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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 This article is also dedicated to the memory of Wolfgang Wagner who sadly and unexpectedly has  
 22 passed away on 12 August 2024. His contributions to TEOS-10 are truly indispensable constituents;  
 23 Wolfgang was an essential co-author of various related documents and articles. He will deeply be  
 24 missed.

25

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

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

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

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

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

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

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

37 Heinrich Hertz: Energiehaushalt der Erde, 1885

38 *The sea surface interaction is obviously*  
 39 *a highly significant quantity in simulating climate.*

40 Andrew Gilchrist, Klaus Hasselmann: Climate Modelling, 1986

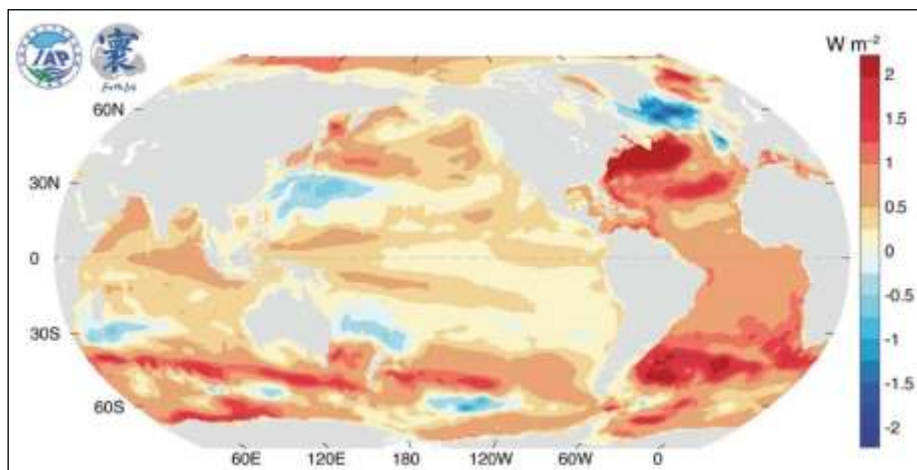
*The climate of the Earth is ultimately determined  
by the temperatures of the oceans.*  
Donald Rapp: Assessing Climate Change, 2014

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## 45 1 Introduction

46 Quite recently in 2024, climate research has published alarming news: “The world’s oceans absorbed  
47 more heat in 2023 than in any other year since records began in the 1950s. ... Data show that the  
48 heat stored in the upper 2,000 metres of oceans increased by 15 zettajoules (1 zettajoule is  $10^{21}$   
49 joules) in 2023 compared with that stored in 2022. This is an enormous amount of energy — for  
50 comparison, the world’s total energy consumption in 2022 was roughly 0.6 zettajoules” (You 2024: p.  
51 434). Dividing this value by the global ocean surface area and by the duration of a year, the reported  
52 ocean’s average warming rate amounts to  $1.3 \text{ W m}^{-2}$ , and is apparently even increasing. “Earth’s net  
53 global energy imbalance (12 months up to September 2023) amounts to  $+1.9 \text{ W m}^{-2}$ , ... ensuring  
54 further heating of the ocean” (Kuhlbrodt et al. 2024: p. E474). „Climate models struggle to explain  
55 why planetary temperatures spiked suddenly. ... No year has confounded climate scientists’  
56 predictive capabilities more than 2023. ... This sudden heat spike greatly exceeds predictions made  
57 by statistical climate models” (Schmidt 2024: p. 467).

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



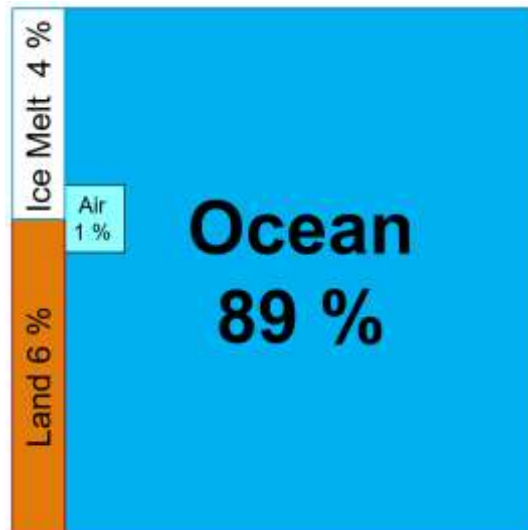
68  
69 Fig. 1: Observed trend 1958 through 2022 of the upper 2000 m ocean heat content (WMO 2024).  
70 Image reproduction permitted by WMO Copyright.

