Deep-Sea Research I 101 (2015) 71–79

Contents lists available at ScienceDirect

Deep-Sea Research I

journal homepage: www.elsevier.com/locate/dsri

The Absolute Salinity of seawater diluted by riverwater

Rich Pawlowicz

Department of Earth Ocean and Atmospheric Sciences, University of British Columbia, 6339 Stores Rd., Vancouver, B.C., Canada, V6T 1Z4

ARTICLE INFO

Article history:
Received 21 January 2015
Received in revised form
19 March 2015
Accepted 21 March 2015
Available online 2 April 2015

keywords:
Seawater
Electrical conductivity
Salinity
Density
TEOS-10

ABSTRACT

Seawater is often assumed to have a constant relative composition of dissolved matter, so that a measurement of one property (e.g., electrical conductivity) can be used with a suitable correlation equation to estimate other properties like density. However, small variations in the relative composition do occur, and the associated variation in seawater properties can be orders of magnitude larger than would be naively assumed from measurement precision. The new seawater standard TEOS-10 provides a mechanism to account for these compositional variations, and correction factors are provided suitable for measurements in the open ocean when composition changes occur due to specific biogeochemical processes. Here variations due to the addition of river salts are considered by combining numerical models for the conductivity, salinity, and density of arbitrary aqueous solutions with a global database of river chemistry. It is found that calculated densities in river diluted waters will typically be too low by 0.02–0.3 kg m^{-3}, but with significant spatial variability.

1. Introduction

Traditionally, the amount of dissolved inorganic matter in seawater, i.e., the salinity, has not been measured directly. Instead it was (and is) computed by measuring a related property such as the chlorinity, refractive index, or most typically electrical conductivity, and then relating that measurement to a numerical salinity using an empirical correlation equation incorporated into a standard. Salinity can then be used to calculate other properties, like density, using additional empirical correlation functions. All such procedures rely on the assumption that the relative chemical composition of seawater is effectively constant.

However, it has long been known that the relative chemical composition of seawater does vary slightly over global scales, affecting relationships between conductivity and salinity, and between salinity and density (Brewer and Bradshaw, 1975; Lewis and Perkin, 1978). If this is ignored, a “salinity” can be numerically determined with perfect accuracy as, for example, a Practical Salinity defined by the Practical Salinity Scale 1978 (PSS-78; UNESCO, 1981b but quantities like density, calculated using an equation of state that takes as an input this salinity, may have measurable errors. Using PSS-78 and the old EOS80 standard (UNESCO, 1981a) for density, these errors in the open ocean can be more than one order of magnitude larger than are implied by the precision and intercomparability to which present-day conductivity measurements are routinely made (Pawlowicz et al., 2011).

The new TEOS-10 seawater standard (IOC et al., 2010) provides a theoretical framework for incorporating the effects of these composition variations on calculations of seawater density through a correction factor (the so-called “salinity anomaly”, denoted δS_A) used when determining the TEOS-10 Absolute Salinity (S_A). With an appropriate δS_A the error in calculated quantities can be reduced to the error of the original laboratory measurements used in creating the equation of state.

There are several practical methods described in the TEOS-10 manual to find the appropriate value of δS_A needed to reduce field measurements, but all are valid only in the open ocean where variations arise from specific biogeochemical uptake and remineralization processes. None of these procedures should be applied in situations where the chemical composition may vary in other ways as a result of different processes. Such situations include measurements near hydrothermal vents, of water samples stored in glass bottles, of water fractionated by sea ice formation, in anoxic basins, or in coastal areas. Quantifying uncertainty in the practical application of TEOS-10 procedures, even in the open ocean, will require better knowledge of δS_A in these other situations.

A full investigation for biases in all thermodynamic properties in a coastal area has already been carried out for Baltic seawater, which is significantly diluted by inflow from many rivers (Feistel et al., 2010a). Conductivity/salinity/density measurements have also been carried out in the St. Lawrence estuary (Poisson, 1980; Millero, 1984), and simple calculations attempted for waters offshore from 4 different American rivers (Conners and Kester, 1974). Results from these limited-area studies suggest that δS_A in coastal waters can sometimes be much larger than in the open ocean.

E-mail address: rpawlowicz@eos.ubc.ca

http://dx.doi.org/10.1016/j.dsr.2015.03.006
0967-0637/

Here I attempt to globally characterize δS_A in oceanic areas where seawater is diluted by river waters. Since there are many rivers in the world, with many different chemical compositions, direct measurements on a global scale would be impractical. Instead I do so by combining the numerical composition/conductivity/density models used previously to understand open-ocean salinity anomalies (Pawlowicz, 2008, 2010; Pawlowicz et al., 2011) with a global database of river chemistry (Meybeck and Ragu, 1997).

2. Methods and data

2.1. Theoretical background: TEOS-10

As described by Wright et al. (2011), the definition of TEOS-10 Absolute Salinity S_A is designed so that the density ρ of a sample of any seawater with salinity S_A can be accurately calculated using

$$\rho = f_{TEOS-10}(S_A, t, p) \tag{1}$$

where $f_{TEOS-10}$ is a precisely specified function derived from the TEOS-10 Gibbs function of seawater (Feistel, 2008), t the temperature, and p the pressure. TEOS-10 Absolute Salinity is "Density Salinity". In addition, the numerical value of S_A can be linked to the chemical composition of a very particular seawater defined by the TEOS-10 Reference Composition (Millero et al., 2008a).

