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## 2 **TEOS-10 and the Climatic Relevance of Ocean-Atmosphere Interaction**

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6 **Abstract:** Unpredicted observations in the climate system, such as recently an excessive ocean  
 7 warming, are often lacking immediate causal explanations and are challenging the numerical models.  
 8 As a highly advanced mathematical tool, the Thermodynamic Equation of Seawater – 2010 (TEOS-10)  
 9 had been established by international bodies as an interdisciplinary standard and is recommended  
 10 for use in geophysics, such as especially in climate research. From its very beginning, the  
 11 development of TEOS-10 was supported by *Ocean Science* through publishing successive stages and  
 12 results. Here, the history and properties of TEOS-10 are briefly reviewed. With focus on the air-sea  
 13 interface, selected current problems of climate research are discussed and tutorial examples for the  
 14 possible use of TEOS-10 in the associated context are presented, such as related to ocean heat  
 15 content, latent heat and rate of marine evaporation, properties of sea spray aerosol, or climatic  
 16 effects of low-level clouds. Appended to this article, a list of publications and their metrics is  
 17 provided for illustrating the uptake of TEOS-10 by the scientific community, along with some  
 18 continued activities, addressing still pending, connected issues such as uniform standard definitions  
 19 of uncertainties, of relative humidity, seawater salinity or pH.

20 This article is dedicated to the Jubilee celebrating 20 years of Ocean Science.

21

22 *All the rivers run into the sea; yet the sea is not full;*  
 23 *unto the place from whence the rivers come, thither they return again.*

24 The King James Bible: Ecclesiastes, 450 – 150 BCE

25 *He wraps up the waters in his clouds,*  
 26 *yet the clouds do not burst under their weight.*

27 Holy Bible: New International Version, Job 26:8

28 *Of the air, the part receiving heat is rising higher.*  
 29 *So, evaporated water is lifted above the lower air.*

30 Leonardo da Vinci: Primo libro delle acque, Arundel Codex, ca. 1508

31 *Two-thirds of the Sun's energy falling on the Earth's surface is needed*  
 32 *to vaporize ... water ... as a heat source for a gigantic steam engine.*

33 Heinrich Hertz: Energiehaushalt der Erde, 1885

34 *The sea surface interaction is obviously*  
 35 *a highly significant quantity in simulating climate.*

36 Andrew Gilchrist, Klaus Hasselmann: Climate Modelling, 1986

37 *The climate of the Earth is ultimately determined*  
 38 *by the temperatures of the oceans.*

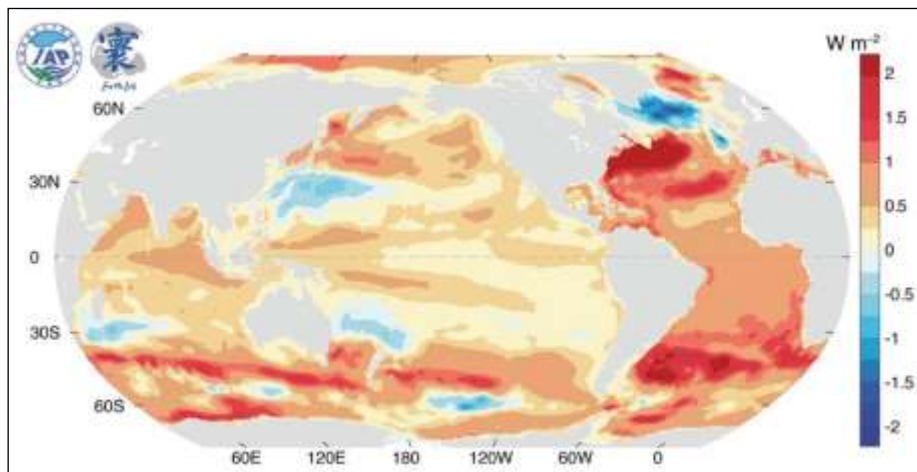
39 Donald Rapp: Assessing Climate Change, 2014

40

## 41 1 Introduction

42 Quite recently in 2024, climate research has published alarming news: “The world’s oceans absorbed  
 43 more heat in 2023 than in any other year since records began in the 1950s. ... Data show that the  
 44 heat stored in the upper 2,000 metres of oceans increased by 15 zettajoules (1 zettajoule is  $10^{21}$   
 45 joules) in 2023 compared with that stored in 2022. This is an enormous amount of energy — for  
 46 comparison, the world’s total energy consumption in 2022 was roughly 0.6 zettajoules” (You 2024: p.  
 47 434). Dividing this value by the global ocean surface area and by the duration of a year, the reported  
 48 ocean’s average warming rate amounts to  $1.3 \text{ W m}^{-2}$ , and is apparently even increasing. “Earth’s net  
 49 global energy imbalance (12 months up to September 2023) amounts to  $+1.9 \text{ W m}^{-2}$ , ... ensuring  
 50 further heating of the ocean” (Kuhlbrodt et al. 2024: p. E474).

51 The currently observed *ocean heat content* (OHC) represents a merely transient maximum after a  
 52 decade-long systematic warming process in the past, see Fig. 18 in Section 6, which may proceed to  
 53 even higher values in the future. In Section 3, thermodynamic aspects of related OHC definitions will  
 54 be considered. Regarding the long-term period since 1971, “the drivers of a larger Earth energy  
 55 imbalance in the 2000s than [before] are still unclear. ... Future studies are needed to further explain  
 56 the drivers of this change” (von Schuckmann et al. 2023: p. 1694). Laterally, the observed heat excess  
 57 is unevenly distributed over the world ocean (Fig. 1), in contrast to what naively may be expected  
 58 from rising atmospheric  $\text{CO}_2$  concentrations. Rather, warming seems to be most pronounced in the  
 59 cloudy austral and boreal west-wind belts. Selected thermodynamic relations between OHC and  
 60 cloudiness are briefly discussed in Section 6.

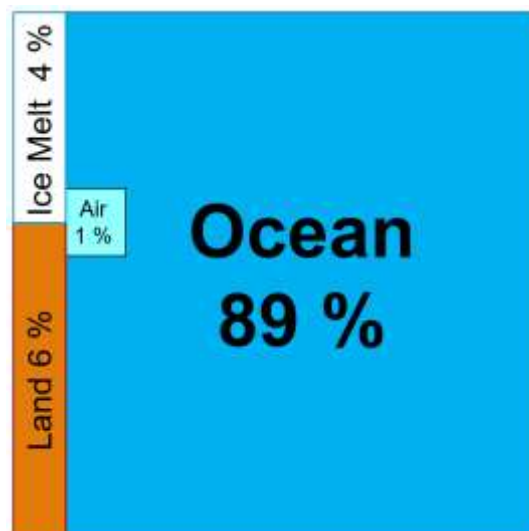


61  
 62 Fig. 1: Observed trend 1958 through 2022 of the upper 2000 m ocean heat content (WMO 2024).  
 63 Image reproduction permitted by WMO Copyright.

64  
 65 Sunlight is the only available heat source of sufficient power to cause the observed warming, while  
 66 the globally averaged geothermal heat flux is estimated to be just  $0.087 \text{ W m}^{-2}$  (Pollack et al. 1993),  
 67 and is not expected to suddenly rise recently due to human impact. Irradiation is hampered by  
 68 clouds, dust and absorbing gases, and water surface reflection such as by whitecaps, waves or  
 69 plankton layers (Cahill et al. 2023). Heat absorbed in the water column may effectively exit the ocean  
 70 again only across the air-sea interface via sensible, radiative and latent heat flux. All these effects  
 71 may vary in the climate system in a complicated, mutually interacting manner. Typically, present  
 72 numerical climate models suffer from an “ocean heat budget closure problem” (Josey et al. 1999)  
 73 and describe the ocean-atmosphere heat flux only to within uncertainties between  $10 \text{ W m}^{-2}$  and  $30$   
 74  $\text{W m}^{-2}$  (Josey et al. 2013). According to recent model comparison studies, many of those “models fail

75 to provide as much heat into the ocean as observed” (Weller et al. 2022: p. E1968). Dynamical  
 76 models, rather than observed correlations, are the most reliable tools for the detection and  
 77 verification of causal relations (Feistel 2023), however, such as in this case of air-sea interaction,  
 78 large uncertainties may prevent any significant conclusions to be drawn regarding the causes of the  
 79 observed ocean warming rate of  $1.3 \text{ W m}^{-2}$ .

80 Of the increasing amount of water vapour contained in the global troposphere, 85 % results from  
 81 ocean evaporation (Gimeno et al. 2013). Corresponding to 1200 mm annual evaporation (Budyko  
 82 1963, 1984, Baumgartner and Reichel 1975, Peters-Lidard et al. 2019), the associated latent heat flux  
 83 of about  $95 \text{ W m}^{-2}$  per ocean surface area represents the strongest energy supply for the  
 84 atmospheric dynamics (Albrecht 1940) and at the same time the strongest cooling process of the sea.  
 85 This flux depends sensitively on the relative humidity (RH) at the water surface; an RH increase by 1  
 86 %rh can be estimated to reduce evaporation by  $5 \text{ W m}^{-2}$  (Feistel 2015, Feistel and Hellmuth 2021,  
 87 2023), so that minor additional 0.2 %rh may already suffice to warm up the ocean by the observed  
 88  $1.3 \text{ W m}^{-2}$ . Unfortunately, marine RH is observed only with uncertainties between 1 and 5 %rh  
 89 (Lovell-Smith et al. 2016), or, accordingly, between 5 and  $25 \text{ W m}^{-2}$  of latent heat flux, which is  
 90 roughly corresponding to unknown variations ranging up to 50 ... 250 mm evaporation per year. It  
 91 remains unclear to what extent minor, yet unnoticed changes in marine RH may be responsible for  
 92 the recent ocean warming.



93

94 Fig. 2: Heat fractions stored additionally in the different parts of the Earth system 1960–2020 (values  
 95 from von Schuckmann et al. 2023), represented graphically by partial areas. Obviously, the oceans  
 96 dominate global warming.

97

98 According to Fig. 2, a paramount share of 94 % of global warming occurs in different phases and  
 99 geophysical mixtures of water, in particular in seawater. Considering this situation, the *Scientific*  
 100 *Committee on Oceanic Research* (SCOR) in cooperation with the *International Association for the*  
 101 *Physical Sciences of the Oceans* (IAPSO) decided at its 2005 Cairns meeting the establishment of the  
 102 *SCOR/IAPSO Working Group 127 on Thermodynamics of Seawater* (WG127) (Millero 2010, Pawlowicz  
 103 et al. 2012, Smythe-Wright et al. 2019), which held its inaugural meeting in 2006 at Warnemünde  
 104 (Fig. 3). It had been recognised that “modelling of the global heat engine needs accurate expressions  
 105 for the entropy, enthalpy, and internal energy of seawater so that heat fluxes can be more accurately  
 106 determined in the ocean” (Millero 2010: p. 28) while such properties were not available from the  
 107 thermodynamic seawater standard at that time, the 1980 Equation of State of Seawater (EOS-80)  
 108 (Fofonoff and Millard Jr. 1983).

109 The foundation of WG127 happened almost coincidentally with the establishment of the *Ocean*  
 110 *Science* journal of the *European Geosciences Union* (EGU) in 2004/05. The development of the new  
 111 standard by WG127, the Thermodynamic Equation of Seawater – 2010 (TEOS-10) was very  
 112 successfully supported by Ocean Science, publishing the Special Issue #14 on “Thermophysical  
 113 Properties of Seawater” with 16 articles between 2008 and 2012 (Feistel et al. 2008a). **Appendix A**  
 114 reports the current metrics of this Special Issue. Also in 2008, at its conference in Berlin, Germany,  
 115 the *International Association for the Properties of Water and Steam* (IAPWS) established a new  
 116 *Subcommittee on Seawater* (SCSW) that cooperated closely with WG127. In the form of carefully  
 117 verified mathematical formulations for properties of water, ice, seawater and humid air, IAPWS  
 118 adopted 9 fundamental documents related to TEOS-10 (IAPWS AN6-16 2016), see **Appendix A**.



119

120 Fig. 3: Participants of the 2006 kick-off meeting of SCOR/IAPSO WG127 at the Leibniz Institute for  
 121 Baltic Sea Research (IOW) in Warnemünde, Germany. From left to right: Chen-Tung Arthur Chen  
 122 (Taiwan), Frank Millero (USA), Brian King (UK), Rainer Feistel (WG vice chair, Germany), Daniel Wright  
 123 (Canada, deceased 2010), Trevor McDougall (WG chair, Australia) and Giles Marion (USA).



124

125 Fig. 4: Participants of the BIPM-IAPWS meeting in February 2012 at the Pavillon de Breteuil, Sèvres.  
 126 From left to right: Dan Friend (IAPWS), Karol Daučik (IAPWS president), Jeff Cooper (IAPWS), Alain  
 127 Picard (BIPM, deceased 2015), Petra Spitzer (WG127), Rainer Feistel (WG127), Michael Kühne  
 128 (director BIPM), Andy Henson (BIPM) and Robert Wielgosz (BIPM).

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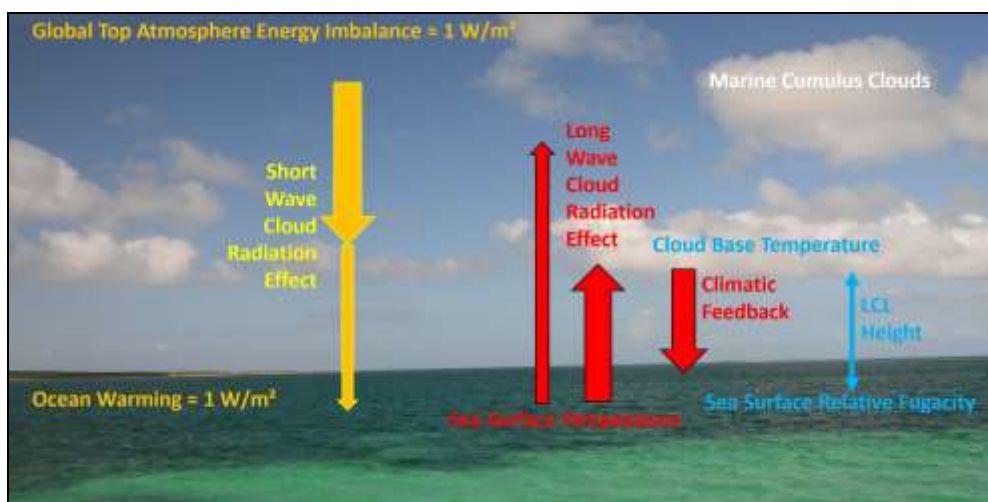
130 With respect to problems yet pending after the official adoption of TEOS-10, especially for the  
 131 preparation of future novel international definitions of seawater salinity, seawater pH and  
 132 atmospheric relative humidity (Feistel et al. 2016, Pawlowicz et al. 2016, Dickson et al. 2016, Lovell-

133 Smith et al. 2016), the standing *IAPSO/SCOR/IAPWS Joint Committee on the Properties of Seawater*  
 134 (JCS) was established in 2012. In 2011, IAPWS also extended its cooperation with the *International*  
 135 *Bureau for Weights and Measures* (BIPM), see Fig. 4. Further details on TEOS-10 (IOC et al. 2010,  
 136 McDougall et al. 2013, Feistel 2018, Wikipedia 2024) are available from the TEOS-10 homepage,  
 137 [www.teos-10.org](http://www.teos-10.org), and are briefly reviewed in **Section 2** and **Appendix B**.

138 In the context of the predecessor EOS-80, the *ocean heat content* (OHC) was defined in terms of  
 139 *potential temperature* (Abraham et al. 2013). Improving this method, TEOS-10 entropy and enthalpy  
 140 of seawater provided a proper quantitative basis for a novel, thermodynamically rigorous definition  
 141 of the OHC in the form of seawater *potential enthalpy* (McDougall 2003, McDougall et al. 2013,  
 142 Graham and McDougall 2013, McDougall et al. 2021), equivalently defined as **Conservative**  
 143 **Temperature** and briefly discussed in **Section 3**.

144 Currently implemented parameterisations of marine evaporation rates in the form of historical  
 145 *Dalton equations* (Stewart 2008, Josey et al. 1999, 2013) may be replaced by TEOS-10 chemical  
 146 potentials which provide the proper quantitative basis for a thermodynamically rigorous formulation  
 147 of non-equilibrium Onsager forces and fluxes in terms of *relative fugacity* (RF) of humid air (Kraus  
 148 and Businger 1994, Feistel and Lovell-Smith 2017, Feistel and Hellmuth 2023, 2024a), as described in  
 149 **Section 4**. *Relative humidity* (RH) is defined relative to the saturation state of moist air, which in turn  
 150 is controlled by the chemical potentials of water in the gas and liquid phase. It is only natural,  
 151 therefore, to define RH in terms of chemical potentials, which in fact is performed by RF. The  
 152 uncertainty of latent heat flux with respect to the uncertainty of surface RH observation is shown to  
 153 be significantly larger than the observed warming of  $1.3 \text{ W m}^{-2}$ , so that this warming may or may  
 154 not be caused by so-far ignored minor RH increase.

155 The conceptual model of sea air as a two-phase composite thermodynamic system is outlined in  
 156 **Section 5**. The roles of enthalpy, chemical potential and entropy are explained by means of explicit  
 157 theoretical descriptions of three simplified tutorial examples, (i) for the latent heat of evaporation,  
 158 (ii) for the heat capacity of humid air containing sea spray, and (iii) for the entropy production of  
 159 irreversible evaporation.



160

161 Fig. 5: Schematic of *cloud radiation effects* (CRE). The *short-wave effect* (SW CRE) controls the  
 162 downward flux of solar irradiation while the *long-wave effect* governs the infrared radiation balance  
 163 between water surface and cloud base. By thermal convection, cumulus clouds emerge at the  
 164 isentropic *lifted condensation level* (LCL). Figure from Feistel and Hellmuth (2024b)

165

166 Clouds do not only release the latent heat which water vapour has carried away from the ocean, they  
 167 also interfere substantially in the global radiation balance, cooling the surface by reflecting short-  
 168 wave solar irradiation, and warming the surface by sending back down long-wave thermal radiation,  
 169 see Fig. 5. In the course of global warming, cloudiness has been found to exhibit a systematic trend of  
 170 reduction, see **Section 6**, which affects the ocean heat content in a non-trivial, non-uniform manner.  
 171 Marine cumulus clouds **arise** by isentropic uplift of thermal convection. Their height controls their  
 172 temperature and **their** thermal downward radiation, affecting the ocean's energy balance. Updating  
 173 previous results (Roms 2017) for the *lifted condensation level* (LCL) of marine cumulus clouds to  
 174 thermodynamically rigorous TEOS-10 standard equations (Feistel and Hellmuth 2024b), the radiative  
 175 effect of those clouds can be estimated from *sea-surface temperature* (SST) and surface relative  
 176 humidity. This effect turns out to be weakly cooling and cannot provide a reasonable explanation for  
 177 the so-far unclear strong ocean warming.