71

72 Sunlight is the only available heat source of sufficient power to cause the observed warming, while  
73 the globally averaged geothermal heat flux is estimated to be just  $0.087 \text{ W m}^{-2}$  (Pollack et al. 1993),

74 and is not expected to suddenly rise recently due to human impact. Irradiation is hampered by  
 75 clouds, dust and absorbing gases, and water surface reflection such as by whitecaps, waves or  
 76 plankton layers (Cahill et al. 2023). Heat absorbed in the water column may effectively exit the ocean  
 77 again only across the air-sea interface via sensible, radiative and latent heat flux. All these effects  
 78 may vary in the climate system in a complicated, mutually interacting manner. Typically, present  
 79 numerical climate models suffer from an “ocean heat budget closure problem” (Josey et al. 1999)  
 80 and describe the ocean-atmosphere heat flux only to within uncertainties between  $10 \text{ W m}^{-2}$  and  $30$   
 81  $\text{W m}^{-2}$  (Josey et al. 2013). According to recent model comparison studies, many of those “models fail  
 82 to provide as much heat into the ocean as observed” (Weller et al. 2022: p. E1968). Dynamical  
 83 models, rather than observed correlations, are the most reliable tools for the detection and  
 84 verification of causal relations (Feistel 2023), however, such as in this case of air-sea interaction,  
 85 large uncertainties may prevent any significant conclusions to be drawn regarding the causes of the  
 86 observed ocean warming rate of  $1.3 \text{ W m}^{-2}$ .

87 Of the increasing amount of water vapour contained in the global troposphere, 85 % results from  
 88 ocean evaporation (Gimeno et al. 2013). Corresponding to 1200 mm annual evaporation (Budyko  
 89 1963, 1984, Baumgartner and Reichel 1975, Peters-Lidard et al. 2019), the associated latent heat flux  
 90 of about  $95 \text{ W m}^{-2}$  per ocean surface area represents the strongest energy supply for the  
 91 atmospheric dynamics (Albrecht 1940) and at the same time the strongest cooling process of the sea.  
 92 This flux depends sensitively on the relative humidity (RH) at the water surface; an RH increase by 1  
 93 %rh can be estimated to reduce evaporation by  $5 \text{ W m}^{-2}$  (Feistel 2015, 2024, Feistel and Hellmuth  
 94 2021, 2023), so that minor additional 0.2 %rh may already suffice to warm up the ocean by the  
 95 observed  $1.3 \text{ W m}^{-2}$ . Unfortunately, marine RH is observed only with uncertainties between 1 and 5  
 96 %rh (Lovell-Smith et al. 2016), or, accordingly, between 5 and  $25 \text{ W m}^{-2}$  of latent heat flux, which is  
 97 roughly corresponding to unknown variations ranging up to 50 ... 250 mm evaporation per year. It  
 98 remains unclear to what extent minor, yet unnoticed changes in marine RH may be responsible for  
 99 the recent ocean warming.



100

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

104

105 According to Fig. 2, a paramount share of 94 % of global warming occurs in different phases and  
 106 geophysical mixtures of water, in particular in seawater. Considering this situation, the *Scientific*  
 107 *Committee on Oceanic Research* (SCOR) in cooperation with the *International Association for the*

108 *Physical Sciences of the Oceans* (IAPSO) decided at its 2005 Cairns meeting the establishment of the  
 109 *SCOR/IAPSO Working Group 127 on Thermodynamics of Seawater* (WG127) (Millero 2010, Pawlowicz  
 110 et al. 2012, Smythe-Wright et al. 2019), which held its inaugural meeting in 2006 at Warnemünde  
 111 (Fig. 3). It had been recognised that “modelling of the global heat engine needs accurate expressions  
 112 for the entropy, enthalpy, and internal energy of seawater so that heat fluxes can be more accurately  
 113 determined in the ocean” (Millero 2010: p. 28) while such properties were not available from the  
 114 thermodynamic seawater standard at that time, the 1980 Equation of State of Seawater (EOS-80)  
 115 (Fofonoff and Millard Jr. 1983).



