of about $0.003\,\mathrm{g\,kg^{-1}}$, even though the exact nature of the composition anomalies that produce the density anomalies can vary with geographic location. If the details of the composition anomalies in TA, DIC, NO_3^- and $Si(OH)_4$ are known, then more accurate inter-relationships can be derived using relatively simple formulas (Pawlowicz et al., 2010; IOC et al., 2010), two of which are reproduced below as Eqs. (9) and (10). In practice, measurements of conductivity and density, or of conductivity and concentrations of major non-conservative parameters (carbonate system and nutrients), along with a few assumptions about the nature of ocean biogeochemical processes, are enough to specify the full seawater system to a useful accuracy, including Density Salinity, Solution Salinity, Added-Mass Salinity and Preformed Salinity.

The largest deviations from Reference Salinity in Table 1a are for Practical Salinity, and it is largely this discrepancy that justifies the introduction of the Reference Salinity as a more accurate measure of absolute salinity. The next largest numerical offset from the Reference Salinity appears in Solution Salinity which is roughly one quarter as large as the offset for Practical Salinity. The final salinity increase for Solution Salinity is significantly larger than for Added-Mass Salinity due to the incorporation of H^+ and OH^- into the anomalous non-conservative contributions to the dissolved material. The values for the Density Salinity S_A^{dens} and Added-Mass Salinity S_A^{add} are closest, and would generally lie (just) within typical measurement error of each other, a determination that is shown to also hold for a variety of laboratory results in Pawlowicz et al. (2010). The smallest deviation from Reference Salinity occurs for Preformed Salinity. However,

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◀ | ▶|

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

even this change is about double the precision to which Reference Salinity can be determined through conductivity measurements. Tables 1a and b emphasize the fact that the single largest factor limiting our knowledge of the spatial variations of thermodynamic properties (like density) is a correct estimation of the effects of compositional variations.

Although no one salinity variable can fully characterize seawater with anomalous composition, the central importance of density to dynamical investigations of the ocean suggests that if a single salinity variable is required, then the Density Salinity is the most useful. However, attempts to use the Density Salinity as loosely defined at the beginning of this section lead almost immediately to a number of technical questions that are addressed in the next section.

4.2 The "Density Salinity" of seawater

In Sect. 2 we noted that the Density Salinity equals the Reference Salinity by construction for the special case of SSW and therefore reproduces the MFWM estimate of the mass fraction of dissolved material in seawater in this case. It is also intended to be a useful measure of salinity effects in the general case when composition anomalies are present but this depends on whether its use with the Gibbs function for SSW returns sufficiently accurate results for density and other thermodynamic quantities over the range of oceanographic conditions. Here we more rigorously define the Density Salinity as a numerical measure that returns the correct value of density when used as an argument of the Gibbs function at a selected $T-P$ reference point, and show that the density values returned at other temperatures and pressures are sufficiently accurate for practical usage. We then discuss alternative methods by which it can be estimated that will be useful in practice.

First, note that for SSW, the TEOS-10 density is given by

$$\rho = \frac{1}{v} = \frac{1}{g_P(S_R, T, P)}, \tag{4}$$

◄ | ►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

where v is the specific volume, g is the Gibbs function for SSW (Feistel, 2008; IAPWS, 2008) and the subscript P indicates partial differentiation with respect to pressure at constant salinity and temperature. For SSW, evaluating Eq. (4) at fixed S_R for different values of T and P will determine the correct values of ρ for a fixed seawater sample.

5 Thus, measurement of ρ at any specified values of T, P and subsequent inversion of Eq. (4) to determine S_R will return the unique value of S_R appropriate to the sample. This unique value of S_R is referred to as the Density Salinity of the SSW sample and is represented by the symbol S_A^{dens}. We wish to extend this definition to apply to seawater samples of arbitrary composition, but in this case the values of S_R determined

10 by measurements of the same sample at different values of T and P are not guaranteed to be the same since thermal expansion and compressibility may be influenced by the presence of composition anomalies in ways that are not accounted for by Eq. (4). Consequently, to use this procedure to define a unique representation of salinity for a seawater sample of arbitrary composition, we must specify reference conditions at

15 which S_A^{dens} is to be determined. For reference conditions, we choose $t=25\,°C$ and $P=101\,325\,Pa$. Thus, for a sample of general composition, with density ρ at $t=25\,°C$ and $P=101\,325\,Pa$, the Density Salinity S_A^{dens} is defined by the implicit equation

$$\rho = \frac{1}{g_P\left(S_A^{dens}, 298.15\,K, 101\,325\,Pa\right)} . \qquad (5)$$

In general, Eq. (5) must be solved numerically as discussed in Feistel et al. (2010a).

20 This is straightforward because it involves the zero of a monotonic function; a routine to perform the inversion is provided in the Sea-Ice-Air library (Wright et al., 2010). S_A^{dens} is thus guaranteed to provide the correct value of density when used as an input to the Gibbs function representation, for any seawater composition at the reference values of temperature and pressure. Below, we show that if Density Salinity is defined

25 by Eq. (5), then it can also be used as the salinity argument in Eq. (4) to determine reliable estimates of the density at other values of temperature and pressure. The demonstration of this point also shows that the value determined for Density Salinity

is not sensitive to the choice of reference conditions so although a choice must be specified for strict consistency, this choice is not important in practice.

To be more specific regarding the need to specify reference conditions for a seawater sample of arbitrary composition, we note that if the density is correctly determined at any reference point T_R, P_R, then we can determine the density at any other temperature and pressure from the equation

$$\rho^{true}\left(S_A^{dens},T,P\right) = \rho\left(S_A^{dens},T_R,P_R\right) + \int_{T_R}^{T} \frac{\partial \rho}{\partial T}\left(S_A^{dens},t,P_R\right) dt + \int_{P_R}^{P} \frac{\partial \rho}{\partial P}\left(S_A^{dens},T,p\right) dp, \qquad (6)$$

where the partial derivatives with respect to temperature and pressure are the true values for the water sample. When the Gibbs function is used to evaluate the density, away from the reference conditions, these derivatives are effectively replaced by the corresponding derivatives for Standard Seawater. The error associated with using the Gibbs function to determine density for an arbitrary seawater sample can therefore be expressed as

$$\Delta\rho\left(S_A^{dens},T,P\right) = \int_{T_R}^{T} \frac{\partial(\rho - \rho^{SSW})}{\partial T}\left(S_A^{dens},t,P_R\right) dt + \int_{P_R}^{P} \frac{\partial(\rho - \rho^{SSW})}{\partial P}\left(S_A^{dens},T,p\right) dp \qquad (7)$$

where ρ^{SSW} is the density determined by the Gibbs function formulation for SSW.

Equation (7) clearly reveals the source of the errors that we wish to consider. Unfortunately, very little experimental work has been done on the influence of composition anomalies on the thermal expansion or compressibility of seawater. However, the FREZCHEM model (Marion and Kargel, 2008; Feistel and Marion, 2007; Feistel et al., 2010b), which is based on Pitzer equations for aqueous electrolyte solutions, can be used to estimate the magnitude of the errors indicated by Eq. (7). These model calculations are subject to considerable uncertainty since they are not validated by direct measurements, and the numerical results are affected by the details of the chosen

compressibility parameterization. However, the basic results discussed below have also been confirmed using the LIMBETA model (Pawlowicz et al., 2010) with different parameterizations of compressibility effects. Thus, although details are uncertain, the model calculations provide a useful indication of the magnitude of the effects of composition anomalies on the evaluation of density using the Gibbs function for SSW.

To provide a relevant example, we consider the effect of anomalies similar to those observed at depth in the North Pacific where the largest known deep ocean anomalies are found. Two (numerical) samples of seawater are created, the first representing Standard Seawater as discussed by Feistel and Marion (2007) and the second including composition anomalies corresponding to North Pacific Intermediate Water (Sect. 4.1 and Pawlowicz et al., 2010). The concentration of solute in the SSW sample is specified to give $S_R = 35\,\mathrm{g\,kg^{-1}}$. NPIW anomalies are then added to a duplicate sample to give a density anomaly of approximately $0.015\,\mathrm{g\,m^{-3}}$, similar to the maximum anomalies observed in the open ocean. Pure water is then added to this NPIW sample to adjust its density to match that of the original SSW sample at $t = 25\,^\circ\mathrm{C}$, $P = 101\,325\,\mathrm{Pa}$, so that the samples of SSW and slightly diluted NPIW have identical Density Salinities.