178 **Section 7** provides a summary of this paper, **Appendix A** reports collections of publications with  
 179 respect to TEOS-10 as well as their metrics, and **Appendix B** **gives** a short introduction into the  
 180 concept of thermodynamic potentials.

181

## 182 2 Thermodynamic Equation of Seawater – 2010 (TEOS-10)

183 In the climate system, the omnipresent and dominant substance is water in various phases and  
 184 mixtures. For example, “water vapor is by far the most important greenhouse gas, in the sense that it  
 185 absorbs more irradiance from the Earth than all other greenhouse gases combined” (Rapp 2014: p.  
 186 381). Textbooks and other publications offer numerous collections of various different property  
 187 equations for water, ice, seawater or moist air, but uncertainties and mutual consistencies of those  
 188 equations are often unclear. To improve this situation, a novel *Thermodynamic Equation of Seawater*  
 189 – 2010 (TEOS-10) was developed by the members of the SCOR/IAPSO Working Group 127 (WG 127)  
 190 in close cooperation with the International Association for the Properties of Water and Steam  
 191 (IAPWS). TEOS-10 is described in a detailed Manual (IOC et al. 2010) and has been adopted and  
 192 recommended by IOC-UNESCO (2009) in Paris and by the IUGG (2011) in Melbourne, see also Feistel  
 193 (2008b, 2012, 2018), Valladares et al. (2011) and Pawlowicz et al. (2012). Starting in 2008 with a  
 194 Special Issue of *Ocean Science* (Feistel et al. 2008a), a large number of scientific publications has  
 195 appeared in the meantime, supporting, extending or exploiting TEOS-10. A collection of selected  
 196 papers related to TEOS-10 is summarised in Appendix A together with metrics that illustrate the  
 197 growing uptake of TEOS-10 by the scientific community.

198 The development of the first numerical thermodynamic Gibbs potentials (see Appendix B) for  
 199 seawater (Feistel 1991, 1993, Feistel and Hagen 1995) was based on the works of Millero and Leung  
 200 (1976) and Millero (1982, 1983), together with high-pressure background data of the previous EOS-  
 201 80 standard (Unesco 1981). Independently of that, a Helmholtz potential for pure fluid water had  
 202 been adopted by IAPWS in 1996 at Fredericia (Harvey 1998, Wagner and Pruß 2002). These were the  
 203 key activities which eventually culminated in the formulation of TEOS-10 about two decades later. By  
 204 combining those equations for pure and seawater, some known pending problems of EOS-80  
 205 (Fofonoff and Millard Jr. 1983) could incidentally be resolved (Feistel 2003). In the end, TEOS-10 has  
 206 been assembled from four basic thermodynamic potentials derived from mutually consistent, most  
 207 comprehensive and accurate datasets of measured properties available at that time. Those  
 208 potentials are:

- 209 (i) A Helmholtz function of fluid water,  $f^F(T, \rho) \equiv f^W(T, \rho) \equiv f^V(T, \rho)$ , known as the  
 210 IAPWS-95 formulation (Wagner and Pruß 2002), which is identical for liquid water,

211  $f^W(T, \rho)$  and for water vapour,  $f^V(T, \rho)$ . It describes de-aerated water of a fixed  
 212 isotopic composition, termed *Standard Mean Ocean Water* (SMOW), with density  $\rho$  and  
 213 temperature  $T$ .

214

215 (ii) A Gibbs function of ambient hexagonal ice I,  $g^{Ih}(T, p)$ , or IAPWS-06 formulation (Feistel  
 216 and Wagner 2006), see Tables A2 and A3 of Appendix A, depending on pressure  $p$ .

217

218

219 (iii) A Gibbs function of *IAPSO Standard Seawater*,  $g^{SW}(S, T, p)$ , or IAPWS-08 formulation  
 220 (Feistel 2008a), see Tables A2 and A3 of Appendix A. The variable  $S$ , at which a subscript  
 221 A is omitted here for simplicity, is the specific or **Absolute Salinity**, the mass fraction of  
 222 dissolved salt in seawater, which differs from **Practical Salinity**,  $S_p$ , measured by **present-**  
 223 **day** oceanographic instruments, **as well as from various other obsolete salinity scales**  
 224 (Millero et al. 2008). **Throughout this paper, the term “salinity” is exclusively short hand**  
 225 **for TEOS-10 Absolute Salinity**. Sea salt is assumed to have stoichiometric *Reference*  
 226 *Composition*. The pure-water limit,  $g^{SW}(0, T, p) = g^W(T, p)$ , is the Gibbs function of  
 227 liquid water computed from the IAPWS-95 Helmholtz function  $f^W(T, \rho)$ . For brackish  
 228 seawater,  $g^{SW}$  has implemented Debye’s root law of dilute electrolyte solutions (Landau  
 229 and Lifschitz 1966, Falkenhagen et al. 1971).

230

231

232 (iv) A Helmholtz function of humid air,  $f^{AV}(A, T, \rho)$ , or IAPWS-10 formulation (Feistel et al.  
 233 2010a), see Tables A1 and A2 of Appendix A. The variable  $A$  is the mass fraction of dry air  
 234 admixed with water vapour, so that  $q = 1 - A$  is the *specific humidity*. The dry-air limit  
 235  $f^{AV}(1, T, \rho) = f^A(T, \rho)$  equals, up to modified reference-state conditions, the equation  
 236 of state of Lemmon et al. (2000). The air-free limit  $f^{AV}(0, T, \rho) = f^V(T, \rho)$  equals the  
 237 IAPWS-95 Helmholtz function. In  $f^{AV}$ , the interaction of water vapour with dry air is  
 238 described by 2<sup>nd</sup> and 3<sup>rd</sup> virial coefficients.

239

240

241 Thermodynamic potentials include certain adjustable constants expressing the absolute energies and  
 242 entropies of the particular substances, which are not available from measurement (Planck 1906,  
 243 Feistel 2019b) and have, in turn, no effect on measurable properties derived from those potentials.

244 **In fact, among the comprehensive experimental data sets from which the TEOS-10 equations were**  
 245 **derived, none of those are suitable for fitting the empirical coefficients that represent absolute**  
 246 **energies and entropies of those equations. For this reason, the International Conference on the**  
 247 **Properties of Steam at London defined in 1967 the common triple point of water as the reference**  
 248 **state at which those absolute values were arbitrarily set. Since then, no evidence has appeared for**  
 249 **putative conflicts caused by such settings with any technical or scientific applications of the**  
 250 **equations. Despite this, Feistel and Wagner (2006) and Feistel et al. (2008b) discuss the**  
 251 **implementation of alternative residual entropies of water, if that should be of interest in exceptional**  
 252 **applications of TEOS-10. For recent discussions of Pauling’s absolute “residual” entropy at zero kelvin**  
 253 **and Nernst’s Third Law of thermodynamics, see Kozliak and Lambert (2008), Gutzow and Schmelzer**  
 254 **(2011), Takada et al. (2015), Schmelzer and Tropin (2018), Feistel (2019b), or Shirai (2023).**

255

256 The TEOS-10 reference states (Feistel et al. 2008b, 2010a) are the triple point of water,  $T_{TP} =$   
 257 273.16 K,  $p_{TP} = 611.654\ 771$  Pa, where the conditions

258

$$259 \quad \eta_{TP}^W = 0, \quad e_{TP}^W = 0, \quad (1)$$

260

261 are imposed, and the standard ocean state,  $S_{SO} = 35.165\ 04\ \text{g kg}^{-1}$ ,  $T_{SO} = 273.15\ \text{K}$ ,  $p_{SO} =$   
 262  $101\ 325\ \text{Pa}$ , with the conditions for sea salt,

263

$$264 \quad \eta_{SO}^{SW} = 0, \quad h_{SO}^{SW} = 0, \quad (2)$$

265

266 and for dry air,

267

$$268 \quad \eta_{SO}^A = 0, \quad h_{SO}^A = 0. \quad (3)$$

269

270 Here,  $\eta$ ,  $e$  and  $h$ , respectively, are specific entropy, internal energy and enthalpy of **water**  
 271 **(superscript W), seawater (superscript SW) and dry air (superscript A)**. The TEOS-10 potential  
 272 functions and properties derived **thereby** are numerically implemented in two different libraries, the  
 273 Sea-Ice-Air (SIA) and the Gibbs-Seawater (GSW) libraries, see Table A4 in Appendix A.

274

275 The SIA library includes empirical coefficients only in the four fundamental potentials (Feistel 2010d,  
 276 Wright et al. 2010). All other potential functions and properties are derived strictly by mathematical  
 277 operations to ensure consistent results, even at the cost of low computation speeds as a result of  
 278 stacked iteration procedures. All quantities are exclusively expressed in basic SI units such as kg, m, J  
 279 or Pa. A more recent extension of SIA code is reported in Feistel et al. (2022) for the computation of  
 280 relative fugacity.

281

282 The GSW library is tailored for oceanographic models, optimised in computation speed (Roquet et al  
 283 2015). For fast numerical evaluation, GSW procedures contain new empirical coefficients determined  
 284 from the SIA library functions by regression. Units and variables are adjusted to common  
 285 oceanographic practice such as pressure in decibars relative to surface pressure, or temperatures in  
 286 °C. *Conservative Temperature* (CT) is used as a new preferred thermal variable. An additional  
 287 thermodynamic potential has been constructed (McDougall et al. 2023) that supports the use of CT  
 288 universally as an independent variable.

289

### 290 **3 Potential Enthalpy and Ocean Heat Content (OHC)**

291 Thermodynamically, the term “Ocean Heat Content” (OHC) is a sloppy wording. “Content” means a  
 292 state quantity of a body or volume while, **by contrast**, “heat” is an exchange quantity rather than a  
 293 state quantity. **“We have ... a right to speak of heat as a measurable quantity, ... however, ... we have**  
 294 **no right to treat heat as a substance”** (Maxwell 1888: p. 7). “The obsolete hypothesis of heat being a  
 295 substance is excluded” (Sommerfeld 1988: p. 6). This distinction is qualitatively fundamental (Feistel  
 296 2023). Physical conservation quantities such as energy or mass have the key property that the  
 297 change of that quantity in a volume equals the flux of that quantity across the boundary (Landau and  
 298 Lifschitz 1966, Glansdorff and Prigogine 1971), but this does not apply to “heat”. For example, a heat  
 299 engine receives a permanent net heat flux without getting permanently hotter. While asking how  
 300 much “heat” is contained in the ocean may find ambiguous answers, it is well defined to say how  
 301 much heat has entered **or** left the ocean across its boundary by a specified process that transfers the  
 302 ocean from a certain state of reference to the current state of interest. In this section, based upon  
 303 TEOS-10, related states and processes are described which may properly specify what is commonly  
 304 termed OHC. This consideration intrinsically connects OHC with ocean-atmosphere exchange  
 305 processes relevant for climate change.



306 Since a long time, measuring and calculating the ocean’s “heat” has been a question of central  
 307 interest to oceanography. Recently, this issue has become even more important and urgent in the  
 308 context of climate change. “The total energy imbalance at the top of atmosphere is best assessed by  
 309 taking an inventory of changes in energy storage. The main storage is in the ocean” (Abraham et al.  
 310 2013: p. 450). The conventional approach is a formally defined mathematical procedure based on  
 311 potential temperatures. “Changes to ocean heat content (OHC) can be calculated from  
 312 measurements of the temperature evolution of the ocean. The OHC is attained from the difference  
 313 of the measured potential temperature profile and the potential temperature climatology. This  
 314 difference is integrated over a particular reference depth (for instance, 700 m) and is multiplied by a  
 315 constant ocean density reference and heat capacity” (Abraham et al. 2013: p. 468). However, this  
 316 OHC definition has no rigorous thermodynamic justification, and the relation to processes of ocean-  
 317 atmosphere heat fluxes is not entirely clear. If a sea-air heat flux of  $1 \text{ W m}^{-2}$  warms up the  
 318 atmosphere, by what rate exactly will that OHC decrease?

319 Making the seawater properties entropy and enthalpy quantitatively available, TEOS-10 has offered a  
 320 thermodynamically improved option for defining OHC (McDougall et al. 2021), in the form of the  
 321 integral over the ocean volume,

$$322 \quad OHC = \int h^{SW}(S, \eta, p_0) \rho^{SW}(S, \eta, p) dV. \quad (4)$$

323 Here,  $h^{SW}(S, \eta, p_0)$  is the *potential enthalpy* (McDougall 2003) relative to the surface pressure,  $p_0$ ,  
 324 and  $\rho^{SW}(S, \eta, p)$  is the in-situ mass density at the pressure  $p$  of a parcel with salinity and entropy  
 325 equal to those before. This definition can be understood in terms of both, a specified process of heat  
 326 exchange, and a reference state relative to which OHC is counted, as follows (Feistel 2024):

- 327 (i) A virtual **heat exchange process** supporting the definition (4) is sketched in Fig. 6. In turn,  
 328 each ocean parcel with in-situ properties  $(S, \eta, p)$  is lifted to the surface pressure  $p_0$ ,  
 329 keeping its salinity and entropy constant. There, it reversibly exchanges heat,  $dh = Td\eta$ ,  
 330 with a measuring device until the parcel’s entropy has reached a certain reference value,  
 331  $\eta_{ref}$ , while the parcel’s salinity remains unchanged. Subsequently, the heat is reversibly  
 332 put back to the parcel which is then returned to its original location. The work required  
 333 to lift and lower the parcel is balanced.
- 334 (ii) The **reference state** relative to which OHC is measured is arbitrary and may be chosen by  
 335 convenience or usefulness. In the case of (4), the **OHC** reference state is zero potential  
 336 enthalpy (or zero Conservative Temperature, McDougall 2003) of all ocean parcels.

337 The process depicted in Fig. 6 measures the total heat flux  $\int dh = \int Td\eta$  which changes the entropy  
 338 of the given sample from the current value,  $\eta$ , to some arbitrary reference value,  $\eta_{ref}$ , and this way,  
 339 the process also changes the parcel’s enthalpy from  $h^{SW}(S, \eta, p_0)$  to  $h^{SW}(S, \eta_{ref}, p_0)$ . Integration  
 340 over all ocean samples results in an OHC value of

$$341 \quad OHC^* = \int [h^{SW}(S, \eta, p_0) - h^{SW}(S, \eta_{ref}, p_0)] \rho^{SW}(S, \eta, p) dV. \quad (5)$$

342 While the choice of the OHC reference state is - in principle - entirely arbitrary, such as simply putting  
 343  $\eta_{ref} = 0$ , it is reasonable to better adapt this selection to the purpose of the OHC definition. The  
 344 main purpose of estimating OHC is keeping track of the ocean’s long-term energy balance, in  
 345 particular of the ocean’s share of global warming. Three conditions appear immediately plausible in  
 346 order to achieve this goal,

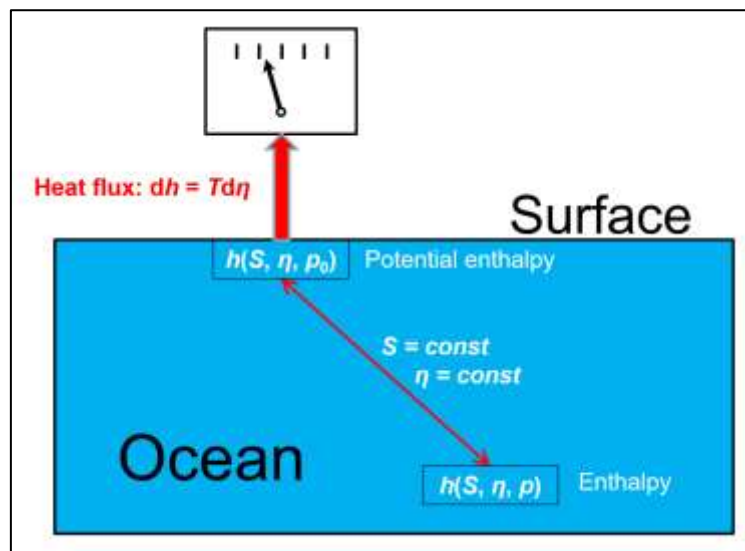
- 347 (i) *The OHC definition should ensure that OHC differences represent a suitable spatial*  
 348 *integral over the heat fluxes crossing the ocean’s boundaries. As discussed in more detail*  
 349 *in Section 5.3, production of entropy,  $d_i\eta$ , caused by irreversible processes between*

350 different parcels within the ocean, does not affect the ocean's total enthalpy budget.  
 351 This is quite in contrast to entropy exchange,  $d_e\eta$ , of the given sample in the form of  
 352 reversible heat flux across its boundary. Such irreversible processes affect the ocean's  
 353 total potential enthalpy much less than its total entropy (McDougall et al. 2021). For this  
 354 reason the OHC reference state should explicitly be defined in terms of potential  
 355 enthalpy,  $h^{SW}(S, \eta_{ref}, p_0)$ , and this way only implicitly in terms of entropy by specifying  
 356  $\eta_{ref}(S)$ .

357  
 358 (ii) Provided that the ocean's mass remains the same between any two ocean states (1) and  
 359 (2), the difference  $OHC(1) - OHC(2)$  should depend only on the surface heat flux balance  
 360 during the time in between. In particular, differences  $OHC(1) - OHC(2)$  should not depend  
 361 on the OHC reference state. For this reason, the OHC reference value should be  
 362 independent of changes occurring in the density distribution,  $\rho^{SW}(S, \eta, p)$ . This can be  
 363 achieved by assigning to each ocean parcel the same reference potential enthalpy,  
 364  $h^{SW}(S, \eta_{ref}, p_0) = \text{const}$ , even though such a state may hardly ever be observed in the  
 365 real ocean.

