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A model for predicting changes in the electrical conductivity, practical salinity, and absolute salinity of seawater due to variations in relative chemical composition

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Abstract

Salinity determination in seawater has been carried out for almost 30 years using the 1978 Practical Salinity Standard. However, the numerical value of so-called practical salinity, computed from electrical conductivity, differs slightly from the true or absolute salinity, defined as the mass of dissolved solids per unit mass of seawater. The difference arises because more recent knowledge about the composition of seawater is not reflected in the definition of practical salinity, which was chosen to maintain historical continuity with previous measures, and because of spatial and temporal variations in the relative composition of seawater. Accounting for these variations in density calculations requires the calculation of a correction factor δS_A , which is known to range from 0 to 0.03 g kg^{-1} in the world oceans. Here a mathematical model relating compositional perturbations to δS_A is developed, by combining a chemical model for the composition of seawater with a mathematical model for predicting the conductivity of multi-component aqueous solutions. Model calculations generally agree with estimates of δS_A based on fits to direct density measurements, and show that biogeochemical perturbations affect conductivity only weakly. However, small systematic differences between model and density-based estimates remain. These may arise for several reasons, including uncertainty about the biogeochemical processes involved in the increase in Total Alkalinity in the North Pacific, uncertainty in the carbon content of IAPSO standard seawater, and uncertainty about the haline contraction coefficient for the constituents involved in biogeochemical processes. This model may then be important in constraining these processes, as well as in future efforts to improve parameterizations for δS_A .

1 Introduction

Procedures for routine estimation of the salinity of seawater have been standardized for nearly 30 years. These procedures are based on combining measurements of the

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electrical conductivity κ of the water with a purely empirical equation relating conductivity and a so-called practical salinity S_{78} :

$$S_{78} = f_{78}(\kappa) \quad (1)$$

The equation $f_{78}(\cdot)$ is specified by the 1978 Practical Salinity Standard, denoted PSS-78 (Perkin and Lewis, 1980b), with a low-salinity correction (Hill et al., 1986a) that extends the range of validity down to near-zero salinities. Temperature and pressure are also important factors in these equations but are omitted from the notation used here.

It was clearly recognized at the time PSS-78 was adopted that the utility of the computed salinities depended on two factors. First, it was necessary that the relative chemical composition of seawater would be constant throughout the world's oceans. Thus waters of the same salinity would have the same conductivity and vice versa. It was known that there were (and are) spatial variations in the composition, but investigations suggested that the numerical effects on salinity estimates arising from these variations remained within limits acceptable to the research standards of the day (Lewis and Perkin, 1978; Hill et al., 1986b). Second, it required a method by which different investigators could intercalibrate their measurements. Procedures providing "standard" seawater from a single source for calibrating chlorinity titrations were adapted to provide batches of labelled IAPSO standard seawater (SSW) for conductivity calibrations; PSS-78 itself is based primarily on measurements of SSW batches P73, P75, and P79 (Perkin and Lewis, 1980a).

However, there is a small numerical difference between the computed practical salinity S_{78} of seawater and its true or absolute salinity S_A in g kg^{-1} , defined as the mass of dissolved solids per unit mass of seawater, i.e.:

$$S_A = \sum_{i=1}^{N_c} M_i c_i \quad (2)$$

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where M_i (Table 2) is the molar mass of the i th of N_c components of seawater (not including dissolved gases), and c_i its concentration. This difference arises for historical reasons (see, e.g., Millero et al., 2008, for more details). For SSW this difference can be accounted for by a simple scaling

$$S_A = \gamma S_{78} \quad (3)$$

where γ incorporates updated knowledge of the true chemical composition of SSW. However, for real ocean waters there are also small spatial and temporal differences in the relationship arising from small variations in the relative chemical composition of seawater. Thus in general:

$$S_A = \gamma S_{78} + \delta S_A \quad (4)$$

The offset δS_A is in the range of 0 to 0.03 g kg^{-1} in the open ocean, with largest values in the North Pacific (McDougall et al., 2009), and can be as large as 0.05 g kg^{-1} in some estuarine waters (Millero, 1984).

In recent years the increasing number of high-quality conductivity measurements of seawater on global scales has led to the realization that these spatio-temporal differences may have practical importance in understanding the global circulation. A reevaluation of the procedures for determining thermodynamic properties of seawater, including density, suggests that more accurate results can be obtained by returning to a procedure in which S_A is used instead of S_{78} as a state variable (Feistel, 2008; Millero et al., 2008). In this procedure a best estimate S_R for the S_A of SSW is made by taking $\gamma = \nu_{PS} \equiv 35.16504/35 \approx 1.004715$. For non-standard seawaters an offset δS_{A08} , found using an algorithm involving a geographic look-up table (McDougall et al., 2009), is added to S_R to calculate S_{A08} as a best estimate for S_A .

S_A can be directly estimated by measuring the density of water samples and then inverting the equation of state which relates density and salinity. The algorithm for S_{A08} is based on a fit of such data against measured Si(OH)_4 concentrations. Other algorithms for estimating δS_A also exist (Brewer and Bradshaw, 1975; Millero, 2000).

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These are also based on purely empirical correlations with concentrations of specific chemical species, typically nutrients and components of the carbonate system.

However, little work has been done on understanding the full theoretical basis for these corrections. A complete chemical theory would include a model for seawater, and a method for determining the variations in conductivity and density that result from compositional variations. Density has been well-studied (e.g. Millero et al., 1976), but in spite of the practical importance of conductivity in ocean measurements there has been virtually no work done in developing a theory of electrical conductivity for natural seawaters. Recently, a model has been developed for calculating the electrical conductivity of natural freshwaters, based on their chemical composition (Pawlowicz, 2008, hereafter Pa08). Although the Pa08 model works well for waters of low salinities (less than a few g kg⁻¹ of dissolved solids), accuracy in waters of higher salinities is not sufficient to directly replace the empirical relationship specified by PSS-78 (Pawlowicz, 2009). However, it will be shown here that the model can be used to quantitatively calculate the effects of small compositional variations on the known PSS-78 conductivity/salinity relationship.

The purpose of this paper is then twofold. First, to develop a seawater conductivity model, based on Pa08, capable of quantitatively determining the effects of small variations in the chemical composition of a model seawater on its conductivity, and consequently on S_{78} . Second, to use this model to compute corrections δS_A directly from a suitable set of observations, independent of density measurements. This model will then be a complement to the available empirical estimates δS_{A08} .

2 Methods

The general approach is based on modelling perturbations about a known base state for SSW. The base state consists of the known PSS-78 relationship (Eq. 1), and a chemical composition C which is a function of S_{78} .

The first step is then to construct the model composition C for SSW, with an assumed

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practical salinity S_{78} , true conductivity $\kappa=f_{78}^{-1}(S_{78})$, and computed absolute salinity $S_A(C)$. The composition C will be based on a model of the changes arising from dilutions and evaporations of a reference composition C_0 for which $S_{78}=35$. Thus our seawater model will mimic the seawater used to develop PSS-78, and can be used to estimate γ .

The second step is to compute conductivity and absolute salinity perturbations, $\delta\kappa$ and δA respectively, arising from compositional changes. There are two kinds of perturbation possible. The most straightforward occurs when a known perturbation δC is added to the base state C . The Pa08 conductivity model is used to estimate $\delta\kappa$. In this calculation a nonzero δS_A arises because both S_A and S_{78} change, but by different amounts. Since these situations often involve composition changes only in the nonconservative elements of seawater, we call this a constant chlorinity calculation. However, estuarine situations when freshwaters (which may contain Cl^- and other so-called conservative elements) are added will also be handled in this way. Results can be simplified into an approximate analytical form, which can then be used to qualitatively understand the effect of perturbations.

In contrast, a more formally correct procedure for the correction of ocean measurements is to compute δS_A when the composition is perturbed, but κ (and hence S_{78}) are fixed. In this constant conductivity calculation the addition of a known concentration of (say) nitrate, which is ionic and would increase conductivity, would be balanced by a small dilution of the SSW composition. The Pa08 model is then used iteratively to calculate the dilution factor. A change $\delta S_A=\delta A$ arises because the concentrations of all components change. The two procedures provide nearly identical δS_A for the examples considered here.

Unless otherwise stated, all calculations are carried out for a temperature of 25°C and a pressure of 0 dbar. This is appropriate for comparisons with laboratory measurements on water samples. The accuracy of the Pa08 conductivity model has also been most comprehensively investigated under these conditions (Pawlowicz, 2009).

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2.1 A composition model for standard seawater ($S_{78}=35$)

Typical oceanic concentrations of virtually all elements in the periodic table are now known (e.g., Nozaki, 1997), but many elements are present in only trace quantities. The model base state (labelled SSW76, see Columns 1-2 of Table 3) is meant to match as closely as possible the composition of the North Atlantic surface seawater circa 1976 used to derive both PSS-78 and the 1980 equation of state (Millero and Poisson, 1981). It includes all components that can affect salinity down to the level of 1 mg kg^{-1} , although traditional practice in not including the dissolved gases N_2 (16 mg kg^{-1}), and O_2 ($0\text{--}8 \text{ mg kg}^{-1}$) is followed. This composition is denoted by a vector $C_0 = \{c_1 \ c_2 \ \dots \ c_{N_c}\}$, where c_i is the concentration (mol kg^{-1} solution) of the i th of N_c constituents. SSW76 is defined to have $S_{78}=35$ (exactly), and constructed to have a chlorinity of 19.374 g kg^{-1} according to the definition (Millero et al., 2008) derived from titration procedures:

$$\text{Chlorinity}/(\text{g kg}^{-1}) \equiv 0.3285234 \times M_{Ag} \times ([\text{Cl}^-] + [\text{Br}^-] + [\text{I}^-]) \quad (5)$$

with $[\cdot]$ denoting concentrations and $M_{Ag}=107.8682 \text{ g mol}^{-1}$ the molar mass of silver. In addition, the reference salinity $S_R \equiv u_{PS} S_{78}$ (Millero et al., 2008), will be (exactly) $35.16504 \text{ g kg}^{-1}$.

The recently defined reference composition of standard seawater (from Millero et al., 2008, hereafter M08) was taken as a starting point in specifying SSW76. However, M08 cannot easily be used directly as a model for seawater in this study for several reasons.

First, the fixed ratios of carbonate system components in M08 are not convenient for studying spatial and temporal variations in seawater composition. Although specification of the carbonate system in seawater requires (at minimum) 7 species (Millero, 1995), some of which appear in amounts much less than 1 mg kg^{-1} , their concentrations are not independent. Rather, they are coupled by constants governing the chemical equilibria between them. Only two parameters from the set $\{T, A, \text{pH}, f\text{CO}_2,$

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DIC} are required to fully specify the carbonate system (with minor corrections arising from borate and SO_4^{2-} concentrations). From these parameters, the equilibrium constants (denoted by K_w, K_0, K_1, K_2, K_B and parameterized in Dickson et al. (2007)) are used to compute the ionic concentrations.

