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Ocean Science

Preface

An historical perspective on the development of the Thermodynamic Equation of Seawater – 2010

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This paper is dedicated to the memory of Daniel Gordon Wright (1952–2010), who contributed so much to all aspects of SCOR/IAPSO WG 127, the IAPWS Subcommittee on Seawater, this special issue, and TEOS-10.

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Abstract. Oceanography is concerned with understanding the mechanisms controlling the movement of seawater and its contents. A fundamental tool in this process is the characterization of the thermophysical properties of seawater as functions of measured temperature and electrical conductivity, the latter used as a proxy for the concentration of dissolved matter in seawater. For many years a collection of algorithms denoted the Equation of State 1980 (EOS-80) has been the internationally accepted standard for calculating such properties. However, modern measurement technology now allows routine observations of temperature and electrical conductivity to be made to at least one order of magnitude more accurately than the uncertainty in this standard.

Recently, a new standard has been developed, the Thermodynamical Equation of Seawater 2010 (TEOS-10). This new standard is thermodynamically consistent, valid over a wider range of temperature and salinity, and includes a mechanism to account for composition variations in seawater. Here we review the scientific development of this standard, and describe the literature involved in its development, which includes many of the articles in this special issue.

1 Introduction

Seawater is a fascinating, complex, and important fluid. Virtually every chemical element known to mankind is dissolved within it (Nozaki, 1997). Spatial changes in the concentrations of these elements, and in the temperature of the water, affect the water's density. These density changes lead to pressure gradients that drive the entire oceanic circulation, which, in turn, acts to redistribute these variations in temperature and solute concentration.

The density changes involved can be extremely small. To demonstrate this, it is important to first note that, rather than measuring density and solute concentrations directly, oceanographers use standardized procedures linking the characteristic physical properties of seawater to measurements of its temperature, as a proxy for the heat content, and its electrical conductivity, as a proxy for the solute concentrations. Oceanographers routinely make measurements of temperature and electrical conductivity to a precision of almost five significant figures, at depths of 1000s of metres, in order to estimate density changes accurately enough for meaningful analysis.

At this level of precision, the internationally accepted definition of temperature is still evolving (Fischer et al., 2011; BIPM, 2011). However, a widely accepted international standard for temperature does exist – the International Temperature Scale of 1990 (ITS-90, Preston-Thomas, 1990) – and the technical effort required in maintaining this standard occurs outside the oceanographic community. More

problematic is the fact that absolute measurements of electrical conductivity, traceable to the seven base units of the International System of Units (SI), can still not be made accurately enough to support the needs of oceanographers (Seitz et al., 2011). Physical oceanographers must then grapple with fundamental measurement issues in a way that does not occur in (and is not easily appreciated by) other areas of earth science.

However, these measurement issues themselves are not directly relevant to most ocean science, which is more concerned with understanding the mechanisms controlling the movement of water and its contents. Thus although operational procedures for making precise conductivity-based measurements are widely known and used (e.g., Hood et al., 2010), many of the scientific details involved in standardizing measurements are obscure and not well understood, except by a few specialists.

This special issue of Ocean Sciences contains a number of papers relating to modern developments in the scientific understanding of the properties of seawater, and the development of new and better procedures to describe these properties. Many of these papers were written by members of SCOR/IAPSO Working Group 127 on the Thermodynamics and Equation of State of Seawater, in the course of research which has culminated in the development of the new international standard for the properties of seawater: the Thermodynamic Equation of Seawater – 2010 (TEOS-10; IOC et al., 2010). This issue therefore encompasses a large part of the historical record of the development of this standard.

A critical component of TEOS-10 is the definition of a new salinity variable, the Absolute Salinity S_A. Absolute Salinity is a measure of the mass fraction of solute in seawater on the carefully defined Reference Composition Salinity Scale. Numerical values of S_A when expressed in units of grams per kilogram of seawater differ from numerical values assigned by previous definitions of salinity by about 0.5 % (i.e. in the third significant digit), so careful attention to the details of calculations and assigned nomenclature is necessary to prevent confusion. A scientifically important advance in TEOS-10 is that variations in the relative composition of seawater can now be accounted for explicitly. In addition, an important conceptual step has been taken: the definition of S_A is now separated from practical issues related to its measurement. This was not the case in previous definitions. With this step oceanographic procedures are now formally consistent with those of the rest of the scientific world and the modern view of a useful standard.

As electrical conductivity is and will remain for the forseeable future the most useful measurement technique for salinity determination, the currently existing logistical infrastructure associated with traditional Practical Salinity S_P measurements (PSS-78, UNESCO, 1981b) is adapted rather than replaced to support TEOS-10. Estimation of S_A using conductivity involves two steps. First, the measured conductivity is used to determine the Absolute Salinity of so-called Reference Composition Seawater by calculation of a Reference Salinity S_R. Then, a correction (the Salinity Anomaly δS_A) which accounts for the effects on conductivity of differences in the relative chemical composition is added:

$$S_A = S_R + \delta S_A \quad (1)$$

The Reference Salinity itself can be estimated by scaling the Practical Salinity:

$$S_R/(\mathrm{g\,kg^{-1}}) \equiv (35.16504/35) \times S_P \quad (2)$$

Additional information is needed to estimate δS_A; in the simplest case the geographic location and depth of the measurement can be used to obtain an estimate from a climatological atlas. However, other methods of obtaining δS_A also exist, and in theory at least other measurement techniques (e.g., direct density measurements) can also be used to estimate S_A independently of its conductivity.

The other scientifically important advance in TEOS-10 is that it allows for the calculation of all thermodynamic properties of seawater, including basic thermodynamic properties like the entropy and enthalpy which are central to "heat budgets", as well as the more familiar physical properties like density and sound speed. These properties are also calculated in a thermodynamically consistent way. That is, they satisfy theoretical interrelationships between different forms of energy and macroscopic system properties that were first derived in the 18th century. These interrelationships are central to many fields of science and engineering, but have not been easily accessible to oceanographers until now.

An apocryphal quotation often attributed to Otto von Bismarck is that "laws are like sausages, it is better not to see them being made" (Anon, 2011). Perhaps this is also true for international standards. However, this article is not a brief practical review of the TEOS-10 standard itself. Such information can be found on the website www.teos-10.org, including a 9 page primer entitled "What every oceanographer needs to know about TEOS-10", documentation of the software available ("Getting started with TEOS-10", 29 pp.) as well as the software itself, and the full 202 page manual that makes up the standard (IOC et al., 2010). Instead this article aims to provide a more detailed historical and personal perspective on the scientific process that motivated and accompanied the development of TEOS-10. A careful reader of the primary literature may notice apparent inconsistencies in the content of different papers. These unavoidably arose as features of the standard evolved in time (or sometimes seemingly appeared from nowhere). Providing a historical overview will allow for more efficient technical evaluation of TEOS-10 and further development in this important area. In addition, a description of the work contained in this special issue and its relationship to the working history of SCOR/IAPSO WG 127 is provided, as well as an outlook to problems that still await solutions beyond TEOS-10.

2 1964-1980: JPOTS and the development of EOS-80

Any attempt at evaluating TEOS-10 must begin with a consideration of the standards it replaced, which include the Practical Salinity Scale 1978 (PSS-78; UNESCO, 1981b), the International Equation of State of Seawater 1980 (EOS-80; UNESCO, 1981a), and a collection of algorithms for other important and useful properties of seawater gathered together and released in the form of FORTRAN computer codes (Fofonoff and Millard, 1983). For convenience, the entire grouping of PSS-78, EOS-80, the formulas for ancillary properties, and the code is sometimes loosely labelled as "EOS-80". Many details of the history behind these standards are provided by Lewis and Perkin (1978), Fofonoff (1985) and Millero (2010).