116

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



121

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

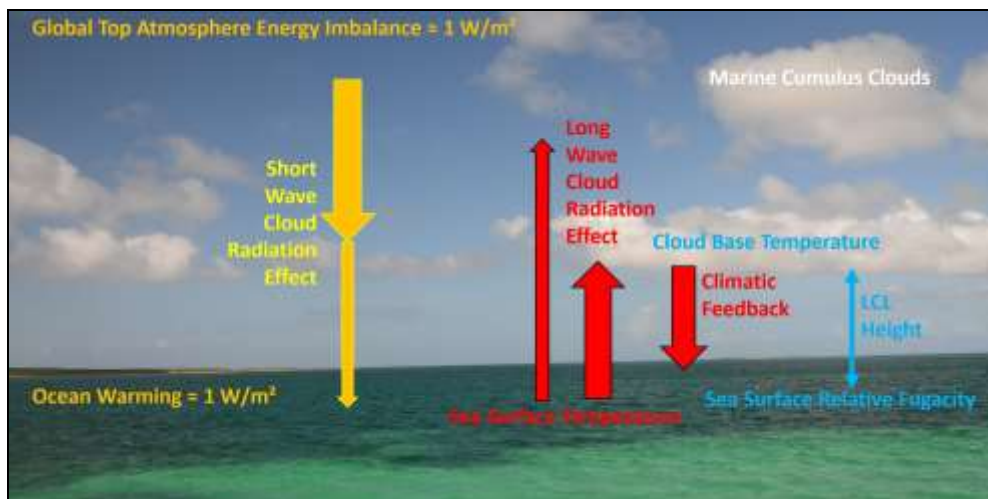
126

127 The foundation of WG127 happened almost coincidentally with the establishment of the *Ocean*  
 128 *Science* journal of the *European Geosciences Union* (EGU) in 2004/05. The development of the new  
 129 standard by WG127, the Thermodynamic Equation of Seawater – 2010 (TEOS-10) was very  
 130 successfully supported by Ocean Science, publishing the Special Issue #14 on “Thermophysical  
 131 Properties of Seawater” with 16 articles between 2008 and 2012 (Feistel et al. 2008a). **Appendix A**

132 reports the current metrics of this Special Issue. Also in 2008, at its conference in Berlin, Germany,  
 133 the *International Association for the Properties of Water and Steam* (IAPWS) established a new  
 134 *Subcommittee on Seawater* (SCSW) that cooperated closely with WG127. In the form of carefully  
 135 verified mathematical formulations for properties of water, ice, seawater and humid air, IAPWS  
 136 adopted nine fundamental documents related to TEOS-10 (IAPWS AN6-16 2016), see **Appendix A**.

137 With respect to problems yet pending after the official adoption of TEOS-10, especially for the  
 138 preparation of future novel international definitions of seawater salinity, seawater pH and  
 139 atmospheric relative humidity (Feistel et al. 2016, Pawlowicz et al. 2016, Dickson et al. 2016, Lovell-  
 140 Smith et al. 2016), the standing *IAPSO/SCOR/IAPWS Joint Committee on the Properties of Seawater*  
 141 (JCS) was established in 2012. In 2011, IAPWS also extended its cooperation with the *International*  
 142 *Bureau for Weights and Measures* (BIPM), see Fig. 4. Further details on TEOS-10 (IOC et al. 2010,  
 143 McDougall et al. 2013, Feistel 2018, Wikipedia 2024) are available from the TEOS-10 homepage,  
 144 [www.teos-10.org](http://www.teos-10.org), and are briefly reviewed in **Section 2** and **Appendix B**.

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



151

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

156

157 Currently implemented parameterisations of marine evaporation rates in the form of historical  
 158 *Dalton equations* (Stewart 2008, Josey et al. 1999, 2013) may be replaced by TEOS-10 chemical  
 159 potentials which provide the proper quantitative basis for a thermodynamically rigorous formulation  
 160 of non-equilibrium Onsager forces and fluxes in terms of *relative fugacity* (RF) of humid air (Kraus  
 161 and Businger 1994, Feistel and Lovell-Smith 2017, Feistel and Hellmuth 2023, 2024a), as described in  
 162 **Section 4**. *Relative humidity* (RH) is defined relative to the saturation state of moist air, which in turn  
 163 is controlled by the chemical potentials of water in the gas and liquid phase. It is only natural,  
 164 therefore, to define RH in terms of chemical potentials, which in fact is performed by RF. The  
 165 uncertainty of latent heat flux with respect to the uncertainty of surface RH observation is shown to

166 be significantly larger than the observed warming of  $1.3 \text{ W m}^{-2}$ , so that this unpredicted warming  
 167 may or may not be caused by so-far ignored minor RH increase.

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

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

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

189

## 190 **2 Thermodynamic Equation of Seawater – 2010 (TEOS-10)**

191 In the climate system, the omnipresent and dominant substance is water in various phases and  
 192 mixtures. For example, “water vapor is by far the most important greenhouse gas, in the sense that it  
 193 absorbs more irradiance from the Earth than all other greenhouse gases combined” (Rapp 2014: p.  
 194 381). Textbooks and other publications offer numerous collections of various different property  
 195 equations for water, ice, seawater or moist air, but uncertainties and mutual consistencies of those  
 196 equations are often unclear. To improve this situation, a novel *Thermodynamic Equation of Seawater*  
 197 – 2010 (TEOS-10) was developed by the members of the SCOR/IAPSO Working Group 127 (WG 127)  
 198 in close cooperation with the International Association for the Properties of Water and Steam  
 199 (IAPWS). TEOS-10 is described in a detailed Manual (IOC et al. 2010) and has been adopted and  
 200 recommended by IOC-UNESCO (2009) in Paris and by the IUGG (2011) in Melbourne, see also Feistel  
 201 (2008b, 2012, 2018), Valladares et al. (2011) and Pawlowicz et al. (2012). Starting in 2008 with a  
 202 Special Issue of *Ocean Science* (Feistel et al. 2008a), a large number of scientific publications has  
 203 appeared in the meantime, supporting, extending or exploiting TEOS-10. A collection of selected  
 204 papers related to TEOS-10 is summarised in Appendix A together with metrics that illustrate the  
 205 growing uptake of TEOS-10 by the scientific community.

