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Metrological challenges for measurements of key climatological observables: Oceanic salinity and pH, and atmospheric humidity. Part 1: Overview

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Abstract

Water in its three ambient phases plays the central thermodynamic role in the terrestrial climate system. Clouds control Earth's radiation balance, atmospheric water vapour is the strongest "greenhouse" gas, and non-equilibrium relative humidity at the air-sea interface drives evaporation and latent heat export from the ocean. On climatic time scales, melting ice caps and regional deviations of the hydrological cycle result in changes of seawater salinity, which in turn may modify the global circulation of the oceans and their ability to store heat and to buffer anthropogenically produced carbon dioxide. In this paper, together with three companion articles, we examine the climatologically relevant quantities ocean salinity, seawater pH and atmospheric relative humidity, noting fundamental deficiencies in the definitions of those key observables, and their lack of secure foundation on the International System of Units, the SI. The metrological histories of those three quantities are reviewed, problems with their current definitions and measurement practices are analysed, and options for future improvements are discussed in

conjunction with the recent seawater standard TEOS-10. It is concluded that the International Bureau of Weights and Measures, BIPM, in cooperation with the International Association for the Properties of Water and Steam, IAPWS, along with other international organisations and institutions, can make significant contributions by developing and recommending state-of-the-art solutions for these long standing metrological problems in climatology.

So wäre es zu wünschen, daß man zukünftig bei der Bestimmung ... immer von denselben Voraussetzungen ausgeht, oder jedenfalls daß die Grundlage des angewandten Verfahrens scharf pointiert wird.

[It is desirable that future estimates ... be always based on the same assumptions, or at least that the method applied be precisely described.]

S.P.L. Sörensen, S. Palitzsch, 1910

1. Introduction

Climate research is a special scientific task that inherently requires close world-wide cooperation over many human generations. Observational data, be they measured directly or derived from equations that transform the original input values, need to be rigorously defined, consistent and comparable between groups that work at distant locations or times. The impossibility of repeating real-time climatological measurements largely prevents correcting erratic or suspicious readings made in the past. Data measured today will likely be exploited in the future and should be unambiguous and reliable to the highest standards currently available. The preferred and most advanced metrological basis to be employed is the International System of Units, the SI (BIPM, 2006). The requisite traceability to the SI of environmental measurement results was only gradually established in recent years, and in several fields this traceability still poses a serious challenge (BIPM, 2010), as will also be emphasised in this paper and its companions. Solving these metrological problems in geosciences demands joint efforts of international organisations and institutions that develop and implement definitions, equations and measurement standards based on the SI.

Water in its three ambient phases is the unrivalled key substance in the complex dynamic terrestrial climate system. Water vapour in the atmosphere accounts for 50 – 60 % of the terrestrial greenhouse effect, in contrast to 20 – 25 % due to carbon dioxide, CO₂ (Trenberth et al., 2007; Schmidt et al., 2010). Water in the atmosphere not only controls the Earth's radiation balance but also the oceanic export of latent heat and entropy as well as the formation and distribution of clouds (Baumgartner and Reichel, 1975; Clement et al., 2009; Dessler, 2010; Feistel and Ebeling, 2011; Wells, 2012; Hellmuth et al., 2013; Tollefsen, 2012; Fasullo and Trenberth, 2012); the latter may contribute another 10 – 25 % to greenhouse warming (Lacis et al., 2010; Schmidt et al., 2010). Melting polar glaciers raise the sea level and influence the surface salinity distribution, and in turn may affect the large-scale vertical and horizontal circulations in the oceans which continuously store, release or displace huge amounts of heat and dissolved gases (Peixoto and Oort, 1992; Reid and Valdés, 2011; Rayner et al., 2011; Barker et al., 2011; Marotzke, 2012; Stocker, 2013; Otto-Bliesner et al., 2014; Schmidt et al., 2014; Böhm et al., 2015). Trends in global distributions of humidity, latent heat flux, evaporation and precipitation are closely

connected with small but precisely measurable systematic shifts and anomalies in sea-surface salinities (Boyer et al., 2005; Stott et al., 2008; Durack and Wijffels, 2010; Durack et al., 2012, 2013; Pierce et al., 2012). Seawater is the largest buffer for anthropogenically produced CO₂, a fact that highlights the risk of ocean acidification and potential damage to the marine ecosystem (Caldeira and Wickett, 2003; Raven et al., 2005; Marion et al., 2009; Kerr, 2010; Le Quéré, 2010; Le Quéré et al., 2014). Seawater pH is an important parameter associated with the distribution of inorganic carbon in the ocean.