5 It is desirable in the model to let the carbonate ions remain in chemical equilibrium in all conditions as this more closely models the behavior of real water. Thus instead of using the M08 ionic concentrations, the carbonate system is defined using two of the standard parameters. The first parameter used is Total Alkalinity (TA), set to $2300 \mu\text{mol kg}^{-1}$, where

$$10 \quad TA \equiv [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{OH}^-] - [\text{H}^+] \quad (6)$$

A total borate component is specified by adding together the B(OH)_4^- and B(OH)_3 components of M08, and SO_4^{2-} concentrations (required for carbonate system calculations) are also taken from M08.

Second, although the TA of SSW76 and M08 are the same, the total dissolved inorganic carbon (DIC) defined as

$$15 \quad \text{DIC} \equiv [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (7)$$

in the two models is different (as are pH and $f\text{CO}_2$). The reason for this is that attempts to match δS_A observations, as well as weak independent evidence, suggests that the DIC content of SSW is somewhat higher than that specified in M08.

20 M08 specifies ionic composition after setting the fugacity $f\text{CO}_2$ to $333 \mu\text{-atm}$ at a temperature of 25°C . This $f\text{CO}_2$ is appropriate for an equilibrium with atmospheric levels when the measurements were made to define PSS-78, and at 25°C implies a DIC of $1963 \mu\text{mol kg}^{-1}$. Typically, after sampling, SSW is filtered and sterilized for ≈ 30 days at temperatures of 28°C before 1991 (batch numbers up to P115), but only $18\text{--}21^\circ\text{C}$ since then (P. Ridout, OSIL, personal communication). Since the solubility of CO_2 is strongly dependent on temperature, the choice of temperature is important. At 20°C equilibrium levels of DIC would be around $2006 \mu\text{mol kg}^{-1}$, and at 28°C they would

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be $1937 \mu\text{mol kg}^{-1}$. The change in DIC due to increasing atmospheric CO_2 levels is slightly smaller. At a temperature of 25°C and a present-day $f\text{CO}_2$ of $380 \mu\text{-atm}$, calculated DIC would be $1992 \mu\text{mol kg}^{-1}$.

However, there are indications that measured DIC values in ampoules of SSW are often (but not always) somewhat higher than these predicted equilibriums at bottling time, and this is generally believed to be caused by the decomposition of residual organic matter after bottling. Unfortunately, although the T_A of standard seawater has been studied (Goyet et al., 1985; Millero et al., 1993), there has been no systematic attempt to analyze the DIC content of standard seawater, and its temporal stability. Brewer and Bradshaw (1975) measured $2238 \mu\text{mol kg}^{-1}$ in SSW batch P61. Recent (September 2009) measurements of DIC in ampoules of old SSW from batches P79 (from 1977), P111 (1989), and bottled P140 (2000) found values of 2610, 2200, and $1803 \mu\text{mol kg}^{-1}$, respectively. The spread between replicates from different ampoules of the same batch was $10\text{--}20 \mu\text{mol kg}^{-1}$, larger than measurement uncertainty, but much smaller than the variations between batches.

In fact, as will be shown later, conductivity is not sensitive to variations in DIC, although S_A (and hence δS_A) are greatly affected. A DIC change of $100 \mu\text{mol kg}^{-1}$ is equivalent to an absolute salinity variation of $\approx 0.006 \text{ g kg}^{-1}$, but will change S_{78} by only 0.0007. Since a primary purpose of our δS_A corrections is (eventually) to calculate densities, it may be more important to choose a model DIC value that will match that of the water used in the measurements defining the 1980 equation of state (Millero and Poisson, 1981), relating salinity and density. This is stated by Millero (2000) to have been $2226 \mu\text{mol kg}^{-1}$. However, density fits to Pacific ocean data published in that paper also suggest zero density anomalies occur when $\text{DIC}=2000 \mu\text{mol kg}^{-1}$.

Since ampoules of SSW are sealed, this large range of uncertainty is ultimately related to the effects of organic material and its neglect in the inorganic seawater chemistry model developed here. This makes it difficult to specify a useful model value for DIC in advance of any calculations, although both density measurements and in-situ observations suggest concentrations somewhat higher than that of M08. It is probably

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desirable that our definition (eventually) imply that $\delta S_A \approx 0$ for observations from the surface North Atlantic. Thus, after some tuning, DIC is set to $2080 \mu\text{mol kg}^{-1}$.

An inappropriate value for the DIC of SSW76 will (eventually) lead to a near-constant offset in all calculated absolute salinity variations. Although this offset is thus potentially significant, it will apply to all calculations and hence may have little effect on comparisons between different seawaters, or on any computation in which additions rather than absolute levels of DIC are specified.

The last difference is that non-conservative nutrient species must be included. Changes in NO_3^- and Si(OH)_4 will exceed 1 mg kg^{-1} in a seawater with $S_A \approx 35 \text{ g kg}^{-1}$ and are related to the salinity variations we seek to model (Brewer and Bradshaw, 1975; Millero, 2000). These nutrients are assumed to have a concentration of zero in SSW76.

Following customary practice the mass of Na^+ is adjusted slightly to maintain charge neutrality, once all other ionic components are specified in SSW76. This may partly account for the contributions of neglected ionic constituents, of which the most important are the conservative elements Li^+ (0.18 mg kg^{-1} , Soffyn-Egli and Mackenzie, 1984), Rb^+ (0.12 mg kg^{-1}), and the nutrient PO_4^- ($0\text{--}0.23 \text{ mg kg}^{-1}$).

The computed absolute salinity $S_A(C_0) = 35.171 \text{ g kg}^{-1}$ for SSW76. This differs by 0.006 g kg^{-1} from the defined value of S_R . The mismatch is within the uncertainty of $\pm 0.007 \text{ g kg}^{-1}$ suggested by Millero et al. (2008), however much of that error arises from uncertainty about the amount of SO_4^{2-} . In contrast, the salinity difference here largely arises from differences in carbonate parameters. However, it should be emphasized that SSW76 is a model of seawater, and not necessarily a better (or worse) description of actual seawater than M08. This is because the assumed precision for some of the constituent concentrations that is greater than that of the best observations.

Strictly speaking, the difference between $\gamma = 35.171/35$ and u_{PS} means that the δS_A computed in this paper, needed to get true absolute salinity S_A , is not exactly the same as that required to get the reference composition salinity S_{A08} . Instead the two

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corrections will be related by a scale factor of $\gamma/u_{PS} \approx 1.00017$. However, the difference is small enough that it is not of any practical importance and the two will be considered interchangeable.

2.2 A model for standard seawater ($S_{78} \neq 35$)

5 The composition of water C at salinities other than $S_{78} = 35$ can be specified in different ways. The simplest is to multiply all constituent concentrations by a constant fraction (i.e. $C^{(3)} = \beta \times C_0$ for $S_{78} = \beta \times 35$). This is a so-called type III Reference Seawater (Millero et al., 2008). However, during the specification of PSS-78, SSW was evaporated or diluted with distilled water in order to change its salinity, and again equilibrated with the atmosphere. This makes it more reasonable to specify a type II Reference Seawater $C^{(2)}$, where only the concentrations of conservative tracers, as well as TA , are multiplied by the constant fraction β for $S_{78} = \beta \times 35$, but fCO_2 is kept constant.

Assuming in advance of our later discussion that the conductivity model can predict the effects of perturbations reasonably well, and realizing that $C^{(2)}$ and $C^{(3)}$ are very similar, the differences in conductivity, absolute salinity, and conductivity-derived practical salinity arising from these two approximations can be estimated as:

$$\delta\kappa' = \kappa_{Pa08}(C^{(2)}) - \kappa_{Pa08}(C^{(3)}) \quad (8)$$

$$\delta S'_A = S_A(C^{(2)}) - S_A(C^{(3)}) \quad (9)$$

$$\delta S'_{78} = f_{78}(\kappa_{Pa08}(C^{(2)})) - f_{78}(\kappa_{Pa08}(C^{(3)})) \quad (10)$$

20 where κ_{Pa08} is the conductivity estimate computed using the Pa08 conductivity model and absolute salinities are calculated using Eq. (2).

Over the range of $5 < S_{78} < 40$, the conductivity differences are $\delta\kappa' < \pm 0.8 \mu S cm^{-1}$ (Fig. 1a), which in turn implies $\delta S'_{78} < \pm 0.0005$ (Fig. 1b). These uncertainties are negligible. However, the changes in absolute salinity $\delta S'_A$ are an order of magnitude larger, and can approach $0.004 g kg^{-1}$ at salinities of about 17 (Fig. 1b) although the differences are not important for typical seawater salinities near 35.

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2.3 A perturbation model for observed seawater

As a particular parcel of seawater is advected through the ocean within the thermohaline circulation, biogeochemical processes alter its composition so it differs from that of SSW. These perturbations are represented by a vector δc , so that the composition becomes $C + \delta c$. Biogeochemical processes will not alter the conservative components of seawater, so these components of δc are zero. Changes occur due to variations in non-conservative nutrients and components of the carbonate system. However, calculations appropriate for estuarine waters may also involve changes in some of the conservative components as they may also be components of freshwaters.

Note that a slight simplification has been made. Actual additions of a particular species to a volume of water will (slightly) change the concentrations of all other species, when concentrations are measured per unit mass of solution (or per unit volume) as is done here. However, modelling this additional complication is not necessary here as we are not tracking individual parcels.

Nutrient changes that lie above our threshold of 1 mg kg^{-1} include nitrate (NO_3^-) and silicate. The latter can appear in the form of SiO_2 , Si(OH)_4 , and SiO(OH)_3^- . Typically in the pH range of seawater all but a few percent appears as nonconductive Si(OH)_4 , and it will therefore be assumed that only a negligible amount appears in the other forms.

Changes to the carbonate system can be determined by measurements of TA and DIC (or any two equivalent measurements, e.g. pH and TA). With the addition of NO_3^- , and a change in TA , the number of positive and negative charges in the composition will probably no longer balance. Other processes must therefore be present in the real ocean to balance this excess (or rather, the change in TA arises to compensate for the effects of these other processes). The dissolution of CaCO_3 is likely the predominant mechanism at work (Sarmiento and Gruber, 2006). The negative charges and carbon from CO_3^- are already accounted for in the increase in TA and DIC respectively. An increase in Ca^{2+} is also known to occur in deep waters (de Villiers, 1998), and we assume that this will balance the change in total charge. That is, we assume

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a relationship between the increase in TA and the increase in concentrations of Ca^{2+} from dissolution and NO_3^- from remineralization:

$$\Delta TA = 2\Delta[Ca^{2+}] - \Delta[NO_3^-] \quad (11)$$

where Δ denotes changes. Thus our perturbations must include measured concentrations of NO_3^- , $Si(OH)_4$, TA , and DIC , as well as an inferred change in Ca^{2+} using Eq. (11). Carbonate parameters are then recomputed using the equilibrium constant formulas described by Dickson et al. (2007).