206 The development of the first numerical thermodynamic Gibbs potentials (see Appendix B) for  
 207 seawater (Feistel 1991, 1993, Feistel and Hagen 1995) was based on the works of Millero and Leung  
 208 (1976) and Millero (1982, 1983), together with high-pressure background data of the previous EOS-  
 209 80 standard (Unesco 1981). Independently of that, a Helmholtz potential for pure fluid water had  
 210 been adopted by IAPWS in 1996 at Fredericia (Harvey 1998, Wagner and Pruß 2002). These were the

211 key activities which eventually culminated in the formulation of TEOS-10 about two decades later. By  
 212 combining those equations for pure and seawater, some known pending problems of EOS-80  
 213 (Fofonoff and Millard Jr. 1983) could incidentally be resolved (Feistel 2003). In the end, TEOS-10 has  
 214 been assembled from four basic thermodynamic potentials derived from mutually consistent, most  
 215 comprehensive and accurate datasets of measured properties available at that time. Those  
 216 potentials are (IAPWS R6-95 2016, IAPWS R10-06 2009, IAPWS R13-08 2008, IAPWS G8-10 2010,  
 217 respectively):

- 218 (i) A Helmholtz function of fluid water,  $f^F(T, \rho) \equiv f^W(T, \rho) \equiv f^V(T, \rho)$ , known as the  
 219 IAPWS-95 formulation (Wagner and Pruß 2002), which is identical for liquid water,  
 220  $f^W(T, \rho)$  and for water vapour,  $f^V(T, \rho)$ . It describes de-aerated water of a fixed  
 221 isotopic composition, termed *Standard Mean Ocean Water (SMOW)*, with density  $\rho$  and  
 222 temperature  $T$ .  
 223
- 224 (ii) A Gibbs function of ambient hexagonal ice I,  $g^{\text{Ih}}(T, p)$ , or IAPWS-06 formulation (Feistel  
 225 and Wagner 2006), see Tables A2 and A3 of Appendix A, depending on pressure  $p$ .  
 226
- 227 (iii) A Gibbs function of *IAPSO Standard Seawater*,  $g^{\text{SW}}(S, T, p)$ , or IAPWS-08 formulation  
 228 (Feistel 2008a), see Tables A2 and A3 of Appendix A. The variable  $S$ , at which a subscript  
 229 A is omitted here for simplicity, is the specific or *Absolute Salinity*, the mass fraction of  
 230 dissolved salt in seawater, which differs from *Practical Salinity*,  $S_p$ , measured by present-  
 231 day oceanographic instruments, as well as from various other obsolete salinity scales  
 232 (Millero et al. 2008). Throughout this paper, the term “salinity” is exclusively short hand  
 233 for TEOS-10 Absolute Salinity. Sea salt is assumed to have stoichiometric *Reference*  
 234 *Composition*. The pure-water limit,  $g^{\text{SW}}(0, T, p) = g^W(T, p)$ , is the Gibbs function of  
 235 liquid water computed from the IAPWS-95 Helmholtz function  $f^W(T, \rho)$ . For brackish  
 236 seawater,  $g^{\text{SW}}$  has implemented Debye’s root law of dilute electrolyte solutions (Landau  
 237 and Lifschitz 1966, Falkenhagen et al. 1971).  
 238
- 239 (iv) A Helmholtz function of humid air,  $f^{\text{AV}}(A, T, \rho)$ , or IAPWS-10 formulation (Feistel et al.  
 240 2010a), see Tables A1 and A2 of Appendix A. The variable  $A$  is the mass fraction of dry air  
 241 admixed with water vapour, so that  $q = 1 - A$  is the *specific humidity*. The dry-air limit  
 242  $f^{\text{AV}}(1, T, \rho) = f^A(T, \rho)$  equals, up to modified reference-state conditions, the equation  
 243 of state of Lemmon et al. (2000). The air-free limit  $f^{\text{AV}}(0, T, \rho) = f^V(T, \rho)$  equals the  
 244 IAPWS-95 Helmholtz function of water vapour. In  $f^{\text{AV}}$ , the interaction of water vapour  
 245 with dry air is described by 2<sup>nd</sup> and 3<sup>rd</sup> virial coefficients.  
 246  
 247