These standards arose at the end of a transition in physical oceanography. During the 1960s and 1970s traditional sampling techniques, requiring reversing thermometers for temperature measurements, and titration-based chemical analyses of water samples for salinity (so-called Chlorinity Salinity or Knudsen Salinity, with units of ppt), were being replaced by newer techniques implemented by electronic instrumentation. These new instruments could be lowered into the ocean or moored to make near-continuous measurements in space or time. The amount of data that could be acquired during a research expedition thus increased dramatically. Measurements were also being archived electronically so that comparison of observations made by different researchers from different institutions, at different times, were now becoming much easier. However, use of these new technologies raised many technical issues that needed to be solved. One important issue was that new methods for determining salinity and density had to be standardized, to supersede old methods first developed in the early part of the 20th century.

In pursuit of this goal, a large number of fundamental measurements were carried out by different researchers, many of which have not been repeated or updated since. These included highly precise estimates of the chemical composition of seawater, as well as its electrical conductivity, density, and other properties at different dilutions. In addition, an international working group (the UNESCO/SCOR/ICES/IAPSO Joint Panel on Oceanographic Tables and Standards, or JPOTS) was formed in 1964. JPOTS produced a number of standards, culminating in the EOS-80 group.

Crucially, PSS-78 defined a proxy for solute concentration denoted as the Practical Salinity. Practical Salinity is calculated using a specified function of measured temperature, pressure, and electrical conductivity (actually a dimensionless ratio of conductivity relative to the conductivity of a reference solution). Since it is based on a dimensionless ratio, Practical Salinity was also defined to be a dimensionless number. EOS-80 provided correlation equations for seawater properties based on its measured temperature, pressure, and Practical Salinity.

These new standards were largely based on empirical polynomial fits to laboratory measurements using particular batches of a reference material unique to oceanographers, so-called IAPSO Standard Seawater. As first suggested by Martin Knudsen at the ICES conference 1899 in Stockholm, Standard Seawater, obtained from near-surface waters in a particular region of the North Atlantic, processed, bottled, labelled, and globally distributed from a single source (originally from Copenhagen, then from the Institute of Ocean Sciences in Wormley, U.K, and from 1989 onwards by a commercial company, Ocean Scientific International Ltd., U.K.) was used for standardizing Chlorinity-Salinity titrations, and had been labelled with its Chlorinity (Knudsen, 1903; Jacobsen and Knudsen, 1940). Standard Seawater would henceforth be used for standardizing Practical Salinity measurements and would be labelled instead with its conductivity ratio and Practical Salinity.

The development of EOS-80 and the standardization of procedures using Standard Seawater was a great step forward in allowing reproducible measurements of seawater properties to be made. A choice was also made to ensure that the new Practical Salinity scale was (as much as possible) numerically continuous with older Chlorinity-Salinities. However, EOS-80 did not address several fundamental issues.

First, since the EOS-80 algorithms are based on measurements of Standard Seawater, they are not well-linked to the actual ocean. Standard Seawater is obtained from a particular part of the North Atlantic, but does undergo some processing before bottling and labelling. It was known even in the 1970s that the densities of real seawater could differ from their EOS-80 calculated values by as much as $0.020\,\mathrm{kg\,m^{-3}}$ in the open ocean (Lewis and Perkin, 1978), and that these differences were largest in the North Pacific because of the effects of added nutrients and inorganic carbon (Brewer and Bradshaw, 1975). Differences could be much larger in coastal areas (e.g., Millero, 1984).

However, it was also known that conductivity measurements partially compensated for these changes in relative composition, since the additional ions also increased conductivity (although not as much as the addition of the same mass of "sea salt"). Thus, even with these inaccuracies, conductivity was thought to be a better measure of the mass fraction of solute in "average seawater" than was the older Chlorinity titration.

It was further rationalized that the remaining errors varied over basin scales, so that their effect over the 100–1000 km scale of typical hydrographic surveys would likely be small, amounting to an offset which would have little effect on regional calculations of transports and circulation, based on gradients. Transport calculations from conductivity-temperature-depth (CTD) profiles were in any case fraught with difficulty because of the classical "level of no motion" problem.

In addition, the accuracy of good salinity measurements via Chlorinity titration was only about $\pm$ 0.02 ppt (equivalent

to a density change of ± 0.015 kg m^{-3}), and it was thought that use of conductivity would improve this only slightly to an equivalent of ± 0.01 ppt. Effects of compositional variations were thus at the extrapolated limit of measurement precision.

Finally, there was little reliable data at the time on carbon parameters in the ocean and methodological issues related to its measurement were still being debated. Thus although the concept of "correcting" salinities for composition variations was considered, it was not clear how this might be routinely accomplished, nor whether such corrections would have practical importance. The issue seemed intractable and was dropped (Dauphinee, 1980; Lewis, 1980).

The second shortcoming of EOS-80 was that no attempt had been made to quantify the fundamental thermodynamics of seawater. In the atmospheric sciences it had been known for at least 80 years that air was quite accurately described by ideal gas laws for which thermodynamic relationships between density, entropy, enthalpy, sound speed, and so on are easily derived. Simple formulas were available to determine potential temperature, which was first used in atmospheric studies by von Bezold (1888). Potential temperature removes the effects of pressure on temperature, but in addition it is simply related to the entropy and the density of an ideal gas. Entropy is a true measure of heat content and hence is of fundamental importance in understanding energy budgets. This simple relationship means that processes in the atmosphere that maintain potential temperature are also isentropic.

The concept of potential temperature was first applied to ocean studies by Helland-Hansen (1912). In seawater, potential temperature is useful to remove effects of pressure on temperature, but it is not easily related to density, entropy, or enthalpy. Also, processes that maintain potential temperature are not necessarily isentropic (similar problems arise with defining moist entropy in the atmosphere). There was no "ideal liquid" that could be used as a useful analytical model, and hence no easy way to estimate the entropy and enthalpy of seawater. Including entropy in the EOS-80 collection was intended (JPOTS, 1974) but never implemented.

In addition, although thermodynamic relationships can be used to derive certain physical properties from measurements of other properties, the collected algorithms of EOS-80 are thermodynamically inconsistent. A particular property, for example the entropy or the sound speed, can be derived in different ways, from different specified correlation equations, with different numerical results. Such problems become highly relevant in numerical situations involving differences where the leading digits cancel, such as in the computation of the buoyancy frequency in abyssal waters.

A theoretical approach that solved this problem had been known for more than a century. So-called fundamental equations of state or thermodynamic potentials can be constructed from which all equilibrium properties of a given substance can be consistently derived by mathematical manipulations alone (Gibbs, 1873). For seawater, this possibility had been studied theoretically (Fofonoff, 1962), but no attempt was made to derive such a potential function from the experimental data available at that time. Perhaps a thermodynamically consistent approach did not seem relevant to research aims being pursued at the time, or perhaps it was ignored because of the complexity of its construction process, or because of the high numerical effort required for its practical evaluation, at least with the common computation tools of that era. Traditionally, thermodynamics has never been part of the basic training of oceanographers.

For whatever reason, this elegant concept remained obscure in the oceanographic community. Even in atmospheric science, where thermodynamical concepts are more widely known, meteorological textbooks offer collections of separate correlation equations for the properties of humid air rather than a single thermodynamic potential function (Feistel et al., 2010d).

The third problem with EOS-80 is that the PSS-78 definition of salinity is intrinsically linked to very specific operational procedures. Since the same was true for previous salinity definitions it may not have been clear that this was an undesirable characteristic. A more modern view, which is intrinsic to virtually every other field of science, is that the definition of a unit should be separate from its operational implementation. One can think of the definition as being words on a piece of paper, which, when handed to someone else, allows them come up with a measurement from first principles (at least in theory). The operational implementations are then the specific techniques or physical artifacts that may be convenient to realize the definition. A set of instructions that allows the definition of a unit to be realized at the highest level of accuracy is now termed a *mise en pratique* in metrology (BIPM, 2008).

As an example of the problems that can arise from this confusion, consider titration methods. Although titrations with silver nitrate for the chloride ion are reproducible, the resulting Chlorinities do not in fact accurately measure chloride concentrations but are biased by the presence of bromine and iodine in seawater and subject to changes in the accepted values of the atomic weights, which for many elements are subject to some uncertainty due to variations in naturally occurring isotopic composition. Also, the scale factor by which Chlorinity is multiplied to get Chlorinity-Salinity was based on measurements, dating back to 1900, of the mass of solid residue left after seawater of known Chlorinity had been evaporated to dryness (Forch et al., 1902). However, it was known that certain constituents other than water were also evaporated during this process, so that the results underestimated the mass of material other than water in seawater.