It is evident from climatology and geosciences that atmospheric relative humidity, ocean salinity and seawater pH are key parameters for observing, modelling and analysing the increasing effects of global warming on ecosystems and society. However, despite their widespread use and relevance, the metrological underpinning of these parameters is inadequate, relies on century-old provisional concepts, lacks traceability to the SI, or suffers from ambiguities and deficiencies of definitions, conventions and measurement techniques. The recent introduction of the international standard TEOS-10, the Thermodynamic Equation of Seawater 2010 (IOC et al., 2010), has raised new awareness of these long standing and increasingly urgent problems, and has at the same time offered new perspectives for overcoming them.

The definition of relative humidity stands out from that of salinity and pH in that a widely accepted and authorised definition, clearly traceable to the SI, and acting as a *de facto* standard, has been established and promulgated by the WMO¹ since 1950. Nevertheless, the definition does not cover the full range of conditions possible under both industrial and extreme natural conditions, and a number of non-standard definitions continue to propagate. The challenge is to provide a definition of relative humidity with a sound thermodynamic basis consistent with the WMO definition yet covering the full range.

TEOS-10 was adopted by the IOC² in 2009 (UNESCO, 2009) for oceanography with respect to thermodynamic properties of seawater and ice, and by the IUGG³ in 2011 (IUGG, 2011) for marine sciences by a resolution that also recommends the use of the TEOS-10 equation for humid air. While TEOS-10 supersedes the previous oceanographic Equation of State of 1980 (EOS-80, see Unesco, 1981), its relation to atmospheric standard equations recommended by JCOMM⁴ and WMO (2008) is left unsettled (JCOMM, 2014). The formulation and successful international adoption of TEOS-10 was the result of close cooperation between the SCOR⁵/IAPSO⁶ Working Group 127 and IAPWS⁷ in the years 2006–2011, until WG 127 was disbanded in accordance with the rules governing SCOR/IAPSO Working Groups (Pawlowicz et al., 2012). In order to address metrological problems beyond TEOS-10, the standing Joint Committee on the Properties of Seawater, JCS, was established by SCOR, IAPSO and IAPWS in 2012. In this context, the plan for this position paper arose during meetings held at the BIPM⁸ at Sèvres in August 2011 and February

¹WMO: World Meteorological Organization, <http://www.wmo.int>

²IOC: Intergovernmental Oceanographic Commission of Unesco, <http://ioc-unesco.org>

³IUGG: International Union of Geodesy and Geophysics, <http://www.iugg.org>

⁴JCOMM: Joint Technical Commission for Oceanography and Marine Meteorology, <http://www.jcomm.info/>

⁵SCOR: Scientific Committee on Oceanic Research, <http://www.scor-int.org/>

⁶IAPSO: International Association for the Physical Sciences of the Oceans, <http://iapso.iugg.org/>

⁷IAPWS: International Association for the Properties of Water and Steam, <http://www.iapws.org>

2012, and became definite during a joint meeting of JCS with representatives of CIPM⁹-CCT¹⁰ and CIPM-CCQM¹¹ at the 16th International Conference on the Properties of Water and Steam in Greenwich, London, UK, in September 2013 (IAPWS, 2013; Feistel, 2013; Hellmuth et al., 2014; Pawlowicz et al., 2014). Under the umbrella of JCS, cooperation commenced between the IAPWS, the international standards developing organisation for properties of water and aqueous systems, and the BIPM, the organisation that ensures and promotes the global comparability of measurements and provides the coherent International System of units (SI), as defined by the CIPM and described by BIPM (2006). The BIPM-IAPWS cooperation was confirmed at the 2012 and 2014 meetings of CCQM and CCT (BIPM, 2012, 2014).

The recent standard for the thermodynamic properties of seawater, TEOS-10, is introduced in the next section. Sections 3, 4 and 5, respectively, briefly introduce the metrological challenges of ocean salinity, seawater pH and atmospheric relative humidity which are then analysed in greater depth in the subsequent Parts 2, 3 and 4, respectively, of this series of articles. Those companion papers review the scientific histories of definition and measurement of seawater salinity, seawater pH and atmospheric relative humidity, explain the key roles of those quantities in the climate system, consider the problems of their current definitions and measurement techniques, and provide options for future improvements. In Appendices A, B and C in the digital supplement of this paper, for easy reference, some relevant thermodynamic definitions and properties of chemical potentials, activities and fugacities are summarised from a metrological perspective. Based on TEOS-10, Appendix D in the supplement provides an example for an axiomatic approach to define humidity quantities in a mutually consistent manner.