366  
 367 (iii) Quantitatively, OHC values estimated at different times or places should be mutually  
 368 comparable without estimation bias resulting from possibly changing methods of OHC  
 369 calculation. For this reason, resulting OHC values should be independent of the inevitable  
 370 arbitrary, physically irrelevant reference-state conditions imposed on energy and  
 371 entropy, such as eqs. (1)-(3). This can be achieved by assigning to each ocean parcel the  
 372 same standard-ocean enthalpy as its reference potential enthalpy,  $h^{SW}(S, \eta_{ref}, p_0) =$   
 373  $h_{SO}$ . In the special case of TEOS-10 enthalpy, this value is defined by eq. (2),  $h_{SO} = 0$ .  
 374 This choice is implicitly made by the definition (4) but needed to be considered explicitly  
 375 as soon as alternative equations for seawater enthalpy or entropy are employed, such as  
 376 those of Millero and Leung (1976) and Millero (1982, 1983).

377



378

379 Fig. 6: Schematic of a conceptual process defining the ocean heat "content" (OHC) by measuring heat  
 380 flux across the ocean boundary according to eqs. (4) and (5).

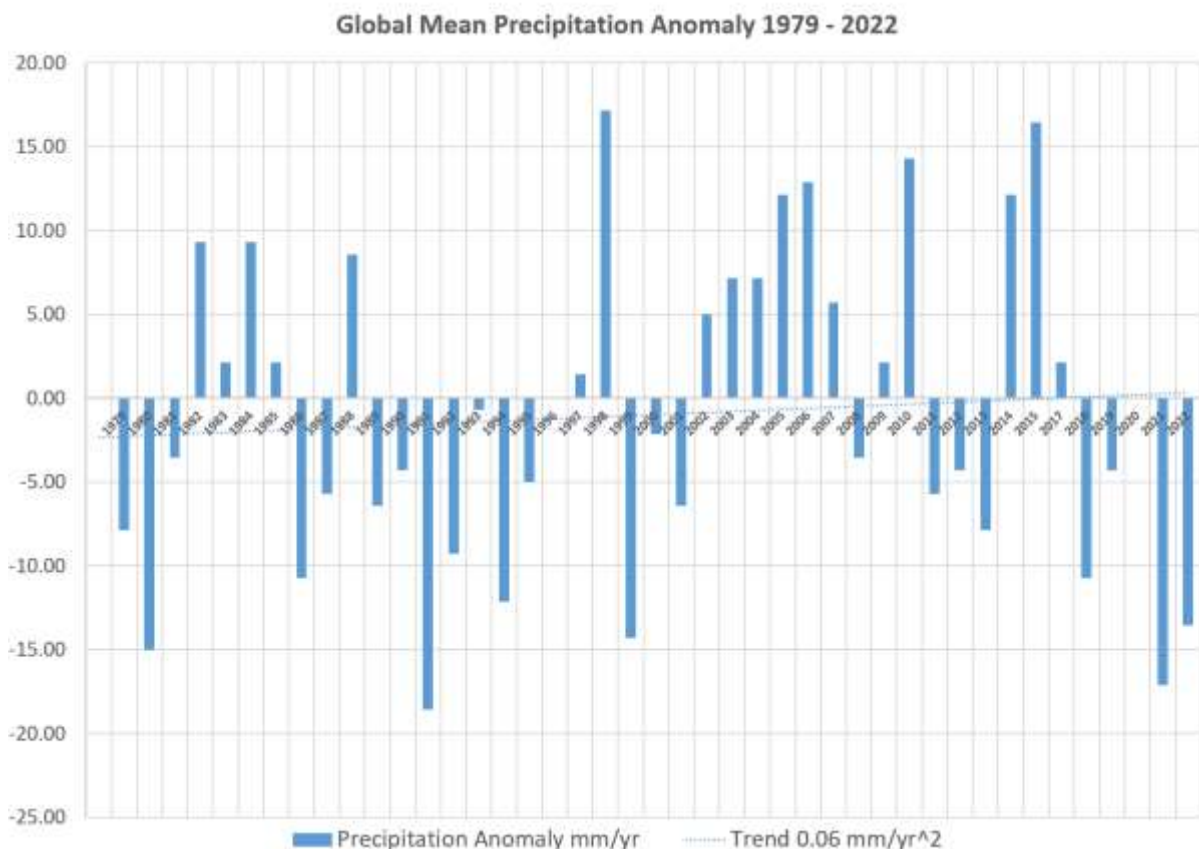
381

382 In a sense consistent with the previous OHC definition (Abraham et al. 2013), also a climatological  
 383 average state could in principle be chosen as the OHC reference. However, this option includes the  
 384 problem that the salinity distribution of the current ocean may differ from the reference ocean, and  
 385 that thermodynamically properly treating the required salt exchange processes at the surface may  
 386 turn the issue unnecessarily complicated. A detailed comparison of the OHC definition (4) with its  
 387 precursor prior to TEOS-10 is provided by McDougall et al. (2021). OHC as a part of the total energy  
 388 balance of the ocean is analysed by Tailleux (2010, 2018) and Tailleux and Dubos (2024).

389

#### 390 4 Relative Fugacity and Ocean Evaporation Rate

391 "The global water cycle and the exchange of freshwater between the atmosphere and ocean is  
 392 poorly understood. ... It has been predicted that increasing global temperatures will lead to an  
 393 enhanced global water cycle" (Holliday et al. 2011: p. 34). In the past, several climate researchers  
 394 have argued that along with global warming the marine evaporation has or will be "amplified" or  
 395 "intensified" (Feistel and Hellmuth 2021). However, it was not always made clear whether this may  
 396 mean that (a) in the course of a year, more water vapour is transferred from the global ocean to the  
 397 atmosphere, or (b) that the global mean evaporation rate remains unchanged while locally or  
 398 temporally, evaporation is more intense, or (c) any combination of the two variants. Conclusions of  
 399 kind (a) were drawn by renowned climatologists such as Budyko (1984), Flohn et al. (1992), Yu  
 400 (2007), Randall (2012), Francis (2021) or Zhang et al. (2021).



401

402 Fig. 7: Global mean precipitation anomaly 1979-2022 in  $\text{mm yr}^{-1}$ . The values displayed exhibit a minor  
 403 increasing trend (dotted line) of  $0.06 \text{ mm yr}^{-2}$ . Data from Vose et al. (2023)

404

405 By contrast, **in favour of option (b)**, the currently observed ocean warming at a rate about  $1 \text{ W m}^{-2}$   
 406 does not support assumptions of an enhanced hydrological cycle with related latent-heat cooling,  
 407 rather, it more likely suggests **a** slight reduction of evaporation. Two decades ago, Held and Soden  
 408 (2006: p. 5687-5689) had already clearly stated that “it is important that the global-mean  
 409 precipitation or evaporation, commonly referred to as the strength of the hydrological cycle, does  
 410 not scale with Clausius–Clapeyron. ... We can, alternatively, speak of the mean residence time of  
 411 water vapor in the troposphere as increasing with increasing temperature.” Subsequent observations  
 412 have underpinned their statement.

413 Between 1979 and 2022, annual mean global precipitation values, see Figure 7, fluctuated by about  
 414  $\pm 10 \text{ mm yr}^{-1}$ , in particular due to La Niña events, but do not exhibit a significant long-term trend  
 415 (Vose et al. 2023). Under the common assumption that global precipitation is balanced against  
 416 evaporation, no substantial strengthening of the hydrological cycle may be observed yet.

417 Probably, the minor trend of  $0.06 \text{ mm yr}^{-2}$  of the data displayed in Fig. 7 is statistically insignificant.  
 418 Associated with this apparent trend, the latent heat transferred to the troposphere can be estimated  
 419 to a negligible putative warming rate of additional  $0.5 \text{ mW m}^{-2}$  per year, which could explain only 10  
 420 % of observed atmospheric warming by  $1.7 \text{ °C}$  per century (Morice et al. 2012, Feistel and Hellmuth  
 421 2021).

422 The thermodynamic driving force for evaporation is the difference between the chemical potentials  
 423 of water in humid air and in seawater at the two sides of the sea-air interface (Kraus and Businger  
 424 1994). TEOS-10 has made this difference numerically available in the form of the water mass  
 425 evaporation rate (Feistel and Hellmuth 2022, 2023)

$$426 \quad J_W = -D_f(u) \ln \frac{\psi_f}{x_W}. \quad (6)$$

427 **Here,  $x_W$**  is the mole fraction of water in seawater. Consistent with Wüst (1920), for the standard  
 428 ocean with Reference Composition, this fraction is (Millero et al. 2008: Table 4),

$$429 \quad x_W = \frac{53.556\ 514\ 4}{54.676\ 283\ 8} = 0.979\ 52, \quad \ln x_W = -0.0206926. \quad (7)$$

430 **In eq. (6),  $D_f(u)$ , the Dalton coefficient, is an empirical transfer coefficient as a function of the wind**  
 431 **speed,  $u$ , as a parameterisation of the turbulent transport processes of water in the vicinity of the**  
 432 **interface. Applications of the Monin-Obukhov Similarity Theory (MOST) in order to estimate the**  
 433 **Dalton coefficient are reviewed by Liu et al. (1979), Foken and Richter (1991), Foken (2004, 2016) and**  
 434 **in the Digital Supplement of Feistel and Hellmuth (2024). A review of empirical Dalton coefficients is**  
 435 **given by Debski (1966).**

436 In eq. (6), the sea-surface humidity is expressed by the *relative fugacity* (RF),  $\psi_f$ , defined by the ratio  
 437 of the water-vapour fugacity in humid air,  $f_v$ , to that fugacity at saturation,  $f_v^{\text{sat}}$  (Feistel and Lovell-  
 438 Smith 2017), see eq. (49). In ideal-gas approximation, RF equals conventional RH (Lovell-Smith et al.  
 439 2016)

$$440 \quad \psi_f \equiv \frac{f_v}{f_v^{\text{sat}}} \approx \psi_x \equiv \frac{x}{x^{\text{sat}}}. \quad (8)$$

441 Here, the mole fraction of water vapour in humid air is  $x$ , and its value at saturation is  $x^{\text{sat}}$ . Further,  
 442  $\psi_x$  is the conventional definition of RF in metrology and meteorology **which, however, is inconsistent**  
 443 **with alternative definitions such as the one employed in climatology** (Lovell-Smith et al. 2016).  
 444 Independent of ideal-gas conditions, but sufficiently close to saturation, such as near the sea surface,  
 445 RF can be estimated in excellent approximation from the Clausius-Clapeyron formula (Feistel et al.  
 446 2022),

$$447 \quad \psi_f \approx \exp \left\{ \frac{L(T_{dp,p})}{R_W} \left( \frac{1}{T} - \frac{1}{T_{dp}} \right) \right\}. \quad (9)$$

448 The evaporation enthalpy of pure water (IAPWS SR1-86 1992) at the dewpoint  $T_{dp}$  is  $L$ , and  $R_W =$   
449  $461.523 \text{ J kg}^{-1} \text{ K}^{-1}$  is the specific gas constant of water. The typical marine RF is

$$450 \quad \psi_f \approx 80 \% \text{rh}, \quad (10)$$

451 and is fairly independent of region, season or global warming (Dai 2006, Randall 2012, Rapp 2014,  
452 MetOffice 2020). Indeed, observed ocean surface RH has no significant climatological trend (Willett  
453 et al. 2023). Similarly, observed ocean wind speeds seem to be unaffected by global warming (Azorin-  
454 Molina et al. 2023). Eq. (6) for the evaporation rate depends only on wind speed and RF, so that it  
455 may be concluded that also the global mean evaporation rate has no significant climatic trend. In  
456 turn, as far as the release of latent heat is the main driving force of marine tropospheric dynamics,  
457 without increase of that release the mean wind speed is not expected to grow. "Latent heat is the  
458 main fuel that powers hurricanes, thunderstorms and normal bouts of lousy weather" (Francis 2021).  
459 Hence, the TEOS-10 approach in the form of eq. (6) appears to be consistent with the prediction of  
460 Held and Soden (2006) that the global evaporation does not increase along with temperature.

461 Various empirical evaporation equations, commonly known as *Dalton equations*, are found in the  
462 literature (Wüst 1920, Sverdrup 1936, 1937, Montgomery 1940, Debski 1966, Baumgartner and  
463 Reichel 1975). Several numerical climate models estimate evaporation from the formula (Stewart  
464 2008, Pinker et al. 2014),

$$465 \quad J_W = D_q(u)(q_0 - q_{10}), \quad (11)$$

466 where  $q_0$  is the specific humidity at the sea surface and  $q_{10}$  is that at 10 m height, or from (Josey et  
467 al. 1999, 2013)

$$468 \quad J_W = D_q(u)(0.98 q^{\text{sat}} - q). \quad (12)$$

469 Here,  $q$  is the near-surface specific humidity, and  $q^{\text{sat}}$  is the saturation value at the same  
470 temperature and pressure. The factor 0.98 accounts for the salinity, see eq. (7). After a few  
471 approximation steps (Feistel and Hellmuth 2023), these Dalton equations can be derived from the  
472 TEOS-version, eq. (6), however, there is an important qualitative difference. At constant RH, due to  
473 global warming, specific humidities such as  $q$  and  $q^{\text{sat}}$ , as well as their difference, are increasing  
474 following the Clausius-Clapeyron saturation formula. Accordingly, eq. (12) implies that also the  
475 evaporation rate  $J_W$  is growing this way, by contrast to eq. (6). This virtual acceleration of the  
476 hydrological cycle is evidently inconsistent with the prediction of Held and Soden (2006). This  
477 parameterisation-caused additional latent heat flux implies a spurious ocean cooling that may  
478 contribute to the finding that many numerical climate models tend to underestimate the observed  
479 ocean warming (Weller et al. 2022).

480 From eq. (6), the sensitivity of the latent heat flux,  $LJ_W$ , with respect to RH variations is easily  
481 estimated. For a mean evaporation rate of 1200 mm per year, the corresponding mass flux is about  
482  $J_W \approx 3.8 \times 10^{-5} \text{ kg m}^{-2} \text{ s}^{-1}$  and the related heat flux is  $LJ_W \approx 95 \text{ W m}^{-2}$  with respect to the ocean  
483 surface area and a specific evaporation enthalpy of  $L = 2501 \text{ kJ kg}^{-1}$ . At a surface humidity of  $\psi_f =$   
484 0.8, a value of  $D_f(u) \approx 1.87 \times 10^{-4} \text{ kg m}^{-2} \text{ s}^{-1}$  can be concluded for the mass transfer coefficient,  
485 and of  $LD_f(u) \approx 468 \text{ W m}^{-2}$  for that of latent heat. Then, from

$$486 \quad \Delta(LJ_W) = L \frac{\partial J_W}{\partial \psi_f} \Delta \psi_f = -LD_f(u) \frac{\Delta \psi_f}{\psi_f} \quad (13)$$

487 it follows that an increase by  $\Delta\psi_f = 1 \text{ \%rh}$  results in a heat flux reduction by  $\Delta(LJ_W) =$   
 488  $5.85 \text{ W m}^{-2}$ . So, the currently observed ocean warming (Cheng et al. 2024) of  $1.3 \text{ W m}^{-2}$  could  
 489 theoretically be caused already by a minor marine humidity increase of  $\Delta\psi_f = 0.2 \text{ \%rh}$ , a value far  
 490 below the present measurement uncertainty between 1 and 5 %rh of relative humidity. The  
 491 resolution of climate models and observation seems to be insufficient yet to identify the possible role  
 492 of RH for the unclear explanation of the warming ocean.

493

## 494 5 Sea Air as a Two-Phase Composite

495 Gibbs' (1873) method of using potential functions can be applied to any systems possessing stable  
 496 thermodynamic equilibria and obeying energy conservation, without being restricted to merely  
 497 homogeneous or single-phase samples. The intentionally strict mutual consistency of the different  
 498 TEOS-10 potential functions permits a mathematical description of multi-phase composites such as  
 499 sea ice, consisting of ice with included brine pockets (Feistel and Hagen 1998, Feistel and Wagner  
 500 2005), or clouds, where liquid water or ice is floating in saturated humid air (Hellmuth et al. 2021).  
 501 Another important model is that of *sea air*, a sample consisting of a mass  $m^{\text{SW}}$  of seawater in  
 502 thermodynamic equilibrium with a mass  $m^{\text{AV}}$  of humid air (Feistel et al. 2010d, Feistel and Hellmuth  
 503 2023). Such a model may serve as a mathematical description for certain thermodynamic properties  
 504 of ocean-atmosphere interaction.

505 Extensive thermodynamic functions such as Gibbs energy or enthalpy are additive with respect to the  
 506 two separate phases of the sample. Equilibrium between those parts requires equal temperatures  
 507 and pressures. For this reason, a Gibbs function of sea air is an appropriate potential for the  
 508 composite system with **the TEOS-10 Gibbs functions**  $g^{\text{SW}}(S, T, p)$  describing the liquid part and  
 509  $g^{\text{AV}}(A, T, p)$  the gas part. Let the masses of the substances in the parts be  $m^{\text{W}}$  of liquid water,  $m^{\text{S}}$  of  
 510 dissolved salt,  $m^{\text{A}}$  of dry air and  $m^{\text{V}}$  of water vapour. Note that TEOS-10 neglects solubility of dry air  
 511 constituents in liquid water. From combinations of the partial masses follow the liquid mass,  $m^{\text{SW}} =$   
 512  $m^{\text{S}} + m^{\text{W}}$ , the gas mass,  $m^{\text{AV}} = m^{\text{A}} + m^{\text{V}}$ , the total mass  $m = m^{\text{SW}} + m^{\text{AV}}$ , the total water mass  
 513  $m^{\text{WV}} = m^{\text{W}} + m^{\text{V}}$ , the salinity  $S = m^{\text{S}}/m^{\text{SW}}$  and the dry-air fraction  $A = 1 - q = m^{\text{A}}/m^{\text{AV}}$ .