Using the algorithms included in the FREZCHEM model, modified to represent a closed system with respect to CO_2 exchange, the density changes predicted for both the SSW sample and the diluted NPIW sample are now determined for t between $-2\,^\circ\mathrm{C}$ and $40\,^\circ\mathrm{C}$ and P between $10^5\,\mathrm{Pa}$ and $10^8\,\mathrm{Pa}$ (roughly between the surface and $10\,000\,\mathrm{m}$ below the ocean's surface), and the density differences between the two samples are determined. If the temperature is below the freezing point of one or both samples then results are determined for metastable liquid states. The results are shown in Fig. 1 and indicate that the density difference between the two samples varies smoothly and is less than $0.2\,\mathrm{g\,m^{-3}}$ over the full range of temperature and pressure conditions considered. This difference is at least a factor of ten smaller than the smallest density differences that can be routinely detected using a densimeter and is certainly negligible for the present purpose. Uncertainties associated with the formulation of FREZCHEM (see, e.g., Marion et al., 2005) may significantly alter the details

Absolute Salinity, Density Salinity, and Reference Salinity

D. G. Wright et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Absolute Salinity, Density Salinity, and Reference Salinity

D. G. Wright et al.

of Fig. 1, but they would not alter the main result that the errors associated with using the TEOS-10 Gibbs function, with S_A^{dens} as the salinity argument, to estimate density changes over the Neptunian range of temperature and pressure changes are negligible. Experimentation with the LIMBETA model (Pawlowicz et al., 2010) confirms that even with different choices for uncertain parameterizations, the errors always remain less than $1\,\text{g}\,\text{m}^{-3}$, which is still negligible for the present purpose.

FREZCHEM has also been used to estimate the corresponding anomalies in the specific heat capacity at atmospheric pressure and in the activity potential for the full Neptunian ranges of temperature and pressure. The differences between the specific heat capacity results for NPIW and SSW with the same Density Salinity are between 0.023 and $0.029\,\text{J}\,\text{kg}^{-1}\,\text{K}^{-1}$ and are entirely negligible compared to the experimental uncertainty of $0.5\,\text{J}\,\text{kg}^{-1}\,\text{K}^{-1}$ for the specific heat capacity of pure water. In fact, even the total changes in heat capacity for an Absolute Salinity change of $0.025\,\text{g}\,\text{kg}^{-1}$ is only about $0.12\,\text{J}\,\text{kg}^{-1}\,\text{K}^{-1}$, which is itself negligible compared to the measurement uncertainty, so we conclude that the influence of composition anomalies on specific heat capacity is safely neglected. For the activity potential, total differences are between 3.5×10^{-5} and 6×10^{-5} with the largest values occurring at the highest temperatures and only a relatively weak dependence on pressure. These values are again negligible compared to the variations for each water sample that are of order 3×10^{-2} (values are in the range -0.40 to -0.43 for the range of oceanographic conditions considered).

Another important quantity to represent accurately is the "heat content" of seawater, which is required in long-term integrations of climate models. The quantity that is very closely proportional to the "heat content" of seawater is Conservative Temperature Θ (McDougall, 2003) being proportional to potential enthalpy with a reference pressure of zero dbar (i.e. zero sea pressure, or an absolute pressure of 101 325 Pa). In appendix A.21 of IOC et al. (2010) it is shown that Conservative Temperature Θ is quite insensitive to small changes in salinity. There it is shown that an uncertainty in the salinity argument of the Gibbs function of $0.025\,\text{g}\,\text{kg}^{-1}$ leads to an uncertainty in Θ of only about $0.5\,\text{mK}$, which is negligible for present purposes. The errors associated

with using the SSW Gibbs function to evaluate the Conservative Temperature with the Density Salinity as an input will be even smaller.

Estimation of the influence of composition anomalies on other quantities is complicated by the almost complete lack of experimental results on the thermodynamic properties of seawater in the presence of known composition anomalies. Feistel et al. (2010b) develop an approach that allows them to estimate the full range of thermophysical properties in the presence of small composition anomalies relative to SSW. Using the FREZCHEM model (Marion and Kargel, 2008), "data" is generated for the specific volume, heat capacity and activity potential of seawater that includes the composition anomaly of interest and this data is then used to determine the Gibbs function for the anomalous seawater (Feistel and Marion, 2007; Feistel et al., 2010b). Note that although the FREZCHEM "data" is limited to only three properties, once the Gibbs function is obtained a much broader range of properties is easily considered. Compared to the significant experimental and numerical effort required for the construction of a highly accurate Gibbs function for a particular solute composition such as SSW (Feistel, 2008), this Gibbs-Pitzer approach is the currently easiest practical method to estimate arbitrary thermodynamic property anomalies with sufficient accuracy.

Although a Gibbs function that explicitly accounts for the composition anomalies present in the open ocean has not yet been developed, Feistel et al. (2010b) have formulated a composition-dependent Gibbs function for the special case of Baltic Sea water in which the primary anomaly is due to the addition of calcium carbonate to SSW. They consider the influence of composition anomalies on several quantities for this special case. Their Fig. 18 shows that the density error $\Delta\rho$ corresponding to Eq. (7) for typical Baltic seawater anomalies depends strongly on the brackish salinity but is less than $5\,\mathrm{g\,m^{-3}}$ for the full range of conditions considered, i.e., for $P=101\,325\,\mathrm{Pa}$, $0\,°\mathrm{C}<t<25\,°\mathrm{C}$ and solute anomalies between 0 and approximately $100\,\mathrm{g\,m^{-3}}$. Note that the maximum solute anomalies in the Baltic are nearly 7 times as large as those in NPIW. Compared to the true density anomaly $\delta\rho$ associated with the presence of anomalous solute, the relative error $|\Delta\rho/\delta\rho|$ is greater than 10% (approaching 16%)

only near $S_A^{\text{dens}}=35\,\text{g}\,\text{kg}^{-1}$ where both the true density anomaly and the absolute error tend to zero. Thus use of Density Salinity represents a useful approach to account for the influence of composition anomalies on density even in the presence of the larger composition anomalies found in the Baltic.

Feistel et al. (2010b) also consider uncertainties associated with using Density Salinity as the salinity argument of the SSW Gibbs function for other thermodynamic properties of Baltic Sea water. They find that this approach consistently provides improved results compared to those obtained using Reference Salinity, which was estimated using the LSEA_DELS model to determine the anomalous conductivity of Baltic Sea water (Pawlowicz, 2010). The improvements vary significantly for different properties, but in no case are results degraded. For only one of the several properties considered, namely the sound speed, was the deviation between the estimated anomaly and the result obtained using Density Salinity in the SSW Gibbs function found to significantly exceed the experimental uncertainty.

We conclude that for the most demanding applications that we are aware of, Density Salinity is very well-suited for use as the salinity argument of the Gibbs function since it produces accurate results for both density and heat-related quantities. Thus the form of absolute salinity best suited to extend the definition of the Absolute Salinity of SSW to seawaters with anomalous composition is the Density Salinity. In addition, the results for Baltic seawater anomalies show that this approach provides results within measurement uncertainties for all considered quantities except sound speed. The latter result is suggestive for general seawater anomalies, but has not been verified except for Baltic seawater anomalies.