To the extent that salinity was only an intermediate variable used in determining density these historical oddities were not particularly important drawbacks, but it did mean that Chlorinity-Salinities were not the best estimates of the mass fraction of solute in seawater, and that other measurement techniques could not necessarily replicate these values

for real seawaters. Attempting to move to a conductivity-based procedure, numerically continuous for at least some batches of Standard Seawater, did not solve these problems. If anything, it made the fundamental underpinnings of the measurements even more convoluted.

3 Developments from 1980-2006

Unfortunately, after the development of EOS-80, fundamental research in the metrological aspects of seawater languished. JPOTS published some additional tables and assisted in resolving some of the issues with measurements of dissolved inorganic carbon, but faded away by 1990. Researchers involved in EOS-80 found it difficult to obtain funding for further work on fundamental properties (F. J. Millero, personal communication). On the other hand, field instrumentation technology based on the new standards advanced rapidly, as did the potential for new discoveries that could come from coordinating large international observational programs using this instrumentation.

By the 1990s the World Ocean Circulation Experiment (WOCE), whose observational program was to consist of long, detailed hydrographic sections across entire ocean basins, could suggest (and attain) a best practice reproducibility of ± 0.002 for in-situ measurements of Practical Salinity (King et al., 2001). This implied that measurements were being made to about an order of magnitude more precision than could be theoretically understood. However, more data was also available: WOCE hydrography programs also included detailed measurements of carbon and nutrient parameters in seawater, a concern of yet another international program, the Joint Global Ocean Flux Study (JGOFS).

Once these data began to be available to the oceanographic community, efforts were made to quantitatively determine the circulation on global scales. The "level of no motion" problem, which traditionally had been the weakest part of transport estimates, was addressed theoretically by the beta-spiral and other inverse methods, and through technology, including satellite altimetry.

These observational and analytical efforts have now multiplied into a plethora of international programs attempting to address climate change issues progressing over time scales of decades to centuries. In addition, global high-resolution 'realistic' models of the ocean are now becoming more widely used. Issues of heat and salt conservation and budgets in both areas are extremely important but cannot be determined to the limits of measurement accuracy under EOS-80.

Although organized metrological research received scant attention, small amounts of research into seawater properties were still being pursued by individual researchers in different parts of the world. An attempt was made to start measuring density anomalies in different ocean basins (Millero, 2000) to quantify the problems arising from changes in the relative composition of seawater. A minor controversy in the underwater acoustics community pertained to questions about which of the existing sound speed equations were more accurate at high pressures (Dushaw et al., 1993). A method of enforcing thermodynamic consistency using a Gibbs function approach was developed (Feistel, 1993; Feistel and Hagen, 1995) by a suitable combination of EOS-80 with other thermal and chemical properties of seawater. Incorporation of a Helmholtz function for pure water developed by Wagner and Pruß (2002) led to an improved Gibbs function (Feistel, 2003). Thermodynamic concepts were also used to develop a proper treatment of energy budgets in the ocean (McDougall, 2003), and the Gibbs function approach was simplified for use in numerical models (McDougall et al., 2003).

Underlying this activity was the issue of Practical Salinity itself. The lack of units in the PSS-78 definition was confusing even to oceanographers, never mind non-specialists, leading to widespread but completely incorrect use of the "PSU" label as a sort of pseudo-unit (Millero, 1993). Numerical values were known to not accurately reflect the mass of dissolved matter in seawater, but were nevertheless used for that purpose. The dependence on conductivity was thought to be unhelpful for some purposes (Parsons, 1982). The lack of traceability to the SI meant uncertainty in long-term comparisons, with some workers suggesting consistent biases on the scale of 0.002 between measurements referenced to different batches of Standard Seawater (Kawano et al., 2006).

There was, however, no oceanographic community consensus that improvements to EOS-80 were needed.

4 2006-2011: IAPWS Subcommittee on Seawater and SCOR/IAPSO Working Group 127

In 2004, R. Feistel (a physicist with a background in thermodynamics, working as an oceanographer in the Baltic Sea), began a collaboration with the International Association for the Properties of Water and Steam (IAPWS). This organization, mainly concerned with developing standards for water and aqueous systems in industrial applications, was particularly interested in characterizing seawater properties for power plant cooling and desalination plants and had produced an international standard Helmholtz function for pure water (the IAPWS-95 standard). The collaboration first led to the 2006 IAPWS Release on a Gibbs function of ice, then to the 2008 IAPWS standard for the thermodynamic properties of seawater, and eventually to the 2010 formulation on humid air. The IAPWS Subcommittee on Seawater was also formally founded in 2008, under the chairmanship of Feistel.

Meanwhile, T. J. McDougall (a theoretical physical oceanographer with training in thermodynamics), realized that converting observational oceanographers into users of the theoretically sound Gibbs function approach would require some kind of international "blessing". He submitted a proposal to the Scientific Committee on Oceanic Research (SCOR) and the International Association for the Physical

Sciences of the Oceans (IAPSO) to form a working group under their auspices in order to more formally explore the possibilities of using Feistel's work to analyze ocean observations and to examine the possibilities of accounting for composition anomalies in seawater. The stated goal was merely to come up with recommendations in the form of a report, and to write some review papers on the matter. In 2005 SCOR and IAPSO jointly approved Working Group 127 on the Thermodynamics and Equation of State of Seawater.

There was considerable overlap in the work of WG 127 and the IAPWS Seawater Subcommittee. This meant that the results were scrutinized by, and benefited from the advice of, a larger scientific and technical community. As an example, the IAPWS had much experience in the process of producing international standards which could have legal standing. Also, for technical applications IAPWS was strongly interested in extending the ranges of validity in salinity and temperature of the resulting standards.

Membership of WG 127 followed SCOR's philosophy of encouraging memberships covering a variety of geographic regions and not being heavily weighted by any one country. In addition to Feistel (Germany) and McDougall (Australia), the group included chemical oceanographers (F. J. Millero, USA, and C.-T. A. Chen, Taiwan) with experience in the density anomaly problem and the development of the EOS-80 standard, a chemical modeller (G. M. Marion, USA) who could provide numerical calculations to explain and extend density and freezing point measurements, a hydrographer (B. A. King, UK) concerned with practical aspect of ocean measurements, and a numerical modeller (D. G. Wright, Canada) who had dealt with equations of state in intermediate complexity ocean models. P. Tremaine (Canada), IAPWS member and chemist with expertise in hydrothermal vents, was also associated with WG 127. In order to develop a firm metrological basis for the work the group also included a metrologist (P. Spitzer, Germany) who could provide expertise with aspects of standards and traceable measurements that were not really known in the oceanographic community. Later they were joined by D. Jackett (Australia, a computer programmer and mathematician), S. Seitz (Germany, another metrologist, specializing in electrolytic conductivity), R. Pawlowicz (Canada, an oceanographer with expertise in the theory of electrical conductivity), and P. Barker (Australia, another oceanographer) who, while not formally a member of the WG, contributed greatly to the software developed to implement the new standard.

SCOR/IAPSO WG 127, chaired by McDougall, had its first meeting in 2006 in Warnemünde near the Baltic Sea. The first task was to find a way to get rid of the endless controversy around the pseudo-unit "PSU" and let 'salinity' have mass fraction units and numerical values that actually reflected best available estimates for their true values. After long and intense discussions on the best way to proceed, this was achieved by the development of the Reference Composition and the Absolute Salinity (Millero et al., 2008).