Of course, other processes also occur in the ocean. For example, TA also varies with changes in phosphate and organic substances, although these contributions will fall below our threshold of importance. A more important process might be sulfate reduction on continental shelves (Chen, 2002), which may be responsible for a large part of TA increases in some areas. In order to model this situation Eq. (11) would be modified to:

$$\Delta TA = 2\Delta[Ca^{2+}] - 2\Delta[SO_4^{2-}] - \Delta[NO_3^-] \quad (12)$$

but now an additional relationship (specifying, e.g., the importance of $CaCO_3$ dissolution relative to SO_4^{2-} reduction) is needed to complete the model. Speculation on this relationship is beyond the scope of this paper.

There is also evidence for significant (relative to our threshold) variations in the concentrations of Mg^{2+} in the vicinity of hydrothermal vents (de Villiers and Nelson, 1999). Again, the wider importance of this process, and a means of parameterizing these variations, is at present unknown.

2.4 A model for seawater conductivity

The Pa08 model estimate κ_{Pa08} of the true electrical conductivity κ of a dilute multi-component aqueous ionic solution like seawater is computed using an equation which

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can be written in a simplified form as (Pawlowicz, 2008)

$$\kappa_{\text{Pa08}}(C) = \sum_{i=1}^{N_c} \bar{\lambda}_i c_i^* z_i \quad (13)$$

The in-situ ionic equivalent conductivities $\bar{\lambda}_i = \lambda_i^\circ f_i \bar{\alpha}_i$ are the product of infinite dilution equivalent conductivities λ_i° for the different ions (set to zero for nonionic species), and two reduction factors: $f_i(I^*) \leq 1$, accounting for relaxation and electrophoresis effects, and $\bar{\alpha}_i(I^*, C) \leq 1$, accounting for ion association effects at finite ionic strength I^* . The stoichiometric ionic strength I^* is

$$I^* = \frac{1}{2} \sum_{i=1}^{N_c} z_i^2 c_i^* \quad (14)$$

The valence of charge on the i th ion is z_i and its stoichiometric concentration c_i^* (mol L⁻¹). This is related to c_i through a density equation (Millero and Poisson, 1981):

$$c_i^* = \rho(S_{78}) c_i \quad (15)$$

where we incur an error of at most 1×10^{-5} by ignoring the fact that the true density will change slightly with composition perturbations δc . As $I^* \rightarrow 0$ we have $f_i \rightarrow 1$ and $\bar{\alpha}_i \rightarrow 1$.

The relaxation/electrophoresis reduction parameter f_i for species i depends on the concentrations of other species $j \neq i$ only through their contribution to I^* . However, the ion association parameter $\bar{\alpha}_i$ depends critically on the concentrations and identities of all other ions (i.e. on the total set of $c_i^*, i = 1, \dots, N_c$), as it is a weighted sum of interactions with all other anions (cations) for a cation (anion). In order to account for this the internal model structure is somewhat more complicated than Eq. (13) suggests. Both the infinite dilution equivalent conductivities, and the in-situ ionic equivalent conductivities determined by Pa08 for SSW76, are listed in Table 2.

The conductivity model used is identical to that described in Pa08, with the addition of parameters for B(OH)_4^- , derived from observations of Corti et al. (1980). All numerical

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parameters are based purely on basic chemical measurements in binary solutions, without reference to any measurements made in seawater (or any other natural water).

The accuracy of the computed conductivity κ_{Pa08} depends on the accuracy of the measured ionic concentrations c_i^* , as well as on biases in the calculation of the reduction factors f_i and $\overline{\alpha_i}$. At salinities $< 4 \text{ g kg}^{-1}$ the relative accuracy $\varepsilon = (\kappa_{Pa08} - \kappa) / \kappa$ of the model is typically limited to ± 0.03 by the accuracy of the chemical analyses used to determine composition (Pawlowicz, 2009). Once this error is reduced, by, e.g., statistical averaging, the true error is less than 0.007 over a range of chemical compositions. For seawater with salinities of $0.1\text{--}1 \text{ g kg}^{-1}$ we find an overestimate of only 0.002. However, at the higher salinities of concern here model biases dominate the error, with ε smoothly varying from about -0.01 at a salinity of 4 ($\kappa \sim 8 \text{ mS cm}^{-1}$) to about -0.10 at a salinity of 35 or $\kappa \sim 50 \text{ mS cm}^{-1}$ (Fig. 2b).

2.5 Conductivity perturbations for non-standard seawaters

A salinity underestimate of order 3 g kg^{-1} resulting from using κ_{Pa08} in Eq. (1) directly will not allow us to directly investigate the small compositional variations in typical seawater that we have discussed above, which are several orders of magnitude smaller. However, not only is $|\varepsilon| \ll 1$, but it is relatively insensitive to changes in chemical composition. A comparison of measured and predicted conductivities for a variety of saline ocean and lake waters in the range of $20\text{--}50 \text{ mS cm}^{-1}$ (Fig. 2b) shows that the resulting error is virtually identical for different compositions at the same conductivity. This is very different from results found when considering baseline predictions formed by taking $f_i = \overline{\alpha_i} = 1$, or equivalently using infinite dilution equivalent conductivities for the different components, ignoring all interionic interactions (Fig. 2a). Not only are these baseline predictions greatly in excess of true conductivities (so that $\varepsilon = O(1)$), but the excess is highly sensitive to the composition. The baseline ε for Mahoney Lake is almost double that for seawater at the same conductivity. The model is therefore accounting for relative chemical composition correctly, but with an overall bias that depends (weakly) on the salinity.

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Thus for model predictions during which only small changes δc in composition are made, we can take the κ_{Pa08} error $\varepsilon \approx$ constant. ε is estimated from

$$\kappa(C) = \kappa_{\text{Pa08}}(C) \cdot (1 + \varepsilon)^{-1} \quad (16)$$

knowing that $\kappa(C) = f_{78}^{-1}(S_{78})$. Since we assume

$$\kappa(C + \delta c) \approx \kappa_{\text{Pa08}}(C + \delta c) \cdot (1 + \varepsilon)^{-1} \quad (17)$$

the change in conductivity $\delta \kappa$ related to small compositional changes is:

$$\begin{aligned} \delta \kappa &\equiv \kappa(C + \delta c) - \kappa(C) \\ &\approx (\kappa_{\text{Pa08}}(C + \delta c) - \kappa_{\text{Pa08}}(C)) \cdot (1 + \varepsilon)^{-1} \\ &= \delta \kappa_{\text{Pa08}} \cdot (1 + \varepsilon)^{-1} \end{aligned} \quad (18)$$

Thus it appears that we can use Pa08 to usefully predict conductivity perturbations.

We can confirm the relationship postulated in Eq. (18) for Pa08, which suggests that increments will be modelled to the same relative accuracy ε as conductivities themselves, by directly comparing numerical estimates from the model of various derivatives and other parameters related to conductivity increments with observations made in seawater.

First, direct estimates of the ionic equivalent conductivities $\lambda_i = \lambda_i^0 f_i$ in seawater have been made using a radioactive tracer technique (Poisson et al., 1979). These parameters can also be extracted from the Pa08 model. When using the baseline (i.e. ignoring all modelled ionic interactions) the parameters are overpredicted with relative errors of 0.34 to 1.5 (Fig. 3a). However, when using the full Pa08 model, predictions are much closer to measured values, and the scatter is also greatly diminished. The mean relative error is -0.09 , almost identical to that found for conductivity itself.

Note that although the equivalent conductivities are generally underpredicted, the results for SO_4^{2-} show a slight overprediction. This ion associates strongly with most other cations. This makes it more difficult to model the equivalent conductivity of the ion, as pairing effects must be subtracted from measurements, but also tends to reduce

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the error when making predictions in actual solutions, as pairing effects are added back in.

More relevant results can be obtained by comparison with so-called partial equivalent conductivities $\bar{\Lambda}_{1i}$, defined by

$$\bar{\Lambda}_{1i} = \left. \frac{\partial \kappa}{\partial E_i} \right|_{P, T, E_{j \neq i}, \dots} \quad (19)$$

These have been evaluated from laboratory measurements in which small changes in equivalent concentrations E_i of the i th of the N_s salts (i.e. binary compounds) in seawater are made by additions to a reference seawater (Park, 1964; Connors and Park, 1967; Connors and Weyl, 1968; Connors and Kester, 1974; Poisson et al., 1979). The data are corrected to show the derivatives when all other other conditions, and concentrations of all other ions, are held fixed. Note that the $\bar{\Lambda}_{1i}$ are not equal to the sum of the corresponding equivalent conductivities for the anion and cation in Eq. (13) when evaluated at the ionic strength of seawater. Differences arise due to changes in the ionic strength, and in the effects of pairing (i.e., when $\bar{\alpha} < 1$) between the components of the added salt and all other constituents in seawater. However, the $\bar{\Lambda}_{1i}$ can easily be computed numerically from the Pa08 model.

For the salts studied, baseline predictions overestimate the partial equivalent conductivities by 0.46 to 3.4 (Fig. 3b and c). When using the full Pa08 model, predictions are much closer to measured values, and the scatter is also greatly diminished (mean relative error -0.12). We also see that added salts containing SO_4^{2-} tend to lie close to the mean, showing that the inclusion of pairing effects does reduce possible problems associated with the ionic equivalent conductivity. In both cases the relative error of these variations is similar to that for conductivity itself. Thus the perturbation estimate Eq. (18) is apparently valid on both theoretical and observational grounds.

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2.6 Salinities of non-standard seawaters

The change in S_{78} resulting from a perturbation δc is given by

$$\delta S_{78} \equiv S_{78}(C + \delta c) - S_{78}(C) \quad (20)$$

$$= f_{78}(\kappa(C + \delta c)) - f_{78}(\kappa(C)) \quad (21)$$

$$\approx f_{78}(\kappa(C) + \delta \kappa_{\text{Pa08}} \cdot (1 + \varepsilon)^{-1}) - f_{78}(\kappa(C)) \quad (22)$$

where ε and $\delta \kappa_{\text{Pa08}}$ are as defined in the previous section. At low salinities where κ_{Pa08} has minimal bias the simpler approximation

$$\delta S_{78} \approx \delta S_{78}^* \equiv f_{78}(\kappa_{\text{Pa08}}(C + \delta c)) - f_{78}(\kappa_{\text{Pa08}}(C)) \quad (23)$$

provides an alternative method of estimating δS_A which does not rely on assumptions about the magnitude of perturbations. In fact the function $f_{78}(\kappa)$ is smooth enough that the approximation holds to a degree of accuracy $\ll \varepsilon$ over all salinities (c.f. Eq. 10), although we continue to use the computationally more intensive Eq. (22) unless otherwise specified. In addition to these changes in S_{78} , perturbations δc also lead to changes in S_A according to:

$$\delta A \equiv S_A(C + \delta c) - S_A(C) = S_A(\delta c) \quad (24)$$

(by the linearity of Eq. 2).