514 The Gibbs energies of the two phases of sea air are additive,

$$515 \quad G^{\text{SA}} = G^{\text{SW}} + G^{\text{AV}} = m g^{\text{SA}}, \quad (14)$$

516 **and**, accordingly, the Gibbs function of sea air,  $g^{\text{SA}}$ , may be constructed from that of seawater,  
 517  $g^{\text{SW}}(S, T, p)$ , with a liquid mass fraction of  $w^{\text{SW}} = m^{\text{SW}}/m$  and that of humid air,  $g^{\text{AV}}(A, T, p)$ , with  
 518 a gaseous mass fraction of  $w^{\text{AV}} = m^{\text{AV}}/m = 1 - w^{\text{SW}}$ ,

$$519 \quad g^{\text{SA}}(S, A, w^{\text{SW}}, T, p) = w^{\text{SW}} g^{\text{SW}}(S, T, p) + (1 - w^{\text{SW}}) g^{\text{AV}}(A, T, p). \quad (15)$$

520 If the two phases are assumed to be at mutual equilibrium, they possess the same temperature,  
 521 pressure and chemical potentials, see eq. (B.11) in Appendix B,  $\mu_{\text{W}}^{\text{SW}} = \mu_{\text{V}}^{\text{AV}}$ , namely that of water in  
 522 seawater,

$$523 \quad \mu_{\text{W}}^{\text{SW}}(S, T, p) = g^{\text{SW}} - S \left( \frac{\partial g^{\text{SW}}}{\partial S} \right)_{T, p}, \quad (15)$$

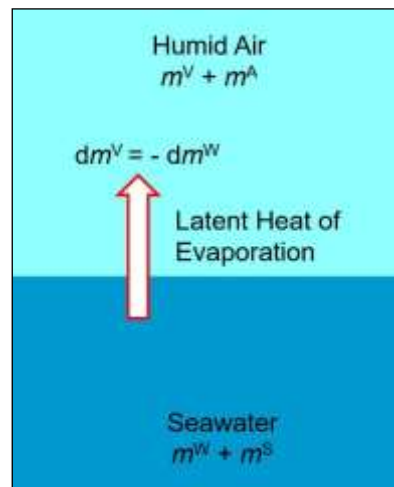
524 **equalling** that of water vapour in humid air,

$$525 \quad \mu_{\text{V}}^{\text{AV}}(A, T, p) = g^{\text{AV}} - A \left( \frac{\partial g^{\text{AV}}}{\partial A} \right)_{T, p}. \quad (16)$$

526

527 *5.1 Sea Air as a Model for Latent Heat of Evaporation*

528 Water evaporated from the ocean surface drives the climate system. “The by far largest part of heat  
 529 conveyed to the air is in the form of latent heat during subsequent condensation along with cloud  
 530 formation. The heat budget over the sea is mainly controlled by the latent heat released to the air”  
 531 (Albrecht 1940). It is the “*heat source for a gigantic steam engine*”, as Heinrich Hertz had put it in his  
 532 1885 inaugural lecture at Karlsruhe (Mulligan and Hertz 1997). The latent heat of evaporation of pure  
 533 liquid water into pure water vapour is numerically well known from experiments (IAPWS SR1-86  
 534 1992, Harvey 1998, Wagner and Pruß 2002). Slightly differing values are reported in various  
 535 textbooks on hydrology (Debski 1966: p. 332), meteorology (Linke and Baur 1970) or geophysics (Gill  
 536 1982, Kraus and Businger 1994). TEOS-10, however, permits the computation of evaporation  
 537 properties from seawater into humid air, based on the first-time availability of standard equations  
 538 for enthalpies and chemical potentials of those non-ideal mixtures.



539

540 Fig. 8: Conceptual thermodynamic “sea air” model of ocean-atmosphere interaction as a two-phase  
 541 composite of seawater and humid air

542

543 “Latent heat is the quantity of heat which must be communicated to a body in a given state in order  
 544 to convert it into another state without changing its temperature” (Maxwell 1888: p.73). If an  
 545 infinitesimal amount of water is transferred from the liquid to the gas phase (Fig. 8), while  
 546 temperature and pressure remain at their equilibrium values, and the total masses of salt,  $m^S$ , dry  
 547 air,  $m^A$ , and water,  $m^{WV}$ , are not affected, the isobaric-isothermal latent heat of evaporation may be  
 548 defined by

$$549 \quad L^{SA} \equiv \left( \frac{\partial H^{SA}}{\partial m^V} \right)_{T,p,m^S,m^A,m^{WV}} \quad (17)$$

550 This latent heat accounts for the loss of total heat of the sea-air sample associated with the loss of  
 551 liquid water and equal gain of water vapour,

$$552 \quad \frac{\partial m^V}{\partial T} = - \frac{\partial m^W}{\partial T}. \quad (18)$$

553 Here,  $H^{SA}$  is the enthalpy of sea air, available from the Gibbs function (15) through the sum

$$554 \quad H^{SA} \equiv m^{SW} h^{SW} + m^{AV} h^{AV}. \quad (19)$$

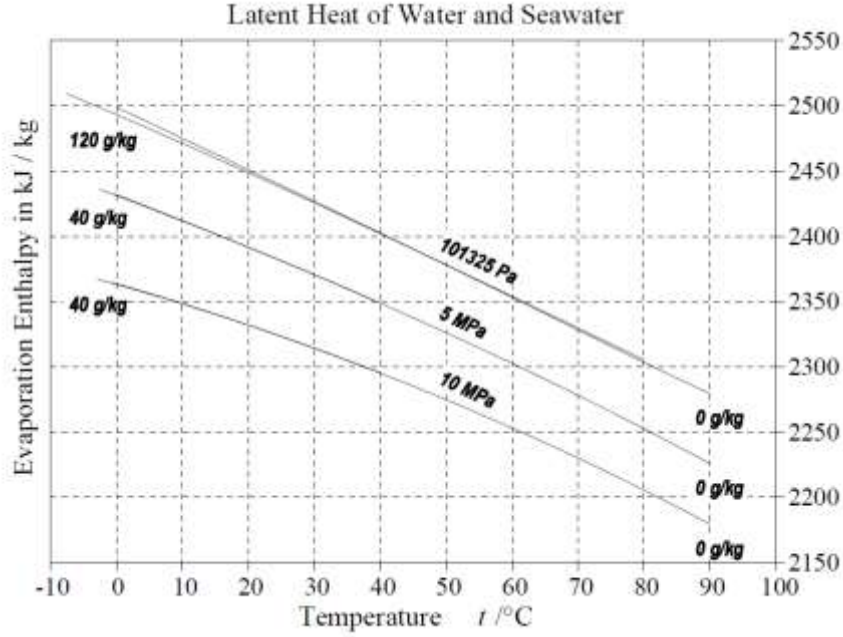
555 Here, the specific enthalpies of seawater,

$$556 \quad h^{\text{SW}} = g^{\text{SW}} - T \left( \frac{\partial g^{\text{SW}}}{\partial T} \right)_{S,p}, \quad (20)$$

557 and of humid air,

$$558 \quad h^{\text{AV}} = g^{\text{AV}} - T \left( \frac{\partial g^{\text{AV}}}{\partial T} \right)_{A,p}, \quad (21)$$

559 are defined in terms of the related Gibbs functions.



560

561 Fig. 9: Evaporation enthalpy, eq. (23), of seawater in equilibrium with humid air at different  
 562 temperatures, pressures and salinities. The dependence on salinity is very weak; graphically, the  
 563 related curves are hardly distinguishable. The nonlinear dependence on temperature is more  
 564 pronounced at elevated pressures. Figure from Feistel et al. (2010a: p. 105)

565

566 The derivative (17) is carried out in the form

$$567 \quad L^{\text{SA}} = -h^{\text{SW}} - m^{\text{SW}} \left( \frac{\partial h^{\text{SW}}}{\partial S} \right)_{T,p} \left( \frac{\partial S}{\partial m^{\text{V}}} \right)_{m^{\text{S}},m^{\text{WV}}} + h^{\text{AV}} + m^{\text{AV}} \left( \frac{\partial h^{\text{AV}}}{\partial A} \right)_{T,p} \left( \frac{\partial A}{\partial m^{\text{V}}} \right)_{m^{\text{A}}}, \quad (22)$$

568 which results in the TEOS-10 latent-heat equation (Feistel et al. 2010a, Feistel and Hellmuth 2023),

$$569 \quad L^{\text{SA}} = h^{\text{AV}} - A \left( \frac{\partial h^{\text{AV}}}{\partial A} \right)_{T,p} - h^{\text{SW}} + S \left( \frac{\partial h^{\text{SW}}}{\partial S} \right)_{T,p}, \quad (23)$$

570 with typical values shown in Fig. 9. If seawater is in mutual equilibrium with humid air at given  
 571 temperature and pressure, salinity and humidity of the parts of sea air satisfy the condition  $\mu_{\text{W}}^{\text{SW}} =$   
 572  $\mu_{\text{V}}^{\text{AV}}$ , given by eqs. (15) and (16),

$$573 \quad \Delta\mu \equiv g^{\text{SW}} - S \left( \frac{\partial g^{\text{SW}}}{\partial S} \right)_{T,p} - g^{\text{AV}} + A \left( \frac{\partial g^{\text{AV}}}{\partial A} \right)_{T,p} = 0 \quad (24)$$

574 At given masses of salt,  $m^{\text{S}}$ , of dry air,  $m^{\text{A}}$ , and of total water,  $m^{\text{WV}} = m^{\text{W}} + m^{\text{V}}$ , eq. (24) controls  
 575 the value of either  $m^{\text{W}}$  or  $m^{\text{V}}$ , and this way also of  $S$  and  $A$  as functions of  $T$ ,  $p$ ,  $m^{\text{S}}$ ,  $m^{\text{A}}$  and  $m^{\text{WV}}$ .  
 576 Related numerical solutions are readily implemented in the TEOS-10 SIA library; the latent heat of



577 sea air can be computed by calling the function `sea_air_enthalpy_evap_si()`, see Wright et al.  
578 (2010).

579 Latent heat of eq. (23) is valid regardless of the equilibrium condition, eq. (24), is satisfied or not. The  
580 non-equilibrium case is considered separately in Section 5.3.

581

## 582 *5.2 Sea Air as a Model of Sea Spray*

583 As a special form of air-sea interaction, sea spray is typically ejected from the crest of a breaking  
584 wave, which may happen all along oceanic coasts but also wherever whitecaps are produced from  
585 swell or stormy sea state, see Fig. 10. In contrast to fresh-water haze, droplets of sea spray cannot  
586 completely evaporate for the salt they contain, and rather develop into a floating persistent Köhler  
587 (1936) equilibrium between droplet size, droplet salinity and ambient relative fugacity (Hellmuth and  
588 Shchekin 2015, Pöhlker et al. 2023). This equilibrium can be described by the TEOS-10 model of sea  
589 air if the additional Kelvin pressure caused by the surface tension is allowed for.



590

591 Fig. 10: Sea spray ejection from a breaking wave crest of Atlantic swell. Photo taken at Cabo Trafalgar  
592 in March 2011.

593

594 In the infrared spectral range, sea spray as well as other aerosols (Carlon 1970, 1980) may be  
595 considered as a black absorber and emitter of thermal radiation. The resulting “gray atmosphere” is a  
596 conveniently simple conceptual model for the long-wave radiative effects of dust or haze in the  
597 climate system (Emden 1913). When heated from below, as in the case of the clear-sky marine  
598 troposphere, a theoretical finding is that the thermally stratified gray troposphere exhibits a special  
599 critical value of the isobaric heat capacity at  $c_p = 4R$  (Pierrehumbert 2010: p. 201),  $R$  being the  
600 molar gas constant. Vertical stability may be lost at  $c_p > 4R$  and turbulent mixing is expected to  
601 commence (Feistel 2011b: eq. 58 therein). Such a kinetic phase transition could substantially modify  
602 the thermal radiation balance between troposphere and ocean surface.

603 The terrestrial atmosphere is dominated by the two-atomic gases  $N_2$  and  $O_2$  with heat capacities  
604 about  $3.5 R$  which prevent the putative radiative vertical instability to occur. This situation may

605 change, however, in the presence of haze or sea spray. To investigate this effect theoretically, in this  
606 section a TEOS-10 equation for the heat capacity of equilibrium sea air is derived from the definition

$$607 \quad c_p^{SA} \equiv \frac{1}{m} \left( \frac{\partial H^{SA}}{\partial T} \right)_{p,m^S,m^A,m^{WV}}. \quad (25)$$

608 The enthalpy of sea air is given by eq. (19). Taking into account water conservation upon  
609 evaporation,  $m^{WV} = \text{const}$ , that is,

$$610 \quad \frac{\partial m^V}{\partial T} = - \frac{\partial m^W}{\partial T}, \quad (26)$$

611 and of eq. (23), the isobaric heat capacity of sea air is concluded to be

$$612 \quad c_p^{SA} = w^{SW} c_p^{SW} + w^{AV} c_p^{AV} + L^{SA} \frac{1}{m} \frac{\partial m^V}{\partial T}. \quad (27)$$

613 To the additive contributions of the partial heat capacities of the liquid and the gas part, there  
614 appears the latent heat of the water mass that evaporates from the liquid as vapour. This  
615 evaporation rate is governed by the mutual equilibrium between seawater and humid air.

616 During the temperature change, sea-air equilibrium, eq. (24), is assumed to be maintained by water  
617 transfer between the phases, changing  $S$  and  $A$  along with  $T$ ,

$$618 \quad \left( \frac{\partial \Delta \mu}{\partial T} \right)_{p,m^S,m^A,m^{WV}} = 0. \quad (28)$$

619 Carrying out the derivative, this condition reads

$$620 \quad \left( \frac{\partial g^{SW}}{\partial T} \right)_{S,p} - S \left( \frac{\partial^2 g^{SW}}{\partial S \partial T} \right)_p - S \left( \frac{\partial^2 g^{SW}}{\partial S^2} \right)_{T,p} \left( \frac{\partial S}{\partial T} \right)_{m^S} \\ 621 \quad = \left( \frac{\partial g^{AV}}{\partial T} \right)_{A,p} - A \left( \frac{\partial^2 g^{AV}}{\partial A \partial T} \right)_p - A \left( \frac{\partial^2 g^{AV}}{\partial A^2} \right)_{T,p} \left( \frac{\partial A}{\partial T} \right)_{m^A}. \quad (29)$$

622 On the other hand, from combining eq. (23) with eq. (24) it follows that the latent heat may be  
623 expressed by,

$$624 \quad L^{SA} = T \left\{ \left( \frac{\partial g^{SW}}{\partial T} \right)_{S,p} - S \left( \frac{\partial^2 g^{SW}}{\partial S \partial T} \right)_p - \left( \frac{\partial g^{AV}}{\partial T} \right)_{A,p} + A \left( \frac{\partial^2 g^{AV}}{\partial A \partial T} \right)_p \right\}, \quad (30)$$

625 so that eq. (29) may be written as

$$626 \quad L^{SA} = T \left\{ S \left( \frac{\partial^2 g^{SW}}{\partial S^2} \right)_{T,p} \left( \frac{\partial S}{\partial T} \right)_{m^S} - A \left( \frac{\partial^2 g^{AV}}{\partial A^2} \right)_{T,p} \left( \frac{\partial A}{\partial T} \right)_{m^A} \right\}. \quad (31)$$

627 Further, the total water mass balance, eq. (26), implies that

$$628 \quad \left( \frac{\partial S}{\partial T} \right)_{m^S} = \left( \frac{\partial S}{\partial m^W} \right)_{m^S} \frac{\partial m^W}{\partial T} = \frac{S}{m^{SW}} \frac{\partial m^V}{\partial T}, \quad (32)$$

629 and similarly,

$$630 \quad \left( \frac{\partial A}{\partial T} \right)_{m^A} = \left( \frac{\partial A}{\partial m^V} \right)_{m^A} \frac{\partial m^V}{\partial T} = - \frac{A}{m^{AV}} \frac{\partial m^V}{\partial T}. \quad (33)$$

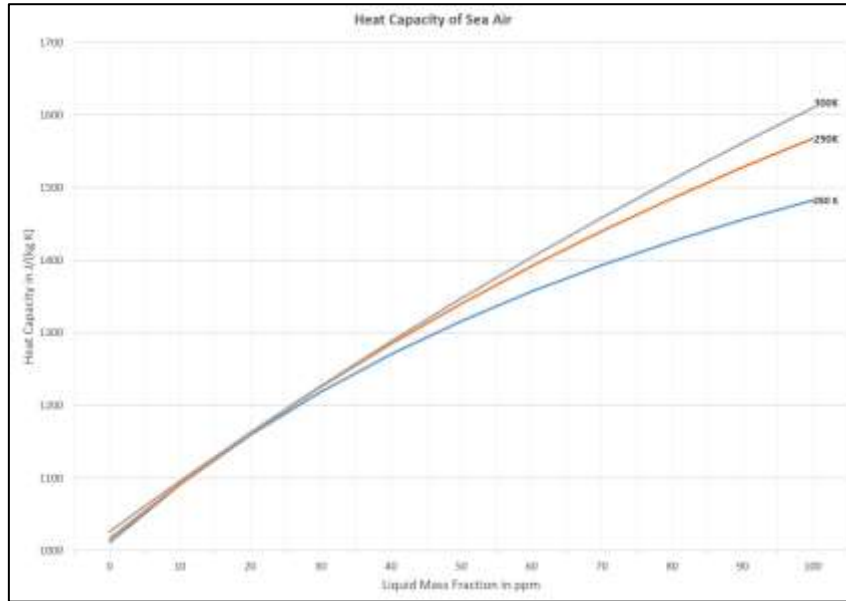
631 Inserting those expressions into eq. (31), the equation for the isobaric evaporation rate of sea air is

$$632 \quad \frac{\partial m^V}{\partial T} = \frac{L^{\text{evap}}}{T} \left\{ \frac{S^2}{m^{SW}} \left( \frac{\partial^2 g^{SW}}{\partial S^2} \right)_{T,p} + \frac{A^2}{m^{AV}} \left( \frac{\partial^2 g^{AV}}{\partial A^2} \right)_{T,p} \right\}^{-1}. \quad (34)$$

633 Together with eq. (34), the desired formula for the isobaric heat capacity (27) of sea air finally  
 634 becomes (Feistel et al. 2010a: eq. 6.22 therein),

$$635 \quad c_p^{SA} = w^{SW} c_p^{SW} + (1 - w^{SW}) c_p^{AV} + \frac{(L^{SA})^2}{T} \left\{ \frac{S^2}{w^{SW}} \left( \frac{\partial^2 g^{SW}}{\partial S^2} \right)_{T,p} + \frac{A^2}{(1-w^{SW})} \left( \frac{\partial^2 g^{AV}}{\partial A^2} \right)_{T,p} \right\}^{-1}. \quad (35)$$

636 Of the *liquid water content*, expressed in form of the liquid mass fraction,  $w^{SW}$ , realistic values may  
 637 typically range between  $10^{-6}$  and  $10^{-4}$  in the troposphere. Growing along with this fraction, related  
 638 heat capacities of sea air, eq. (35), may substantially exceed that of liquid-free humid air,  $c_p^{AV}$ , see  
 639 Fig. 11.