In essence the salinity concept was formalized using a carefully defined artificial seawater, which would in practice be most easily realized as a physical artifact by Standard Seawater. The idea that salinity involves a mass of ions and neutral molecules in solution and not the mass of dissolved solids (a distinction that had been poorly understood and/or mostly ignored in the past) was implicit in this process, and led to the concept of Reference Composition Salinity. The Reference Composition Salinity is the mass fraction of the constituent inorganic ions and compounds in Reference Composition seawater, and can be calculated by summing up the molar concentrations of the constituents of Reference Composition Seawater, multiplied by their atomic weights.

Since the stoichiometry of dissolved substances in chemical equilibria (e.g., in the carbonate system) depends on temperature, pressure, and overall concentrations, this sum is computed only after bringing the seawater to a reference point with fixed temperature $t = 25°\mathrm{C}$ and pressure $p = 101325$ Pa, and removing or adding pure water until a measurement of Practical Salinity is exactly 35.000. At this point the calculated mass fraction of solute is 35.16504 g kg^{-1}, and the Absolute Salinity of the original seawater before the addition/removal of pure water is just this value, scaled by the dilution factor.

Since the mass fraction of solute in Reference Composition Seawater is precisely defined, it is then possible to scale Practical Salinity (S_P) measurements (retroactively considered to be measurements on the best physical realization of this Reference Composition after addition/removal of pure water, at different temperatures and pressures) to form a Reference Salinity (denoted by the symbol S_R), which is the best conductivity-based estimate of the Absolute Salinity of Reference Composition Seawater (Eq. 2). When applied to Standard Seawater, these numerical values may not be true estimates of the mass of solute, but instead lie on a scale (the Reference Composition Salinity Scale) defined to be as close as possible to these true values. This is similar to the case for temperatures, whose measurements according to ITS-90 are not necessarily true in a thermodynamic sense, but instead lie on a scale defined to be as close as possible to these true values.

Then, in order to account for composition changes in real seawaters, a correction factor of some sort is required. The eventual choice was to correct Reference Salinity for the composition variations that occur in real seawater by adding to it a Salinity Anomaly δS_A to more generally estimate the Absolute Salinity (Eq. 1). For Standard Seawater the best currently available estimate of δS_A is zero, although this may not necessarily be true in future if, for example, long-term variations are found to occur in the properties of Standard Seawater. For real seawater, δS_A is almost always non-zero (cf. Fig. 1), and some practical (but as it turned out incomplete) recommendations were made at that time about how δS_A should be defined.

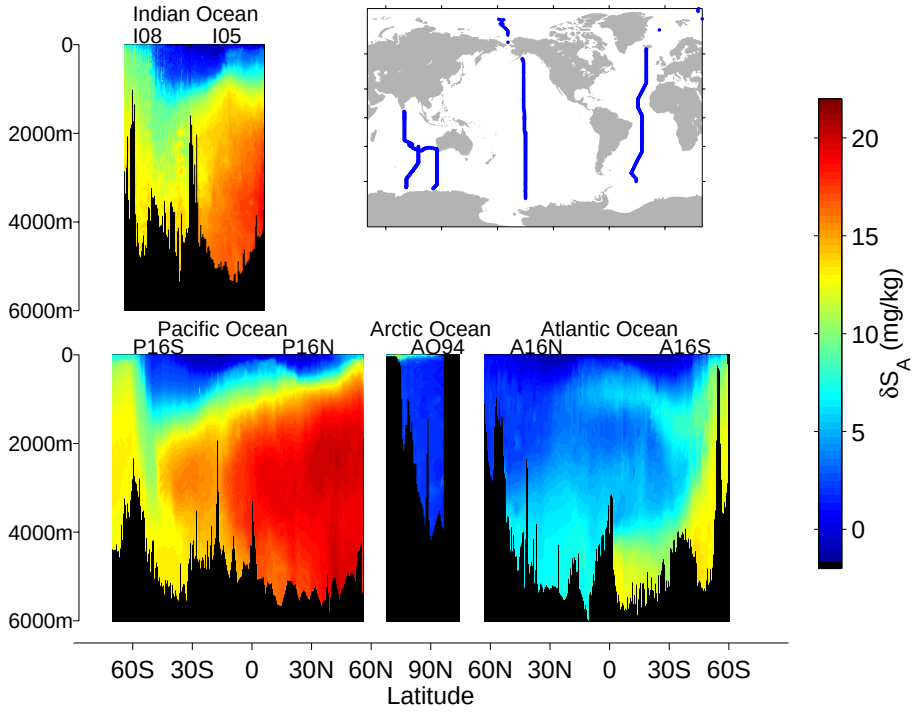

Fig. 1. Salinity anomalies δS_A for trans-oceanic hydrographic sections in different oceanic basins. Values are calculated by the numerical model of Pawlowicz et al., (2011) using archived observations of carbon parameters and nutrients along these sections. Data obtained from the CLIVAR and Carbon Hydrographic Data Office (cchdo.ucsd.edu).

The second task of the Working Group was to develop a consistent formulation of the thermodynamic properties of seawater. This new formulation (Feistel, 2008) has a firm theoretical grounding in principles of both thermodynamics and physical chemistry. It is valid in selected properties over the entire range of salinity from pure water to brines at the point of calcium carbonate precipitation. In addition, properties of ice and humid air (Feistel and Wagner, 2006; Feistel et al., 2010d) have also been formulated in the same way, so that the entire realm of oceanographers is now consistently described, including, e.g., the latent heats of melting and evaporation.

The first important product of this reformulation was a new heat content variable, the Conservative Temperature, which is a scaled potential enthalpy (McDougall, 2003). Loosely speaking, a potential variable is one whose value remains constant under pressure changes, whereas a conservative variable is one whose total amount in a sample is conserved during advection even when mixing occurs within the sample (IOC et al., 2010). Potential temperature accounts for the effects of pressure on in-situ temperatures, but does not account for the fact that the heat capacity of seawater varies by about 5 % over the full range of temperature and salinity. Thus the potential temperature of a mixture of two water parcels is not the average of the potential temperatures of the two original parcels. On the other hand, enthalpy is conserved under isobaric mixing, but not by changes in pressure.

Conservative Temperature combines the two properties. Although no measure of heat can ever be exactly conservative, since this would imply that no compression/expansion work (what is generally referred to as “useful work” in thermodynamics) could be produced by heat (for details see Tailleux (2012)), the nonconservative terms in evolution equations can be of different magnitudes for different heat variables. Conservative Temperature is in practice about two orders of magnitude more conservative than potential temperature (Graham and McDougall, 2012), and for the purposes of ocean modelling, the nonconservative production of potential enthalpy is an even smaller diabatic source of heating/cooling than viscous dissipation, and can be safely ignored in almost all circumstances.

An important next step was the decision (made at the 2nd WG meeting in 2007 in Reggio, Calabria) to formulate the new Thermodynamic Equation of Seawater in terms of the Absolute Salinity, rather than the traditional Practical Salinity. This was partly because the contortions of PSS-78, familiar to oceanographers, were less satisfying to the metrologists and engineers in the IAPWS. However, once this step was taken, it became clear (over beers at the 3rd meeting in 2008 at Goetz near Berlin, Germany) that cutting the direct link between conductivity and the definition of salinity then provided a way forward in developing SI traceability using

direct density measurements. Although this promising approach is still in its preliminary stages, the reformulation in terms of Absolute Salinities should make it possible to create an SI-traceable link without changing routine operational procedures (Seitz et al., 2011).

The second important outcome of the 2007 WG meeting was the realization that only by coming up with a practical algorithm for the salinity anomaly δS_A could oceanographers be convinced that a change in longstanding procedures was necessary and desirable. The addition of measurements in the Indian, South Pacific, and Southern Oceans in 2007 and 2008 resulted in a database of about 800 density anomaly measurements from 100 stations in all basins of the global ocean except the Arctic. By regressing these anomalies onto silicic acid concentrations (as a proxy for the complete composition anomaly arising from biogeochemical processes) and dividing by the haline contraction coefficient, basin-dependent correlations for salinity anomalies were obtained. These were then extended through the whole ocean using a global silicic acid climatology (McDougall et al., 2009). The result was a kind of look-up table for the Salinity Anomaly with some extra complications in the vicinity of the Baltic, the isthmus of Panama and other places where different oceans meet.