248 Thermodynamic potentials include certain adjustable constants expressing the absolute energies and  
 249 entropies of the particular substances, which are not available from measurement (Planck 1906,  
 250 Feistel 2019b) and have, in turn, no effect on measurable properties derived from those potentials.  
 251 In fact, among the comprehensive experimental data sets from which the TEOS-10 equations were  
 252 derived, none of those are suitable for fitting the empirical coefficients that represent absolute  
 253 energies and entropies of those equations. For this reason, the International Conference on the  
 254 Properties of Steam at London defined in 1967 the common triple point of water as the reference  
 255 state at which those absolute values were arbitrarily set. Since then, no evidence has appeared for  
 256 putative conflicts caused by such settings with any technical or scientific applications of the  
 257 equations. Despite this, Feistel and Wagner (2006) and Feistel et al. (2008b) discuss the  
 258 implementation of alternative residual entropies of water, if that should be of interest in exceptional

259 applications of TEOS-10. For recent discussions of Pauling’s absolute “residual” entropy at zero kelvin  
 260 and Nernst’s Third Law of thermodynamics, see Kozliak and Lambert (2008), Gutzow and Schmelzer  
 261 (2011), Takada et al. (2015), Schmelzer and Tropin (2018), Feistel (2019b), or Shirai (2023).

262  
 263 The TEOS-10 reference states (Feistel et al. 2008b, 2010a) are the triple point of water,  $T_{\text{TP}} =$   
 264  $273.16 \text{ K}$ ,  $p_{\text{TP}} = 611.654 \text{ 771 Pa}$ , where the conditions

$$265 \quad \eta_{\text{TP}}^{\text{W}} = 0, \quad e_{\text{TP}}^{\text{W}} = 0, \quad (1)$$

266  
 267 are imposed, and the standard ocean state at Absolute Salinity,  $S_{\text{SO}} = 35.165 \text{ 04 g kg}^{-1}$ , absolute  
 268 temperature,  $T_{\text{SO}} = 273.15 \text{ K}$ , and absolute pressure,  $p_{\text{SO}} = 101 \text{ 325 Pa}$ , with the conditions for sea  
 269 salt,  
 270

$$271 \quad \eta_{\text{SO}}^{\text{SW}} = 0, \quad h_{\text{SO}}^{\text{SW}} = 0, \quad (2)$$

272  
 273 and for dry air,

$$274 \quad \eta_{\text{SO}}^{\text{A}} = 0, \quad h_{\text{SO}}^{\text{A}} = 0. \quad (3)$$

275  
 276 Here,  $\eta$ ,  $e$  and  $h$ , respectively, are specific entropy, internal energy and enthalpy of water  
 277 (superscript W), seawater (superscript SW) and dry air (superscript A). The TEOS-10 potential  
 278 functions and properties derived thereby are numerically implemented in two different libraries, the  
 279 Sea-Ice-Air (SIA) and the Gibbs-Seawater (GSW) libraries, see Table A4 in Appendix A.  
 280  
 281

282  
 283 The SIA library includes empirical coefficients only in the four fundamental potentials (Feistel 2010d,  
 284 Wright et al. 2010). All other potential functions and properties are derived strictly by mathematical  
 285 operations to ensure consistent results, even at the cost of low computation speeds as a result of  
 286 stacked iteration procedures. All quantities are exclusively expressed in basic SI units such as kg, m, J  
 287 or Pa. A more recent extension of SIA code is reported in Feistel et al. (2022) for the computation of  
 288 relative fugacity.  
 289

290 The GSW library is tailored for oceanographic models, optimised in computation speed (Roquet et al  
 291 2015). For fast numerical evaluation, GSW procedures contain new empirical coefficients determined  
 292 from the SIA library functions by regression. Units and variables are adjusted to common  
 293 oceanographic practice such as pressure in decibars relative to surface pressure, or temperatures in  
 294 °C. *Conservative Temperature* (CT) is used as a new preferred thermal variable. An additional  
 295 thermodynamic potential has been constructed (McDougall et al. 2023) that supports the use of CT  
 296 universally as an independent variable.  
 297

297

### 298 **3 Potential Enthalpy and Ocean Heat Content (OHC)**

299 Thermodynamically, the term “Ocean Heat Content” (OHC) is a sloppy wording. “Content” means a  
 300 state quantity of a body or volume while, by contrast, “heat” is an exchange quantity rather than a  
 301 state quantity. “We have ... a right to speak of heat as a *measurable quantity*, ... however, ... we have  
 302 no right to treat heat as a *substance*” (Maxwell 1888: p. 7). “The obsolete hypothesis of heat being a  
 303 substance is excluded” (Sommerfeld 1988: p. 6). “Heat is not a substance! More formally: Heat is not  
 304 a thermodynamic function of state” (Romer 2001: p. 107). This distinction is qualitatively  
 305 fundamental (Feistel 2023). Physical conservation quantities such as energy or mass have the key