The authors of the present series of articles are specialists in the different fields of research and technology involved; they are active in several National Metrological Institutes (NMIs) as well as in national and international organisations and institutions such as ASHRAE¹², BIPM, IAPSO, IAPWS, IUPAC¹³, JCOMM, OSIL¹⁴, SCOR or WMO. Despite this, it is understood that the perspectives and opinions expressed in these papers do not necessarily reflect official policies of those organisations.

2. Thermodynamic Equation of Seawater – 2010 (TEOS-10)

The need for accurate, consistent and comprehensive descriptions of the thermodynamic properties of seawater and its equilibria in contact with ice and humid air led to the development of the new oceanographic standard TEOS-10, the Thermodynamic Equation of Seawater 2010 (IOC et al., 2010). At the core of TEOS-10 are four empirical thermodynamic potentials, officially adopted as IAPWS formulations,

⁸BIPM: International Bureau for Weights and Measures, <http://www.bipm.org/en/about-us/>

⁹CIPM: Comité International des Poids et Mesures, <http://www.bipm.org/en/committees/cipm/>

¹⁰CCT: Consultative Committee on Thermometry, <http://www.bipm.org/en/committees/cc/cct/>

¹¹CCQM: Consultative Committee for Amount of Substance, <http://www.bipm.org/en/committees/cc/ccqm/>

¹²ASHRAE: American Society of Heating, Refrigerating and Air-Conditioning Engineers, <http://www.ashrae.org/>

¹³IUPAC: International Union of Pure and Applied Chemistry, <http://www.iupac.org>

¹⁴OSIL: Ocean Scientific International Ltd., <http://www.osil.co.uk>

- i. the specific Helmholtz energy of pure fluid water, $f^F(T, \rho)$, as a function of ITS-90 temperature, T , and mass density, ρ , commonly known as the IAPWS-95 formulation (IAPWS, 2014; Wagner and Pruß, 2002),
- ii. the specific Gibbs energy of hexagonal ice I, $g^{\text{Ih}}(T, p)$, as a function of temperature and pressure, p (IAPWS, 2009b; Feistel and Wagner, 2006),
- iii. the specific Gibbs energy of IAPSO Standard Seawater, $g^{\text{SW}}(S_A, T, p)$, as a function of Absolute Salinity, S_A , temperature and pressure (IAPWS, 2008; Feistel, 2008), and
- iv. the specific Helmholtz energy of humid air, $f^{\text{AV}}(A, T, \rho)$, as a function of dry-air mass fraction, A , temperature and mass density (IAPWS, 2010; Feistel et al., 2010a).

By design, the identity $f^{\text{AV}}(0, T, \rho) \equiv f^F(T, \rho)$ holds for humid air in the limiting case of air-free water vapour, and similarly $g^{\text{SW}}(0, T, p) \equiv f^F(T, \rho) + p/\rho$ is obeyed in the zero-salinity limit of pure liquid water. The four thermodynamic potentials of TEOS-10 therefore satisfy axiomatic conditions of *completeness*, *consistency* and *independence*. Here, completeness means that all thermodynamic properties of the pure phases, their phase equilibria and composites can be computed from algebraic combinations of partial derivatives of the potentials (Feistel et al. 2008, 2010b; IOC et al., 2010). Consistency means the impossibility of deriving from the potentials two different results for the same quantity. Finally, independence excludes the possibility of deriving the same quantity alternatively from different parts of the four potentials. This rigorous axiomatic approach distinguishes TEOS-10 from earlier collections of empirical correlations for thermodynamic properties of aqueous geophysical systems, such as those recommended by JPOTS¹⁵ in the context of the 1980 Equation of State of Seawater, EOS-80 (Unesco 1981, 1983; Millero, 2010; Pawlowicz et al., 2012), or those recommended by WMO (2008) for the atmosphere.

A rigorous axiomatic approach has many advantages. Special thermodynamic quantities such as fugacity coefficients or enhancement factors of humid air (WMO, 2008; Feistel, 2012) are sometimes introduced in textbooks on a merely empirical basis in terms of selected correlation equations. In contrast, as a consequence of consistency, independence and completeness, not only can such quantities be computed from TEOS-10 (or its improved successors) in a way that is consistent with virtually any other measured thermodynamic property of the related substances, such quantities can also be defined unambiguously in terms of the corresponding thermodynamic potentials and their independent variables, see Appendix D in the digital supplement. Such a uniform method of formally defining and representing all thermodynamic properties with respect to a minimum common set of basic functions may avoid confusion, may more easily permit identification and quantification of differences between seemingly equivalent quantities such as various alternative available definitions of relative humidity, and may establish solid thermodynamic links between quantities that were originally introduced separately and independently, such as correlations for the heat capacity and for the sublimation pressure of ice.