Note that modifying the salinity argument to the Gibbs function for real seawaters with a non-zero δS_A, rather than correcting all of the thermodynamic properties separately, trivially ensures the thermodynamic consistency of the results. Although the McDougall et al. (2009) algorithm defines δS_A solely to improve density estimates, thermodynamic consistency may even improve the accuracy of properties other than density. Attempts were made to verify this hypothesis by modelling and making measurements of Baltic seawater (Feistel et al., 2010b,a). Results show that errors introduced by the composition anomaly in the Baltic are generally small and exceed measurement uncertainty only for conductivity, density, and at the detection limit, sound speed.

Although the procedures used to develop the McDougall et al. (2009) algorithm were purely empirical, the result was a practical algorithm that could be used on a routine basis. Salinity anomalies can be as large at $0.02\,\mathrm{g\,kg^{-1}}$, an order of magnitude larger than the precision to which conductivity measurements are now made (Fig. 1). Initial calculations suggest that including Salinity Anomalies in calculations changes global meridional density gradients below 1000 m by more than 2 % for 58 % of the world ocean, and by more than 10 % for 60 % of the North Pacific.

With a separation between the definition of salinity and its operational determination, the thermodynamics now handled properly, and with a workable solution developed to address composition variations, the WG realized that it was now possible to develop a new standard that would be a significant improvement over EOS-80. Several aspects of this problem were released as IAPWS-approved formulations in 2008. The IOC and IAPSO also became very interested in the possibility of improving EOS-80 and began urging the WG to go beyond their mandate and develop a new standard to be formally approved in 2009. The 3rd WG meeting in 2008 was then heavily concerned with making plans for this process.

At this point McDougall and the WG began writing the "TEOS-10 manual" (IOC et al., 2010), which would comprehensively outline all aspects of the new procedures, in a single place, and could be formally adopted as an international standard in the oceanographic community. In early 2009 the IOC distributed a 105-page version of the manual and a link to a dedicated web site containing version 1 of software (written by Jackett) to governmental and academic ocean scientists in 142 countries, via each country's official IOC representative, to solicit reviews as part of a formal adoption process.

However, four important issues still remained. First, was the whole process too complicated? The EOS-80 density equation relied on polynomial functions with 41 coefficients specified to about 6 significant digits, whereas the new standard included many more coefficients, specified to 17 significant digits. A reduced-complexity model was therefore developed over the purely oceanographic regions of interest.

Also, EOS-80 consisted of less than a dozen mathematical functions, not overly difficult to program. In contrast, TEOS-10 currently consists of hundreds of functions as it attempts to unify the treatment of every thermodynamic property and derived quantity in current usage. To address this issue comprehensive attempts were made to create software libraries implementing the entire suite of useful features developed, and to distribute them via a web site (www.teos-10.org).

In fact, a great deal of code was written during the course of the WG, albeit in a slightly haphazard way. Beginning in 2006, the extended Sea-Ice-Air (SIA) library implementing the thermodynamic potentials of liquid water, ice, water vapour, seawater and humid air as well as numerous properties derived thereof, in total 680 functions, was first coded in Visual Basic by Feistel and translated to FORTRAN 90 by Wright (Feistel et al., 2010c; Wright et al., 2010). The code additionally included extended automated cross checks between the languages specifically developed and written together with J. Reissmann. In 2008, Jackett implemented the algorithms for the calculation of Absolute Salinity in FORTRAN. Then, between 2009 and 2011, the Gibbs-SeaWater (GSW) library, a collection of routines tailored for oceanographic use, was implemented in Matlab (a commercial software package in widespread use by physical oceanographers) and FORTRAN by Barker and McDougall. Currently, implementations in C and Python are also being developed.

Second, although the overall plan looked clear and reasonable from a theoretical viewpoint and would result in significant improvements in density gradient estimates, it was clear that the increase in the types of salinity available (e.g., Practical, Reference, Absolute, Chlorinity) could result in chaos in archives (and in the minds of oceanographers), especially as it would not always be clear which type of salinity was in

fact submitted. Should Reference Salinity be archived? How to ensure that submissions were properly handled?

Fortunately, precedent was available. The practice of archiving in-situ temperature but publishing and analyzing potential temperature suggested that a strategy of continuing to archive in-situ temperature and Practical Salinity (as a "quasi-measured" temperature- and pressure-normalized conductivity) but publishing and analyzing Conservative Temperature and Absolute Salinity would be completely workable. The nomenclature issue was temporarily put aside.

Third, there remained at this point a nagging feeling in the WG that aspects of electrical conductivity, at the heart of Practical Salinity determination, had not really been scrutinized or understood. Attempts to improve the traceability of electrical conductivity back to the 7 fundamental parameters of the International System of Units (SI) had only shown that the scientific needs of oceanographers still outstripped, by about one order of magnitude, the ingenuity and expertise of metrologists in attempting to make absolute measurements of conductivity (Seitz et al., 2010, 2011).

Finally, there was also the important question about how density anomalies and composition anomalies were actually related in theory. This question in particular was the subject of robust and unresolved discussion at the 3rd WG meeting! At the time Absolute Salinity was thought of as representing the mass of solute (in any seawater, Standard, Reference Composition, or otherwise), under a long-standing heuristic that suggested thermodynamic properties were a function of the solute mass and not dependent on the solute composition. The procedure of correcting the Reference Salinity S_R obtained from a conductivity measurement by adding δS_A anomalies estimated from measurements of density anomalies was believed to be more correct than simply correcting density itself, because it was a shortcoming of the conductivity/salinity relationship that was largely to blame for the anomaly. Biogeochemical processes add material to seawater which is inherently less conductive than "sea salt". However, the anomaly itself was only being calculated by assuming that the increase in solute had the same effect on density as a similar mass of added "sea salt". There was no independent way of investigating this assumption.

Fortunately, the final pieces of the puzzle were solved when a comprehensive theoretical analysis of seawater conductivity/composition and density/composition relationships was developed in the context of open ocean biogeochemistry (Pawlowicz, 2010; Pawlowicz et al., 2011; Wright et al., 2011). This work was an important (but previously unforeseen) outcome of the 4th WG meeting in 2009 at Arnhem, The Netherlands, that came about when Pawlowicz (then considering some limnological problems, since the oceanographic problem seemed "solved") and the WG became aware of each other in 2008.

With this theoretical understanding, as well as quantitative estimates of the limitations of different definitions of salinity, came the realization (perhaps obvious in retrospect) that no single definition of salinity could be useful for all purposes. Instead it would be necessary to understand the distinctions between at least 4 different types of absolute salinity (many more are possible, and even in the WG discussions sometimes became bogged down in confusion until a systematic nomenclature, described by Wright et al. (2011) was developed). This is because no single definition can capture all of the implications of independently changing the concentrations of a number of the constituents of seawater. Some changes affect density more than conductivity, and some the reverse. In either case, similar mass fraction changes of different chemical composition can affect density, conductivity (and perhaps other properties) sometimes more than and sometimes less than the effects arising from an equivalent change in the mass fraction of "sea salt". These changes are on the order of 0.1 %, small in absolute terms, but they have measurable consequences and are large enough to have practical significance in ocean circulation research.

Since density is the property of primary interest in geophysical fluid dynamics, it was decided that the Absolute Salinity of real seawater should be defined to be the mass fraction salinity (on the Reference Composition Scale) of Reference Composition Seawater with the same density as that of the sample being measured at a specified temperature and pressure (Wright et al., 2011). The density of the two waters will differ at other temperatures and pressures, but the differences are well within typical measurement errors. This definition of Absolute Salinity is numerically identical to Reference Salinity for Reference Composition Seawater, but for other seawaters generally differs from it by δS_A (Eq. 1), which now has a well-defined meaning.

There is another direct analogy here to long-standing procedures in atmospheric science. Small amounts of water vapour affect the density of air, but these changes can be incorporated in the definition of a "virtual temperature" for moist air. This is the temperature of a parcel of dry air with the same density as that of the moist parcel. Here small changes in the composition of seawater are incorporated into a "virtual salinity", which in TEOS-10 is called Absolute Salinity.