If we consider a parcel of water with fixed chlorinity, additions δc will therefore affect both the measured S_{78} and calculated S_A . These changes will generally be different, giving rise to a salinity correction which can be estimated as:

$$\delta S_A^* \equiv S_A(C + \delta c) - \gamma S_{78}(C + \delta c) \quad (25)$$

$$= \delta A - \gamma \delta S_{78} \quad (26)$$

$$\approx \delta A - \delta S_{78} \quad (27)$$

This implies that δS_A is approximately the change in absolute salinity, minus whatever compensating effects arise from conductivity. If a nonionic substance is added, δA will

dominate the correction. On the other hand, adding very light but extremely conductive ions could lead to negative corrections arising mostly from changes in S_{78} .

However, when converting ocean measurements to absolute salinity we are concerned with the corrections that arise when S_{78} is held constant, rather than those for fixed chlorinity. For non-standard seawater with a measured S_{78} the composition is not C but rather $\beta C + \delta c$. That is, the addition of other solids that dissociate into ions which increase conductivity must be matched by a slight dilution of our standard seawater composition in order to keep conductivity constant. The dilution factor β for the SSW composition can be found by solving

$$\kappa(\beta C + \delta c) = \kappa(C) \quad (28)$$

which can be done iteratively, using κ_{Pa08} in place of κ on both sides of the equation. Then from Eqs. (4) and (28) the true correction is:

$$\delta S_A = S_A(\beta C + \delta c) - S_A(C) = \delta A - (1 - \beta)S_A(C) \quad (29)$$

Typically β is very close to 1 and δS_A^* is within a few percent of δS_A for the small perturbations of concern here. Although the latter is technically more correct, the advantage of the former is that we can separately estimate effects of changing mass and changing number of electrical charges.

3 Results

To illustrate the effects of compositional changes δc first consider an extreme, but realistic, scenario. Investigations of the relationship between salinity and density suggest that largest δS_A (of order 0.03 g kg^{-1}) occur in the intermediate North Pacific (McDougall et al., 2009). This water represents the endpoint of the subsurface branch of the thermohaline circulation and thus provides an appropriate extreme. For comparative purposes model “North Pacific Intermediate Water” (NPIW) is normalized to have the same chlorinity as SSW76, although actual chlorinities in the North Pacific

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are about 0.3 g kg^{-1} lower. Based on typical observations, take this water to contain $\text{Si(OH)}_4 = 170 \text{ } \mu\text{mol kg}^{-1}$ and $\text{NO}_3^- = 40 \text{ } \mu\text{mol kg}^{-1}$, with TA and DIC larger than in SSW76 by values of $150 \text{ } \mu\text{eq kg}^{-1}$ and $300 \text{ } \mu\text{mol kg}^{-1}$ respectively. Columns 4–5 of Table 3 then contain the model composition $C_0 + \delta c$ representing NPIW, with the perturbation δc in columns 6–8.

Carbonate equilibria are recalculated from the new TA and DIC . pH on the Total scale drops to about 7.5 (again, all calculations are at 25°C). The increases we specify actually cause concentrations of CO_3^{2-} and B(OH)_4^- to decrease significantly. In addition, charge balance considerations require that the concentration of Ca^{2+} increase by $0.095 \text{ mmol kg}^{-1}$ or a little less than 1% over its value in SSW76. Measured increases in Ca^{2+} at depth in the North Pacific are of this order (de Villiers, 1998).

Applying the model directly (i.e. under conditions of fixed chlorinity) $\delta S_{78} \approx 0.0062$ and $\delta A \approx 0.0405 \text{ g kg}^{-1}$, and hence from Eq. (27) $\delta S_A^* \approx 0.034 \text{ g kg}^{-1}$. The cruder approximation $\delta S_{78}^* \approx 0.0054$ underestimates δS_A with a relative error of only -0.12. A similar calculation, i.e., one with the same changes in TA , DIC , NO_3^- , and Si(OH)_4 , under conditions of fixed conductivity, results in a dilution factor of $\beta = 0.9998105$, and from Eq. (29) $\delta S_A \approx 0.034 \text{ g kg}^{-1}$.

The two calculations result in almost exactly the same answer. From Eq. (27) we can consider the correction as the difference between changes in absolute and practical salinity. The Si(OH)_4 component alone contributes about 0.016 g kg^{-1} to δS_A , or almost half of the correction. Much of the remainder arises primarily due to increases in HCO_3^- , but there are both increases and decreases in other constituents. In fact, the changes in S_A due to the increase in carbonates outweigh those due to the increase in Si(OH)_4 , but some of this carbonate ion increase is compensated by an increase in S_{78} .

In order to better understand these values we investigate the conductivity. Model calculated ionic equivalent conductivities $\bar{\lambda}_i$ within our seawater are all significantly smaller than the infinite dilution equivalent conductivities λ_i° (Columns 3 and 4 of Table 2), but

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with the exception of H^+ and OH^- are all of order $30 \text{ mS cm}^{-1} (\text{mol L}^{-1})^{-1}$. Very roughly then, conductivity changes will be proportional to changes in the number of charge pairs present. There are large changes in the concentrations of individual negative ions (last column of Table 3), but overall the increases and decreases in negative ions tend to balance out, matching (in total) the smaller increase in positive charges from Ca^{2+} produced by CaCO_3 dissolution. Thus changes in S_A are most strongly influenced by changes in Si(OH)_4 and DIC, but changes in S_{78} occur mostly due to CaCO_3 dissolution.

Further insight can be obtained by deriving an approximate relationship between δS_A and δc . Seawater conductivity per unit mass of salt at 25°C in the model is $\bar{\psi} = \kappa_{\text{Pa08}} / S_A \approx 1.35 \text{ mS cm}^{-1} (\text{g kg}^{-1})^{-1}$. Combining Eqs. (2), (4), and (13) and defining $\psi_i = \lambda_i z_i \rho / M_i$ as the conductivity per unit mass of the i th component:

$$\delta S_A \approx \sum_i M_i \left(1 - \frac{\psi_i}{\bar{\psi}}\right) \delta c_i \quad (30)$$

with numerical values appropriate for $S_{78}=35$ given in Table 2. This expression illustrates the way in which the contribution of individual ions to δS_A depends on the degree by which conductivity per unit mass ψ_i differs from the average $\bar{\psi}$. The relationship is only approximate because the ψ are not in fact constant, but will also vary with δc . In using this formula it is also important to recall that only charge balanced perturbations are meaningful, so that any scenario must involve changes in at least one cation and anion.

Examination of the mass effect coefficients $(1 - \psi_i / \bar{\psi})$ for different ions (listed in Column 6 of Table 2) shows concentration perturbations in some ions (e.g., Na^+ , Ca^{2+} , Mg^{2+} , K^+ , Cl^- , F^-) result in little change to δS_A . These ions contribute to conductivity in an “average” way, with $\psi_i \approx \bar{\psi}$. Contrariwise, concentration changes in other ions do not affect conductivity in an average way and hence must be accounted for with a non-zero δS_A . Some of these (e.g., Sr^{2+} , Br^-) vary with the other conservative ions and hence will not appear in realistic perturbations that arise from biogeochemical

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processes. Nonconductive species contribute exactly their added mass. Several ions (H^+ , OH^-) have an extremely large effect on conductivity, relative to their mass. However, the actual in-situ mass changes in these ions are so small that the overall effect on conductivity is minimal.

5 Seawater is composed primarily of Na^+ and Cl^- ions (Table 3). These contribute to conductivity in an average way, and so if there are small perturbations in their mass S_{78} will approximately account for the salinity change. When using the full model, and ignoring nonconductive $\text{Si}(\text{OH})_4$, the change in absolute salinity δA is ≈ 0.024 , about 4 times larger than δS_{78} . However, our salinity perturbation for modelling NPIW
 10 is composed largely of HCO_3^- , for which ψ_i is significantly different than $\bar{\psi}$. Using Eq. (30) we expect that an HCO_3^- perturbation will give rise to a conductivity change that (when converted to salinity using the average factor $\bar{\psi}$) will only account for ≈ 0.3 of the actual salinity change. The dominance of HCO_3^- changes in δc , and their relatively uncondutive nature, explains the insensitivity of predicted conductivity to variations in
 15 our assumptions about how seawater dilution should be modelled (c.f. Sect. 2.2).

The choice between Eqs. (11) and (12) to balance TA changes will also have some consequences. An addition of Ca^{2+} will result in a compensating increase in conductivity, not affecting δS_A , but an equal decrease of SO_4^{2-} (which has an equivalent effect on TA) will not result in a fully compensating decrease in conductivity and hence will
 20 result in a smaller δS_A . For a concentration change of order $100 \mu\text{mol kg}^{-1}$ (i.e. for NPIW) the difference in δS_A computed using the different scenarios is 0.005 g kg^{-1} using Eq. (30) or 0.008 g kg^{-1} using the full model. Since we do not have a good knowledge of the actual δc_i for all constituents of seawater, we must rely on assumptions about biogeochemical processes to parameterize them. However, our prediction
 25 accuracy is then limited by the extent of our knowledge about these processes.

By considering only those ions both important in typical biogeochemical perturbations (i.e. large values in column 7 of Table 3) and with strong effect on δS_A (i.e., with large values in the last column of Table 2), Eq. (30) can be further simplified. Only HCO_3^- , CO_3^{2-} , CO_2 , $\text{B}(\text{OH})_3$, $\text{B}(\text{OH})_4^-$, NO_3^- and $\text{Si}(\text{OH})_4$ will have significant effects

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on δS_A . Since all of the carbonate parameters are related, and relationships such as Eq. (11) mean that the NO_3^- term is not really independent either, a more sophisticated understanding of the carbonate system may allow a formula for δS_A to be written more simply in terms of more general parameters such as TA and DIC .

5 However, for accurate calculations the full model is required. Unfortunately, although our model can be used to directly compute δS_A in any situation, the computational process by which these values are derived is complex and relatively opaque. Previous workers have fitted simple empirical relationships to measurements, and these appear to be sufficient for practical purposes. Such formulas can also be fitted to “measure-
10 ments” calculated by the perturbation model. This is a simpler way to derive more straightforward formulas.