4.3 Operational aspects of Density Salinity

The solution of Eq. (5) for an arbitrary seawater sample constitutes the definition of the Density Salinity, S_A^{dens} but results are insensitive to the reference values of T and P. The most direct approach to determining the value of S_A^{dens} for a particular water

sample is then to determine its density using an instrument such as a vibrating-tube densimeter (Wolf, 2008) or perhaps an optical salinity sensor (Grosso et al., 2010) to measure ρ and invert Eq. (5) at the temperature and pressure at which the density is measured. To estimate the accuracy to which $S_\mathrm{A}^\mathrm{dens}$ can be determined using Eq. (5) in practice, we first note that using a densimeter, density can be routinely measured to an accuracy of order $10\,\mathrm{g\,m^{-3}}$ (with a coverage factor of 2), and it is possible to reduce this uncertainty to less than $2\,\mathrm{g\,m^{-3}}$ at atmospheric pressure with careful use of the substitution method (Wolf, 2008; Feistel et al., 2010a). Given this uncertainty in density and the fact that the haline contraction coefficient for SSW is approximately 0.75 $(\mathrm{g\,g^{-1}})^{-1}$, we conclude that the above approach can be used to routinely make individual Density Salinity measurements with an accuracy of order $0.013\,\mathrm{g\,kg^{-1}}$ and that using the methodology described by Wolf (2008) this can be reduced to about $0.003\,\mathrm{g\,kg^{-1}}$, comparable to the precision of Practical Salinity measurements.

An important advantage of any approach using density to specify salinity is that density measurement results that are obtained by the substitution method (for example) are traceable to the SI (Seitz et al., 2010b). Although at present this linkage is still immature, the introduction of Density Salinity should facilitate future attempts to bring ocean salinity measurements within the general framework of physical standards. This also makes it more suitable for long-term monitoring than Practical Salinity alone because the accuracy of the latter is approximately one order of magnitude less than its precision (Seitz et al., 2010a).

The definition of $S_\mathrm{A}^\mathrm{dens}$ using Eq. (5) is most useful when density, temperature and pressure are known and one wishes to calculate other thermodynamic properties of seawater. The Density Salinity can then be determined and used to estimate a wide range of thermodynamic properties as discussed by Feistel et al. (2010a) and Wright et al. (2010). Of course, measurements of density require some experimental effort and are not always available. Further, in applications such as numerical ocean circulation modelling the salinity is normally updated using a prognostic equation and then used to determine the density; a definition of $S_\mathrm{A}^\mathrm{dens}$ that assumes knowledge of ρ is not

particularly useful for such applications. To use S_A^{dens} as an input to the Gibbs function in such cases, an alternative approach is required to estimate it. Three approaches to achieve this are discussed below.

The first approximation for S_A^{dens} is provided by the Reference Salinity

$$S_R = (35.16504/35)S_P \text{ gkg}^{-1}, \tag{8}$$

(Millero et al., 2008) which neglects the generally small composition anomalies in seawater and therefore provides results essentially equivalent to past practice with the commonly used Practical Salinity S_P. The extensions of the Practical Salinity Scale to cover $0 < S_P < 2$ by Hill et al. (1986) and $42 < S_P < 50$ by Poisson and Gadhoumi (1993), permit Eq. (8) to be directly applied over the full range $0 < S_P < 50$. (Note, however, that the high-salinity densities measured by Poisson and Gadhoumi 1993) possess larger uncertainties than originally estimated by the authors (Millero and Huang, 2009; Feistel, 2003, 2010).) Use of this approximation in the Gibbs function already provides more and improved estimates of the thermodynamic properties of SSW than were previously available from EOS-80 (Fofonoff and Millard, 1983; Feistel, 2003, 2008, 2010).

A more sophisticated approach that can be used to provide improved estimates of the Density Salinity in the presence of composition anomalies is developed in McDougall et al. (2009) and used to determine a global atlas of $\delta S_R^{dens} = S_A^{dens} - S_R$ (referred to as δS_A by McDougall et al., 2009). The method is based on semi-empirical results presented in a series of papers in which measured density anomalies are regressed onto the concentrations of other variables that are easier to measure (Millero and Kremling, 1976; Millero, 2000; Millero et al., 1976a,b, 1978, 2008b, 2009; Feistel et al., 2010a,b).

McDougall et al. (2009) make use of Density Salinity estimates determined from direct density measurements using Eq. (5) as well as Reference Salinity estimates determined from conductivity measurements and composition anomaly estimates determined by various analytical measurement techniques. Using these results, $\delta S_R^{dens} = S_A^{dens} - S_R$ is estimated and compared with the estimates of composition anomalies. A linear relation between the Density Salinity anomaly δS_R^{dens} and sili-

Absolute Salinity, Density Salinity, and Reference Salinity

D. G. Wright et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

cate anomalies is empirically determined, with different latitude-dependent proportionality constants in each ocean basin that all agree where they connect with the Southern Ocean. The root-mean-square variations of observed values about this empirical estimate vary with location but are typically of order $0.005\,\mathrm{g\,kg^{-1}}$, which should be compared to root-mean-square spatial variations of order $0.01\,\mathrm{g\,kg^{-1}}$ and maximum anomalies of order $0.015\,\mathrm{g\,kg^{-1}}$ for the Density Salinity anomaly itself (McDougall et al., 2009). The uncertainty estimate of $0.01\,\mathrm{g\,kg^{-1}}$ obtained using a coverage factor of 2 is already comparable with the uncertainty in individual estimates of $\delta S_{\mathrm{R}}^{\mathrm{dens}}$ obtained directly from densimeter and CTD measurements. The second columns of Tables 1a and b gives the various salinity anomaly measures in terms of the quantity tabulated by McDougall et al. (2009). The use of these in numerical modelling studies of present-day conditions is considered in Sect. 5.

The third method for estimating Density Salinity will be useful for studies in which salinity anomalies might be expected to change, as in paleoclimate or climate change simulations. In such cases, it is desirable to have expressions that relate to variables that can (eventually) be modelled rather than specified based on climatological conditions. This requires an alternative approach to that of McDougall et al. (2009) for the calculation of Density Salinity. For such purposes, the results of Pawlowicz et al. (2010) should prove useful. They show that Density Salinity anomalies relative to Reference Salinity S_{R} can be related to composition anomalies relative to SSW76 using the equation

$$\delta S_{\mathrm{R}}^{\mathrm{dens}}/(\mathrm{mg\,kg^{-1}}) = \{55.6\Delta\mathrm{TA} + 4.7\Delta\mathrm{DIC} + 38.9\Delta[\mathrm{NO_3^-}] + 50.7\Delta[\mathrm{Si(OH)_4}]\}/$$
$$(\mathrm{mmol\,kg^{-1}}), \tag{9}$$

with a standard uncertainty for the fit to their model "data" of $0.08\,\mathrm{mg\,kg^{-1}}$ over the oceanic range of parameters if all quantities on the right side are known precisely. Similar formulas are also given for conversion to the other salinity variables discussed above. In particular, the difference between Density Salinity and Preformed Salinity

can be determined using

$$\delta S_*^{\text{dens}}/(\text{mg kg}^{-1}) = \{73.7\Delta\text{TA} + 11.8\Delta\text{DIC} + 81.9\Delta[\text{NO}_3^-] + 50.6\Delta[\text{Si(OH)}_4]\}/$$
$$(\text{mmol kg}^{-1}), \tag{10}$$

with a standard uncertainty for the fit to their model "data" of only about 0.01 mg kg^{-1}.
The uncertainty is substantially smaller than for Eq. (9) due to the fact that conductivity results are not involved in the determination of Eq. (10). This equation is ideally suited for use in coupled biophysical models in which one wishes to account for the influence of composition anomalies of biological origin on the density and hence on the ocean circulation.

The fact that Density Salinity ensures an accurate estimate for density is particularly useful for physical oceanographic applications since the density and quantities such as compressibility, thermal expansion and haline contraction that are derived directly from it are the most crucial properties to determine accurately. Indeed, the salinity argument for the Gibbs function must return accurate results for density to be useful in many oceanographic applications. Our definition of Density Salinity guarantees its utility for the most demanding oceanographic applications even in the presence of significant composition anomalies. Its usage in numerical ocean circulation models is considered next.

5 The representation of salinity in numerical models

Any attempt to include the influence of composition anomalies on salinity estimates naturally raises questions about how salinity should be treated in numerical models. Here, we consider a general approach to allow for the effects of non-conservative biogeochemical source terms. To achieve this, Density Salinity S_A^{dens} is used as the argument of the Gibbs function or the equivalent "equation of state" used in the model to determine density. In the first case considered, Density Salinity is represented as the sum of Preformed Salinity determined by the model conservation equation plus

Absolute Salinity, Density Salinity, and Reference Salinity

D. G. Wright et al.

an anomaly representing the effects of non-conservative biogeochemical processes, which are empirically accounted for. Simplifications of this approach are then considered followed by a discussion of a less empirical route forward using biogeochemical models to determine the anomalies.