¹⁵JPOTS: Unesco/SCOR/ICES/IAPSO Joint Panel on Oceanographic Tables and Standards (until 1990, Pawlowicz et al., 2012)

TEOS-10 is also highly accurate. For example, within their common ranges of validity, TEOS-10 is consistent within mutual uncertainties with the CIPM-2001 equation for the density of liquid water (Tanaka et al., 2001; IAPWS, 2009c; Harvey et al., 2009) and with the CIPM-2007 equation for the density of humid air (Picard et al., 2008), which are recommended for metrology by the International Committee for Weights and Measures (CIPM).

However, the advantages of TEOS-10 over other collections of equations are not without some computational cost. For convenience of use, easier numerical implementation, and increased computation speed, IAPWS has released tailored “secondary” correlation equations for selected properties that are consistent (within small tolerances) with the four “primary” potential functions of TEOS-10 but are not independent of the latter. Those fits to data points computed from the original equations may possess smaller ranges of validity, or larger uncertainties, or may be expressed in terms of more convenient independent variables. Available are, for example, a Gibbs function of liquid water for oceanographic use (IAPWS, 2009a; Feistel, 2003), a description of water properties at pressures in the vicinity of 0.1 MPa (IAPWS, 2011a; Pátek et al., 2009), and simple equations for the melting and sublimation curves of pure ice in the p - T diagram (IAPWS, 2011b; Wagner et al., 2011). The Gibbs-Seawater (GSW) library is a collection of tailored equations for high-speed oceanographic applications, derived from the four basic formulations of TEOS-10 (McDougall and Barker, 2011).

Possible future applications of TEOS-10 and IAPWS equations to the atmosphere may be supported additionally by low-temperature extensions for water vapour below 130 K (IAPWS, 2012) and for supercooled liquid water (Holten et al., 2014). While IAPWS-95 describes air-free liquid water, equations for Henry’s constants and partial molar volumes are available for the calculation of properties of dilute aqueous solutions of gases (IAPWS, 2004; Fernández-Prini et al., 2003; Harvey et al., 2005) whose effects exceed the measurement uncertainty in particular for colligative properties. For example, due to the dissolution of air, the very accurate TEOS-10 pure-water freezing point of 273.152 519 K at 101 325 Pa (with an uncertainty of only 2 μ K because the triple point is at exactly 273.16 K by definition, Feistel and Wagner, 2006) is lowered to the common ice point of 273.150 019 K (with an estimated uncertainty of 5 μ K, Harvey et al., 2013). In contrast, effects of dissolved air on the humid-air saturation pressure, even though of similar magnitude (relative saturation-pressure change of about 2×10^{-5} at standard ocean surface conditions, McDonald, 1963), are irrelevant in practice (Harvey et al., 2005).

3. Seawater salinity

Salinity, or more precisely, *Absolute Salinity* (Wright et al., 2011), is a term used to quantify the total mass of substances dissolved in pure water to form a given mass of seawater. Seawater salinity changes as a result of mixing processes in the water column and, more dramatically, by precipitation and evaporation at the surface, by freezing and melting of sea ice, and by freshwater discharge from rivers and glaciers. In the form of latent heat, the oceans export 50 – 90 % of the absorbed solar energy to the atmosphere by evaporating water (Josey et al., 1999, 2013; Emery et al., 2006; Pierrehumbert, 2010; Feistel and

Ebeling, 2011; Wells, 2012). The related global hydrological cycle is reflected in the distribution of sea-surface salinities; arid regions in the trade-wind belts show higher, and humid regions at the equator and at mid-latitudes lower salinities than the global average. While observations of latent heat fluxes are technically demanding and subject to large uncertainties on the order of 20 %, or 30 W m^{-2} (Katsaros, 2001; Josey et al., 2013), local long-term trends in salinity are precisely measurable indicators for climatic changes in the terrestrial water cycle (Durack and Wijffels, 2010; Durack et al., 2012, 2013; Pierce et al., 2012). Salinity deviations, in turn, affect the density gradients in the ocean and in this way modify the world-wide marine “conveyor belt” of heat transports. Along with temperature and pressure as key parameters for ocean modelling and observation, salinity significantly influences almost every property of seawater, including its heat capacity, sound speed, refractive index and viscosity (IOC et al., 2010).