Currently the best physical realization of Reference Composition seawater is a certified reference solution called IAPSO Standard Seawater (SSW). To maintain worldwide intercalibration, SSW is acquired by researchers from a single source (Ocean Scientific International Ltd., UK), which is endorsed by the International Association for the Physical Sciences of the Ocean (IAPSO). Laboratory measurements of SSW properties are incorporated into $f_{TEOS-10}$. However, the definition of S_A under TEOS-10 also takes into account variations in relative chemical composition that occur in real seawaters, and this required resolving some important practical issues.

The first issue concerns the numerical value of Absolute Salinity in real seawaters. An alternative definition of salinity, known as the solution salinity S_a^{soln} according to TEOS-10 nomenclature (Wright et al., 2011; Pawlowicz et al., 2011), is essentially based on adding up the mass of solute in a seawater sample:

$$S_a^{soln} = \frac{1}{\rho}\sum_{i=1}^{N} M_i c_i \tag{2}$$

where there are N constituents with concentrations c_i and molar masses M_i. For seawater with Reference Composition, S_A is defined to be numerically identical to S_a^{soln}. However, for real seawaters with a slightly different composition, Eqs. (1) and (2) cannot both be satisfied with the same numerical value (Pawlowicz et al., 2011), and so TEOS-10 chooses to continue satisfying Eq. (1), implying that $S_A \neq S_a^{soln}$ in general. However, if S_a^{soln} is required, TEOS-10 provides conversion formulas.

The basic operational procedure outlined by TEOS-10 to include the effects of chemical composition variations is to first make a measurement of electrical conductivity in a water sample and compute the Reference Salinity S_R. Reference Salinity is the mass fraction of dissolved inorganic matter (i.e., solution salinity) in a seawater with TEOS-10 Reference Composition, which has the same conductivity as that of the sample. In practical terms this is done by computing the Practical Salinity S_P as defined by the Practical Salinity Scale 1978 (UNESCO, 1981b), which would now be considered a normalization for the effects of temperature and pressure, and multiplying it by a scale factor (Millero et al., 2008a):

$$S_R/(\mathrm{g\ kg^{-1}}) \equiv 35.16504/35 \times S_P. \tag{3}$$

Then, for real seawaters, a correction factor, the δS_A, is added:

$$S_A = S_R + \delta S_A \tag{4}$$

to find the Absolute Salinity that will satisfy Eq. (1) within the limits of measurement accuracy. Typically δS_A in the open ocean is in the range of -0.002 to $+0.03\ \mathrm{g\ kg^{-1}}$; decisions to include or ignore the δS_A correction will obviously depend on the accuracy required for a particular application.

Note that these steps need not be applied only for measurements in seawater. In fact they can also be modified (albeit with lower accuracy) for use in lakes and rivers, which contain small amounts of dissolved material and have a measurable electrical conductivity (Pawlowicz and Feistel, 2012).

The second issue is then the determination of δS_A. Since δS_A cannot be determined from the conductivity alone, TEOS-10 also provides several practical algorithms for numerically estimating the δS_A in the open ocean, where composition variations are driven primarily by biogeochemical processes (see IOC et al., 2010, Section A.4). The usual method is to 'look up' the value at the desired location/depth from a global climatological atlas (McDougall et al., 2012). This atlas is based on empirical correlations between a database of measured open-ocean salinity anomalies (determined by solving Eqs. (1), (3), and (4)) for δS_A from direct measurements of both density and conductivity), with co-located observations of nutrients, in combination with a global atlas of nutrients.

Alternatively, δS_A can be derived from a simple equation, fitted to results of a complex numerical model, that summarizes the effects of variations in total alkalinity (TA) and dissolved inorganic carbon (DIC) as well as additions of nutrients nitrate (NO_3^-) and silicic acid (mostly in the form of $Si(OH)_4$ at the pH of seawater; Duedall et al., 1976) on seawater conductivity and density directly (Pawlowicz et al., 2011):

$$\begin{aligned}\delta S_A/(\mathrm{mg\ kg^{-1}}) = (&55.6 \times (\mathrm{TA} - 2.300 \times S_P/35)\\ &+ 4.7 \times (\mathrm{DIC} - 2.080 \times S_P/35)\\ &+ 38.9 \times [NO_3^-]\\ &+ 50.7 \times [Si(OH)_4])/(\mathrm{mmol\ kg^{-1}})\end{aligned} \tag{5}$$

This requires ancillary measurements of the chemical concentrations of carbon and nutrient parameters. It is assumed that compensating variations in $[Ca^{2+}]$ occur to maintain charge balance (which would otherwise be broken with changes in NO_3^- and TA) and this assumption is built into the coefficients of Eq. (5).

Other more empirical formulas have also been proposed (e.g., Millero et al., 2008), based on regressions between measurements of salinity anomaly in different seawater samples with a variety of factors. These other formulas generally have fewer terms than Eq. (5) because they implicitly rely on correlations between the different parameters in Eq. (5) that occur in the real ocean, or because the sensitivity to some factors (like DIC) is small.

2.2. Numerical modelling of salinity anomalies

An aqueous solution containing specified concentrations of dissolved matter, i.e., with a known solution salinity S_a^{soln}, will have a given density and electrical conductivity, both of which will vary with temperature and pressure. The relationships between salinity, density, and electrical conductivity are known empirically to a very high degree of precision for SSW mixed with pure water. In order to investigate salinity anomalies in coastal areas, the relationships between salinity, density, and electrical conductivity in river waters, and mixtures of river and seawaters, must be determined. This is done here using numerical models for the properties of multi-component solutions.

The density of an aqueous solution containing a salt will be different from that of water. Crudely, ions and uncharged