5   An ocean model needs to calculate salinity at every time step as a necessary prelude to using the equation of state to determine ρ and its derivatives (for use in the hydrostatic relationship and frequently in neutral mixing algorithms). The current practice in numerical models is to treat salinity as a perfectly conservative quantity in the interior of the ocean. It changes at the surface and at coastal boundaries due to evaporation, pre-

10 cipitation, brine rejection, ice melt and river runoff and satisfies an advection-diffusion equation away from these boundaries. The inclusion of composition anomalies requires changes in this approach for several reasons, the relative importance of which vary in space and time and are not yet fully understood. The changes can be divided into two broad categories. First, in addition to fresh water inputs and brine rejection, all

15 sources and sinks of dissolved material entering or exiting through coastal boundaries, the surface or the sea floor (e.g., the sediment, hydrothermal vents, benthic populations) should be considered as possible sources of composition anomalies. Second, within the interior of the model, changes due to the growth, decay and remineralization of biological material must be considered. We begin by outlining an approach that could

20 take advantage of currently available information to gain insight into how important the presence of composition anomalies might be.

    The notion of Preformed Salinity, S_*, introduced in Sect. 3.1, is useful in considering how to account for composition anomalies in ocean models. The basic idea is that the dissolved material in the ocean can be separated into a salinity component S_* that is

25 conservative (just like we have assumed for decades for the total salinity variable in numerical models) plus anomalies from this form, $\delta S_*^{\text{dens}} = S_A^{\text{dens}} - S_*$. These anomalies are caused primarily by biogeochemical processes but may also be locally influenced by surface and coastal boundary inputs (e.g., Millero, 2000; Feistel et al., 2009).

    Since S_* is a conservative variable, given initial values and appropriate boundary

conditions, it evolves according to the equation

$$\frac{d}{dt}S_* = \nabla \cdot (K, D; S_*) \tag{11}$$

where the left-hand side is the material derivative following the appropriately averaged residual-mean velocity (see, for example, IOC et al., 2010 and Griffies, 2004) and the right-hand side is a schematic shorthand for the turbulent diffusion of the conservative quantity S_* by isopycnal mixing with turbulent diffusivity K and by small-scale vertical mixing with turbulent diffusivity D.

Currently, we do not know how to reliably model the non-conservative contribution $\delta S_*^{\text{dens}} = S_A^{\text{dens}} - S_*$ so we insist that it remains consistent with observational estimates. One possibility is then to determine global observational estimates of $\delta S_*^{\text{dens}}(x, y, p)$ and simply add this to the model variable S_* to complete the determination of S_A^{dens}. However, experience has shown that even a smooth field of density errors can result in significant anomalies in diagnostic model calculations, primarily due to unrealistic misalignments between the model density field and the model bottom topography. Indeed, even if the correct mean density could somehow be determined, approximations associated with the specification of the model bottom topography can result in significant errors in bottom pressure torques that can degrade the model solution. One way to minimize such errors is to allow some dynamical adjustment of the specified density field so that, for example, density contours tend to align with bottom depth contours where the flow is constrained to follow bottom topography. This simple idea is the key to the success of the robust diagnostic approach (Sarmiento and Bryan, 1982). To allow dynamical adjustment of the salinity anomaly field while still constraining it to be near to the observational estimate $\delta S_*^{\text{dens}}(\text{obs})$, we recommend carrying an evolution equation for δS_*^{dens} that includes advection and diffusion exactly the same as for S_* plus an additional restoring term towards observational estimates that is intended to represent unknown (or poorly known) sources and sinks:

$$\frac{d}{dt}\delta S_*^{\text{dens}} = \nabla \cdot \left(K, D; \delta S_*^{\text{dens}}\right) + \frac{1}{\tau}\left(\delta S_*^{\text{dens}}(\text{obs}) - \delta S_*^{\text{dens}}\right), \tag{12}$$

Absolute Salinity, Density Salinity, and Reference Salinity

D. G. Wright et al.

where τ is a restoring time. The Density Salinity S_A^{dens} that is needed for the equation of state in the model is then computed using

$$S_A^{dens} = S_* + \delta S_*^{dens}. \tag{13}$$

Equations (11) and (12) are our basic equations for the determination of salinity variations. To apply this approach, it remains to determine credible observational estimates for S_* and δS_*^{dens}, specify appropriate initial and boundary values and provide a value for the restoring time.

A variety of different approximations that can be used to represent S_* and δS_*^{dens} in ocean models are discussed in IOC et al. (2010). Here we consider a range of possibilities that includes the most complete and the simplest approaches envisioned. Note that coupling to, for example, a sea ice model that also uses a salinity variable may involve further technical details, but since the sensitivity of the circulation to the small variations we are considering here is largest in the deep ocean we shall not consider these details in our discussion.

Approach (i): S_* and δS_*^{dens} consistent with Pawlowicz et al. (2010) and McDougall et al. (2009)

In this case, we make use of the full Eqs. (11) through (13). From the results of Pawlowicz et al. (2010) summarized in Table 1b, we know that the simple estimate $S_R - S_* \approx 0.35 \delta S_R^{dens}$ models the results of more detailed calculations to within an acceptable error. Hence a global observational estimate of S_* can be determined from an available S_P climatology (to determine S_R) and the global observational estimates of δS_R^{dens} provided by McDougall et al. (2009). To obtain an observational estimate of δS_*^{dens}, we use $\delta S_*^{dens} \approx 1.35 \delta S_R^{dens}$ (Table 1b) and again use the global estimate of δS_R^{dens} from McDougall et al. (2009). Once the observational estimates are determined, they can be used both as initial conditions for Eqs. (11) and (12) and to specify the deviation from observations that appears in the restoring term in Eq. (12). S_* and

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

δS_*^{dens} are updated using Eqs. (11) and (12) and the absolute salinity is calculated using Eq. (13) which is then used in the equation of state to determine density and any other thermodynamic properties used in the model.

To complete our system, we must specify the restoring time that appears in Eq. (12).
5 Determination of a "best choice" will require experimentation but an appropriate value is likely in the range of one month to a few years. The lower bound is based on a very rough estimate of the time required for the density field to align with local topography through advective processes. The upper bound is set by the requirement to have the restoring time relatively short compared to vertical and basin-scale horizontal redistri-
10 bution times.

Finally, we note that the nudging term $\tau^{-1}(\delta S_*^{\text{dens}}(\text{obs}) - \delta S_*^{\text{dens}})$ in Eq. (12) is a rather crude representation of the influences of many complicated and poorly understood biogeochemical processes. If inclusion of composition anomalies turns out to have significant consequences, then biogeochemical models will be required to properly
15 model the interior sources and sinks that are believed to dominate the occurrence of composition anomalies in seawater. In this case, Eq. (10) will be very useful. If a biogeochemical model produces estimates of the quantities on the right hand side of this equation, it can be immediately integrated into an ocean model to diagnose the effects of the included biogeochemical processes on the model's density and its
20 circulation.

Approach (ii): Treat salinity as a conservative variable

It is convenient at this point to add Eqs. (11) and (12) and use Eq. (13) to obtain

$$\frac{\text{d}}{\text{d}t} S_A^{\text{dens}} = \nabla \cdot \left(K, D; S_A^{\text{dens}} \right) + \frac{1}{\tau} \left(\delta S_*^{\text{dens}}(\text{obs}) - \delta S_*^{\text{dens}} \right). \tag{14}$$

Implementation of Eqs. (12)–(14) is clearly equivalent to approach (i), with S_A^{dens} now
25 given by Eq. (14) and S_* determined by Eq. (13). There is no computational advantage to implementing Eq. (14) rather than Eq. (11); Eq. (14) merely provides a single equation for the Density Salinity.