However, the demonstrated usefulness of salinity in oceanography is in striking contrast to the practical inability to directly measure it (Lewis, 1980; Millero et al., 2008). During the last century, only two methods of measuring this total dissolved mass were successfully exploited to establish salinity scales that were officially adopted by oceanography, namely by drying a sample and weighing the residue (Forch et al., 1902), or by carrying out a complete chemical analysis of the sample’s composition and adding up the constituent masses (Millero et al., 2008). Neither method is appropriate for the frequent regular measurements required in oceanographic studies, nor are they mutually consistent with one another within requisite accuracy. In practice, oceanographers, for many years, have used the fast, reliable and robust technique described by the Practical Salinity Scale of 1978 (PSS-78; see Unesco, 1981) to approximate these other methods. This *Practical Salinity* is defined by using proxy measurements of electrical conductivity relative to that of a bottled standard, natural seawater, reference material called *IAPSO Standard Seawater* (SSW), commercially provided by OSIL¹⁶. Use of this proxy measurement is possible because the chemical composition of seawater is largely ionic, and the relative proportions of the different ions are almost constant.

An uncertainty level of 0.002 g kg^{-1} in dissolved mass fraction (i.e., a relative uncertainty of 6×10^{-5} for typical seawater with a dissolved mass fraction of about 35 g kg^{-1}) is required for routine research and monitoring purposes (SUN, 1985; Seitz et al., 2011). Significant efforts have been made to ensure consistency of salinity measurements to this level over the past century; unfortunately, no robust link has yet been established between any of the salinity definitions and the International System of Units (SI) despite the fact that Practical Salinity was recommended for oceanography in the context of SI units (SUN, 1985; Siedler, 1998).

As part of the development of TEOS-10, a first step was taken to move away from reliance on the electrical conductivity of SSW as an artefact reference material used to define other seawater properties. Instead, the best available stoichiometric data for the composition of SSW was used to define a *Reference Composition* of seawater. The resulting salinity

¹⁶Certain commercial products are identified in this paper, but only in order to adequately specify the procedure. Such identification neither constitutes nor implies recommendation or endorsement by any of the organisations represented by the authors.

measure was termed *Reference-Composition Salinity* (Millero et al., 2008). Although the new TEOS-10 Reference-Composition Salinity Scale has many advantages, there still remain two fundamental problems with the current definition and measurement technology of seawater salinity: (i) a lack of traceability of salinity measurement results to the SI at the uncertainty required, and (ii) an incomplete knowledge of methods to handle small deviations in the chemical composition of the dissolved salts from the Reference Composition, which regionally occur in the oceans and marginal seas and may have relevant effects on seawater properties.

A proposed new concept that takes advantage of currently available density measurement technology and at the same time leaves established oceanographic practice largely unaffected is a combination of conductivity and SI-traceable density measurement (Seitz et al., 2011). In this concept, the salinity of SSW samples can be additionally certified (or at least checked) by density measurements in combination with the TEOS-10 equation of state. Implementing a degree of traceability to the SI will significantly improve the reliability of long-term comparisons of observational data, and this may be possible by making additional measurements of density.

A more thorough review of climatological relevance of seawater salinity, its measurement history, current definition and practice, related problems and deficiencies as well as suggestions for overcoming them are given in the Part 2 companion paper.

4. Seawater pH

Seawater pH is a critical parameter for characterising many important processes in the ocean, and is in turn affected by these processes. In particular, the ocean carbon dioxide (CO₂) system is central to a wide variety of biological processes in the ocean, with CO₂ being taken up by photosynthetic organisms, and remineralised by a variety of respiration processes. Furthermore, a wide variety of calcifying organisms rely on their ability to form calcium carbonate (CaCO₃) for shells or skeletons from the surrounding seawater (Smith et al., 2012; Bednaršek et al., 2012). All of these processes affect and are affected by seawater pH, which can exhibit pronounced diurnal and seasonal cycles as well as strong irregular fluctuations related to local mixing and many other factors (Buch, 1945; Hofmann et al. 2011; Doney, 2013; Omstedt et al., 2014).

Over the past two centuries, the release of CO₂ from human industrial and agricultural practices has resulted in atmospheric CO₂ levels that are now higher than has been experienced on the Earth for at least the last 800 000 years (Lüthi et al., 2008). During this period, the oceans have taken up about 30 % of the total amount of CO₂ produced by human activities (Khatiwala et al., 2013; IPCC, 2013). This addition of anthropogenic CO₂ to the ocean has reduced the surface ocean pH by about 0.13 to date and is expected to reduce pH by a further 0.3 by the end of this century (Feely et al., 2004).