640

641 Fig. 11: TEOS-10 values for the isobaric specific heat capacity, eq. (35), of sea air at atmospheric  
 642 pressure and sea-spray standard-ocean salinity,  $S = 35.165\ 04\ \text{g kg}^{-1}$ , at temperatures of 280 K (lower  
 643 curve), 290 K (middle curve) and 300 K (upper curve) as functions of the liquid mass fraction,  $w^{SW}$ ,  
 644 up to 100 ppm.

645

### 646 5.3 Sea Air as a Model for Irreversible Evaporation

647 The climate system functions far from thermodynamic equilibrium, permanently producing and  
 648 exporting entropy at an average rate **about**  $1\ \text{W m}^{-2}\ \text{K}^{-1}$  per global surface area (Ebeling and Feistel  
 649 1982, Feistel and Ebeling 2011). By contrast, TEOS-10 is a mathematical description of equilibrium  
 650 properties (Appendix B). The latter is applicable to states away from thermodynamic equilibrium  
 651 under the assumption of *local equilibrium* as introduced by Ilya Prigogine (1947, 1978). This  
 652 assumption means that spatially extended substances such as ocean or atmosphere consist of  
 653 sufficiently small volume elements that may reasonably be described as macroscopic equilibrium  
 654 states, homogeneous in temperature, pressure and chemical potentials. TEOS-10 thermodynamic  
 655 potentials can be used to describe those local states.

656 By definition, if a volume at equilibrium is divided into partial volumes, each of those parts is at  
 657 equilibrium itself, and each pair of those is at mutual equilibrium also. The combination of several  
 658 local-equilibrium elements forms a non-equilibrium state if pairs of elements exist that are out of  
 659 mutual equilibrium. Extensive properties such as mass, energy, entropy or enthalpy can be added up  
 660 to give correct values of the entire system. When exchange processes between those elements

661 occur, gains and losses of masses, energies or enthalpies are mutually balanced by conservation laws,  
662 however, this is not the case for entropy.

663 A tutorial case of a local equilibrium system may be the model of sea air (Feistel and Hellmuth 2024a)  
664 depicted in Fig. 8. It consists of a mass  $m^{\text{SW}} = m^{\text{S}} + m^{\text{W}}$  of seawater in contact with a mass  $m^{\text{AV}} =$   
665  $m^{\text{A}} + m^{\text{V}}$  of humid air. Both fluids are assumed to be at internal equilibrium themselves but not  
666 necessarily in mutual equilibrium with one another. This is a natural geophysical situation – marine  
667 RH has typical values of 80 %rh while the equilibrium of humid air with seawater, eq. (24), is  
668 established at about 98 %rh. For simplicity, let all parts have equal temperatures and pressures.

669 If evaporation takes place, the partial water masses involved will change by a mass flux across the  
670 sea surface,

$$671 \quad J_m \equiv \frac{dm^{\text{AV}}}{dt} = \frac{dm^{\text{V}}}{dt} = -\frac{dm^{\text{SW}}}{dt} = -\frac{dm^{\text{W}}}{dt}. \quad (36)$$

672 The change of the total enthalpy of the sea-air sample is available from eqs. (17) and (23),

$$673 \quad \frac{dH^{\text{SA}}}{dt} = \left( \frac{\partial H^{\text{SA}}}{\partial m^{\text{V}}} \right)_{T,p,m^{\text{S}},m^{\text{A}},m^{\text{WV}}} \frac{dm^{\text{V}}}{dt} = L^{\text{SA}} J_m. \quad (37)$$

674 This expression of energy conservation, the 1<sup>st</sup> law of thermodynamics, is similarly valid for  
675 equilibrium and non-equilibrium conditions of the sample. For comparison, of the total entropy  
676 defined by,

$$677 \quad N^{\text{SA}} \equiv m^{\text{SW}} \eta^{\text{SW}} + m^{\text{AV}} \eta^{\text{AV}}, \quad (38)$$

678 the change is given by

$$679 \quad \frac{dN^{\text{SA}}}{dt} = \left( \frac{\partial N^{\text{SA}}}{\partial m^{\text{V}}} \right)_{T,p,m^{\text{S}},m^{\text{A}},m^{\text{WV}}} \frac{dm^{\text{V}}}{dt}. \quad (39)$$

680 In terms of its two parts, eq. (38), this change takes the form,

$$681 \quad \frac{dN^{\text{SA}}}{dt} = \left[ \eta^{\text{AV}} - A \left( \frac{\partial \eta^{\text{AV}}}{\partial A} \right)_{T,p} - \eta^{\text{SW}} + S \left( \frac{\partial \eta^{\text{SW}}}{\partial S} \right)_{T,p} \right] J_m. \quad (40)$$

682 In oceanography, the symbol  $N$  for entropy was suggested by Fofonoff (1962) to avoid confusion  
683 with salinity  $S$ . Making use of their local equilibria, specific entropy of each part can be expressed by  
684 the difference, eq. (B.6),

$$685 \quad \eta = \frac{h-g}{T}, \quad (41)$$

686 between specific enthalpy,  $h$ , and specific Gibbs energy,  $g$ , so that the entropy change (40) becomes

$$687 \quad T \frac{dN^{\text{SA}}}{dt} = (L^{\text{SA}} + \Delta\mu) J_m. \quad (42)$$

688 Here, the latent heat,  $L^{\text{SA}}$ , is given by eq. (23), and the distance from mutual equilibrium,  $\Delta\mu$ , by eq.  
689 (24).

690 The first term,

$$691 \quad T \frac{d_e N^{\text{SA}}}{dt} \equiv L^{\text{SA}} J_m, \quad (43)$$

692 is the *external* entropy change (subscript e) in the form of the heat flux required to maintain the  
693 sample's temperature, in the sense of Maxwell's (1888) definition of latent heat, compensating the  
694 storage of latent heat by emitting water vapour.

695 The second term,

$$696 \quad T \frac{d_i N^{SA}}{dt} \equiv J_m \Delta \mu. \quad (44)$$

697 is the *internal* entropy change (subscript i), or *entropy production*, of the non-equilibrium sea-air  
698 sample. It represents the additional entropy gain of humid air compared to the entropy loss of  
699 seawater. This production happens at the air-sea interface and disappears as soon as mutual  
700 equilibrium,  $\Delta \mu = 0$ , is approached.

701 It is important to be aware that the external part,  $\frac{d_e N^{SA}}{dt}$ , *always* constitutes a contribution to the  
702 system's energy balance while, by contrast, the internal part,  $\frac{d_i N^{SA}}{dt}$ , is *never* any such contribution.  
703 The irreversible production of entropy is an internal conversion or redistribution of energy rather  
704 than a change of it. This implies that irreversible processes violate Gibbs' fundamental equation (B.8)  
705 in the sense that

$$706 \quad \frac{dH^{SA}}{dt} = -T \frac{d_e N^{SA}}{dt} + V^{SA} \frac{dp}{dt} + \sum_i \mu_i \frac{dm_i}{dt} > -T \frac{dN^{SA}}{dt} + V^{SA} \frac{dp}{dt} + \sum_i \mu_i \frac{dm_i}{dt}, \quad (45)$$

707 even though each of its local-equilibrium elements strictly satisfies the related fundamental equation  
708 (B.13), valid for reversible processes only,

$$709 \quad dh = -T d\eta + v dp + \sum_{i=1}^{n-1} (\mu_i - \mu_0) dw_i. \quad (46)$$

710 Entropy production appears wherever a flux is passing its driving gradient. Near equilibrium, this flux  
711 is proportional to its driving force (Glansdorff and Prigogine 1971, Landau and Lifschitz 1974, Kraus  
712 and Businger 1994, Feistel and Hellmuth 2024a), usually termed *Onsager force*. For example, the  
713 evaporation mass flux of water, eq. (6),

$$714 \quad J_m = C \Delta \mu \quad (47)$$

715 may be assumed as being proportional to the difference between the chemical potentials of water  
716 across the air-sea interface. The related *Dalton equation* (6) was discussed in Section 4. The  
717 associated entropy production, eq. (44), obeys the 2<sup>nd</sup> law of thermodynamics by the inequality

$$718 \quad \frac{d_i N^{SA}}{dt} = C (\Delta \mu)^2 \geq 0, \quad (48)$$

719 while the total entropy change, eq. (42) may possess any sign. In other words, the 2<sup>nd</sup> law forbids that  
720 *Onsager fluxes* may be directed against their causing Onsager forces. **The Prigogine Theorem predicts**  
721 **that in linear irreversible thermodynamics, entropy production approaches minimum values at**  
722 **steady states (Glansdorff and Prigogine 1971).**

723 Processes accompanied by entropy production are termed *irreversible* ones, since entropy once  
724 created may never be destroyed again. Related processes cannot be reversed unless lasting changes  
725 are left behind in the external world. By contrast, processes which transform an equilibrium state  
726 into another equilibrium state may *reversibly* be performed without producing entropy. Entropy  
727 production is possible only under non-equilibrium conditions.

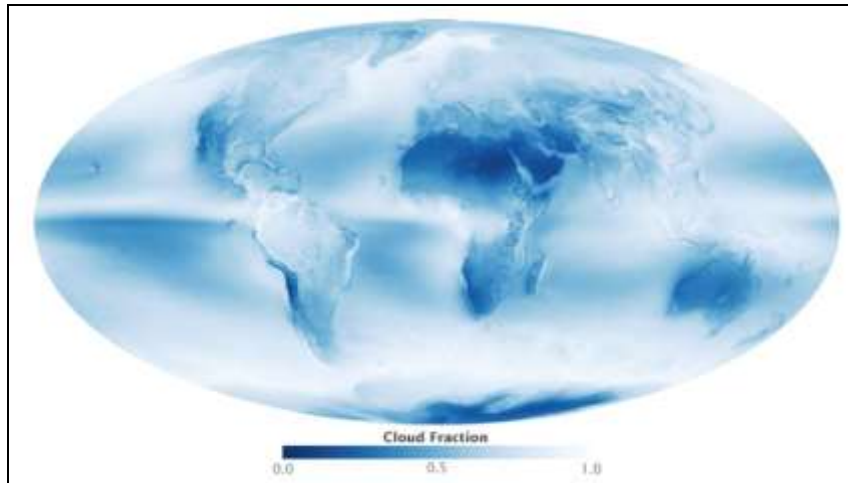
728 Under typical marine circumstances, the entropy production density of ocean evaporation can be  
729 estimated to about  $4 \text{ mW K}^{-1} \text{ m}^{-2}$ , contributing roughly 0.4 % to the global entropy production  
730 (Feistel and Ebeling 2011, Feistel and Hellmuth 2024a).

731

732

## 733 6 Cloudiness and Ocean Warming

734 “Cloud feedback on climate represents the largest uncertainty in our ability to understand the  
 735 sensitivity of the planet to radiative forcing” (Gettelman and Sherwood 2016). On the long-term  
 736 average, cloudiness is particularly strong in the low-pressure belts of the global tropospheric  
 737 circulation, where air is ascending and its humidity is condensing, see Fig. 12. Except for the  
 738 equatorial zone, those spatial cloudiness pattern correlate visibly with those of recent ocean  
 739 warming, compare Fig. 1. It is a plausible working hypothesis that this correlation could also indicate  
 740 a causal relation between the two phenomena. However, such correlations imply **chicken**-and-egg  
 741 problems (Rapp 2014): putative causality relations between those trends cannot be derived from  
 742 observation but only be concluded from reliable prediction models (Feistel 2023). May the observed  
 743 systematic reduction of global cloudiness (Fasullo and Trenberth 2012) actually be responsible for  
 744 the currently recorded excessive ocean warming (You 2024)? Unfortunately, and somewhat  
 745 surprisingly, this assumption can apparently not be underpinned yet by closer investigation. Some  
 746 related issues will be discussed in this section.



747  
 748 Fig. 12: Global distribution of cloudiness July 2002 – April 2015 (Allen and Ward 2015). Image  
 749 reproduction permitted by NASA Copyright.

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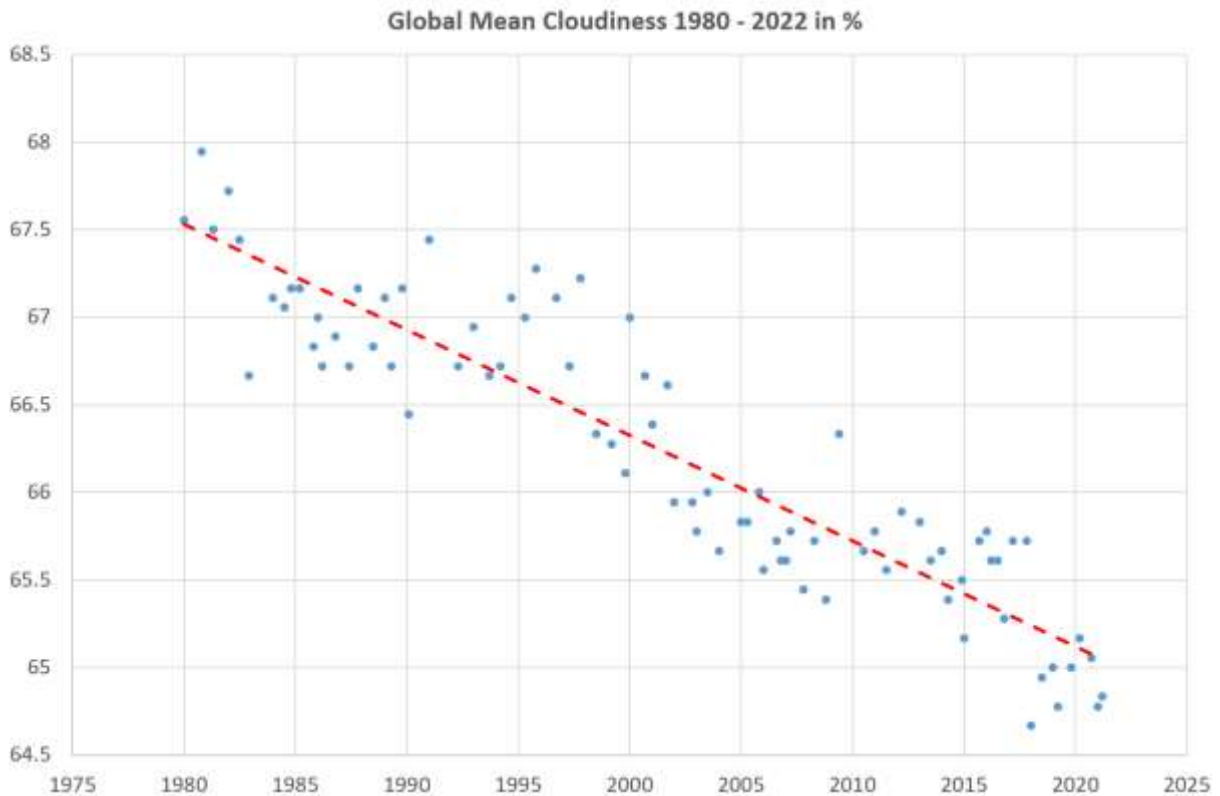
### 751 6.1 Cloudiness Trend

752 Global cloud-covered surface area fraction  $C$  has systematically been reducing by about 6 % per  
 753 century, see Fig. 13, from  $C \approx 67.5$  % in 1980 to  $C \approx 65$  % in 2022 (Foster et al. 2023, Phillips and  
 754 Foster 2023). Observed cloudiness values depend strongly on the way clouds are defined (Spänkuch  
 755 et al. 2022) and on the measurement technology applied. For example, Rapp (2014: Fig. 6.20)  
 756 reported a decrease in cloudiness in 30 years from 70 % in 1983 down to 63.5 % in, likely, 2013. This  
 757 reduction rate of more than 20 % per century is three times as fast as that given in Fig. 13 and may  
 758 result from different observation techniques.

759 Assuming that this shrinking occurred in a similar way above both land and sea, the ocean is  
 760 expected to receive increasingly more solar irradiation. This phenomenon is known as the *short-wave*  
 761 *cloud radiative effect* (SW CRE), see Fig. 14.

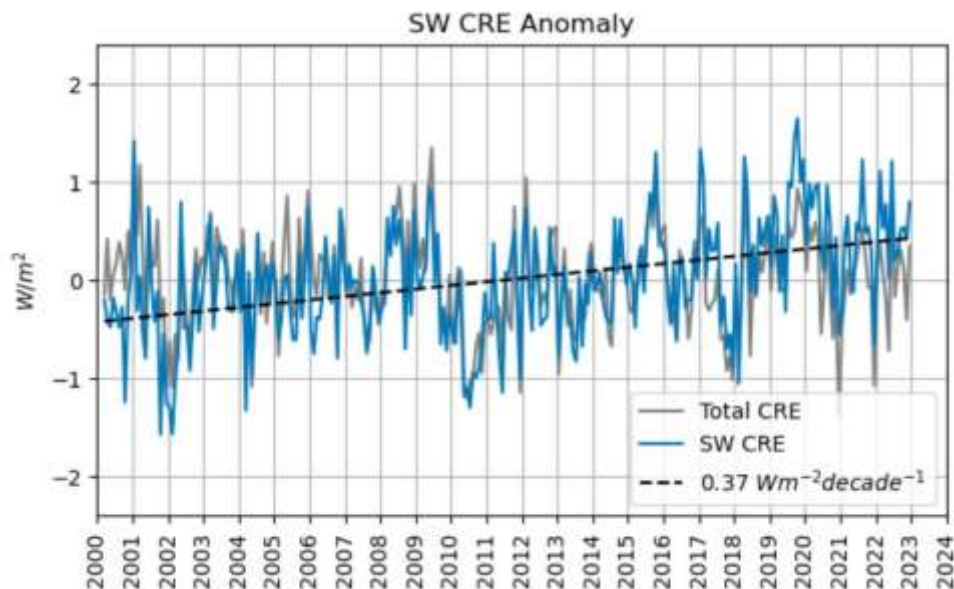
762 On the other hand, clouds are opaque with respect to oceanic upward thermal radiation and emit  
 763 themselves downward infrared radiation. This phenomenon is known as the *long-wave cloud*  
 764 *radiative effect* (LW CRE), see Fig. 15. Radiation models show that on the global average these two  
 765 effects cancel each other almost completely up to minor **residual** of  $-1 \text{ mW m}^{-2} \text{ yr}^{-1}$ , so that the

766 continuously shrinking cloudiness may be assumed to have practically no net effect on the ocean's  
 767 radiation balance (Phillips and Foster 2023, Feistel and Hellmuth 2024b). However, more detailed  
 768 investigations in the future may reveal more rigorous results for the ocean than this simplified  
 769 picture.