An obvious simplification of Eq. (14) is to neglect the restoring term on the right hand side. Under this approximation, Eq. (14) reduces to

$$\frac{d}{dt}S = \nabla \cdot (K, D; S),\tag{15}$$

where the variable S has been used to represent the resulting approximation for Absolute Salinity. Use of Eq. (15) will save the computational expense of carrying Eq. (12) since it is no longer required to determine the evolution of the model salinity, but it must be emphasized that S will not provide the best available estimate for S_A^{dens}. Under this approximation, the model's salinity variable is represented as a conservative quantity, which is consistent with the approach used for the past few decades to represent salinity in numerical models. However the influences of biogeochemical processes that result in composition anomalies are ignored.

It remains to specify initial and boundary conditions to complete the estimation of salinity under the approximation (15). Three sub-cases are of interest which we refer to as options (ii-a), (ii-b) and (ii-c). Option (ii-a) explicitly allows for the influence of composition anomalies in the specification of initial and boundary conditions, option (ii-b) allows for composition anomalies only to the extent that they are captured by conductivity measurements and option (ii-c) explicitly removes the influence of composition anomalies from the specification of initial and boundary conditions.

Option (ii-a): In this case, initial and boundary conditions are specified consistent with observational estimates of Density Salinity S_A^{dens}. The model is initialized with the best available climatological estimate of S_A^{dens} which would currently be determined from a climatological estimate of S_R (=(35.16504/35) S_P g kg^{-1}) plus the correction term δS_R^{dens} obtained from the McDougall et al. (2009) global atlas. Specification of the fluxes of water across the model boundaries then completes the system. If restoring boundary conditions are desirable, then S is restored to observational estimates of S_A^{dens}. Using this approach, the equation of state in the model receives the correct salinity argument initially, but over some longer time scale determined by circulation

and mixing processes, the absence of the non-conservative source terms (the last term in Eq. 14) will reduce the fidelity of the solution; the model salinity will degrade as an estimate of Density Salinity and the representation of density will degrade as a result. An advantage of this approach is that it initially takes into account the influence of the spatial variations in seawater composition, but the fidelity of the solution will inevitably degrade over time due to the omission of non-conservation effects from the right hand side of Eq. (15).

Option (ii-b): This option is considered as a close approximation to past (and current) practice. The model salinity is initialized with a climatological estimate of S_R (the best approximation for S_A^{dens} that doesn't explicitly account for composition anomalies) and the fluxes of water are specified across the boundaries of the model. If restoring boundary conditions are desirable, then S would be restored to observational estimates of Reference Salinity. If the resulting salinity estimates are then substituted into the TEOS-10 equation for density, results will be very similar to those obtained with the current practice of initializing a model with a climatological estimate of S_P, specifying water fluxes across the boundaries or restoring to observational estimates of Practical Salinity to determine the evolution of the model salinity and then using EOS-80 to determine density.

Option (ii-c): A third option is to acknowledge that Eq. (15) is really only appropriate in the absence of the biogeochemical processes that result in composition anomalies. Since this is only correct for Preformed Salinity, it is consistent to initialize the model with a climatological estimate of S_* and either specify fluxes of water across the model boundaries or restore surface values to observational estimates of S_*. TEOS-10 would then be used to estimate density based on the resulting salinity estimates. The results of this case are of interest since comparison with those obtained using option (i) discussed above would provide a direct estimate the influences of biogeochemical processes on the large scale deep ocean circulation. In particular, one could compare robust diagnostic results obtained with option (ii-c) to the corresponding results obtained with approach (i) to determine a reasonable estimate of the influence of composition

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◀ | ▶

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Absolute Salinity, Density Salinity, and Reference Salinity

D. G. Wright et al.

anomalies on the large scale ocean circulation without requiring major computations.

An immediate indication of the errors associated with using either approach (ii-b) or (ii-c) rather than approach (i) is provided by Fig. 2. Similar errors will develop over time for approach (ii-a). The vertical axis in this figure is the difference between the northward density gradient at constant pressure when the equation of state is evaluated with observational estimates of S_A^{dens} and with S_R as the salinity argument. The figure shows that for all the data in the world ocean below a depth of 1000 m, 60% of this data is in error by more than 2%. If this graph were done with S_* rather than S_R as the reference with which results are compared then the error would be increased by the factor 1.35.

While the differences shown in Fig. 2 are not large, they are also not insignificant. Noting that the geostrophic transport associated with a vertically uniform horizontal density difference of $\delta\rho$ across a box of arbitrary width L and thickness H is approximately $g\delta\rho H^2/(2\rho f)$, it is easily seen that a density change of just 10 g/m^3 over a depth of 1000 m is associated with a 0.5 Sv change in volume transport through the section, which is not entirely negligible. We also note that the systematic density gradient anomalies in the north-south direction are likely to result in robust changes in the bottom pressure torque with a potentially more significant effect on the circulation. Investigation of the resulting changes is certainly warranted.

Obviously, each of the approaches discussed above represents a rather crude method to include the effects of composition anomalies on the results of ocean circulation models. Nevertheless, we suggest that examination of such simplified formulations will provide useful new insights with minimal effort. We therefore believe that the systematic examination of approaches (i) and (ii) and comparison of the results will represent a useful starting point for the examination of the effects of composition anomalies.

6 Summary and conclusions

Both the Reference Composition (RC) and the Reference-Composition Salinity Scale (RCSS) have been defined precisely and we recommend that they remain unchanged in the future to provide stable benchmarks for the composition of Standard Seawater and a stable scale for the presentation of salinity results.

The RC was defined by Millero et al. (2008) as a "best estimate" of the composition of SSW that was analyzed during the mid-1970s and RCSW is seawater with the RC. The RCSS was defined to provide a best estimate of the mass fraction of dissolved material in RCSW and the SSW that it approximates. The use of RCSW as an approximation for SSW improves our numerical estimates of its absolute salinity by about $0.165\,\mathrm{g\,kg^{-1}}$ in water with a Practical Salinity of 35. Nevertheless, uncertainties remain. Subsequent investigations (Pawlowicz, 2009; Lee et al., 2010) have already identified smaller but quantifiable differences between RCSW and SSW, and given the current limitations of our knowledge of the true composition of seawater, it is likely that future investigations will show even more changes. It might be tempting to modify the definition of the RC and also the RCSS to continue to provide a best estimate for the composition and absolute salinity of SSW in the future. However, such adjustments would inevitably cause confusion and could result in problems detecting long-term changes in ocean salinity and in providing reliable estimates of the thermodynamic properties of seawater. We therefore recommend that both the RC and the RCSS remain unchanged. If improved estimates of the mass fraction of SSW are available and situations arise in which it is desirable to have more precise estimates of the mass fraction, corrected values can be determined for special-purpose applications. Such corrections would be easily achieved since the RCSS has been defined so that the Absolute Salinity of SSW on this scale can differ from the true mass fraction only by a fixed proportionality constant.

The next largest uncertainty in our ability to predict the properties of seawater arises from spatial (and temporal) variations in the composition of seawater. These give rise to

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◀ | ▶

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

salinity variations of up to $0.03\,\mathrm{g\,kg^{-1}}$ in the open ocean and may exceed $0.1\,\mathrm{g\,kg^{-1}}$ in coastal waters or estuaries. In order to correctly understand these effects a number of different salinity variables are defined, each of which is useful in different applications. The term Solution Salinity is introduced for the mass fraction of dissolved material after it is in solution and in thermodynamic equilibrium. This is also the most "intuitive" definition of absolute salinity. The name Solution Salinity emphasizes that the mass fraction is determined for the dissolved material actually in solution, accounting for the fact that chemical reactions that occur when material is added can convert H_2O to (or from) chemical forms defined to be part of the "solute". The term Added-Mass Salinity is used to refer to the mass fraction based on the mass of solute added to SSW before entering solution. The Density Salinity is the Solution Salinity of SSW that has the measured density of our anomalous seawater. This is not the same as the actual Solution Salinity when the relative composition differs from that of SSW, but it is a measureable and SI-traceable quantity that is probably of most relevance to dynamical investigations as it allows for the correct calculation of density when used as an argument in the TEOS-10 Gibbs function. When considering seawater that includes anomalies, MFWM used the term Absolute Salinity to refer to Density Salinity and we continue this practice with the recognition that Density Salinity may deviate significantly from Solution Salinity when composition anomalies are present.