The concept of pH was introduced by Sørensen (Sørensen, 1909) in terms of a logarithmic function of the hydrogen ion concentration, $\text{pH} = -\lg [c(\text{H}^+)/(\text{1 mol L}^{-1})]$, later replaced by the reduced practical activity (as defined by eq. (B.11) in Appendix B in the supplement),

$$\text{pH} = -\lg a(\text{H}^+), \quad (1)$$

to better account for ionic interactions in the solution (Sørensen and Linderstrøm-Lang, 1924). In recent decades, because of the impossibility of measuring single-ion activities and other, more technical issues, a variety of related but different operationally-defined pH-like quantities have been introduced (IUPAC, 1985). However, as Bates and Popovych (1981) noted more than 30 years ago, related problems of incompatibility are inevitable. Only for a few selected calibration procedures in media of low ionic strength can the traceability hierarchy between the conceptually defined values, eq. (1), and experimentally assessed pH values with inherent uncertainties be established successfully (Buck et al., 2002; Baucke, 2002).

These technical issues are particularly problematic in seawater studies. First, seawater has a high ionic strength, which causes problems when using conventional pH calibration standards. Second, some current research problems such as detection of the long-term anthropogenically-driven changes in ocean carbon chemistry over multi-decadal timescales would benefit from an extremely small standard uncertainty in pH measurements such as 0.003 (Newton et al., 2014), albeit over a fairly narrow range of pH, and this is far smaller than the differences between many of the available operationally defined ‘pH’ quantities (Marion et al., 2011). The notation ‘pH’ in quotation marks is used to emphasise that, although commonly called pH, these various operationally defined quantities are not identical to the accepted definition, eq. (1). It is the decision to define pH as the single-ion activity, eq. (1), which causes additional difficulties. Such a single-ion activity is immeasurable by any thermodynamic method and requires a convention for its evaluation (Buck et al., 2002).

As a result of critical assessments (Marion et al., 2011) of the various concepts that have been adopted by different groups for pH of seawater, the following steps are suggested for improvement:

First, a suitable nomenclature is needed to keep pH terminology less ambiguous and to make more transparent the alternative definitions and conventions. It is the task of international bodies such as IUPAC or IOC to develop and promote such conventions.

Second, it is recommended that ocean scientists be encouraged to use the same chemical quantity, namely the free concentration or activity of the hydrogen ion, to examine the effect of pH on processes in the oceans. pH can be estimated from measurement (potentiometric, spectrophotometric) and modelling approaches. Accuracy via different definitions and conventions clearly requires consistency with respect to experimental measurements, equilibrium constants, activity coefficients, and buffer solutions that are used for specific approaches.

A third suggestion is that standard formulas be developed for the accurate and unambiguous conversion between the different pH scales that are in practical use, and that their uncertainty budgets be developed. Similar to existing standard equations for conductivity or

density of seawater, future empirical correlation equations for the pH of Standard Seawater (or artificial seawater) as functions of salinity, temperature, pressure, CO₂ fugacity and other relevant involved parameters, consistent with the IAPWS formulation for the dissociation constant of pure water (IAPWS, 2007; Bandura and Lvov, 2006), should be envisaged as helpful tools to ensure international comparability of measurement results.

Fourth, the development of appropriate numerical models should be pursued to find a suitable convention for activity of the hydrogen ion in seawater or in other aqueous solutions. With the existence of such a convention, metrological traceability to the SI can be developed.

Finally, as a related though separate issue, the development is needed of pH standard buffer solutions which can be used directly to calibrate pH electrodes in potentiometric pH measurements and also in the experimental determination of pK_a values, $pK_a \equiv -\lg(K_a)$, where K_a is the equilibrium constant for the acid ionisation of the indicator dyes for spectrophotometric seawater pH measurements. This requires the development of an artificial seawater and its characterisation under different conditions.

A more thorough review of climatological relevance of seawater pH, its oceanographic measurement history, current definition and practice, related problems and deficiencies as well as suggestions for overcoming them are given in the Part 3 companion paper.

5. Atmospheric relative humidity

The term *humidity* indicates water vapour, normally admixed with air or other dry gas. Above liquid water and aqueous solutions, above ice, and in pore spaces lined with adsorbed water, water vapour will be found, often with an interface-crossing net flux of molecules. The irreversible net flux only ceases at equilibrium, at which point the chemical potential of water is the same in all coexisting phases. The chemical potential depends primarily on the temperature, but also on the curvature of the interface between gas and liquid, the surface material, the gas mixture, the substances dissolved in the condensed phase and the total pressure. If at equilibrium the condensed phase - either pure liquid water or ice - has a planar interface with the vapour phase, the vapour (or more loosely, the humid gas) is said to be *saturated* and the system is said to be *at saturation*.