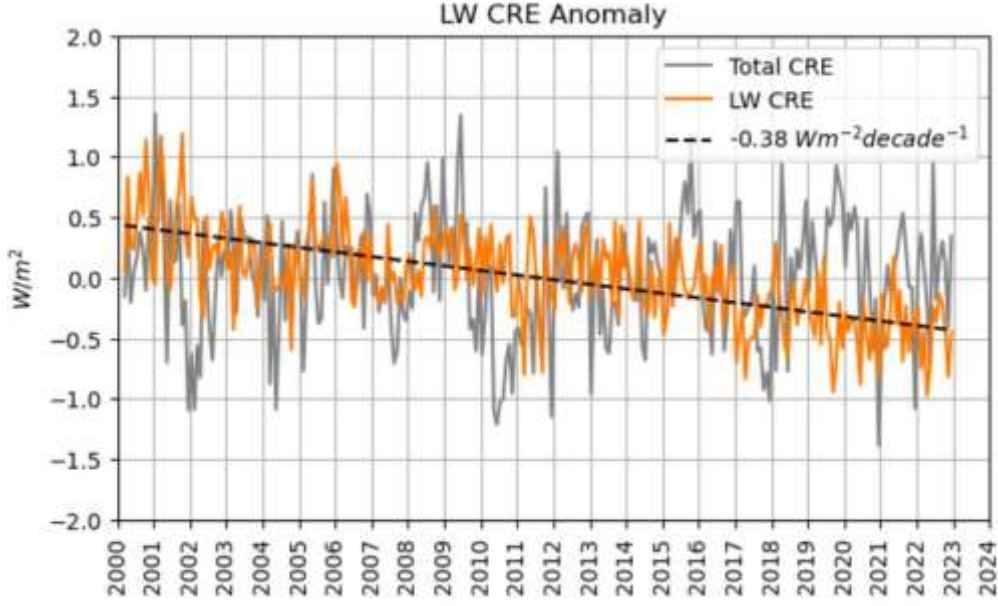
770

771 Fig. 13: Dots: satellite-derived global mean cloud area fractions 1980-2022 in percent. Data from  
 772 Foster et al. (2023). Dashed line: present cloudiness is 65 % with a climatological linear shrinking  
 773 trend of  $-6.2\%$  per century.



774

775 Fig. 14: Short-wave cloud radiative effect (SW CRE) of increasing solar irradiation. Image kindly  
 776 provided by Coda Phillips (priv. comm.), with minor correction compared to the similar previous  
 777 publication (Phillips and Foster 2023). Total CRE is the net effect of SW and LW CRE, see Fig. 15



778

779 Fig. 15: Long-wave cloud radiative effect (LW CRE) of decreasing net thermal radiation. Image kindly  
 780 provided by Coda Phillips (priv. comm.), with minor correction compared to the **similar previous**  
 781 publication (Phillips and Foster 2023). Total CRE is the net effect of SW and LW CRE, see Fig. 14.

782

### 783 6.2 Cumulus Clouds

784 Cumulus clouds are often formed in the course of diurnal convection by isentropic uplift of humid air  
 785 parcels from the sea surface to the condensation level, mostly located at low heights between 200  
 786 and 500 m. This process permits a thermodynamic description of such clouds (Romps 2014) by  
 787 calculating the *lifted condensation level* (LCL) as the cumulus cloud base. **In distinction to previous**  
 788 **studies**, as the first such international geophysical standard, TEOS-10 provides explicit equations for  
 789 entropy, enthalpy and chemical potentials of humid air which may be used to derive reference  
 790 equations and values of the LCL (Feistel and Hellmuth 2024b).

791 At the sea surface pressure,  $p_{SS}$ , the air parcel may possess the temperature  $T_{SS}$  and the relative  
 792 fugacity  $\psi_f$ , which is a real-gas definition of relative humidity (Feistel and Lovell-Smith 2017) in terms  
 793 of the chemical potential of water vapour in humid air,  $\mu_V^{AV}$ , and that of liquid water,  $\mu_W$ ,

$$794 R_W T_{SS} \ln \psi_f = \mu_V^{AV}(A, T_{SS}, p_{SS}) - \mu_W(T_{SS}, p_{SS}). \quad (49)$$

795 Here,  $R_W = 461.523 \text{ J kg}^{-1} \text{ K}^{-1}$  is the specific gas constant of water, and  $A = 1 - q$  is the dry-air  
 796 mass fraction of the parcel, to be determined from  $\psi_f$  by this condition.

797 At the LCL, the parcel is saturated at  $\psi_f = 1$ , i.e.,

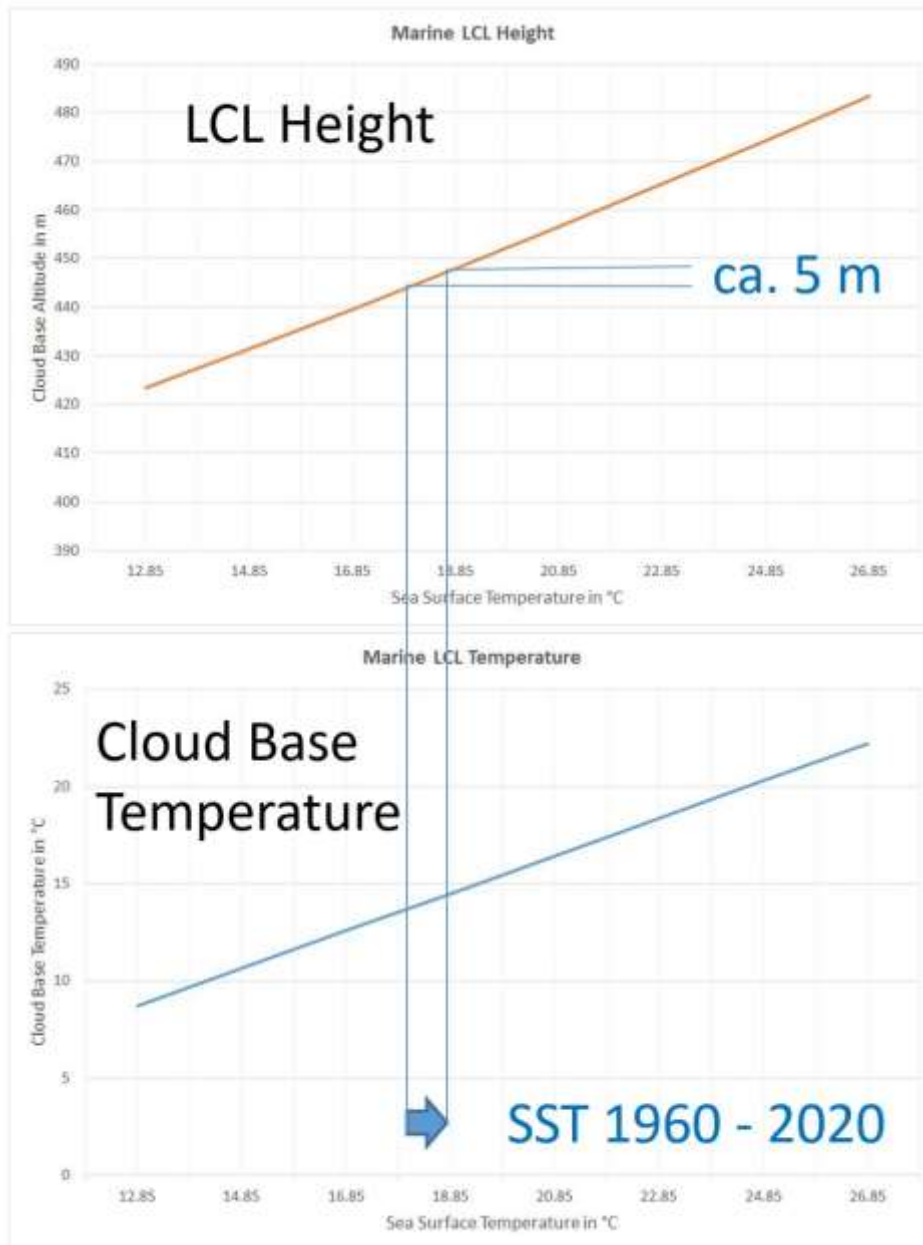
$$798 0 = \mu_V^{AV}(A, T_{LCL}, p_{LCL}) - \mu_W(T_{LCL}, p_{LCL}). \quad (50)$$

799 During uplift,  $A$  is assumed to remain constant, as well as the parcel's entropy,  $\eta^{AV}$ ,

$$800 \eta^{AV}(A, T_{SS}, p_{SS}) = \eta^{AV}(A, T_{LCL}, p_{LCL}). \quad (51)$$

801



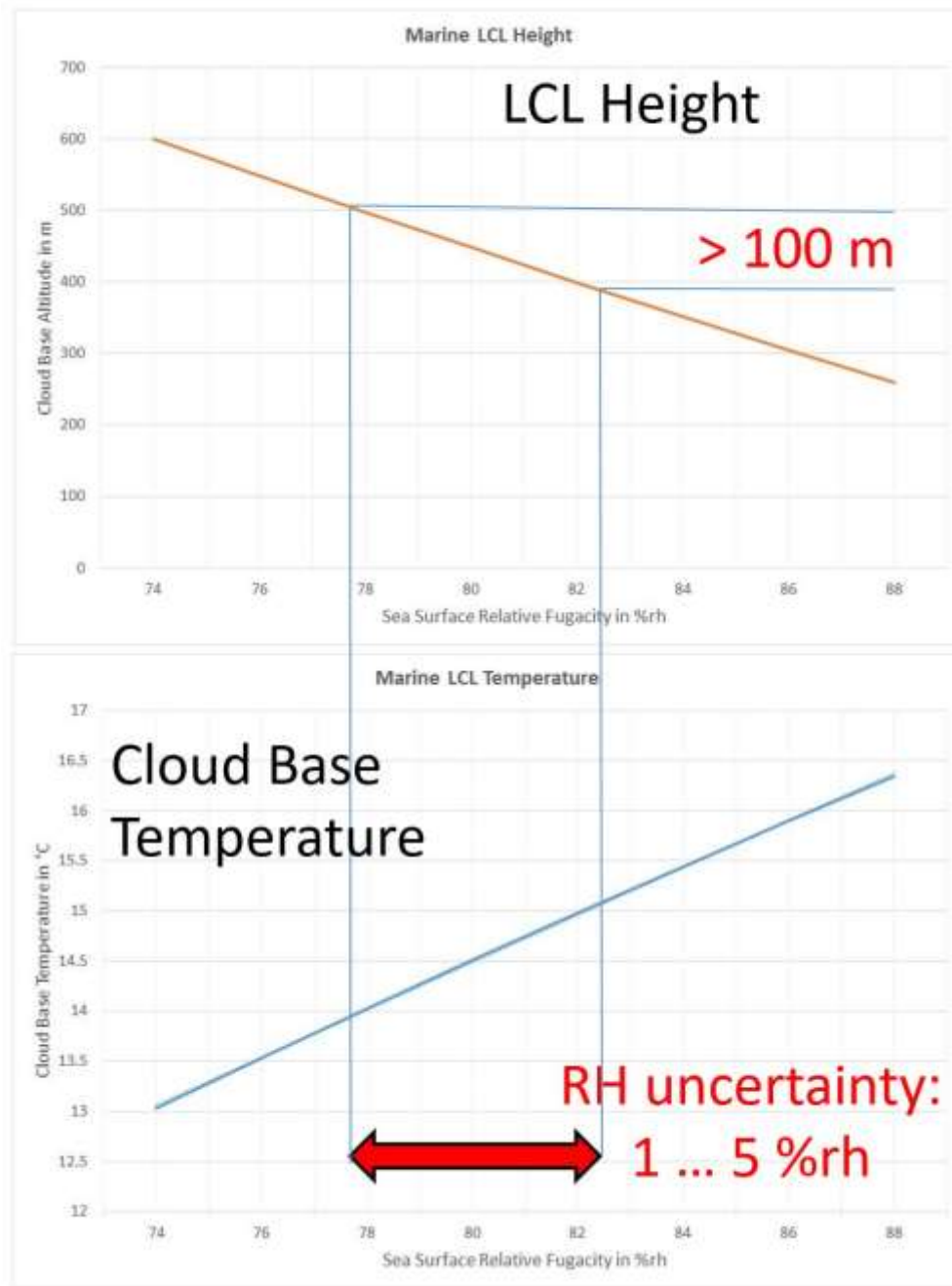


802

803 Fig. 16: As a function of typical low-latitude sea-surface temperatures, LCL height (top) and LCL  
 804 temperature (bottom) are computed from the TEOS-10 equations (49) – (52) at a typical marine  
 805 surface RH of 80 %rh. The added interval indicates the global mean SST change between 1960 and  
 806 2020 which has resulted in an increase of the cloud base altitude by about 5 m.

807

808



809

810 Fig. 17: As a function of typical marine RH values, LCL height (top) and LCL temperature (bottom) are  
 811 computed from the TEOS-10 equations (49) – (52) at a sea surface temperature of 292 K, close to the  
 812 current global mean SST of 18.8 °C, see Fig. 18. The added interval indicates the observation  
 813 uncertainty of sea surface RH which corresponds to an uncertainty of the cloud base altitude of more  
 814 than 100 m.

815

816 Finally, the LCL altitude,  $z_{LCL}$ , above sea level follows from the isentropic integral of the hydrostatic  
 817 equation in terms of the enthalpy,  $h^{AV}$ , of humid air,

$$818 \quad z_{LCL} = \frac{1}{g_E} [h^{AV}(A, \eta^{AV}, p_{SS}) - h^{AV}(A, \eta^{AV}, p_{LCL})]. \quad (52)$$

819 The gravity acceleration is  $g_E = 9.81 \text{ m s}^{-2}$ . The functions  $\mu_V^{AV}$ ,  $\eta^{AV}$ ,  $h^{AV}$  and  $\mu_W$  can be expressed  
 820 by partial derivatives of the TEOS-10 thermodynamic potentials of humid air and liquid water, and

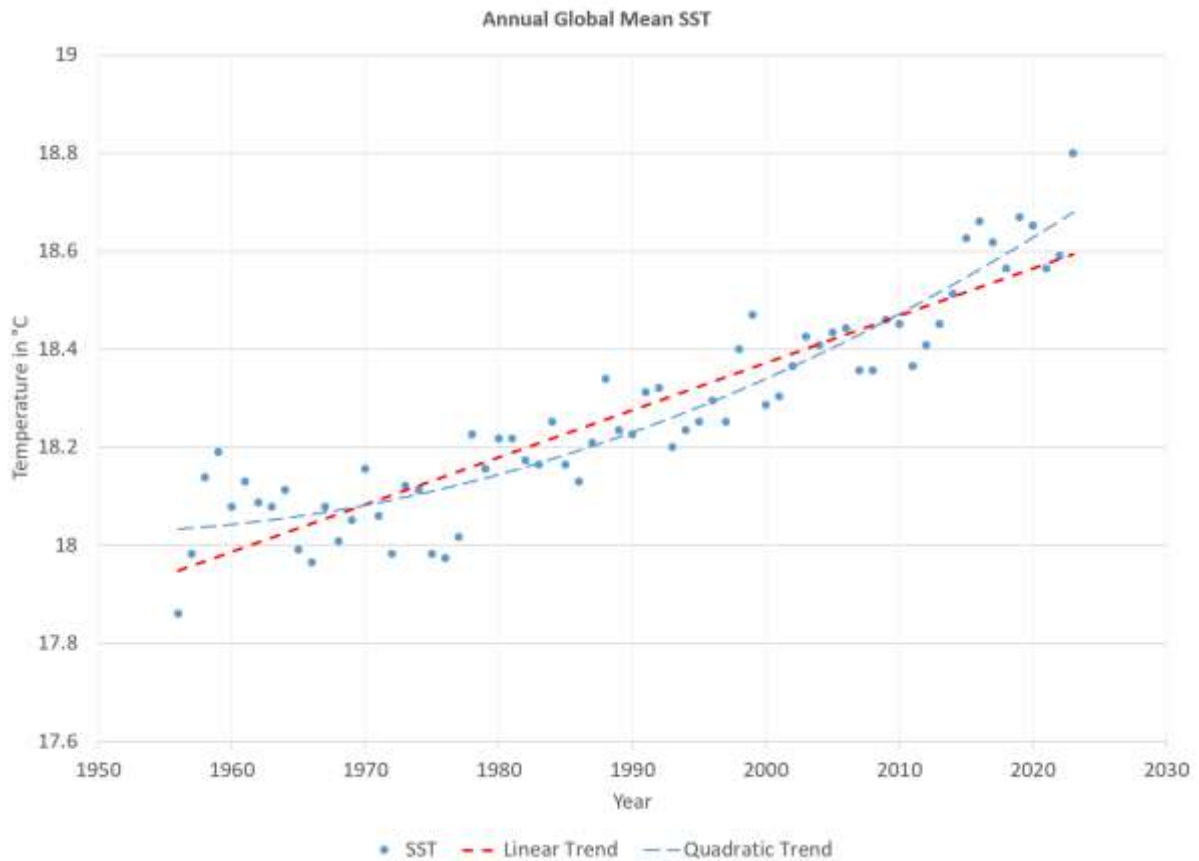
821 are numerically available from the *Sea-Ice-Air (SIA) library* (Feistel et al. 2010d, Wright et al. 2010).  
 822 Solving eqs. (49) – (52) numerically, the LCL properties ( $A, T_{LCL}, p_{LCL}, z_{LCL}$ ) are obtained from the  
 823 given surface properties, ( $\psi_f, T_{SS}, p_{SS}$ ).