We emphasize that our choice of salinity argument for use in the Gibbs function is the Density Salinity which is defined such that it will provide the most accurate results possible for density even though it may not provide equally accurate results for the mass fraction of dissolved material. The inclusion of composition anomalies necessarily introduces some inconsistencies between these two quantities. Our choice ensures that density and related quantities, as well as Conservative Temperature ("heat content" per unit mass) are accurately represented by the Gibbs function. Consequently, we believe that our choice for the representation of salinity is the most relevant generalization to allow for composition anomalies. To improve on this measure of salinity, it seems likely that an additional parameter (or parameters) representing the effects of composition

Absolute Salinity, Density Salinity, and Reference Salinity

D. G. Wright et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

⏮ | ⏭

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

anomalies would be required as an input to the Gibbs function. Such an extension has been implemented for the Baltic Sea (Feistel et al., 2010b) and it may be useful in the future to develop a similar extension for the open ocean.

There are currently three methods available to estimate the Density Salinity for use as an argument of the Gibbs function. If only measurements of Practical Salinity and geographic sampling position are available, then Density Salinity can be estimated using the Reference Salinity determined from Eq. (8) plus the salinity anomaly determined from a lookup table (McDougall et al., 2009). If on the other hand, one measures density in the lab at known values of temperature and pressure, ideally at the reference conditions of 25 °C and 101 325 Pa, then a direct estimate of Density Salinity is available through the solution of Eq. (5). If the Practical Salinity is also measured, then an independent estimate of $\delta S_{\mathrm{R}}^{\mathrm{dens}}$ is available which can be used to improve the reliability of the lookup table. Finally, relationships like Eq. (9) have been proposed (Brewer and Bradshaw, 1975; Millero, 2000; Millero et al., 2008, 2009; Pawlowicz et al., 2010) to estimate the density anomaly from direct measurements of some or all of the non-conservative parameters in seawater. Collection of information to verify all of these approaches is particularly important for semi-enclosed basins where current estimates of $\delta S_{\mathrm{R}}^{\mathrm{dens}}$ are most uncertain.

We have stressed that the most appropriate input to the Gibbs function for most dynamical physical oceanographic applications is *Density Salinity*. Nevertheless, use of *Reference Salinity* will be more appropriate in some applications where maximum simplicity is desirable and reduced accuracy is acceptable as well as for studies such as the detection of salinity variations associated with climate change where precision may be more critical than accuracy. Regarding the latter point, we note that the reproducibility of Reference Salinity is roughly 0.002 g kg^{-1} and is not subject to future changes provided the RCSS is not altered. On the other hand, the uncertainties in estimates of Density Salinity are several times larger in some situations. At present, the most well tested way to determine the influence of composition anomalies on global estimates of density salinity involves use of a lookup table that is based on a spatially varying

correlation between Density Salinity anomalies and silicate anomalies estimated using less than a thousand individual measurements from just 105 locations. As the number and distribution of the measurements available to determine the global variation of the composition anomalies improves, this lookup table will be refined and changes of order $0.01\,\mathrm{g\,kg^{-1}}$ are likely to occur in some regions where the current data coverage is sparse and of order $0.003\,\mathrm{g\,kg^{-1}}$ more generally throughout the ocean. Further, use of relations such as Eqs. (9) and (10) will be desirable in some cases and these might also change estimates by similar amounts in some regions. It is therefore anticipated that methodological changes will result in changes in Density Salinity estimates that may be substantially larger than the precision with which we can determine Reference Salinity. Consequently, Reference Salinity should be used in applications where precision is more critical than accuracy, but we recommend that Density Salinity be used whenever the highest available accuracy is required for density.

The inclusion of the effects of composition anomalies on density and other thermodynamic properties of seawater represents a new and challenging area of research. We have discussed one approach to evaluating the potential significance of these effects through the use of numerical models. Initially we propose an empirical approach that can be used to provide new insights into the significance of this effect. If the effects prove to be significant, then more sophisticated models that account for variable inputs through surface and coastal boundaries as well as chemical and biological processes will be required.

Appendix A

Nomenclature

This appendix provides a reference for the definitions of various forms of salinity and density variables used here and the relations between them. The notation used is a consistent simplification of that used in Pawlowicz et al. (2010). The basic symbols

used are summarized in Table A1 and the relations between them are illustrated in Fig. A1.

The notation is chosen to maintain consistency with previous usage but extended to deal with composition anomalies in a manner that is intended to be intuitively obvious. We retain the symbols S_P and S_R for the commonly used Practical Salinity variable and the Reference Salinity variable introduced by MFWM. An additional symbol of this style S_* is used to represent Preformed Salinity which is introduced as a conservative parameter to which anomalies, primarily of biochemical origin, are added. In previous publications, the symbol S_A and term Absolute Salinity has been used to represent the mass fraction of dissolved material in seawater (here defined as the Solution Salinity). In practice however, Absolute Salinity was approximated by the Density Salinity. With the addition of composition anomalies, distinctions arise between quantities that were previously treated as equivalent, and so new variable names are required to distinguish them. In particular, based on the work of Pawlowicz, et al. (2010), we now know that the Density Salinity anomalies do not provide a good approximation for the anomalies in the mass fraction of dissolved material in seawater. To make the distinction between these different forms of salinity while maintaining a connection with previous usage, we represent the Density Salinity and the Solution Salinity (i.e., the mass fraction of dissolved material in solution) by the symbols S_A^{dens} and S_A^{soln}. In addition, Added-Mass Salinity, denoted by S_A^{add}, represents the form of salinity obtained when the mass of anomalous solute is determined prior to adding it to solution rather than after its dissolution and equilibration at reference values of temperature, pressure and concentration. When S_A is used without a superscript, it will be taken to refer to Density Salinity, consistent with the assignment made in practice in most previous studies and justified in this paper.

The special case of Standard Seawater is particularly simple as illustrated in the upper panel of Fig. A1. In this case, the Reference Salinity, Density Salinity, Solution Salinity, Added-Mass Salinity and Preformed Salinity are all equivalent to within measurement uncertainties and they can be unambiguously determined simply by mea-

Absolute Salinity, Density Salinity, and Reference Salinity

D. G. Wright et al.

suring conductivity. An optimal estimate of the true density is then determined using any of these salinity variables as an input to the equation of state. In this case, the Practical Salinity is (35/35.16504) times any of the other salinity variables when they are expressed in $g\,kg^{-1}$ (e.g. $S_P \approx (35/35.16504) \times S_A/(g/kg)$ for SSW).

In studies involving composition anomalies, each of the different salinity variables is distinct and it is convenient to consider them in terms of base quantities and anomalies from these base quantities. For situations in which the Reference Salinity is known and an improved estimate of one of the other salinity variables is required, the base quantity is chosen as the Reference Salinity S_R or the density ρ_R determined from the SSW Gibbs function using the Reference Salinity as an input. When considering the effects of composition anomalies of biogeochemical origin (or in discussion of laboratory studies) it is more convenient to use the "preformed" quantities S_* and ρ_* as base quantities.

Increments relative to either Reference or Preformed values all begin with the symbol δ. The increment relative to Reference values is $\delta\rho_R = \rho - \rho_R$ where the true density is indicated by ρ. If the density increment relative to the preformed density is required, it should be represented by $\delta\rho_* = \rho - \rho_*$.

For salinity, the increments begin at either the Reference or Preformed base values and end at any of the five possibilities Reference (R), Preformed (*), Density (dens), Solution (soln) or Added-Mass (add) Salinities. The subscript R is used to indicate use of the Reference Salinity as the base quantity and subscript * is used to indicate use of Preformed Salinity as the base quantity. The five target values listed above are indicated by R, *, dens, soln and add. Thus for example, $\delta S_R^* = S_* - S_R$, $\delta S_R^{dens} = S_A^{dens} - S_R$ and $\delta S_*^{dens} = S_A^{dens} - S_*$.