First consider perturbations when $S_{78} = 35$. The model is used to calculate δS_A over a grid of δc points within a range of $0 \leq \Delta TA \leq 0.3 \text{ meq kg}^{-1}$, $0 \leq \Delta DIC \leq 0.3 \text{ mmol kg}^{-1}$, and $0 \leq \Delta \text{NO}_3^- \leq 0.040 \text{ mmol kg}^{-1}$, with Ca^{2+} again varying according to Eq. (11). In-
15 spection of the results shows that δS_A varies quasi-linearly with the components of the perturbation, and by least-squares fitting the equation

$$\delta S_A / (g \text{ kg}^{-1}) = (47.11 \Delta DIC + 7.17 \Delta TA + 36.57 \Delta [\text{NO}_3^-]) \times 10^{-3} \quad (31)$$

agrees very well with the full calculations, with a misfit standard error of $\pm 0.00007 \text{ g kg}^{-1}$ and a maximum misfit of 0.0003 g kg^{-1} .

20 The DIC coefficient is similar to the theoretical coefficient for HCO_3^- (Column 7 Table 2), and both the theoretical and fitted NO_3^- coefficients are roughly comparable. The $\approx 20\%$ difference results from both the biogeochemical relationships, as well as variations in the interionic interactions involved in conductivity.

Repeating the above procedure for $25 \leq S_{78} \leq 40$, we find that the coefficients in the
25 fit for δS_A vary with salinity (Fig. 4). The coefficients for ΔDIC and NO_3^- vary only weakly (with a change of $< 10\%$ over the salinity range chosen) and in practical terms the variation can be ignored. However, the coefficient for ΔTA varies strongly ($> 50\%$ change over the salinity range chosen), and almost linearly with S_{78} . This suggests

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that Eq. (31) should be modified for situations when $S_{78} \neq 35$ by replacing ΔTA with $\Delta TA \times S_{78}/35$. Note that the Δ signifies the change from SSW values at the specified salinity, e.g. the difference between observed TA and $2300 \times S_{78}/35 \mu\text{mol kg}^{-1}$. We also add in the total mass of Si(OH)_4 to produce this final prediction formula:

$$\delta S_A / (g \text{ kg}^{-1}) = (47.11 \Delta \text{DIC} + 7.17 (S_{78}/35) \Delta TA + 36.57 \Delta [\text{NO}_3^-] + 96.11 \Delta [\text{Si(OH)}_4]) \times 10^{-3} \quad (32)$$

Note that there may be no easy way to empirically verify the different coefficients with ocean measurements. An empirical fit to data has resulted in the following relationship

$$\delta S_A / (g \text{ kg}^{-1}) = (50.13 (\Delta NT A - 0.215) + 63.10 \Delta [\text{NO}_3^-] + 96.30 \Delta [\text{Si(OH)}_4]) \times 10^{-3} \quad (33)$$

(Millero, 2000, eq. 3) which has a similar coefficient for Si(OH)_4 , but otherwise is numerically somewhat different. However, the different constituents included are strongly correlated in the ocean. A least-squares fit to a restricted set of actual observations may therefore be rather insensitive in certain directions of the parameter space of coefficients. Thus it is most appropriate at this stage to compare these different formulas only by examining their effect on measured ocean profiles.

The full calculation procedure can easily be applied to actual ocean profiles, as long as they include observations of S_{78} , TA , DIC , Si(OH)_4 and NO_3^- . These parameters are now considered to be standard for deep-ocean hydrographic observations so no modification is needed in routine procedures. The latter 4 are enough to specify the non-conservative elements, with changes in Ca^{2+} inferred from Eq. (11) to maintain charge neutrality.

As an example, consider several recent high-quality hydrographic profiles from the North Atlantic, Arctic, and North Pacific, and Southern Ocean (Fig. 5–7). Previous δS_A estimates have been made in all regions except the Arctic.

Surface nutrients are low in all profiles except in the Southern Ocean, and surface pH relatively high, although lower than in SSW (Fig. 5). The Arctic profile has a high surface TA , which implies higher Ca^{2+} , and DIC , due to cold temperatures. Nutrients,

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TA , and DIC at depth are much higher in the North Pacific than in the other profiles. However, deep pH is much lower. Deep nutrient levels are typically higher than surface nutrients in all cases. Inferred ΔCa^{2+} is high in the Arctic and Southern Ocean, and high in the deep North Pacific.

The computed salinity correction δS_A is close to zero in the surface waters of the N. Pacific (Fig. 6a) and N. Atlantic (Fig. 6b), but is almost 0.008 in the surface waters of the Arctic (Fig. 6c). On the other hand, the correction is lowest at depth in the Arctic (only 0.003), but is as high as 0.033 in the deep North Pacific. The surface correction is highest in the Southern Ocean. The correction itself is dominated by the δ_A in all cases with $\delta S_A \approx 0.8\delta A$. The increase in ionic content does result in a small change in conductivity which partially compensates for the compositional change, but as before $\delta S_{78} \ll \delta A$.

Comparison of calculated δS_A with those produced by Eq. (33) and McDougall et al. (2009) for these stations are relatively good (Fig. 7). The general shape of depth profiles and overall magnitudes are similar, although our estimates appear to be systematically slightly larger. Correction factors in the deep Pacific and shallow Arctic are large, whereas the δS_A are small in both Pacific and Atlantic surface waters, and deep Arctic waters. Our corrections are about 0.005 larger in the deep Pacific and not very different when $\delta S_A \approx 0$. Widest disagreement between the three estimates occurs in the Southern Ocean. For all profiles, the model δS_A is the largest of the 3 estimates, and the predictions of McDougall et al. (2009) the smallest.

As a final comparison, the model is used to replicate the measurements in a controlled situation where the chemistry is more precisely known. Millero (1984) measured δS_A (Fig. 8) for various mixtures composed of a known fraction a of SSW and an artificial river water of known composition C_R (Table 4):

$$C_{mixture} = aC_0 + (1 - a)C_R \quad (34)$$

with $0 \leq a \leq 1$. Here we take the dilution $C = aC_0$ as a base state (the difference between $C^{(2)}$ and $C^{(3)}$ dilutions does not materially affect the results here), and $\delta c = (1 - a)C_R$ as

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a perturbation in a fixed-chlorinity calculation. The name is somewhat misleading here because the river water also contains Cl^- but this does not affect the mathematical details of the calculation. Calculations must be modified slightly when $S_{78} < 5$, since the usual seawater parameterizations of the carbonate equilibria are no longer valid in this low-salinity range. They do not extrapolate correctly to pure-water limits. Instead we use low-salinity parameterizations more suitable for river and lake waters (Pawlowicz, 2009; Millero, 1995). The change of δS_A across the transition between the two regimes is not smooth, but the size of the step is small enough that it cannot be seen in Fig. 8.

The δS_A^* arising from perturbation computations almost exactly lies within the scatter of the observations (Fig. 8). As salinity drops and the riverine addition becomes a larger fraction of the composition, δS_A^* increases. One unexpected result is that δS_A^* increases roughly linearly with decreases in salinity only at high salinities. When S_R drops below about 10 g kg^{-1} , δS_{78} curves upwards quite sharply, so that the δS_A^* curve flattens and even decreases at very low salinities. The observations do not appear to show this, although their scatter is large enough that this behavior cannot be ruled out. However, at low salinities where the Pa08 model is known to be accurate (Pawlowicz, 2009), it can be applied directly to C_{mixture} and the alternative estimate δS_{78}^* used in place of the perturbation calculation for δS_{78} . Results agree almost exactly with the perturbation model, showing the same curvature. Agreement is good at low salinities because the bias in Pa08 is small, and is good at high salinities because the river water perturbation is very small.

Finally, for $a=0$ Pa08 directly predicts a conductivity of $142 \mu\text{S cm}^{-1}$, which can then be used with PSS-78 to compute $S_{78}=0.0686$ and hence $\delta S_A = 0.0388 \text{ g kg}^{-1}$ independently of the seawater perturbation model. The perturbation model does approach these values in the limit as $a \rightarrow 0$. Note however that this limit is not a good indicator of the zero-salinity intercept of a best-fit line through the observations, especially those from salinities $> 5 \text{ g kg}^{-1}$, typical of most estuarine waters, because of the curvature in δS_{78} . Such a best fit line would intercept the left axis at rather higher values. Overall, however, although the particular chemistry of the oceanic perturbations may result in

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different errors than those associated with riverine dilutions, there do not appear to be any general biases present.

4 Discussion and conclusions

The combination of a chemical model of seawater and a conductivity model allows the effects of compositional perturbations on conductivity-based methods of salinity determination to be estimated. An immediate result is that conductivity itself is relatively insensitive to biogeochemical perturbations to the chemical composition of seawater. In fixed chlorinity calculations, δS_{78} increases by less than 0.007 over the range of waters investigated in the world ocean, while S_A increases by up to 0.04 g kg^{-1} . Numerical values of S_R (i.e. the scaled S_{78}) lie somewhere between a chlorinity-based measure and the true absolute salinity, although much closer to the former. This also accounts for the stability of conductivity in SSW (Bacon et al., 2007), in spite of the known variations in DIC that occur within samples.

A second result is that the observed δS_A are almost entirely explained by changes in nutrients and the carbonate system. Although this fact is already known empirically and is the basis for existing estimates of δS_A (e.g., McDougall et al., 2009; Millero, 2000) the model calculations provide a more theoretical confirmation. In addition, the model shows that variations in Ca^{2+} and/or SO_4^{2-} are as important as changes in NO_3^- , although they are linked via biogeochemical relationships.

Another result is that the effects of perturbations at typical oceanic salinities are approximately linear functions of salinity, but that this linear behavior does not extrapolate well to behavior at low salinities ($S_{78} < 5$). At low salinities carbonate composition and δS_{78} become much more nonlinear functions of salinity. Thus generalizations based on infinite dilution quantities, or river endpoints, are qualitatively useful but may in practice be less relevant to oceanic situations than might be otherwise be expected. Conversely, extrapolations of linear fits to measurements in estuarine waters will not necessarily agree with observations of river end-members.

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However, although the general agreement between calculated δS_A and density-based estimates like δS_{A08} is good, differences remain. The differences are not very much larger than the typical uncertainty arising from density measurements, but are systematic. There are several possible explanations for these differences.

First, the Pa08 conductivity model may be inadequate to correctly calculate perturbations in this application. The scatter in comparisons between predictions and observations in Fig. 3 suggests that the model bias may still depend to some extent on chemical composition. It is difficult to fully address this issue without more data for comparison. However, the good agreement with the dataset on mixtures of artificial river water and seawater (Fig. 8) suggests that model performance is adequate in at least some cases, even when the perturbations become very large. Agreement between the fixed chlorinity calculation for δS_A^* (Eq. 27) and the fixed conductivity calculation for δS_A (Eq. 29) for the case of biogeochemical perturbations is also very good. The maximum difference between the two is only 0.0007 g kg^{-1} . Since each calculation involves somewhat different changes to the chemical composition, and different assumptions about bias correction, this also suggests that these composition-dependent model errors are almost an order of magnitude smaller compared to the differences between model-estimated and density estimated δS_A .