824 Table 1: LCL cloud-base temperatures,  $T_{LCL}$ , pressures,  $p_{LCL}$ , and heights,  $z_{LCL}$ , as functions of the  
 825 SST,  $T_{SS}$ , at marine surface relative fugacity of  $\psi_f = 80$  %rh, computed from TEOS-10 eqs. (49) –  
 826 (52), as well as climatic LCL sensitivities,  $\alpha, \beta, \gamma$ , eq. (53), with respect to increasing SST (Feistel and  
 827 Hellmuth 2024). The row printed in bold approximates the current global mean SST, see Fig. 18.

$T_{SS}$ K	$T_{LCL}$ K	$p_{LCL}$ hPa	$z_{LCL}$ m	$\alpha$ % K <sup>-1</sup>	$\beta$ K K <sup>-1</sup>	$\gamma$ hPa K <sup>-1</sup>
286	281.883	963.093	423.468	-0.0483	0.9634	-0.2742
288	283.810	962.542	431.481	-0.0542	0.9629	-0.2773
290	285.735	961.984	439.660	-0.0608	0.9624	-0.2806
<b>292</b>	<b>287.659</b>	<b>961.419</b>	<b>448.017</b>	<b>-0.0680</b>	<b>0.9619</b>	<b>-0.2841</b>
294	289.583	960.847	456.561	-0.0759	0.9614	-0.2878
296	291.505	960.268	465.305	-0.0846	0.9608	-0.2917
298	293.426	959.680	474.263	-0.0942	0.9603	-0.2959
300	295.346	959.084	483.449	-0.1047	0.9597	-0.3004

828

829



830

831 Fig. 18: Estimated increase 1957 – 2023 of global annual mean sea-surface temperatures (source:  
 832 Cheng et al. 2024). The linear trend (red) is  $t/^\circ\text{C} \approx 18 + 0.01 \times (yr - 1961)$ . The quadratic trend  
 833 curve (blue) suggests an acceleration of warming.

834

835 As solutions of eqs. (49) – (52), height and base temperature of marine cumulus clouds, as a function  
 836 of the sea-surface temperature  $T_0$  at a sea-surface relative fugacity of  $\psi_f = 80$  %rh, are displayed in  
 837 Fig. 16. Similarly, height and base temperature, as a function of the sea-surface relative fugacity **RF** of  
 838  $\psi_f$  at a sea-surface temperature  $T_{SS} = 292$  K, close to the current global mean SST, are displayed in  
 839 Fig. 17. **It is obvious that the LCL effect of the range of RF uncertainty exceeds significantly the effect**  
 840 **caused by global SST rise, so that unknown minor systematic RF changes may easily disguise the**  
 841 **thermal effects on marine cumulus clouds.**

842 Global mean sea-surface temperature has risen from about 17.9 °C in 1956 to 18.8 °C in 2023 (Cheng  
 843 et al. 2024), see Fig. 18. This pronounced climatic trend is expected to let the cumulus cloud base lift  
 844 up while at the same time warming it, see Fig. 16, but **not as much as** the SST itself is increasing. The  
 845 related climatic sensitivities possess complicated dependencies but may directly be derived by taking  
 846 the related derivatives

$$847 \quad \alpha \equiv \left( \frac{\partial A}{\partial T_{SS}} \right)_{p_{SS}, \psi_f} = - \left( \frac{\partial q}{\partial T_{SS}} \right)_{p_{SS}, \psi_f}, \quad \beta \equiv \left( \frac{\partial T_{LCL}}{\partial T_{SS}} \right)_{p_{SS}, \psi_f} \quad \text{and} \quad \gamma \equiv \left( \frac{\partial p_{LCL}}{\partial T_{SS}} \right)_{p_{SS}, \psi_f}, \quad (53)$$

848 of the TEOS-10 LCL equations (49) – (52) with respect to the surface temperature while keeping  
 849 surface RH fixed (Feistel and Hellmuth 2024). Selected results for those sensitivities are given in Table  
 850 1 relative to 1 °C rise of SST, similar to that in the past 70 years (Fig. 16). Here,  $\alpha \approx -0.07$  % K<sup>-1</sup>  
 851 describes the rate of increase of specific humidity at the sea surface, often dubbed the “Clausius-  
 852 Clapeyron effect”. The value of  $\beta \approx 0.96$  indicates that the cumulus cloud base warms up slower  
 853 than the ocean by about 4 %, and  $\gamma \approx -0.28$  hPa K<sup>-1</sup> is the LCL pressure lowering caused by ocean  
 854 warming, corresponding to ascending clouds. The value  $\beta < 1$  implies that the thermal downward  
 855 radiation from the cloud base does not keep pace with the ocean upward radiation, so that the net  
 856 climatic feedback of cumulus clouds is negative and acts against ocean warming. These clouds do not  
 857 provide a physical explanation for the observed enhanced ocean warming.

858

### 859 6.3 Stratocumulus and Other Clouds

860 **“Marine low clouds strongly cool the planet” (Myers et al. 2021). Over the Atlantic, “the strongest**  
 861 **surface longwave cloud effects were shown in the presence of low level clouds” (Kalisch and Macke**  
 862 **2012). “Low-cloud feedbacks are also a leading cause of uncertainty in future climate prediction**  
 863 **because even small changes in cloud coverage and thickness have a major impact on the radiation**  
 864 **budget” (Wood 2012: p. 2373).**

865 **Generally, however, the** dominating cloud type over the ocean is stratocumulus (Eastman et al.  
 866 2011). “They are common over the cooler regions of subtropical and midlatitude oceans where their  
 867 coverage can exceed 50% in the annual mean” (Wood 2012: p. 2373) with a typical thickness about  
 868 320 m and “a tendency for thicker clouds (median 420 m) in mid- and high latitudes” (Wood 2012: p.  
 869 2378). “Stratocumuli tend to form under statically stable lower-tropospheric conditions” (Wood  
 870 2012: p. 2374). On the annual average, stratocumulus is particularly frequent (up to 60 % coverage)  
 871 at the subtropical coastal upwelling regions such as the cold Benguela, Humboldt and California  
 872 Currents (Wood 2012: Fig. 4a, Muhlbauer et al. 2014: Fig. 2). However, in those areas there is no  
 873 obvious correlation of cloud cover with ocean warming (Fig. 1). Stratocumulus also forms large cloud  
 874 cover (about 20 % coverage) in the boreal and austral west-wind bands (Wood 2012: Fig. 4a) where  
 875 the ocean is strongly warming up (Fig. 1).

876 “Only small changes in the coverage and thickness of stratocumulus clouds are required to produce a  
 877 radiative effect comparable to those associated with increasing greenhouse gases” (Wood 2012: p.

878 2374). Marine stratocumulus cloud feedback is still a major challenge and source of uncertainty of  
 879 climate models (Hirota et al. 2021). However, “similar to other low-cloud types in the marine  
 880 boundary layer, the impact of stratocumulus clouds on the outgoing longwave radiation is marginal  
 881 due to the lack of contrast between the temperature of stratocumulus cloud tops and the  
 882 temperature of the sea surface over which they form. Thus, the net radiative effect of stratocumulus  
 883 clouds is primarily controlled by factors influencing their shortwave cloud forcing such as the cloud  
 884 albedo and the cloud coverage” (Muhlbauer et al. 2014: p. 6695).

885 Following this argumentation and assuming that the short-wave cloud effect of stratocumuli on the  
 886 ocean radiation balance by far outweighs their long-wave effects, then the short-wave warming  
 887 effect (Fig. 14) of decreasing cloudiness may dominate over the long-wave cooling (Fig. 15). Possibly,  
 888 this could make stratocumulus a potential candidate for causing the unclear recent ocean warming.

889 Similarly, in the diurnal cycle, short-wave effects (Fig. 14) have an impact at daytime only, while long-  
 890 wave effects (Fig. 15) are present all 24 hours. In this respect, Luo et al. (2024) report that low-level  
 891 cloudiness has an asymmetric day/night trend which enhances ocean warming. Regionally, where in  
 892 spring the days get longer, and the heavy cloudiness of the west-wind belt becomes replaced by  
 893 fewer subtropical clouds (see Fig. 12), the systematic reduction of cloudiness may be expected to  
 894 produce local excess warming such as near the subtropical fronts (see Fig. 1). Only dedicated future  
 895 model studies, however, may reliably verify such speculations. As a recent example for the  
 896 complexity of SST warming “by suppressing the evaporative cooling” of the ocean, Wang et al. (2024)  
 897 explain dramatic but yet elusive warming events in the North-East Pacific by changes in ocean-  
 898 atmosphere mechanisms caused by reduced Chinese aerosol emissions. Also, Berthou et al. (2024)  
 899 describe cloud cover feedback over the sea during an unprecedented marine heatwave off northwest  
 900 Europe in 2023.

901

## 902 7 Summary

903 Substantial uncertainties of estimated heat fluxes at the ocean-atmosphere interface, such as the  
 904 “ocean heat budget closure problem”, prevent reliable model predictions and causal explanations of  
 905 climate phenomena that may take place within the range of those uncertainties. Among such  
 906 “surprises” is the currently registered excessive ocean warming, but are also the subsequent  
 907 consequences of this warming, such as those expected for global weather processes.

908 Intending to reduce model uncertainties of thermal energies and heat fluxes in the climate system  
 909 associated with the global circulation of water in its different phases and mixtures, the new  
 910 geophysical thermodynamic standard TEOS-10 had been adopted internationally in 2009 and 2011.  
 911 Meanwhile, the uptake of TEOS-10 by the scientific community is mainly focussed on ocean  
 912 observations and modelling, as the related publication metrics are suggesting (Appendix A).

913 TEOS-10 is advanced over previous similar standards and various collections of tailored empirical  
 914 property equations by (i) its completeness in describing all thermodynamic properties of seawater,  
 915 humid air and ice, including their entropies, enthalpies and chemical potentials, by (ii) its perfect  
 916 mutual consistency between different phases and mixtures, and by (iii) its minimum uncertainty over  
 917 maximum ranges of validity. Among its particularly favourable fields of application are composite  
 918 systems with internal phase boundaries such as air sea interaction or cloud formation.

919 In addition to entropies, enthalpies and chemical potentials, TEOS-10 has made available certain new  
 920 quantities for the description and modelling of climate processes, such as (i) Absolute Salinity of the  
 921 ocean with a specified Reference Composition, (ii) Conservative Temperature as a measure of

922 Potential Enthalpy of seawater representing a definite heat content, and (iii) Relative Fugacity as the  
 923 thermodynamic driving force of evaporation, suggesting an improved full-range definition of relative  
 924 humidity as a substitute for mutually inconsistent and restricted such definitions in practical use in  
 925 climatology, meteorology and physical chemistry.

926 This paper explains some tutorial examples for the application of TEOS-10 to selected current climate  
 927 problems. There is (i) the two-phase conceptual model of “sea air” which provides rigorous equations  
 928 for the latent heat of evaporation, for the heat capacity of humid air including salty aerosols (sea  
 929 spray), and for the irreversible production of entropy by evaporation into the marine troposphere.  
 930 There is also (ii) the formation of low marine cumulus clouds by isentropic thermal convection up to  
 931 their condensation level, and their climatic feedback to surface temperature and humidity  
 932 concerning their infrared radiation effects.

933 It is currently unclear why and how the ocean warming is intensifying, and when and how the related  
 934 enormous amount of heat may transfer to the atmosphere. The observed systematic reduction of  
 935 cloudiness may play an important role in this process, but responsible details and theoretical causes  
 936 are unknown. Marine surface relative humidity is an important and rather sensitive “control valve”  
 937 for the supply of the troposphere with latent heat, however, the common assumption of constant  
 938 relative humidity during climate change lacks rigorous explanation and leaves open the question of  
 939 its possible trends below the insufficiently high level of observational uncertainty. TEOS-10 may  
 940 further assist climate modellers to address such issues.

941 Ocean Science has proved a scientifically well-reputable, reliable and successful partner journal for  
 942 the publication of advanced results and methods in oceanography and geophysics. Cooperation with  
 943 international bodies such as IUGG, UNESCO/IOC, IAPSO, SCOR, IAPWS and BIPM has made possible  
 944 the development and international introduction of TEOS-10. The established standing committee JCS  
 945 remains active with respect to related fundamental problems yet to be solved. It is hoped and  
 946 expected that TEOS-10 may constitute a reliable long-term thermodynamic basis for interdisciplinary  
 947 climate research.

948

#### 949 **Appendix A: Summary and Metrics of Selected Publications Related to TEOS-10**

950 Between December 2008 and December 2012, supporting the activities of SCOR/IAPSO WG127,  
 951 *Ocean Science* had published 16 articles open-access in its Special Issue #14, “Thermophysical  
 952 properties of seawater” (Feistel et al. 2008a). From February 2013 on, monthly metrics have been  
 953 recorded by the journal. Table A1 reports those metrics of the last decade.

954 For comparison, metrics – as far as published elsewhere by 04 April 2024 – of selected TEOS-10  
 955 articles listed at [www.teos-10.org](http://www.teos-10.org) are reported in Table A2.

956 **Table A1:** Metrics of articles in the *Ocean Science* Special Issue #14, “Thermophysical properties of  
 957 seawater” (Feistel et al. 2008a), from February 2013 till March 2024. “SIA” stands for the TEOS-10  
 958 Sea-Ice-Air open source code library.

Reference	Topic	Accessed	PDF Downloads	Cited
Millero and Huang (2009)	Seawater at High $T,S$	16 462	11 061	79
Feistel et al. (2010c)	Baltic Sea Density/Salinity	15 435	11 385	92
Pawlowicz et al. (2011)	Seawater Biogeochemistry	9 663	6 444	47
McDougall et al. (2012)	Global Absolute Salinity	9 290	5 489	116
Feistel et al. (2010a)	Humid Air Helmholtz Function	8 737	5 346	31

Safarov et al. (2009)	Seawater at High $T,p$	7 356	4 308	68
Wright et al. (2011)	Density Salinity	5 268	2 891	49
Marion et al. (2009)	CaCO <sub>3</sub> Solubility	5 169	3 170	36
Pawlowicz (2010)	Composition Variation	4 471	2 666	27
Feistel et al. (2010d)	SIA Library Equations	4 255	2 416	23
Wright et al. (2010)	SIA Library Routines	4 049	1 733	19
Feistel et al. (2008b)	Consistent New Potentials	3 585	1 527	27
Seitz et al. (2011)	Salinity Traceability	3 363	1 705	24
Feistel et al. (2010b)	Baltic Property Anomalies	3 183	1 500	12
Tailleux (2009)	Mixing Efficiency	2 752	1 303	11
Millero and Huang (2010)	Seawater at High $T,S$ (corrig.)	2 189	909	1

959

960 **Table A2:** Metrics published by March 2024 of selected TEOS-10 related articles apart from *Ocean*  
 961 *Science* **Special Issue #14**. “Ice Ih” is the ambient, hexagonal ice I phase of water.

Reference	Topic	Accessed	PDF Downloads	Cited
Wagner and Pruß (2002)	Water Helmholtz Function	7 516	7 516	3 457
Jackett et al. (2006)	Algorithms for Seawater	2 877	2 364	119
Feistel (2005)	Seawater Gibbs Function	2 584	1 126	10
Feistel et al. (2005)	Ice Ih Gibbs Function	2 288	1 015	5
Lemmon et al. (2000)	Dry Air Helmholtz Function	2 279	2 279	381
McDougall (2003)	Potential Enthalpy	1 970	1 367	50
Wagner et al. (2011)	Ice Melting/Sublimation	1 467	510	102
Seitz et al. (2010)	Salinity Determination	1 332		15
Feistel (2008b)	IAPWS-06 and IAPWS-08	1 279		4
Millero et al. (2008)	Seawater Composition	970		780
Feistel and Wagner (2006)	Ice Ih Gibbs Function	843	843	286
Feistel and Wagner (2005)	Ice Ih Gibbs Function	833		58
Graham and McDougall (2013)	Conservative Temperature	651	467	28
Feistel (2012)	New TEOS-10 Standard	436		27
Spall et al. (2013)	TEOS-10 for oceanography	230	128	3
Feistel (2008a)	Seawater Gibbs Function	134		133
Roquet et al. (2015)	TEOS-10 Polynomials	111		97
Feistel and Wagner (2007)	Ice Ih Sublimation >20 K	105		112
Feistel (2003)	Seawater Gibbs Function	100		105
McDougall et al. (2013)	Thermodynamics of Seawater	35		10
Feistel and Marion (2007)	Seawater Gibbs-Pitzer	25		32
Valladares et al. (2011)	Replacement of EOS-80	14+5		4+1
Feistel et al. (2006)	New Seawater Equation			

962

963 **Table A3:** IAPWS documents supporting TEOS-10, openly accessible at [www.iapws.org](http://www.iapws.org). IAPWS  
 964 documents are independently and painstakingly verified before they may become adopted at an  
 965 annual meeting. No metrics available.