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Absolute Salinity, Density Salinity, and Reference Salinity

D. G. Wright et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper

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Absolute Salinity, Density Salinity, and Reference Salinity

D. G. Wright et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

| ◄◄ | ►► |
| ◄ | ► |

| Back | Close |

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Absolute Salinity, Density Salinity, and Reference Salinity

D. G. Wright et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

|◄ ►|

◄ ►

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◀ | ▶|

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table 1a. Salinity corrections for water from the deep North Pacific, with $\delta\rho_R = 0.015\,\mathrm{kg\,m^{-3}}$, normalized to $S_R = 35\,\mathrm{g\,kg^{-1}}$. $\delta\rho_R = \rho - \rho_R$, is the estimated difference between the true density and the density evaluated from the Reference Salinity using the TEOS-10 Gibbs function. The corresponding Density Salinity anomaly is given by $\delta S_R^{\mathrm{dens}} = \delta\rho_R/(\rho_R\beta_R)$. The relations given in the second column are derived from formulae given in Pawlowicz et al. (2010) (see also IOC et al., 2010).

Salinity measure	Anomaly relation to $\delta S_R^{\mathrm{dens}}$	Value	Offset from $S_R/(\mathrm{g/kg})$
S_P (Practical Salinity)	–	34.836	−0.164
$S_R = (35.16504/35)\,S_P$ (Reference Salinity)	–	35.000 g/kg	–
$S_* = S_R + \delta S_R^*$ (Preformed Salinity)	$S_* - S_R \approx -0.35\delta S_R^{\mathrm{dens}}$	34.993 g/kg	−0.007
$S_A^{\mathrm{dens}} = S_R + \delta S_R^{\mathrm{dens}}$ (Density Salinity)	$S_A^{\mathrm{dens}} - S_R \approx 1.0\delta S_R^{\mathrm{dens}}$	35.020 g/kg	+0.020
$S_A^{\mathrm{soln}} = S_R + \delta S_R^{\mathrm{soln}}$ (Solution Salinity)	$S_A^{\mathrm{soln}} - S_R \approx 1.75\delta S_R^{\mathrm{dens}}$	35.034 g/kg	+0.034
$S_A^{\mathrm{add}} = S_R + \delta S_R^{\mathrm{add}}$ (Added-Mass Salinity)	$S_A^{\mathrm{add}} - S_R \approx 0.78\delta S_R^{\mathrm{dens}}$	35.016 g/kg	+0.016

Absolute Salinity, Density Salinity, and Reference Salinity

D. G. Wright et al.

Table 1b. Salinity corrections for water from the deep North Pacific, with $\delta\rho_R = 0.015\,\mathrm{kg\,m^{-3}}$, defined as in Table 1a and $\delta S_R^{dens} = \delta\rho_R/(\rho_R\beta_R)$. This table is for a Preformed Salinity of $35.000\,\mathrm{g\,kg^{-1}}$. The relations given in the second column are derived from formulae given in Pawlowicz et al. (2010) (see also IOC et al., 2010).

Salinity measure	Anomaly relation to δS_R^{dens}	Value	Offset from $S_*/(\mathrm{g/kg})$
S_P (Practical Salinity)	–	34.843	−0.157
S_* (Preformed Salinity)	–	35.000 g/kg	–
$S_R = S_* + \delta S_*^R$ (Reference Salinity)	$S_R - S_* \approx 0.35\,\delta S_R^{dens}$	35.007 g/kg	+0.007
$S_A^{dens} = S_* + \delta S_*^{dens}$ (Density Salinity)	$S_A^{dens} - S_* \approx 1.35\,\delta S_R^{dens}$	35.027 g/kg	+0.027
$S_A^{soln} = S_* + \delta S_*^{soln}$ (Solution Salinity)	$S_A^{soln} - S_* \approx 2.1\,\delta S_R^{dens}$	35.041 g/kg	+0.041
$S_A^{add} = S_* + \delta S_*^{add}$ (Added-Mass Salinity)	$S_A^{add} - S_* \approx 1.13\,\delta S_R^{dens}$	35.023 g/kg	+0.023

Table A1. The various salinity variables and the relations between them.

Quantity	Symbols	Equations	Comments
Practical Salinity	S_P	PSS-78	Unitless conductivity-based salinity
Reference Salinity	S_R	$(35.16504/35)S_P$ g/kg	Absolute Salinity of RCSW. For a general seawater parcel, S_R is influenced by H_2O exchange and conductive anomalies
Preformed Salinity	S_*	$S_R - \delta S_*^R$	Standard Seawater to which anomalies are added; influenced by H_2O exchange. S_* can be calculated from other salinity measures by subtracting off the effect of composition anomalies.
Density Salinity	S_A^{dens}	$S_R + \delta S_R^{dens}, S_* + \delta S_*^{dens}$	Provides the best estimate of density using TEOS-10
Solution Salinity	S_A^{soln}	$S_R + \delta S_R^{soln}, S_* + \delta S_*^{soln}$	mass fraction of material actually dissolved in solution, as in MFWM
Added-Mass Salinity	S_A^{add}	$S_R + \delta S_R^{add}, S_* + \delta S_*^{add}$	Salinity measure used in lab analyses
Preformed – Reference	δS_R^*	$S_* - S_R$	
Density – Reference	δS_R^{dens}	$S_A^{dens} - S_R$	Additions used to adjust from Reference Salinity to the other salinity parameters
Solution – Reference	δS_R^{soln}	$S_A^{soln} - S_R$	
Added-mass – Reference	δS_R^{add}	$S_A^{add} - S_R$	
Reference – Preformed	δS_*^R	$S_R - S_*$	
Density – Preformed	δS_*^{dens}	$S_A^{dens} - S_*$	Additions used to adjust from Preformed Salinity to the other salinity parameters
Solution – Preformed	δS_*^{soln}	$S_A^{soln} - S_*$	
Added-mass – Preformed	δS_*^{add}	$S_A^{add} - S_*$	
Haline contraction coefficient for RCSW	β_R	$\frac{1}{\rho_R}\frac{\partial \rho}{\partial S_R}$	Calculated from the TEOS-10 Gibbs function

Table A2. Glossary of abbreviations.

|	
Cl	Chlorinity
DIC	Dissolved Inorganic Carbon
EOS-80	Equation Of State defined in 1980
IAPSO	International Association for the Physical Sciences of the Oceans
IAPWS	International Association for the Properties of Water and Steam
IOC	International Oceanographic Commision
IPTS-68	International Practical Temperature scale defined in 1968
ITS-90	International Temperature Scale of 1990
KCl-normalized	Seawater normalized to a Practical Salinity of 35
MFWM	Millero et al. (2008)
PSS-78	Practical Salinity Scale defined in 1978
RC	Reference Composition – the composition model for Standard Seawater introduced by MFWM
RCSS	Reference-Composition Salinity Scale
RCSW	Reference-Composition Seawater
SI	International System of Units
SonCl	The ratio Of Practical Salinity to Chlorinity for SSW which is also used as an approximation for RCSW in (1)
SSW	IAPSO Standard Seawater
SSW76	The composition model for SSW introduced by Pawlowicz (2010)
TA	Total Alkalinity
TEOS-10	Thermodynamic Equation of Seawater 2010
UNESCO	United Nations Educational, Scientific and Cultural Organization
VSMOW	Vienna Standard Mean Ocean Water