At this point it also became necessary to make explicit the notion that capitalization of particular names (like the Absolute Salinity) in TEOS-10 implied very specific definitions, and was necessary to distinguish these concepts from more generic versions that might be applied in other contexts. For example, numerical estimates of the the mass fraction of solute in lakes or brines (found, e.g., by summing up the constituents in a full chemical analysis) may be denoted absolute salinities, but would likely be numerically different from their TEOS-10 Absolute Salinity.

In time it is anticipated that further extensions to the TEOS-10 definitions and procedures can be formalized to account for such situations. Of particular interest to oceanographers would be an extension to coastal areas and marginal seas, where the composition changes arising from

the addition of river salts, and their effects on conductivity and density, may differ from those that occur due to open ocean biogeochemical processes. At present a relatively simple approximation for these areas is included in the δS_A algorithm of McDougall et al. (2009), but in future more accurate algorithms may be developed.

Other absolute salinity variables in seawater have other purposes. If one is interested in the mass of solute itself, then the proper salinity variable is the Solution Salinity, which is the absolute salinity of Reference Composition Seawater with the same mass of solute. It can be estimated by adding a different correction factor to the Reference Salinity. If one is interested in a conservative tracer, then the effects of non-conservative biogeochemical processes must be accounted for. The Preformed Salinity is the salinity that would result if all of the effects of biogeochemical processes were subtracted from a sample of seawater. Preformed Salinity is then a conservative tracer of solute in ocean circulation, and the correct choice for the kinematic parts of ocean general circulation models.

Of course, none of these definitions stand alone and workable methods to convert from one to another have also been developed (Pawlowicz et al., 2011). Uses of these methods all depend on additional measurements to quantify the composition anomaly. At present, conversion factors are available using either estimates of the density anomaly from direct density measurements, or from measurements of carbon and nutrient parameters with concentrations of calcium modified to maintain charge balance (appropriate in open-ocean situations). Developing procedures in other situations is largely limited by the lack of knowledge about the actual composition changes that might be expected.

These final developments were added to the manual (IOC et al., 2010), which, under the name Thermodynamic Equation of Seawater 2010 (TEOS-10) has now been accepted by the Intergovernmental Oceanographic Commission and the International Union of Geodesy and Geophysics as the official international standard for the properties of seawater.

Finally, in the course of developing the work described above, WG 127 also considered and (mostly) solved a large number of detailed technical issues that could affect the viability and future use of this standard. These are described in the last publication of Dan Wright (Wright et al., 2011) who had become a close friend to these authors and whose unfortunate and untimely death in the summer of 2010 has deeply affected the members of the Group. As a glance at the publications list of the WG in this special issue suggests, Dan was heavily involved in almost all aspects of the WG and his insight was greatly appreciated.

5 The future of seawater

Is this work finished? WG 127 was deliberately created with a short and finite lifetime, but much work still remains. Far from exhausting the list of topics planned to be addressed in the original terms of reference for WG 127, not only are there still areas virtually untouched, but a long list of new topics has appeared.

Traceability to the SI is an important issue both for the long-term ability of oceanographers to address climate change issues and for integration into the rest of the world's scientific community. This will also involve a more comprehensive examination of the accuracy of TEOS-10. The true composition of the major constituents of seawater, and their relationship to ocean biogeochemical processes on shelves, in marginal seas, and in other areas remains to be fully explored. Ocean acidification by rising atmospheric CO_2 levels and its effects on composition and pH values is not yet sufficiently understood. More measurements of density anomalies are needed in the centers and at the edges of different basins. Still little-known are issues related to the solubility of gases and their effects on density, which must be scrutinized as part of any evolution to SI traceability. Studies in these areas will lead to improvements in the δS_A algorithms.

In addition to these technical details, new advances and improvements in fundamental understanding of ocean processes, facilitated by TEOS-10, are also anticipated. By using the new heat and salinity variables provided by TEOS-10, ocean circulation processes can be diagnosed with much greater accuracy. Also, the importance of large-scale feedbacks of biogeochemical processes into the global ocean circulation (by modifying density fields) can now be explored.

6 The special issue

As should now be clear, a large number of journal articles were written by members of WG 127. This special issue was initially conceived as a conference proceedings from the 2008 International Conference on the Properties of Water and Steam (Berlin), which was attended by many members of the WG. However the open-source nature of the journal has meant that it has become a repository of much of the technical detail that was required to underpin the new standard. Work could be formally described and circulated for discussion relatively quickly, but could then be modified to take into account comments and later work before a final version was prepared. As the history outlined above attempts to show, the new standard evolved in time. Some aspects of the discussion in earlier papers in particular are superseded by later work.

A number of papers are concerned with extending the original Gibbs function formulation for seawater to sea ice and moist air in a consistent way. The extension to fluid water and ice was addressed by Feistel et al. (2008) and to moist air by Feistel et al. (2010d). Such developments are required to ensure the mutual consistency of the thermodynamic descriptions of the liquid and gas phases, for instance, by ensuring that the chemical potentials for two different phases

are equal at thermodynamic equilibrium. This is because the Gibbs function for each different property requires the fixing of a number of arbitrary constants, the values of which are not fully independent of each other. This fact may not necessarily be recognized when thermodynamic formulations are developed independently of each other. Such mutually consistent formulations can be used, for instance, to evaluate the salinity dependence of the saturation water vapour pressure of moist air in thermodynamic equilibrium with seawater.

Note that the formulation of moist air considered by Feistel et al. (2010d) is based on the most accurate available data compiled by the IAPWS and does not assume moist air to behave as a perfect gas. As a result, the description achieved is significantly more involved than descriptions usually found in the atmospheric and meteorological literature, which are traditionally based on a number of mutually inconsistent, although usually much simpler, correlation formulae.

In developing thermodynamic formulations, a key issue is determining the range of validity in (temperature, salinity, pressure) space, and in assessing the accuracy of the formula in different regions of this space. The paper by Marion et al. (2009) discusses the effect of the precipitation of calcium carbonates in setting validity bounds at high salinities, the problem being that the precipitation of calcium carbonate modifies the relative composition of the different constituents of seawater.

In addition to the above, papers by Safarov et al. (2009) and Millero and Huang (2009, 2010) report on new experimental data that go significantly beyond the usual range of temperature and pressure encountered in the oceans, but which are relevant for desalination studies.

Because the different thermodynamic formulations described above have been developed to achieve the highest possible degree of accuracy consistent with the precision of available data, the numerical implementation of dedicated routines to evaluate such properties requires special care and some degree of numerical expertise. As discussed above, this motivated WG 127 to undertake a significant effort to develop an extensive library of routines for which the theoretical basis was described by Feistel et al. (2010c) while the documentation of all routines was described by Wright et al. (2010).

The issue of SI traceability of the oceanic salinity measurements will become extremely important in understanding long-term variations in oceanic salinity. Seitz et al. (2011) discusses the general issue of measuring salinity from the metrology viewpoint, and how consistency and traceability with the international system of units can be achieved.

A number of papers are concerned with the issue of composition variations in real seawater and their effects on conductivity/salinity/density relationships. A fundamental part of the new TEOS-10 standard is a practical algorithm to estimate the salinity anomaly δS_A. An approach based more-or-less on an empirically determined look-up table is described by McDougall et al. (2009). There are some significant changes in the content of the discussion and the final published paper; these relate to the way in which anomalies are handled in the coastal limit of low salinity.

Pawlowicz (2010) and Pawlowicz et al. (2011) seek to provide a theoretical framework for the anomaly problem, based on principles of physical chemistry and an understanding of the composition variations in real seawater, to gain insights into the empirical approach undertaken by McDougall et al. (2009). The first paper describes a numerical model that can predict conductivity changes arising from specified composition anomalies, and the second describes a combined conductivity/density model. Model calculations can replicate the available database of density measurements in different ocean basins. This provides a verification of the measurements and also implies a degree of reliability in the models which can then be used to explore the effects of arbitrary compositional variations. Simple formulas are developed to calculate the salinity anomalies from measurements of carbon parameters and nutrients in open-ocean regions.