Second, the overall comparison between the model and the other predictions in Fig. 7 can (perhaps) be improved by decreasing all calculated δS_A by a small (constant) amount. Differences between the predictions will then be both positive and negative, instead of mostly positive. Constant increases or decreases will result from changes in the specified DIC content of SSW76. As discussed in Sect. 2.1 it is not possible at this time to precisely define the DIC content of SSW, and the appropriate value may have to be “tuned” to allow predictions and observations of δS_A to match. The value used in this paper results in $\delta S_A \approx 0$ in the surface North Atlantic. However, reducing DIC in SSW76 to provide a better match in the North Pacific would result in a negative δS_A in the surface North Atlantic.

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A third possibility is that the biogeochemical model (Eq. 11) is in error. Imagine that instead of increasing Ca^{2+} by $\approx 100 \mu\text{mol kg}^{-1}$ SO_4^{2-} is decreased by a similar amount according to Eq. (12). Since these ions have different effects on conductivity, the change would decrease δS_A in the North Pacific by as much as 0.007 g kg^{-1} from our present estimates, which would (again) account for much of the difference. Sulfate reduction may be an important process on shelves (and in anoxic basins), but its importance in the open ocean is less easy to determine.

Fourth, it is possible that these differences reflect inadequacies in the empirical algorithms of Millero (2000) and McDougall et al. (2009) used to calculate the corrections. The database of density measurements used to determine these different algorithms may simply not be large enough to correctly characterize the whole ocean and extrapolations to unsampled regions may not be completely valid. A more detailed comparison with the existing database of density measurements may help to resolve this issue.

A different and more fundamental explanation for disagreements, especially in the North Pacific, may be that the true δS_A value calculated from our model might not be equivalent to the “effective” δS_A computed from density measurements, which is merely chosen to produce the correct density when the equation of state is applied using salinity as a state variable. Agreement between the two estimates depends partly on the definition of salinity, and partly on the haline contraction coefficient being similar for perturbations with different composition.

The haline contraction coefficient is a measure of the density change related to a particular salinity change. The working assumption for S_{A08} is that the density change arising from a given mass change will be insensitive to the composition of the change. The haline contraction coefficient is then calculated from the equation of state, equivalent to assuming that all constituents change in the proportions already found in seawater. This assumption has been shown to be true within practical limits for typical low-salinity river waters, and for mixtures of artificial river and seawaters (Millero, 1975). The agreement between the perturbation model and density-based measurements for the case of artificial river water mixtures (Fig. 8) also suggests that this is likely not

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a large factor at least in some cases. However, this previous work has not considered the full range of compositional variations, and, in particular, the biogeochemical perturbations in seawater.

Biogeochemical perturbations involve nutrients, carbonates, and dissolved gases. Perhaps fortuitously, changes in the concentrations of the dissolved gases (which for O_2 in particular are well above the 1 mg kg^{-1} threshold) have virtually no effect of density (Watanabe and Iizuka, 1985). Thus their neglect in the usual definition of salinity has not been important in the past. However, the haline contraction coefficient for $Si(OH)_4$ at least is slightly less than half of that for typical ions in natural freshwaters and seawaters (Wüest et al., 1996). That is, the density change resulting from a given change in the mass of $Si(OH)_4$ is slightly less than half that for a change of the same mass of the typical ions in natural waters. Thus density measurements converted to mass changes using a haline contraction coefficient derived from the density equation will underestimate the true salinity variation arising from silicate addition. Investigation of this issue should be possible using an appropriate model for density.

An additional issue is that the definition of salinity S_A (Eq. 2), although apparently straightforward, is not completely suitable for the purpose of quantifying small compositional changes in the ocean. Chemical reactions within seawater mean that the chemical formulas for ions present are not identical to the solids added. Si is actually added to seawater in the form of SiO_2 which then dissolves and combines with H_2O , so the appropriate weighting factor for $Si(OH)_4$, say in Eq. (33), may be the molar mass of SiO_2 , (60.08 g mol^{-1}) rather than that of $Si(OH)_4$. That is, the added $2H_2O$ may be inappropriately included in the estimate of the mass of dissolved solids. Thus the calculated δS_A overestimates the actual salinity change.

Reducing the $Si(OH)_4$ coefficient in Eq. (33) in this way reduces δS_A by 0.006 g kg^{-1} in our model NPIW (Table 3) and removes much of the difference in the North Pacific at depths greater than 2000 m (Fig. 7). However, other factors must also be important because there are only very small changes in predictions for the Arctic and North Atlantic, or indeed in any profile at depths shallower than 1000 m. Changes in the

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Southern Ocean are larger, but still not sufficient to completely explain the differences.

A similar argument may be made for the mass of NO_3^- , which results from the remineralization of organic N and is therefore associated with a decrease in O_2 already present in the water column. The dissolved gas O_2 is not included in the definition of salinity, but when these atoms combine with N their mass then becomes part of the calculated salinity. However, the resulting changes in calculated salinity due to this inconsistency are only 0.002 g kg^{-1} for model NPIW, relatively small compared to those that arise from Si reactions.

Larger corrections arise from consideration of the O_2 and H_2O that accompany the dissolution of organic carbon and its conversion to carbonates. In model NPIW the DIC increase is $300 \mu\text{mol kg}^{-1}$ and the carbonate component of S_A increases by 0.018 g kg^{-1} (Table 3) using the definition of Eq. (2). However, the true added mass of dissolved carbon-related material, partly remineralized organic C and partly CO_3^{2-} from dissolved CaCO_3 , is only 0.008 g kg^{-1} . Remineralization involves the combination of 0.0025 g kg^{-1} of organic C with almost 0.007 g kg^{-1} of O_2 to produce CO_2 . The remainder of the discrepancy is due to the dissolution of H_2O in the chemical reactions governing the carbonate equilibria.

Thus it is possible that by rewriting the definition for the absolute salinity of compositional perturbations, to more precisely reflect the actual addition of dissolved material, the numerical values for δS_A can be made smaller by as much as 0.018 g kg^{-1} for NPIW. This can be accomplished without any change in the actual composition, conductivity, or density of the water. Such a variation is more than enough to account for the observed differences. Again, a more detailed comparison with measured δS_A would be required to determine whether this would be useful. One drawback of this approach is that such a redefinition would involve specifying the biogeochemical processes involved, which would make the result less general. In addition, including O_2 decreases in the definition of salinity perturbations, but not in the definition of S_A itself, could create other inconsistencies.

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The differences do not arise because the temperature of calculations was set at 25°C, even though in-situ conductivities used to determine observations of S_{78} are generally measured at much lower temperatures. Conductivity is highly temperature-dependent, and this dependence varies with composition. For SSW, changes in temperature will not result in a change in S_{78} because the PSS-78 formula (Eq. 1) accounts for the effects of temperature variations. However, the temperature effect is slightly different for perturbed compositions. The correction factor τ when comparing conductivities at 25° to those at a temperature θ , defined as:

$$\frac{\kappa(\beta C_0 + \delta c, 25^\circ\text{C})}{\kappa(\beta C_0 + \delta c, \theta)} = \frac{\kappa(C_0, 25^\circ\text{C})}{\kappa(C_0, \theta)} \times (1 + \tau) \quad (35)$$

can be estimated using κ_{Pa08} for κ . For δc representing model NPIW, and $\theta=1^\circ\text{C}$, $\tau \approx -1 \times 10^{-5}$, which changes δS_A by less than $-0.0004 \text{ g kg}^{-1}$. This is negligible relative to the other effects discussed above.

Although the temperature effect is not important, we cannot determine at present which (if any) of the other possible explanations is most important in resolving the differences. However, it appears more likely that they result from uncertainties in the chemical model and/or the definition of salinity rather than from any fundamental problems with the conductivity calculation. It will be important to model density as well as conductivity to fully understand the source of these differences in ocean observations.

In summary, although conductivity measurements have been of primary importance to oceanographic studies for at least a generation our knowledge of the relationship between conductivity and salinity has been purely empirical. There remain many uncertainties about the reliability and predictability of standard procedures. Development of a theory with which variations can be studied is therefore potentially important for studies in many different areas.

For example, it has been shown here that biogeochemical processes have a measurable effect on the conductivity/salinity relationship. This suggests that comparisons between more comprehensive datasets of direct density measurements and our

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predictions may be useful in constraining future research into these processes. Even in the shallow ocean, the changing composition due to changes in atmospheric CO₂ may affect salinity estimates and this model provides a way of investigating the effects of such changes. In coastal and estuarine systems, compositional variations are known to affect density and other properties (e.g. Millero et al., 1976). Comparisons of density and S_{78} measurements may then be useful in estimating the pools (and eventually residence times) of the constituents of these variations.

In addition to these purely scientific concerns, the availability of this theory may be useful in solving a number of technical issues arising in current practices. The extrapolation of δS_{A08} estimates into waters for which no density measurements are available (as done by McDougall et al. (2009) to provide correction factors in coastal and Arctic regions) can be confirmed if information is available about compositional perturbations. The effects of pressure, which can lead to small changes in the chemical equilibria of the carbonate system, can also be investigated. Finally, there are possible uncertainties in the reliability of SSW for highest precision measurements (Kawano et al., 2006), although it is unclear why these variations arise (Bacon et al., 2007). Again, the model developed here may be useful in resolving some of these technical issues.

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Table 1. List of important symbols and abbreviations.

C	Chemical composition of standard seawater
C_0	Chemical composition of standard seawater when $S_{78}=35$.
c_i	Concentration (mol kg^{-1}) of i th constituent of seawater
c_i^*	Concentration (mol L^{-1}) of i th constituent of seawater
δc	Small composition perturbation (added to C)
δS_{78}	Practical Salinity change resulting from compositional perturbation
δS_{78}^*	Simpler estimate of Practical Salinity change resulting from compositional perturbation
δA	Absolute salinity change resulting from compositional perturbation
δS_A	True correction to reference salinity
δS_A^*	Correction estimate using fixed chlorinity calculation
δS_{A08}	Estimate of δS_A developed by McDougall et al. (2009)
ϵ	relative error of Pa08 prediction
I^*	Ionic strength (mol L^{-1})
I_m	Ionic strength (mol kg^{-1})
κ	True conductivity
κ_{Pa08}	Conductivity estimated using Pa08
λ_i^0	infinite dilution ionic equivalent conductivity
λ_i	ionic equivalent conductivity
M_i	Molar mass of i th constituent of seawater
M08	Chemical model of seawater in Millero et al. (2008)
Pa08	Conductivity model described by Pawlowicz (2008)
ρ	Density of seawater
S_{78}	Practical salinity
S_A	Absolute salinity
S_{A08}	Absolute salinity using procedure of Millero et al. (2008); McDougall et al. (2009)
S_R	Reference salinity (Millero et al., 2008)
SSW	IAPSO Standard Seawater
SSW76	Chemical model for SSW circa 1976 in this work
z_i	Valence of i th constituent of seawater

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Table 2. Model parameters including molar masses M_i , infinite dilution equivalent conductivities λ_i° , ionic equivalent conductivities $\bar{\lambda}_i$ in SSW76, conductivities per unit mass ψ_i , and coefficients multiplying δc_i in the approximate δS_A Eq. (30).