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion
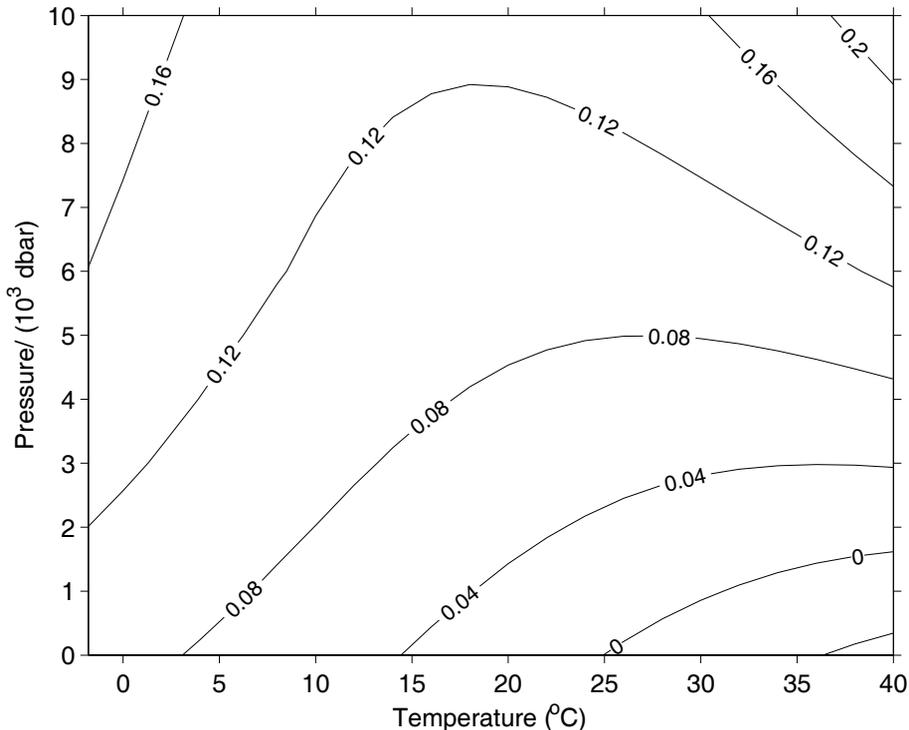
Fig. 1. The estimated density difference ($g\,m^{-3}$, ppm) between two water samples used to represent NPIW and SSW that have been adjusted to give identical densities at $t=25\,°C$ and $P=101\,325\,Pa$. These estimates are obtained using the FREZCHEM model and should be treated as rough estimates. However, even given the associated uncertainties, the differences are negligible compared to the total density changes associated with composition anomalies in the open ocean.
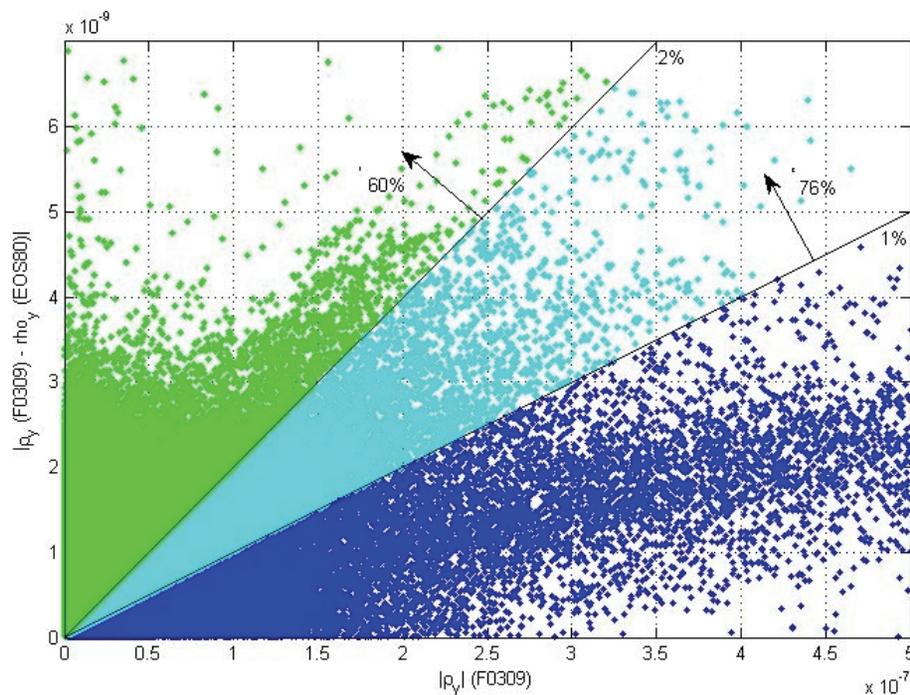
Fig. 2. The northward density gradient at constant pressure (the horizontal axis) for all the data in the ocean atlas of Gouretski and Koltermann (2004) for $p > 1000$ dbar. The vertical axis is the magnitude of the difference between evaluating the density gradient using S_A^{dens} as the salinity argument in the TEOS-10 expression for density compared with using S_P in the EOS-80 algorithm for density. The latter corresponds to current practice and is not significantly different from using S_R in TEOS-10.

Fig. A1.

Absolute Salinity, Density Salinity, and Reference Salinity

D. G. Wright et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►
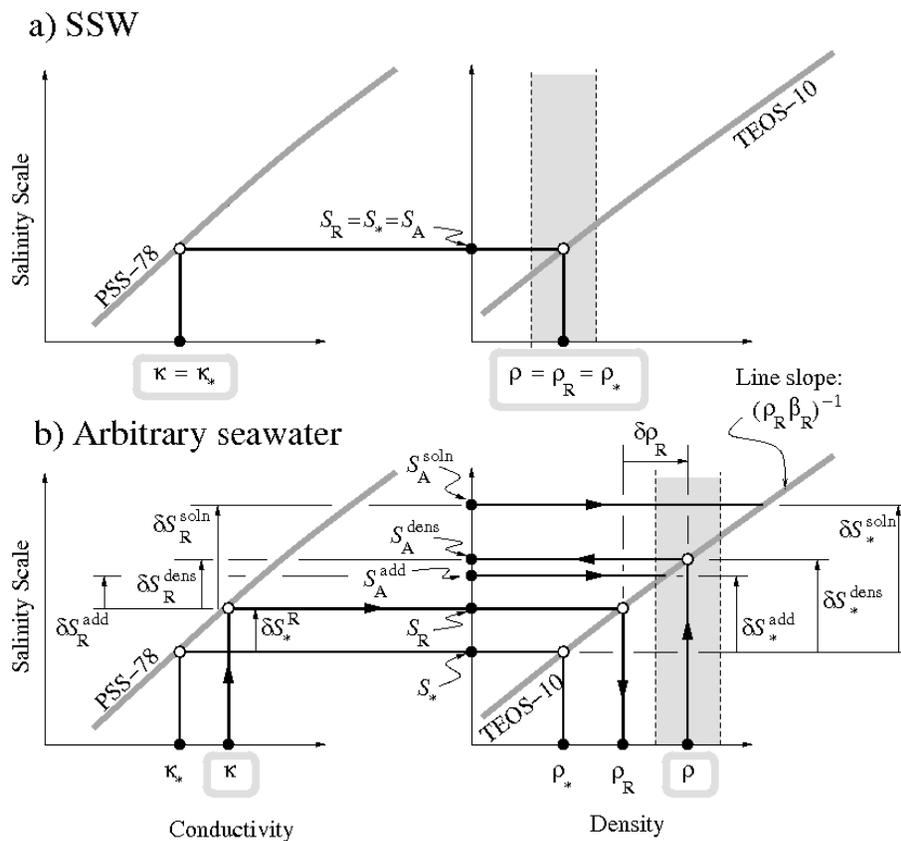
Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Fig. A1. This figure schematically shows the relationships between different variables used to characterize seawater. **(a)** For SSW, the estimate S_R of the Absolute Salinity S_A is used to define a conductivity/salinity relationship (schematically shown as the scaled PSS-78 curve on the left hand graph), and a density/salinity relationship (schematically shown as the TEOS-10 curve on the right hand graph). The vertical gray bar indicates the uncertainty range of measured densities around the TEOS-10 prediction. **(b)** For arbitrary seawater, composed of a preformed SSW component with Absolute Salinity S_*, plus a composition anomaly. Observed values are indicated by labels outlines in gray along the horizontal axes. The observed conductivity κ is related to a Reference Salinity S_R and a reference density ρ_R using relationships developed for SSW. However, the observed density ρ, or density anomaly $\delta\rho_R$, is related to the Density Salinity $S_A^{dens} \neq S_R$. Estimates of mass fraction salinities S_A^{add} and S_A^{soln} directly determined from the full chemical composition are, respectively defined based on whether the mass of anomalous solutes are accounted for before or after their addition to the Preformed Salinity. The difference between the two estimates reflects the effects of equilibrium chemistry within seawater, which converts some H_2O into the chemical forms comprising the solute. Empirically, the relationship in the ocean between S_A^{add} and measured densities ρ can be described, within typical observational error, by TEOS-10. This is not true in general for the relationship between S_A^{soln} and ρ.