Document	Code	Topic	Meeting	Year
Release	R06-95	Water Helmholtz Function	Dresden	2016
Release	R10-06	Ice Ih Gibbs Function	Doorwerth	2009
Release	R13-08	Seawater Gibbs Function	Berlin	2008
Release	R14-08	Ice Melting/Sublimation	Pilsen	2011

Suppl. Release	SR1-86	Water Saturation Properties	St. Petersburg	1992
Suppl. Release	SR6-08	Liquid Water at 0.1 MPa	Pilsen	2011
Suppl. Release	SR7-09	Liquid Water Gibbs Function	Doorwerth	2009
Guideline	G05-01	Fundamental Constants	Virtual Online	2020
Guideline	G08-10	Humid Air Helmholtz Function	Niagara Falls	2010
Guideline	G09-12	Cold Water Vapour < 130 K	Boulder	2012
Guideline	G11-15	Fugacity Virial Equation	Stockholm	2015
Guideline	G12-15	Supercooled Water	Stockholm	2015
Advisory Note	AN4-09	IAPWS/CIPM Water Density	Doorwerth	2009
Advisory Note	AN5-13	Industrial Seawater	Dresden	2016
Advisory Note	AN6-16	IAPWS support for TEOS-10	Dresden	2016

966

967 **Table A4:** Numbers of unique internet downloads 2011-2023 of supporting material from the TEOS-  
968 10 homepage at [www.teos-10.org](http://www.teos-10.org). "GSW" stands for the TEOS-10 Gibbs Seawater open source code  
969 library. Data from Pawlowicz (2023)

Item	2011 -13	2013 -14	2014 -15	2015 -16	2016 -17	2017 -18	2018 -19	2019 -20	2020 -21	2021 -22	2022 -23
TEOS-10 Manual	920	360	535	552	418	427	349	472	479	482	530
Getting Started	879	362	558	547	427	475	349	444	460	483	479
Lecture Slides	704	284	374	318	219	248	204	272	272	231	272
TEOS-10 Primer	584	197	289	297	222	217	187	253	260	226	268
GSW MATLAB	1920	1102	1485	1814	1235	1552	1233	1556	1504	1747	1897
GSW FORTRAN	366	222	171	162	127	116	82	98	83	92	87
GSW C	202	84	133	151	85	96	59	81	58	49	57
GSW PHP	-	55	61	43	29	60	28	52	22	22	21
SIA VB	72	100	46	45	45	48	43	47	47	38	30
SIA FORTRAN	59	118	58	44	36	42	37	42	31	33	31

970

971 **Table A5:** Selected additional TEOS-10 related readings, metrics by March 2024

Reference	Topic	Accessed	PDF Downloads	Cited
Turner et al. (2016)	Seawater Pitzer Model	13 780	1 175	21
Lovell-Smith et al. (2016)	Relative Humidity Challenges		6 502	27
Schmidt et al. (2018)	Density-Salinity Relation	9 421	5 481	28
Feistel et al. (2016a)	Challenges beyond TEOS-10		5 023	49
Dickson et al. (2016)	Seawater pH Challenges		2 818	43
Pawlowicz et al. (2016)	Seawater Salinity Challenges		2 738	40
Smythe-Wright et al. (2019)	IAPSO's history and roles	5 893	384	3
Foken et al. (2021)	Atmospheric Measurements	5 709		2
Feistel (2018)	TEOS-10 Review	5 441	1 632	38
Feistel and Hellmuth (2023)	Dalton Equation	5 068		1



McDougall et al. (2021)	Ocean Heat Flux and Content	4 993	1 425	5
Hellmuth et al. (2020)	Ice-Crystal Nucleation	4 811		6
Uchida et al. (2019)	Optical Density Sensor	3 513		19
Hellmuth et al. (2021)	Mass Density of Humid Air	2 643		4
Feistel and Lovell-Smith (2017)	Relative Fugacity Part 1		1 335	18
Le Menn et al. (2018)	Seawater Salinity Measurands		1 136	13
Schmidt et al. (2016)	Seawater Density up to 1 ppm		950	21
Von Rohden et al (2016)	Baltic Sound Speed	2 122	784	1
Feistel et al. (2016b)	Uncertainty of Correlation Eqs.		662	14
Martins and Cross (2022)	TEOS-10 Excel Code	2 087	542	2
Hellmuth and Feistel (2020)	Low-Density Subcooled Water	1 827		1
Feistel (2011a)	Stochastic Potential Functions	1 217		6
McDougall et al. (2014)	Sea Ice Formation	1 124	771	16
Feistel and Hellmuth (2024a)	Evaporation Entropy	1 038		0
Young (2010)	Boussinesq Approximation	928	724	56
Harvey et al. (2023)	Water Properties	874	369	9
Tailleux (2018)	Local Available Potential Energy	807	409	11
Uchida et al. (2020)	Seawater Intercomparison	707	764	6
Sharkawy et al. (2010)	Review of Seawater Correlations	701		946
Feistel (2019a)	Relative Fugacity Part 2		267	3
Feistel et al. (2022)	Relative Fugacity Part 3		252	4
McDougall et al. (2023)	Seawater Potential of (S, CT, p)	629	122	1
Feistel et al. (2015)	Virial Fugacity Equation	581		17
Nayar et al. (2016)	Seawater Property Review	553		366
Marion et al. (2011)	Seawater pH	491		170
Feistel and Lovell-Smith (2023)	Systematic Error in Regression	428	41	
Holzappel and Klotz (2024)	H <sub>2</sub> O and D <sub>2</sub> O Ice Ih	285	58	
Holzappel and Klotz (2021)	Thermal Expansion of Ice Ih	245	77	1
Pawlowicz and Feistel (2012)	TEOS-10 in Limnology			22
Kretzschmar et al. (2015)	Industrial Seawater Equation	104		0
Ebeling et al. (2020)	Individual Ionic Activities	99		10
Marion et al. (2010)	FREZCHEM Solution Model	82		74
Sun et al. (2008)	Saline Thermal Fluid Equations	79		84
Almeida et al. (2018)	TEOS-10 Atlantic Impact	53		5
Safarov et al. (2012)	High-Salinity Seawater	42		21
Woosley et al. (2014)	World Ocean Absolute Salinity	39		16
Safarov et al. (2013)	Brackish Seawater Properties	35		15
Ulfsbo et al. (2015)	Seawater Activity Coefficients	34		11
Feistel and Hagen (1998)	Sea Ice Gibbs Function	24		31
Feistel (2010)	Seawater Gibbs Function	23		24
Tailleux (2010)	Buoyancy Power Input			20
Millero and Huang (2011)	Seawater Compressibility	19		19
Tchijov et al. (2008)	Ice at High $p$ and Low $T$	19		6
Von Rohden et al. (2015)	Seawater Sound Speed 0.1 MPa			18
Budéus (2018)	TEOS-10 Density Bias ?	8		5
Lago et al. (2015)	Seawater Sound Speed < 70 MPa	8		4
Manaure et al. (2021)	Individual Ionic Activities	8		2
Weinreben and Feistel (2019)	Anomalous Salinity Density	8		1
Ebeling et al. (2022)	Individual Ionic Activities	2		6
Waldmann et al. (2022)	Uncertainty of Ocean Variables	2		
Tailleux and Dubos (2024)	Seawater Static Energy	1		1

Pawlowicz (2013):	Physical Variables in the Ocean			
Laliberte (2015)	TEOS-10 Python Code			
Thol et al. (2024)	N <sub>2</sub> -O <sub>2</sub> -Ar Helmholtz Function			

972

973 **Appendix B: Thermodynamic Potentials**

974 This Appendix provides a short introduction to thermodynamic potentials, supporting the equations  
 975 and topics discussed in this article. Alternative presentations from different perspectives are  
 976 available from numerous textbooks such as Guggenheim (1949), Margenau and Murphy (1964),  
 977 Landau and Lifschitz (1966) or Kittel (1969). For seawater, the use of a Gibbs thermodynamic  
 978 potential was first suggested theoretically by Fofonoff (1958, 1962), see also Craig (1960).

979 A key theoretical tool for the physical investigation of the globally warming climate and the related  
 980 energy balances is *thermodynamics*. It is known from experience that there exists a distinguished  
 981 state of various ambient substances that is known as a *thermodynamic equilibrium state*. If a sample  
 982 of matter is in this state, it may never spontaneously alter its measurable macroscopic properties  
 983 unless it becomes disturbed by external contact and exchange of energy or matter with its  
 984 surrounding. Typical properties which characterise a particular equilibrium state are the total mass of  
 985 a sample,  $m$ , its volume,  $V$ , its temperature,  $T$ , or its pressure,  $p$ . Of a given sample, different  
 986 equilibrium states may exist that differ in those quantities, but there exists a specific relation  
 987 between those variables, known as an *equation of state*, which is characteristic for the given  
 988 substance and remains universally valid at any of its possible equilibrium states. The most general  
 989 and comprehensive equation of state of a given substance is a *thermodynamic potential* of that  
 990 substance.

991 Thermodynamics is a mathematical theory for the construction and exploitation of equations of state  
 992 and of properties derived **therefrom** for the prediction or verification of observations or experiments.  
 993 Depending on the properties of interest, equations of state may be formulated in various different  
 994 mathematical forms. It was discovered by J. Willard Gibbs (1873) that from a suitable thermodynamic  
 995 potential all thermodynamic properties of a given substance at any of its equilibrium states can be  
 996 derived by appropriate mathematical methods.

997 For theoretical reasons (namely, the statistical so-called *canonical ensemble*, Landau and Lifschitz  
 998 1966: §31; Kittel 1969: Ch. 18), a preferred thermodynamic potential of a pure substance is its  
 999 *Helmholtz Energy*, or *Free Energy*,  $F(m, T, V)$ , expressed in terms of the sample's mass,  $m$ , its  
 1000 temperature and volume. For mixtures, the single mass must be replaced by the set of partial masses  
 1001 of the species involved. Here, mass is used as a measure for the amount of substance, rather than  
 1002 particle or mole numbers, for the practical reason that in oceanography masses are easier measured  
 1003 than moles, and so TEOS-10 is following that tradition and is a mass-based description. Classical  
 1004 empirical thermodynamics **of Clausius and Gibbs was formulated independently** of the existence and  
 1005 properties of atoms or molecules which presently define the mole (BIPM 2019).

1006 To the **Internal Energy**  $E$  of the sample, the Helmholtz energy is related by the Helmholtz Differential  
 1007 Equation,

$$1008 \quad E = F - T \left( \frac{\partial F}{\partial T} \right)_{m,V} \quad (\text{B.1})$$

1009 **Note that IOC et al. (2010) uses the symbol  $U$  for the Internal Energy rather than  $E$  in eq. (B.1). This**  
 1010 **replacement is done here for denoting with  $u$  the wind speed, eq. (6), rather than specific internal**  
 1011 **energy, which is defined here by  $e = E/m$ , eqs. (1) and (B.3). The symbol  $E$  is frequently used in the**  
 1012 **thermodynamic literature, for example by Gibbs (1873a) and Landau and Lifschitz (1966).**

1013 The potential function  $F$  is extensive, which means that for instance  $F(2m, T, 2V) = 2F(m, T, V)$  is  
 1014 valid for an equilibrium sample of twice the mass. It follows that the mass-specific Helmholtz  
 1015 function,  $F/m \equiv f(T, \rho)$ , depends on two variables only,  $T$  and the mass density,  $\rho \equiv m/V$ , and is  
 1016 mathematically simpler and more convenient than  $F$ , which may always be retrieved from a given  $f$   
 1017 by

$$1018 \quad F(m, T, V) = m \times f\left(T, \frac{m}{V}\right). \quad (\text{B.2})$$

1019 The quantitative description of a substance of interest in the form of a thermodynamic potential such  
 1020 as  $f(T, \rho)$  has axiomatic properties. The description is *complete*, i.e., all thermodynamic properties of  
 1021 that substance are available, it is *consistent*, i.e., for any property one and only one result can be  
 1022 derived, and it is *independent*, i.e., no part of this description may be omitted without losing the  
 1023 completeness. It is obvious that such axiomatic properties are very desirable for the description of  
 1024 geophysical substances, however, such thermodynamic potentials are rarely found in the  
 1025 corresponding literature. In particular in climate research which combines results and data from  
 1026 different disciplines, such as meteorology and oceanography, from research carried out all over the  
 1027 globe and over the years by subsequent generations of specialists, international binding standards  
 1028 such as the International System of Units (SI) are required that ensure mutual consistency and  
 1029 metrological comparability of any involved data produced from experiments, observations and  
 1030 models.

1031 Gibbs' (1873a) original potential function was (internal) energy,  $e = E/m$ . It is known that a sample's  
 1032 energy can be increased by compression,  $-pdv$ , where  $v = 1/\rho$  is the specific volume, or by input of  
 1033 heat,  $Td\eta$ , where  $\eta = N/m$  is the specific entropy. As an extensive quantity, entropy introduced by  
 1034 Clausius (1865, 1976) is denoted here by  $N$  to avoid confusion with seawater salinity,  $S$ . Energy  
 1035 conservation implies that

$$1036 \quad de = Td\eta - pdv. \quad (\text{B.3})$$

1037 Any such change between different equilibrium states of the same sample takes place along a  
 1038 definite, substance-specific surface  $e(\eta, v)$  so that  $de$  in eq. (B.3) is mathematically an exact  
 1039 differential and the partial derivatives of  $e$  possess the physical meanings that

$$1040 \quad T = \left(\frac{\partial e}{\partial \eta}\right)_v, \quad -p = \left(\frac{\partial e}{\partial v}\right)_\eta. \quad (\text{B.4})$$

1041 Gibbs (1873b) also demonstrated that for several equilibrium samples in contact with one another, in  
 1042 absence of gravity or accelerated motion, the samples are in mutual equilibrium only if they have  
 1043 equal values of the coefficients  $T$  and  $p$  of eq. (2.3).

1044 In the geophysical practice, the quantities  $\eta$  and  $v$  are difficult to measure, in contrast to, say,  $T$  or  $p$ .  
 1045 Mathematically equivalent to  $e(\eta, v)$ , thermodynamic potentials in terms of the other three possible  
 1046 pairs of independent variables are formally obtained from so-called Legendre transforms (Alberty  
 1047 2001), namely the *Helmholtz function*  $f(T, v) \equiv e - T\eta$  with the differential

$$1048 \quad df = -\eta dT - pdv, \quad (\text{B.5})$$

1049 the *Gibbs function*  $g(T, p) \equiv f + pv = e - T\eta + pv$  with

$$1050 \quad dg = -\eta dT + vdp, \quad (\text{B.6})$$

1051 and the specific *enthalpy*  $h(\eta, p) \equiv g + T\eta = f + T\eta + pv = e + pv$  with

$$1052 \quad dh = Td\eta + vdp. \quad (\text{B.7})$$

1053 Depending on the application purpose, each of these potential functions has certain advantages and  
 1054 disadvantages, and having all of them optionally at hand in mutually consistent versions is most  
 1055 useful.

1056 Gibbs (1874-78) also considered a situation in which a given sample may exchange substance with its  
 1057 surrounding. If the exchanged mass of substance  $i$  is  $dm_i$ , the related change of the sample's  
 1058 (extensive) energy  $E$  at constant entropy and volume is termed the *chemical potential*  $\mu_i$  of that  
 1059 substance,

$$1060 \quad dE = TdN - pdV + \sum_i \mu_i dm_i, \quad (B.8)$$

1061 so that this exact differential implies that the chemical potential is obtained from

$$1062 \quad \mu_i \equiv \left( \frac{\partial E}{\partial m_i} \right)_{N,V,m_{j \neq i}} = \left( \frac{\partial F}{\partial m_i} \right)_{T,V,m_{j \neq i}} = \left( \frac{\partial G}{\partial m_i} \right)_{T,p,m_{j \neq i}} = \left( \frac{\partial H}{\partial m_i} \right)_{N,p,m_{j \neq i}}. \quad (B.9)$$

1063 Equilibrium of a spatially extended substance, in absence of gravity or accelerated motion, requires  
 1064 that in addition to  $T$  and  $p$ , also the chemical potential  $\mu_i$  separately for each present substance  
 1065 needs to possess the same value anywhere in the volume. "The potential for each component  
 1066 substance must be constant throughout the whole mass" (Gibbs 1874-78: p. 119).

1067 As intensive properties, the specific energies cannot depend on the total mass but only on the mass  
 1068 fractions,  $w_i \equiv m_i/m$ . Because by definition  $\sum w_i = 1$ , only  $(n - 1)$  different fractions may be  
 1069 independent variables describing the  $n$  components of a mixture. For example, one of the  
 1070 components may be chosen as a master species, "0", such as a solvent, and the remaining ones,  $i =$   
 1071  $1, \dots, n - 1$ , may denote the solutes.

1072 In terms of  $T$  and  $p$ , chemical potentials are computed from the Gibbs function,  $g$ , through the Gibbs  
 1073 energy,  $G$ , of eq. (B.9). Because the Gibbs function depends only on the independent intensive  
 1074 variables,  $g(w_1, \dots, w_{n-1}, T, p)$ , the solutes' chemical potentials,  $i > 0$ , are

$$1075 \quad \mu_i = \left( \frac{\partial G}{\partial m_i} \right)_{T,p,m_{j \neq i}} = \left( \frac{\partial(mg)}{\partial m_i} \right)_{T,p,m_{j \neq i}} = g + \left( \frac{\partial g}{\partial w_i} \right)_{T,p,w_{j \neq i}} - \sum_{j=1}^{n-1} w_j \left( \frac{\partial g}{\partial w_j} \right)_{T,p,w_{k \neq j}} \quad (B.10)$$

1076 Similarly, the solvent's chemical potential is

$$1077 \quad \mu_0 = \left( \frac{\partial G}{\partial m_0} \right)_{T,p,m_{j>0}} = \left( \frac{\partial(mg)}{\partial m_0} \right)_{T,p,m_{j>0}} = g - \sum_{j=1}^{n-1} w_j \left( \frac{\partial g}{\partial w_j} \right)_{T,p,w_{k \neq j}}. \quad (B.11)$$

1078 Therefore, the *relative chemical potentials* of the solutes are simply the partial derivatives,

$$1079 \quad \mu_i - \mu_0 = \left( \frac{\partial g}{\partial w_i} \right)_{T,p,w_{j \neq i}}. \quad (B.12)$$

1080 For mixtures,  $n > 1$ , the differential (B.6) of the Gibbs function takes the more general form

$$1081 \quad dg = -\eta dT + v dp + \sum_{i=1}^{n-1} (\mu_i - \mu_0) dw_i. \quad (B.13)$$

1082 It follows straightforwardly from (B.10), (B.11) that the sum,

$$1083 \quad \sum_{i=0}^{n-1} \mu_i m_i = m g = G, \quad (B.14)$$

1084 equals the Gibbs energy itself (Gibbs 1874-78: eq. (96) therein, Guggenheim 1949, Landau and  
 1085 Lifschitz 1966, Kittel 1969). In particular, if  $n = 1$ , the Gibbs function  $g$  of a pure substance  
 1086 represents its chemical potential,

$$1087 \quad g = \mu. \quad (B.15)$$

1088 Where two phases of a pure substance are in contact at mutual equilibrium, such as saturated water  
 1089 vapour at the liquid water surface, the mathematically distinct Gibbs functions of those phases take  
 1090 equal values. This indispensable condition for mutual consistency between the thermodynamic  
 1091 potentials of TEOS-10 is rigorously obeyed by virtue of appropriate reference-state conditions (Feistel  
 1092 et al. 2008b).

1093

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