Species	M_i [g mol ⁻¹]	λ_i° [mS cm ⁻¹ (mol L ⁻¹) ⁻¹]	$\bar{\lambda}_i$ [mS cm ⁻¹ (g kg ⁻¹) ⁻¹]	ψ_i	$1 - \frac{\psi_i}{\psi}$ –	$M_i(1 - \frac{\psi_i}{\psi})$ $\times 10^{-3}$
Na ⁺	22.9898	50.1	29.9	1.33	0.02	0.40
Mg ²⁺	24.3050	53.0	20.5	1.73	–0.28	–6.78
Ca ²⁺	40.0780	59.5	23.8	1.21	0.10	4.14
K ⁺	39.0983	73.5	48.2	1.26	0.07	2.67
Str ²⁺	87.6200	59.4	24.3	0.57	0.58	50.88
Cl [–]	35.4530	76.3	50.1	1.45	–0.07	–2.43
SO ₄ ^{2–}	96.0626	80.0	33.5	0.71	0.47	45.38
Br [–]	79.9040	78.1	51.8	0.66	0.51	40.69
F [–]	18.9984	55.4	33.1	1.78	–0.32	–6.01
HCO ₃ [–]	61.0168	44.5	24.8	0.42	0.69	42.28
CO ₃ ^{2–}	60.0089	69.3	26.7	0.91	0.33	19.57
B(OH) ₃	61.8330	–	–	–	1.00	61.83
B(OH) ₄ [–]	78.8404	35.2	17.1	0.22	0.84	65.89
CO ₂	44.0095	–	–	–	1.00	44.01
OH [–]	17.0073	198.0	156.9	9.44	–5.98	–101.69
H ⁺	1.0079	349.6	279.0	283.23	–208.36	–210.02
NO ₃ [–]	62.0049	71.4	43.9	0.73	0.46	28.77
Si(OH) ₄	96.1149	–	–	–	1.00	96.11

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Table 3. The chemical compositions of model SSW76, NPIW, and their differences. For both water types we show concentrations in molar units and their contribution to mass-based salinities. The upper 9 species are conservative. Both SSW76 and NPIW have a chlorinity of 19 374 mg kg⁻¹, but chlorinity is not exactly the same as the concentration of Cl⁻ (Millero et al., 2008). The next 7 species form the carbonate system, followed by the two nutrients. We also list other parameters that can be used to specify the equilibria involved in the carbonate system. S_A , κ , S_{78} , and S_R are computed according to the formulas discussed in the text. The charge differences in the right-most column are indicated with two signs. The first represents the net change (increase or decrease), and the second whether these are positive or negative charges.

Species	SSW76		NPIW		NPIW-SSW76		$\mu\text{eq kg}^{-1}$
	mmol kg ⁻¹	mg kg ⁻¹	mmol kg ⁻¹	mg kg ⁻¹	mmol kg ⁻¹	mg kg ⁻¹	
Na ⁺	468.96335	10781.35913	468.96335	10781.35913	0.00000	0.00000	0.00
Mg ²⁺	52.81702	1283.71757	52.81702	1283.71757	0.00000	0.00000	0.00
Ca ²⁺	10.28205	412.08380	10.37705	415.89129	0.09500	3.80748	+ +190.00
K ⁺	10.20769	399.10324	10.20769	399.10324	0.00000	0.00000	0.00
Sr ²⁺	0.09066	7.94332	0.09066	7.94332	0.00000	0.00000	0.00
Cl ⁻	545.86954	19352.71293	545.86954	19352.71293	0.00000	0.00000	0.00
SO ₄ ²⁻	28.23526	2712.35228	28.23526	2712.35228	0.00000	0.00000	0.00
Br ⁻	0.84208	67.28578	0.84208	67.28578	0.00000	0.00000	0.00
F ⁻	0.06832	1.29805	0.06832	1.29805	0.00000	0.00000	0.00
HCO ₃ ⁻	1.90028	115.94926	2.25090	137.34304	0.35062	21.39378	+ -350.62
CO ₃ ²⁻	0.16285	9.77242	0.08222	4.93414	-0.08063	-4.83828	- -161.25
B(OH) ₃	0.34579	21.38143	0.38239	23.64422	0.03660	2.26279	0.00
B(OH) ₄ ⁻	0.06923	5.45779	0.03263	2.57262	-0.03660	-2.88517	- -36.60
CO ₂	0.01687	0.74233	0.04687	2.06284	0.03001	1.32051	0.00
OH ⁻	0.00480	0.08172	0.00205	0.03483	-0.00276	-0.04688	- -2.76
H ⁺	0.00001	0.00001	0.00002	0.00002	0.00001	0.00001	+ +0.01

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Table 3. Continued.

Species	SSW76		NPIW		NPIW-SSW76		
	mmol kg ⁻¹	mg kg ⁻¹	mmol kg ⁻¹	mg kg ⁻¹	mmol kg ⁻¹	mg kg ⁻¹	μeq kg ⁻¹
NO ₃ ⁻	0.00000	0.00000	0.04000	2.48020	0.04000	2.48020	+ -40.00
Si(OH) ₄	0.00000	0.00000	0.17000	16.33953	0.17000	16.33953	0.00
<i>T A</i>	2300.0 μeq kg ⁻¹		2450.0 μeq kg ⁻¹		150.0 μeq kg ⁻¹		
DIC	2080.0 μmol kg ⁻¹		2380.0 μmol kg ⁻¹		300.0 μmol kg ⁻¹		
pH _{TOT}	7.89892		7.52859		-0.37033		
<i>S_A</i>	35.17124 g kg ⁻¹		35.21175 g kg ⁻¹		δ <i>A</i> =0.04051 g kg ⁻¹		
<i>κ</i>	53064.8 μS cm ⁻¹		53073.1 μS cm ⁻¹		δ <i>κ</i> =8.324 μS cm ⁻¹		
<i>S₇₈</i>	35.00000		35.00618		δ <i>S₇₈</i> =0.00618		
<i>S_R</i>	35.16504		35.17125				

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Table 4. Composition C_R of artificial river water used by Millero (1984). Numbers have been adjusted to correct for typographical errors in Millero et al. (1976) and to agree best with stated values of both molar and mass concentrations in that paper, after rounding. TA is set by charge balance, with DIC carbonate ion concentrations computed from TA and pH using the low-salinity carbonate system parameterizations of Millero (1995) when $S_{78} < 5$.

Species	Concentration (mmol kg ⁻¹)
Ca ²⁺	0.3745
Mg ²⁺	0.1685
Na ⁺	0.2740
K ⁺	0.0590
SO ₄ ²⁻	0.1165
Cl ⁻	0.2200
NO ₃ ⁻	0.0160
HCO ₃ ⁻	0.9434
CO ₃ ²⁻	0.0031
CO ₂	0.0440
OH ⁻	0.0004
pH	7.60
TA	0.9500 meq kg ⁻¹
DIC	0.9905
S_A	0.1074 g kg ⁻¹

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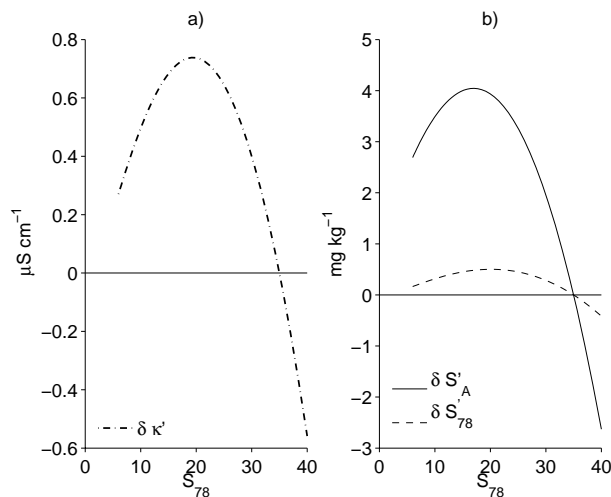


Fig. 1. Comparison between constant $f\text{CO}_2$ and constant fraction models for dilution of seawater. **(a)** Difference in conductivities. **(b)** Differences in practical and absolute salinity.

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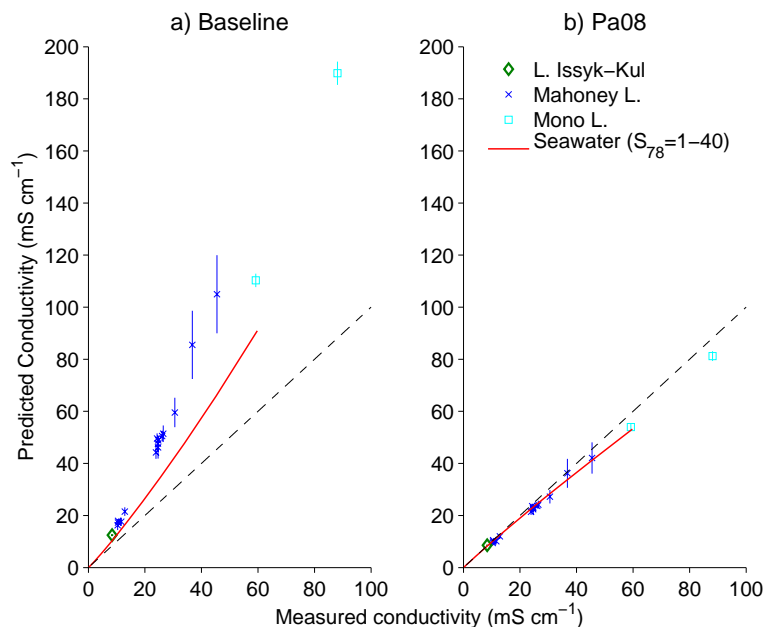


Fig. 2. Predicted versus measured κ at 25°C for saline lakes Mahoney (Hall and Northcote, 1986), Mono (Jellison et al., 1999), and Issyk-Kul (Vollmer et al., 2002), as well as for seawater. **(a)** Baseline predictions without ionic interactions. **(b)** Pa08 predictions that include ionic interactions. Vertical bars show uncertainty based on the computed charge imbalance in the published chemical composition used for predictions. Lake Issyk-Kul is a warm deep lake with roughly equal amounts of NaCl and MgSO₄, meromictic Mahoney Lake is dominated by NaSO₄, Mono Lake contains a Na–CO₃–Cl–SO₄ brine and seawater is primarily composed of NaCl.