306 property that the change of that quantity in a volume equals the flux of that quantity across the  
 307 boundary (Landau and Lifschitz 1966, Glansdorff and Prigogine 1971), but this does not apply to  
 308 “heat”. For example, a heat engine receives a permanent net heat flux without getting permanently  
 309 hotter. While asking how much “heat” is contained in the ocean may find ambiguous answers, it is  
 310 well defined to say how much heat has entered or left the ocean across its boundary by a specified  
 311 process that transfers the ocean from a certain state of reference to the current state of interest. In  
 312 this section, based upon TEOS-10, related states and processes are described which may properly  
 313 specify what is commonly termed OHC. This consideration intrinsically connects OHC with ocean-  
 314 atmosphere exchange processes relevant for climate change.

315 Since a long time, measuring and calculating the ocean’s “heat” has been a question of central  
 316 interest to oceanography. Recently, this issue has become even more important and urgent in the  
 317 context of climate change. “The total energy imbalance at the top of atmosphere is best assessed by  
 318 taking an inventory of changes in energy storage. The main storage is in the ocean” (Abraham et al.  
 319 2013: p. 450). The conventional approach is a formally defined mathematical procedure based on  
 320 potential temperatures. “Changes to ocean heat content (OHC) can be calculated from  
 321 measurements of the temperature evolution of the ocean. The OHC is attained from the difference  
 322 of the measured potential temperature profile and the potential temperature climatology. This  
 323 difference is integrated over a particular reference depth (for instance, 700 m) and is multiplied by a  
 324 constant ocean density reference and heat capacity” (Abraham et al. 2013: p. 468). However, in  
 325 representing a kind of “heat substance”, this OHC definition has no rigorous thermodynamic  
 326 justification, and the relation to processes of ocean-atmosphere heat fluxes is not entirely clear. If a  
 327 sea-air heat flux of  $1 \text{ W m}^{-2}$  warms up the atmosphere, by what rate exactly will that OHC decrease?

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

$$331 \quad OHC = \int h^{SW}(S, \eta, p_0) \rho^{SW}(S, \eta, p) dV . \quad (4)$$

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

- 336 (i) A virtual **heat exchange process** supporting the definition (4) is sketched in Fig. 6. In turn,  
 337 each ocean parcel with in-situ properties  $(S, \eta, p)$  is lifted to the surface pressure  $p_0$ ,  
 338 keeping its salinity and entropy constant. There, it reversibly exchanges heat,  $dh = Td\eta$ ,  
 339 with a measuring device until the parcel’s entropy has reached a certain reference value,  
 340  $\eta_{ref}$ , while the parcel’s salinity remains unchanged. Subsequently, the heat is reversibly  
 341 put back to the parcel which is then returned to its original location. The work required  
 342 to lift and lower the parcel is balanced because the parcel’s thermodynamic state is  
 343 exactly the same before and after the balanced reversible heat exchange across the  
 344 surface. The “heat content” defined this way for a single parcel is added up then over all  
 345 ocean parcels to result in its total OHC value.
- 346 (ii) The **reference state** relative to which OHC is measured may freely be specified at will,  
 347 but beneficially be chosen with respect to its convenience or usefulness. In the case of  
 348 eq. (4), the OHC reference state is zero potential enthalpy (or zero Conservative  
 349 Temperature, McDougall 2003) of all ocean parcels.

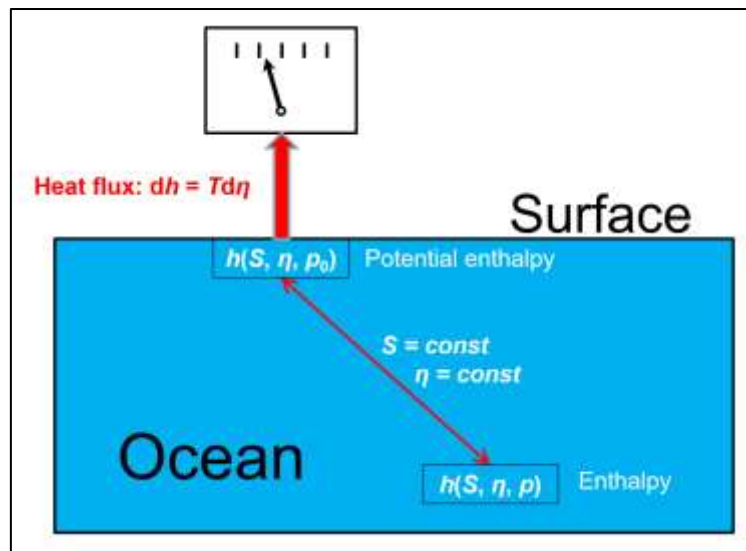
350 The process depicted in Fig. 6 measures the total heat flux  $\int dh = \int Td\eta$  which changes the entropy  
 351 of the given sample from the current value,  $\eta$ , to some arbitrary reference value,  $\eta_{\text{ref}}$ , and this way,  
 352 the process also changes the parcel's enthalpy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

$$354 \quad \text{OHC}^* = \int [h^{\text{SW}}(S, \eta, p_0) - h^{\text{SW}}(S, \eta_{\text{ref}}, p_0)] \rho^{\text{SW}}(S, \eta, p) dV. \quad (5)$$