In general, the *relative humidity* of a humid gas is the ratio of some humidity quantity to the same quantity at saturation at the same temperature. In particular, the *de facto* standard definition, which has been authorised by the WMO since 1950 (WMO, 2008, p. 1.4–27) and by many other organisations, chooses the optional humidity quantity to be the water-vapour mole fraction. Nevertheless, a variety of alternative definitions using different ratios continue to propagate in particular in climatological and meteorological textbooks or research articles (Katsaros, 2001). The problems of definition of relative humidity relate in part to the resulting ambiguity and the lack of a fundamental basis that would support one definition over another. An equally serious and related problem is the inability of the WMO definition (and of most alternative definitions) to cover the full range over which other humidity quantities apply and relative-humidity sensors respond usefully.

The state of a humid gas can be characterised by a wide variety of humidity quantities, including the mixing ratio, the specific humidity, the vapour mole fraction, the vapour pressure, the water-vapour partial pressure and the water fugacity (for details of the definitions see the digital supplement of this paper and the Part 4 companion paper). Of these quantities, it is only the water fugacity that is equal in each phase at equilibrium and it is only the relative fugacity that constitutes the proper thermodynamic driving force to saturation.

In irreversible thermodynamics, fluxes of heat and matter result from Onsager forces which are combinations of gradients of temperature and chemical potentials (de Groot and Mazur, 1962; Glansdorff and Prigogine, 1971; Falkenhagen et al., 1971; Landau and Lifschitz, 1974). In the climate system, the most relevant differences of chemical potentials are those of water between ocean, ice cover and humid air, at the boundary of and within the atmosphere. These differences can be exactly expressed in terms of the relative fugacity (see Appendix C in the supplement) of water vapour in the atmosphere, which is one of the options for defining relative humidity. To a reasonable approximation, the spatial distribution of the relative fugacity of water vapour can be described by that of the relative humidity in the WMO definition (Erikson, 1965; Kraus, 1972; Hansen and Takahashi, 1984; IOC et al., 2010; Feistel et al., 2010a; Feistel and Ebeling, 2011; Li and Chylek, 2012; Li et al., 2014). At the sea surface, the thermodynamic driving force for evaporation is the difference between the chemical potentials of water in the ocean and in the atmosphere (Kraus and Businger, 1994; IOC et al., 2010). Thus, relative humidity immediately above the sea surface essentially controls the latent heat export from the ocean, which in turn constitutes the dominant energy source driving global weather and climate processes (Chahine, 1992; Trenberth et al., 2005; Schneider et al., 2010; Pierce et al., 2011; Josey et al., 2013; Bony et al., 2015; Schiermeier, 2015).

TEOS-10 has demonstrated the possibility and value of a rigorous axiomatic foundation of the description of seawater-ice-air thermodynamic properties. Using the same approach, development of a consistent “axiomatic” definition and nomenclature of humidity quantities, as derived from a small set of empirical fundamental equations, will help to provide clarity and consistency within the wider humidity community. One such axiomatic approach to humidity, which uses an enhanced subset of TEOS-10, is outlined in Appendix D in the supplement.

A more thorough review of climatological relevance of relative humidity, its measurement history, current definition and practice, related problems and deficiencies as well as suggestions for overcoming them are given in the Part 4 companion paper.

6. Discussion and Conclusion

Long-term data records of meteorological and oceanographic observations covering several decades are fundamental for the detection and quantification of climatic changes and for the verification of numerical climate models developed for the prediction of future physical and chemical conditions in the atmosphere and in the ocean. For this purpose, it is indispensable that the measurement results collected over the years from locations all over the globe are

mutually comparable and free of spurious trends and discontinuities. Metrological comparability of measurement results for quantities of a given kind requires metrological traceability to the same reference (VIM, 2012). It is demonstrated in detail in the articles of this review that salinity, pH and relative humidity only incompletely satisfy important conditions implied by comparability, namely

- metrological traceability to shared primary standards possessing high temporal stability, preferably to the International System of Units (SI),
- unambiguous and clearly specified definitions of the measured quantities,
- consistency of empirical equations applied for the conversion, combination or correction of different values involved in the measurement or comparison procedures, and
- provision of realistic uncertainty estimates for each measurement result and each derived quantity.