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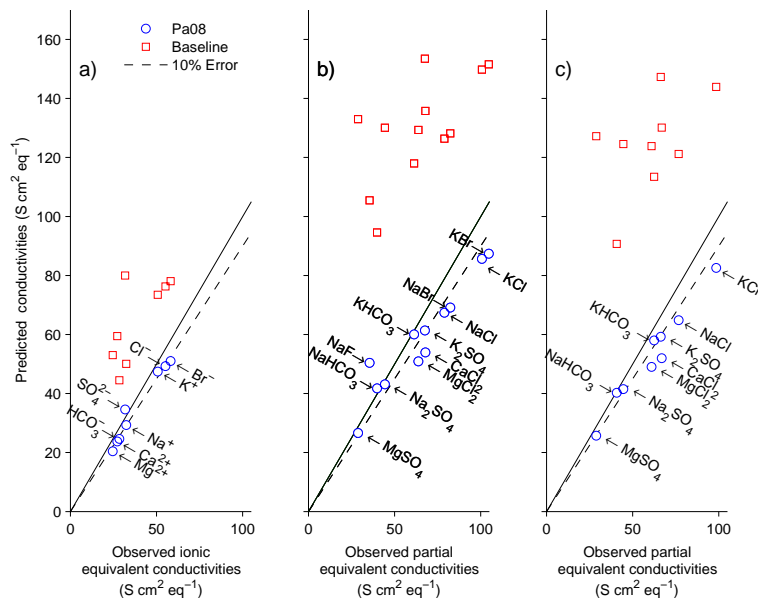


Fig. 3. Comparison between different Pa08 model-derived and measured parameters related to conductivity, for seawater. **(a)** Ionic equivalent conductivities in seawater of $S_{78}=38.38$ at 25°C . Original data from Poisson et al. (1979, Table 3). **(b)** Partial equivalent conductivities for various salts in seawater of $S_{78}=35.13$ at 25°C . Original data from Poisson et al. (1979, Table 4). **(c)** Partial equivalent conductivities for various salts in seawater of $S_{78}=35.04$ at 23°C . Original data from Connors and Weyl (1968, Table 4). Dashed line shows a relative error of -0.10 . Baseline predictions are made by ignoring all ionic interactions (i.e. using only infinite dilution equivalent conductivities). Pa08 results include relaxation/electrophoresis and ion pairing effects, with the former accounting for most of the reductions from baseline.

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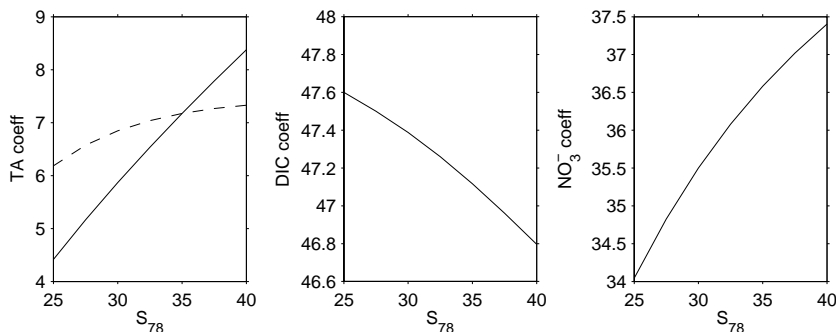


Fig. 4. Coefficients of the best fit equation $\delta S_A = aTA + bDIC + c[\text{NO}_3^-]$ to model predictions, as a function of salinity. **(a)** Coefficient a . Dashed line shows a best fit curve as a function $TA \times S_{78}/35$ rather than TA . **(b)** Coefficient b . **(c)** Coefficient c .

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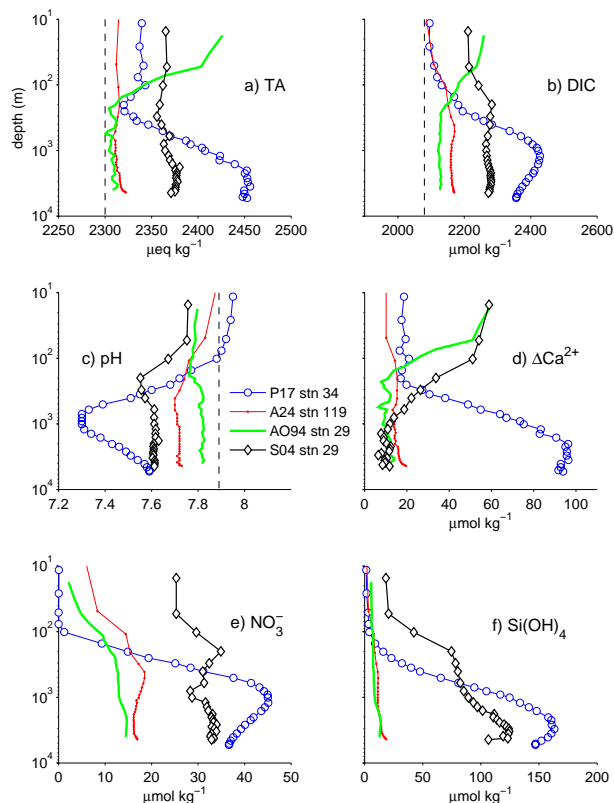


Fig. 5. Composition perturbations for example stations: North Pacific (WOCE line P17, station 34, 37.5° N, 135.0° W, 10 August 2001), North Atlantic (WOCE line A24, station 119, 52.73° N, 34.71° W, 22 June 1997) Arctic (AO94 station 29, 87.16° N, 160.71° E, 17 August 1994) and Southern Ocean (WOCE line S04, station 29, 62.02° S, 134.18° E, 9 January 1995). **(a)** TA for all profiles. **(b)** DIC . **(c)** pH on the Total scale. **(d)** Computed change ΔCa^{2+} **(e)** NO_3^- . **(f)** $Si(OH)_4$. Vertical dashed lines show values in SSW76.

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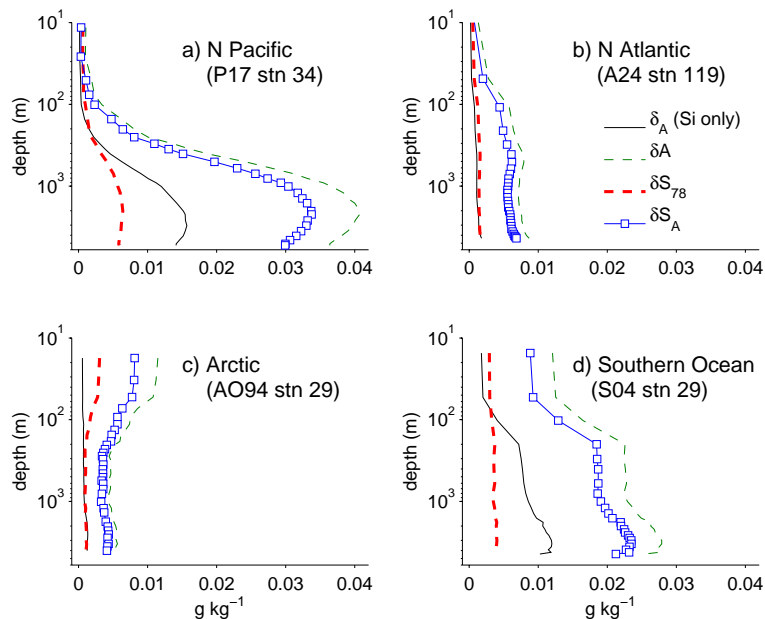


Fig. 6. Predicted corrections for measured water column profiles. Shown are the total fixed-conductivity correction δS_A , as well as the components of the fixed-chlorinity correction $\delta S_A^* = \delta A - \delta S_{78}$ (with $\delta S_A^* \approx \delta S_A$), and the component of the correction due to silicate alone, $\delta_A(\text{Si})$. **(a)** N. Pacific profile. **(b)** N. Atlantic profile. **(c)** Arctic profile. **(d)** Southern Ocean profile.

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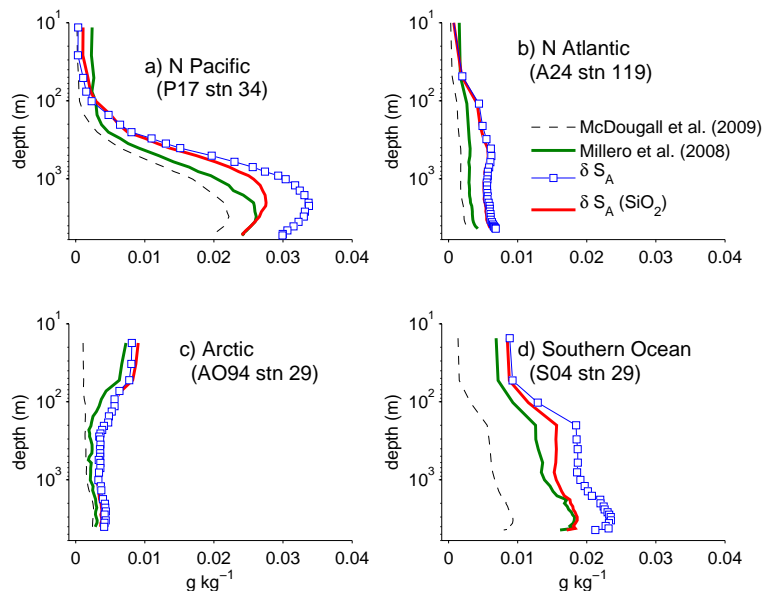


Fig. 7. Comparison between δS_A computed with the full conductivity model in this paper with the results of empirical formulas provided by Millero et al. (2008) and McDougall et al. (2009). The latter provides corrections as a function of ocean basin, latitude, and measured Si(OH)_4 . Also shown are calculations using a reduced mass for added Si. **(a)** North Pacific. **(b)** North Atlantic. **(c)** Arctic. **(d)** Southern Ocean.

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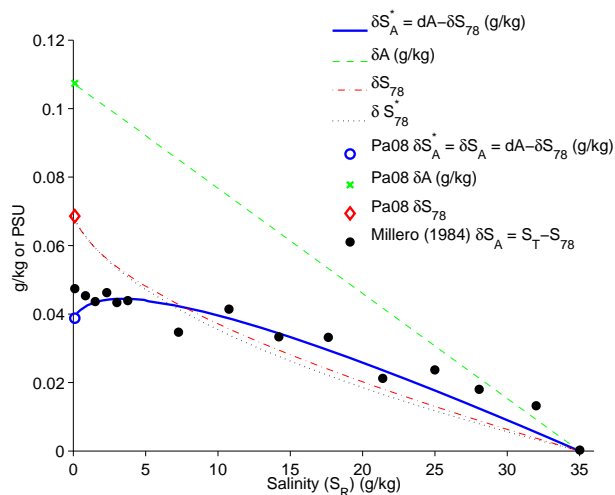


Fig. 8. Comparison between δS_A^* computed with the full perturbation model in this paper with the measurements of Millero (1984) in mixtures of SSW and artificial river water. Also shown are direct estimates δS_{78}^* using the Pa08 model, as well as limiting case estimates for pure river water.

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