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

- 360 (i) *The OHC definition should ensure that OHC differences represent a suitable spatial*  
 361 *integral over the heat fluxes crossing the ocean's boundaries.* As discussed in more detail  
 362 in Section 5.3, production of entropy,  $d_i\eta$ , caused by irreversible processes between  
 363 different parcels within the ocean, does not affect the ocean's total enthalpy budget.  
 364 This is quite in contrast to entropy exchange,  $d_e\eta$ , of the given sample in the form of  
 365 reversible heat flux across its boundary. Such irreversible processes affect the ocean's  
 366 total potential enthalpy much less than its total entropy (McDougall et al. 2021). For this  
 367 reason the OHC reference state should explicitly be defined in terms of potential  
 368 enthalpy,  $h^{\text{SW}}(S, \eta_{\text{ref}}, p_0)$ , and this way only implicitly in terms of entropy by specifying  
 369  $\eta_{\text{ref}}(S)$ .  
 370
- 371 (ii) *Provided that the ocean's mass remains the same between any two ocean states (1) and*  
 372 *(2), the difference OHC(1) – OHC(2) should depend only on the surface heat flux balance*  
 373 *during the time in between. In particular, differences OHC(1) – OHC(2) should not depend*  
 374 *on the OHC reference state.* For this reason, the OHC reference value should be  
 375 independent of changes occurring in the density distribution,  $\rho^{\text{SW}}(S, \eta, p)$ . This can be  
 376 achieved by assigning to each ocean parcel the same reference potential enthalpy,  
 377  $h^{\text{SW}}(S, \eta_{\text{ref}}, p_0) = \text{const}$ , even though such a state may hardly ever be observed in the  
 378 real ocean.  
 379
- 380 (iii) *Quantitatively, OHC values estimated at different times or places should be mutually*  
 381 *comparable without estimation bias resulting from possibly changing methods of OHC*  
 382 *calculation.* For this reason, resulting OHC values should be independent of the inevitable  
 383 arbitrary, physically irrelevant reference-state conditions imposed on energy and  
 384 entropy, such as eqs. (1)-(3). This can be achieved by assigning to each ocean parcel the  
 385 same standard-ocean enthalpy as its reference potential enthalpy,  $h^{\text{SW}}(S, \eta_{\text{ref}}, p_0) =$   
 386  $h_{\text{SO}}$ . In the special case of TEOS-10 enthalpy, this value is defined by eq. (2),  $h_{\text{SO}} = 0$ .  
 387 This choice is implicitly made by the definition (4) but needed to be considered explicitly  
 388 as soon as alternative equations for seawater enthalpy or entropy are employed, such as  
 389 those of Millero and Leung (1976) and Millero (1982, 1983).