While Absolute Salinity is designed by construction to yield the correct value of density, it remains to be verified that it is also able to accurately predict the values of all other thermodynamic properties, such as entropy or the speed of sound, when used as the salinity argument of the TEOS-10 Gibbs functions in cases of variable composition. The paper by Feistel et al. (2010a) is one of the first to address this issue, in the particular context of composition anomalies pertaining to the Baltic sea, whose properties are documented in Feistel et al. (2010b). In order to evaluate the thermodynamic properties for a wide range of temperature and salinity, a theoretical approach based on the use of the FREZCHEM model was used.

One important conclusion is that while Absolute Salinity appears to yields reasonable predictions for a number of thermodynamic properties in the Baltic, this may not be true for all of them. Note that the earliest definitions of salinity had some strange features that resulted from the use of relatively fresh seawater samples from the Baltic in their analyses so it is particularly satisfying to be able to provide a modern perspective on one of the oldest issues in oceanography.

Theoretical investigations into seawater properties are also concerned with the essential nonlinearity of the equation of state. Tailleux (2009) seeks to understand some of the implications of these nonlinearities for our understanding of the concept of mixing efficiency, which is a central quantity in the study of turbulent mixing in stratified fluids. Until now, the mixing efficiency had been primarily studied and defined for a Boussinesq fluid with a linear equation of state. In this case three standard but distinct definitions of mixing efficiency can be used which all give the same numerical value for a turbulent mixing event associated with shear flow instability. However, the values may become radically different for other types of mixing events, or when the nonlinearities of the equation of state are retained. Tailleux (2009) establishes that defining mixing efficiency as the ratio of the

available potential energy dissipation rate over the turbulent kinetic energy dissipation rate provides least sensitivity to the nonlinearities of the equation of state.

Finally, many of the technical details developed in the above papers were synthesized and extended into a practical discussion of the nature of TEOS-10 by Wright et al. (2011). This paper then is probably the most useful starting point in any comprehensive attempt to understand the scientific basis of TEOS-10 and to develop practical applications.

7 Perspective

The historical progression described above illustrates the way in which an important oceanographic standard was developed. It was not at all clear that WG 127 would have a successful outcome, nor were the eventual results exactly as originally envisaged. There were many uncertainties at every stage, and a certain degree of retroactive correction as more work was done. McDougall summarized the process as: "we were often feeling around in the dark for a solution. This was true of the meetings, and especially so of the out-of session emails. So there was always a sense of the work being true research, not just turning a handle (which a lot of oceanography has become these days). This also meant that sometimes I felt the whole edifice could perhaps collapse in a heap. But thankfully, we always found a sensible solution as each pesky issue raised its ugly head."

Many of these solutions required a great deal of intellectual discussion, both during meetings and between them, with emails being generated and answered "around the clock" as members in different time zones began and finished work. However, members of WG 127 (including the authors) remember this as some of the most intense, exciting, and productive work of their careers. The impressive efficiency and the extremely productive meetings were even more surprising since most of the members were meeting each other face to face for the first time.

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References

Anon: http://en.wikiquote.org/wiki/Otto_von_Bismarck, 2011.

BIPM: Report of the 97th meeting of the CIPM, Bureau international des poids et mesures, October 2008, Pavillon de Breteuil, Sevres, http://www.bipm.org/utils/en/pdf/CIPM2008-EN.pdf, 2008.

BIPM: Resolutions adopted by the General Conference on Weights and Measures (24th meeting), Paris, 17–21 October 2011, http://www.bipm.org/en/convention/cgpm/resolutions.html, 2011.

Brewer, P. G. and Bradshaw, A.: The effect of the non-ideal composition of seawater on salinity and density, J. Mar. Res., 33, 157–175, 1975.

Dauphinee, T. M.: Introduction to the Special Issue on the Practical Salinity Scale 1978, IEEE J. Oceanic Eng., OE-5, 1–2, 1980.

Dushaw, B. D., Worcester, P. F., Cornuelle, B. D., and Howe, B. M.: On equations for the speed of sound in seawater, J. Acoust. Soc. Am., 94, 255–275, 1993.

Feistel, R.: Equilibrium thermodynamics of seawater revisited, Prog. Oceanogr., 31, 101–179, 1993.

Feistel, R.: A new extended Gibbs thermodynamic potential of seawater, Prog. Oceanogr., 58, 43–114, 2003.

Feistel, R.: A Gibbs Function for Seawater Thermodynamics for -6 to 80°C and Salinity up to 120 g kg^{-1}, Deep Sea Res. Pt. I, 55, 1619–1671, 2008.

Feistel, R. and Hagen, E.: On the GIBBS thermodynamic potential of seawater, Prog. Oceanogr., 36, 249–327, 1995.

Feistel, R. and Wagner, W.: A new equation of state for H_2O ice Ih, J. Phys. Chem. Ref. Data, 35, 1021–1047, 2006.

Feistel, R., Wright, D. G., Miyagawa, K., Harvey, A. H., Hruby, J., Jackett, D. R., McDougall, T. J., and Wagner, W.: Mutually consistent thermodynamic potentials for fluid water, ice and seawater: a new standard for oceanography, Ocean Sci., 4, 275–291, doi:10.5194/os-4-275-2008, 2008.

Feistel, R., Marion, G. M., Pawlowicz, R., and Wright, D. G.: Thermophysical property anomalies of Baltic seawater, Ocean Sci., 6, 949–981, doi:10.5194/os-6-949-2010, 2010a.

Feistel, R., Weinreben, S., Wolf, H., Seitz, S., Spitzer, P., Adel, B., Nausch, G., Schneider, B., and Wright, D. G.: Density and Absolute Salinity of the Baltic Sea 2006-2009, Ocean Sci., 6, 3–24, doi:10.5194/os-6-3-2010, 2010b.

Feistel, R., Weinreben, S., Wolf, H., Seitz, S., Spitzer, P., Adel, B., Nausch, G., Schneider, B., and Wright, D. G.: Density and Absolute Salinity of the Baltic Sea 2006-2009, Ocean Sci., 6, 3–24, doi:10.5194/os-6-3-2010, 2010c.

Feistel, R., Wright, D. G., Kretzschmar, H.-J., Hagen, E., Herrmann, S., and Span, R.: Thermodynamic properties of sea air, Ocean Sci., 6, 91–141, doi:10.5194/os-6-91-2010, 2010.

Fischer, J., de Podesta, M., Hill, K. D., Moldover, M., Pitre, L., Rusby, R., Steur, P., Tamura, O., White, R., and Wolber, L.: Present Estimates of the Differences Between Thermodynamic Temperatures and the ITS-90, Int. J. Thermophys., 32, 12–25, doi:10.1007/s10765-011-0922-1, 2011.

Fofonoff, N. P.: Physical properties of sea-water, in: The Sea, edited by: Hill, M. N., 3–30, Wiley, New York, 1962.

Fofonoff, N. P.: Physical Properties of Seawater: A New Salinity Scale and Equation of State for Seawater, J. Geophys. Res., 90, 3332–3342, 1985.

Fofonoff, N. P. and Millard, R. C.: Algorithms for the computation of fundamental properties of seawater, Unesco Technical Papers in Marine Science 44, Paris, 1983.

Forch, C., Knudsen, M., and Sørensen, S. P. L.: Berichte über die Konstantenbestimmungen zur Aufstellung der hydrographischen Tabellen, D. Kgl. Danske Vidensk. Selsk. Skrifter 6. Raekke, naturvidensk. og mathem. Afd. XII, 1, Bianco Lunos Bogtr., Copenhagen, 1902.

Gibbs, J. W.: Graphical methods in the thermodynamics of fluids, Trans. Connecticut Acad. Arts and Sci., 2, 309–342, 1873.

Graham, F. S. and McDougall, T. J.: Quantifying the non-

conservative production of Conservative Temperature, potential temperature and entropy, submitted to J. Phys. Oceanogr., 2012.