Seawater salinity, seawater pH and atmospheric relative humidity are key climatological observables whose long-term trends are known to be small but fundamental indicators for changes in the global hydrological cycle, in ocean-atmosphere interaction and in the terrestrial balances of energy and matter. With the Thermodynamic Equation of Seawater 2010 (TEOS-10), a new axiomatic set of equations has recently become available that consistently and comprehensively describes the thermodynamic properties of seawater, ice and humid air, as well as their mutual phase equilibria and composites such as sea ice or clouds. The development of TEOS-10 by the SCOR/IAPSO Working Group 127 in close cooperation with IAPWS has raised new awareness of various deficiencies in the definition and measurement practice of seawater salinity, seawater pH and atmospheric relative humidity regarding traceability to the SI or inconsistent, incomplete or ambiguous definitions or measurement techniques.

More than a century ago, Knudsen and Sørensen developed the first official international salinity scale along with the definition of standard seawater as a metrological primary reference material for oceanographic salinity measurements (Culkin and Smed, 1979). At about the same time, Sørensen defined pH as a measure of acidity of solutions such as seawater (Sørensen, 1909), and Lewis introduced fugacity as a real-gas substitute for the ideal-gas partial pressure of gaseous mixtures (Lewis, 1901). Notwithstanding, partial pressure of water vapour has been the basis of international standards for relative humidity since 1950, and further alternative, inconsistent definitions are frequently used in textbooks, research papers or numerical models in climatology and meteorology. Seawater salinity and pH have been measured with respect to many different scales, however, none of them provided proper traceability to the SI.

The conclusion from this review is that new SI-based definitions need to be introduced or new methods must be established which uniquely link the quantities of interest to SI-traceable measurement results. Such links may consist of equations (or “conventions”), such as the TEOS-10 equation for the density of standard seawater which permits the calculation of Absolute Salinity from measurements of temperature, pressure and density, all of the

latter traceable to the SI (Seitz et al., 2011). A similar approach is possible for the relative fugacity making use of the TEOS-10 equation of state of humid air (Feistel, 2012; Feistel et al., 2015). The development of an equation for the activity of the hydrogen ion in seawater derived from Pitzer equations has also been suggested recently (Marion et al., 2011).

The general metrological concept of separating the definition of a quantity from the set of instructions (“mise en pratique”, see BIPM, 2006, or “operational definition”) that in practice allows its measurement at the lowest level of uncertainty, is also promising for the climatological key observables seawater salinity, pH and atmospheric relative humidity. For example, the options of defining salinity in terms of the solute mass fraction, pH in terms of the hydrogen-ion activity, and relative humidity in terms of the water-vapour fugacity are theoretically well-founded and consistent with traditional use. For practical measurements, alternative quantities may be more suitable *surrogate measurands* if they are traceable to the SI and linked to the quantity in question by a robust theoretical or empirical relation. In the cases considered in this series of papers, preferred surrogate properties that obey these conditions may be seawater density, optical attenuation of an indicator dye, and dew-point temperature, which may be measured and used to calculate salinity, pH and relative fugacity, respectively, rather than measuring or realising these quantities directly. The target quantities are then calculated from those measurands by certain, explicitly specified empirical equations (such as those of TEOS-10) that should constitute an integral part of the particular measurement standard.

Following this approach, establishing traceability to SI of salinity, pH and relative-humidity measurement results may include (Hellmuth et al., 2014; Feistel, 2013, 2015)

- i.** the rigorous theoretical definition of those key quantities in terms of thermodynamic properties of seawater and humid air, such as composition variables or chemical potentials,
- ii.** the specification of one or several surrogate properties that strongly correlate with the respective original quantity, that are traceable to the SI, and are conveniently measurable in practice to the requisite accuracy,
- iii.** the development and formal adoption of equations that relate the original quantities to their surrogates,
- iv.** the development and subsequent specification of best-practice procedures for measuring the surrogate properties, including the calibration rules that establish the links to SI units,
- v.** the estimate of uncertainties involved in steps (i) to (iv),
- vi.** the development of recommended conversion procedures between legacy data and the new quantities, and
- vii.** the release of recommendations regarding steps (i) to (vi) on an international and interdisciplinary level in the form of published resolutions, guides or manuals.

First steps in these directions have been undertaken in the cooperation between BIPM and IAPWS under the umbrella of the Joint SCOR/IAPWS/IAPSO Committee on the Properties of Seawater, JCS (BIPM, 2012, 2014).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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