Helland-Hansen, B.: The Ocean Waters, Internat. Rev. Hydrobiol. Hydrograph., Hydrog. Supp. Ser. 1 No. 2, 1912.

Hood, E. M., Sabine, C. L., and Sloyan, B. M., eds.: The GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and Guidelines, IOCCP Report Number 14, ICPO Publication Series Number 143, available at: http://www.go-ship.org/HydroMan.html, 2010.

IOC, SCOR, and IAPSO: The international thermodynamic equation of seawater - 2010: Calculation and use of thermodynamic properties, Manual and Guides No. 56, Intergovernmental Oceanographic Commission, UNESCO (English), available from: http://www.TEOS-10.org, 2010.

Jacobsen, J. P. and Knudsen, M.: Urnormal 1937 or Primary Standard Sea-Water 1937, Publication scientifique no. 7, International Association of Physical Oceanography, 1940.

JPOTS: Sixth report of the joint panel on oceanographic tables and standards. Kiel, 24–26 January 1973, Unesco technical papers in marine science, Paris, 1974.

Kawano, T., Aoyama, M., Joyce, T., Uchida, H., Takatsuki, Y., and Fukasawa, M.: The Latest batch-to-batch Difference Table of Standard Seawater and Its Application to the WOCE Onetime Sections, J. Oceanography, 62, 777–792, 2006.

King, B. A., Firing, E., and Joyce, T. M.: Shipboard Observations during WOCE, in: Ocean Circulation and Climate, International Geophysics Series Vol 77, p. 715, Academic Press, San Diego, 2001.

Knudsen, M.: On the standard-water used in the hydrographical research until July 1903, Publications de circonstance no. 2, Conseil Permanent International pour l'Exploration de la Mer, Copenhagen, 1903.

Lewis, E. L.: The Practical Salinity Scale 1978 and Its Antecendents, IEEE J. Oceanic Eng., OS-5, 3–8, 1980.

Lewis, E. L. and Perkin, R. G.: Salinity: Its definition and Calculation, J. Geophys. Res., 83, 466–478, 1978.

Marion, G. M., Millero, F. J., and Feistel, R.: Precipitation of solid phase calcium carbonates and their effect on application of seawater $S_A - T - P$ models, Ocean Sci., 5, 285–291, doi:10.5194/os-5-285-2009, 2009.

McDougall, T. J.: Potential enthalpy: a conservative oceanic variable for evaluating heat content and heat fluxes, J. Phys. Oceanogr., 33, 945–963, 2003.

McDougall, T. J., Jackett, D. R., Wright, D. G., and Feistel, R.: Accurate and computationally efficient algorithms for the potential temperature and density of seawater, J. Atmos. Ocean. Tech., 20, 730–741, 2003.

McDougall, T. J., Jackett, D. R., and Millero, F. J.: An algorithm for estimating Absolute Salinity in the global ocean, Ocean Sci. Discuss., 6, 215–242, doi:10.5194/osd-6-215-2009, 2009.

Millero, F. J.: The conductivity-density-salinity-chlorinity relationships for estuarine waters, Limnol. Oceanog., 29, 1317–1321, 1984.

Millero, F. J.: What is PSU?, Oceanography, 6(3), 67, 1993.

Millero, F. J.: Effect of changes in the composition of seawater on the density-salinity relationship, Deep Sea Res. Pt. I, 47, 1583–1590, 2000.

Millero, F. J.: History of the Equation of State of Seawater, Oceanography, 23(3), 18–33, 2010.

Millero, F. J. and Huang, F.: The density of seawater as a function of salinity (5 to 70 g kg-1) and temperature (273.15 to 363.15 K), Ocean Sci., 5, 91–100, doi:10.5194/os-5-91-2009, 2009.

Millero, F. J. and Huang, F.: Corrigendum to "The density of seawater as a function of salinity (5 to 70 g kg-1) and temperature (273.15 to 363.15 K)" published in Ocean Sci., 5, 91-100, 2009, Ocean Sci., 6, 379–379, doi:10.5194/os-6-379-2010, 2010.

Millero, F. J., Feistel, R., Wright, D. G., and McDougall, T. J.: The composition of Standard Seawater and the definition of the Reference-Composition Salinity Scale, Deep Sea Res. Pt. 1, 55, 50–72, 2008.

Nozaki, Y.: A fresh look at element distribution in the North Pacific Ocean, EOS, Trans. Amer. Geophys. Union, 78, 221–221, doi:10.1029/97EO00148, 1997.

Parsons, T. R.: The New Physical Definition of Salinity – Biologists Beware, Limnol. Oceanog., 27, 384–385, 1982.

Pawlowicz, R.: A model for predicting changes in the electrical conductivity, practical salinity, and absolute salinity of seawater due to variations in relative chemical composition, Ocean Sci., 6, 361–378, doi:10.5194/os-6-361-2010, 2010.

Pawlowicz, R., Wright, D. G., and Millero, F. J.: The effects of biogeochemical processes on oceanic conductivity/salinity/density relationships and the characterization of real seawater, Ocean Sci., 7, 363–387, doi:10.5194/os-7-363-2011, 2011.

Preston-Thomas, H.: The International Temperature Scale of 1990 (ITS-90), Metrologia, 27, 3–10, 1990.

Safarov, J., Millero, F., Feistel, R., Heintz, A., and Hassel, E.: Thermodynamic properties of standard seawater: extensions to high temperatures and pressures, Ocean Sci., 5, 235–246, doi:10.5194/os-5-235-2009, 2009.

Seitz, S., Spitzer, P., and Brown, R. J. C.: CCQM-P111 study on traceable determination of Practical Salinity and mass fraction of major seawater components, Accred. Qual. Assur., 15, 9–17, doi:10.1007/s00769-009-0578-8, 2010.

Seitz, S., Feistel, R., Wright, D. G., Weinreben, S., Spitzer, P., and De Biévre, P.: Metrological traceability of oceanographic salinity measurement results, Ocean Sci., 7, 45–62, doi:10.5194/os-7-45-2011, 2011.

Tailleux, R.: Understanding mixing efficiency in the oceans: do the nonlinearities of the equation of state for seawater matter?, Ocean Sci., 5, 271–283, doi:10.5194/os-5-271-2009, 2009.

Tailleux, R.: Thermoydnamics/Dynamics coupling in weakly compressible turbulent stratified fluids, ISRN Thermodynamics, p. in press, 2012.

UNESCO: Background papers and supporting data on the International Equation of State of Seawater 1980, Unesco Technical Papers in Marine Science 38, Paris, 1981a.

UNESCO: Background papers and supporting data on the Practical Salinity Scale 1978, Unesco Technical Papers in Marine Science 37, Paris, 1981b.

von Bezold, W.: Zur Thermodynamik der Atmosphaere. Zweite Mittheilung. Potentielle Temperatur. Verticaler Temperaturgradient. Zusammengesetzte Convection, Sitz. ber. Königl. Preuss. Akad. Wiss. Berlin, 46, 1189–1206, available at: http://bibliothek.bbaw.de/bibliothek-digital/digitalequellen/schriften/anzeige/index_html?band=10-sitz/1888-2\&seite:int=530, 1888.

Wagner, W. and Pruß, A.: The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for

General and Scientific Use, J. Phys. Chem. Ref. Data, 31, 387–535, 2002.

Wright, D. G., Feistel, R., Reissmann, J. H., Miyagawa, K., Jackett, D. R., Wagner, W., Overhoff, U., Guder, C., Feistel, A., and Marion, G. M.: Numerical implementation and oceanographic application of the thermodynamic potentials of liquid water, water vapour, ice, seawater and humid air - Part 2: The library routines, Ocean Sci., 6, 695–718, doi:10.5194/os-6-695-2010, 2010.

Wright, D. G., Pawlowicz, R., McDougall, T. J., Feistel, R., and Marion, G. M.: Absolute Salinity, "Density Salinity" and the Reference-Composition Salinity Scale: present and future use in the seawater standard TEOS-10, Ocean Sci., 7, 1–26, doi:10.5194/os-7-1-2011, 2011.