390



391

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

394

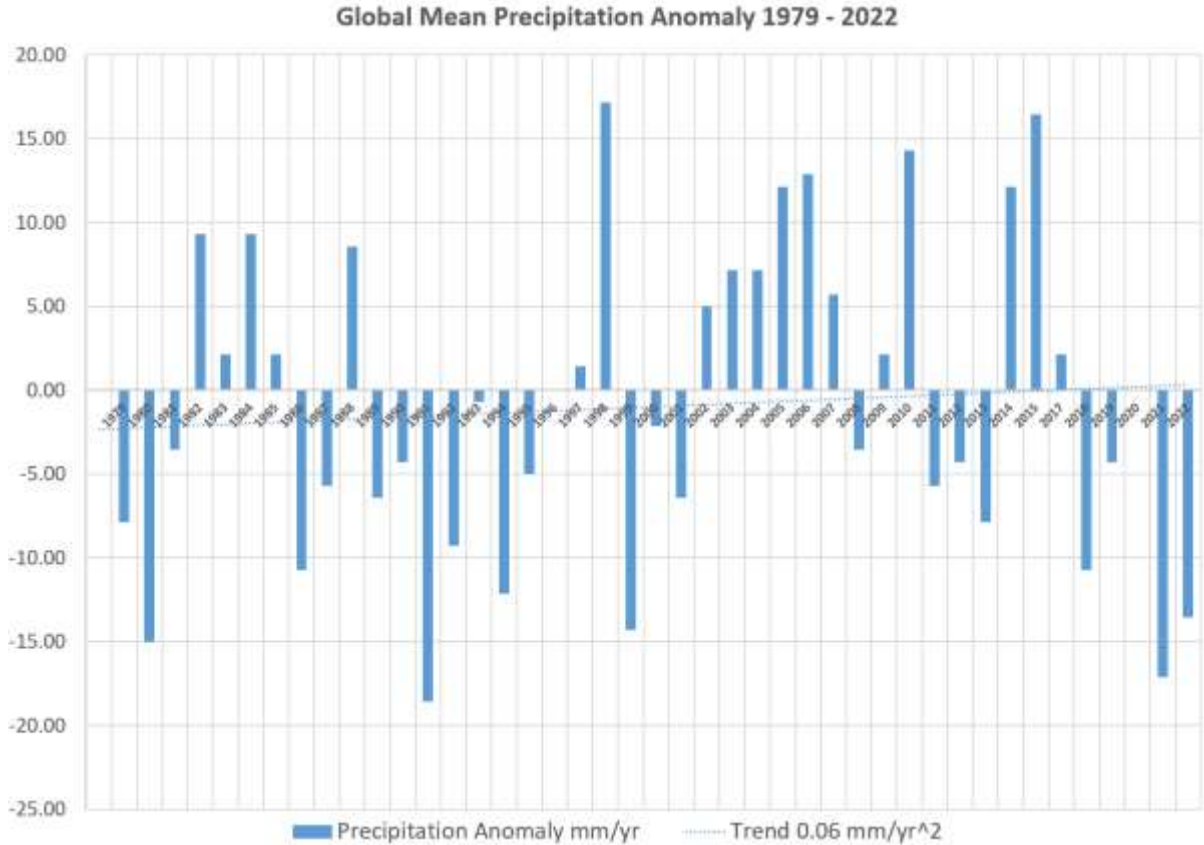
395 In a sense consistent with the previous OHC definition (Abraham et al. 2013), also a climatological  
 396 average state could in principle be chosen as the OHC reference. However, this option includes the  
 397 problem that the salinity distribution of the current ocean may differ from the reference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

402

#### 403 4 Relative Fugacity and Ocean Evaporation Rate

404 "The global water cycle and the exchange of freshwater between the atmosphere and ocean is  
 405 poorly understood. ... It has been predicted that increasing global temperatures will lead to an  
 406 enhanced global water cycle" (Holliday et al. 2011: p. 34). In the past, several climate researchers  
 407 have argued that along with global warming the marine evaporation has or will be “amplified” or  
 408 “intensified” (Feistel and Hellmuth 2021). However, it was not always made clear whether this may  
 409 mean that (a) in the course of a year, more water vapour is transferred from the global ocean to the  
 410 atmosphere, or (b) that the global mean evaporation rate remains unchanged while locally or  
 411 temporally, evaporation is more intense, or (c) any combination of the two variants. Conclusions of  
 412 kind (a) were drawn by renowned climatologists such as Budyko (1984), Flohn et al. (1992), Yu  
 413 (2007), Randall (2012), Francis (2021) or Zhang et al. (2021).

414 By contrast, in favour of option (b), the currently observed ocean warming at a rate about  $1 \text{ W m}^{-2}$   
 415 does not support assumptions of an enhanced hydrological cycle with related latent-heat cooling,  
 416 rather, it more likely suggests a slight reduction of evaporation. Two decades ago, Held and Soden  
 417 (2006: p. 5687-5689) had already clearly stated that “it is important that the global-mean  
 418 precipitation or evaporation, commonly referred to as the strength of the hydrological cycle, does  
 419 not scale with Clausius–Clapeyron. ... We can, alternatively, speak of the mean residence time of  
 420 water vapor in the troposphere as increasing with increasing temperature.” Subsequent observations  
 421 have underpinned their statement.



422

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

425

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

430 Probably, the minor trend of  $0.06 \text{ mm yr}^{-2}$  of the data displayed in Fig. 7 is statistically insignificant.  
 431 Associated with this apparent trend, the latent heat transferred to the troposphere can be estimated  
 432 to a negligible putative warming rate of additional  $0.5 \text{ mW m}^{-2}$  per year, which could explain only 10  
 433 % of observed atmospheric warming by  $1.7 \text{ °C}$  per century (Morice et al. 2012, Feistel and Hellmuth  
 434 2021).

435 The thermodynamic driving force for evaporation is the difference between the chemical potentials  
 436 of water in humid air and in seawater at the two sides of the sea-air interface (Kraus and Businger  
 437 1994). TEOS-10 has made this difference numerically available in the form of the water mass  
 438 evaporation rate (Feistel and Hellmuth 2022, 2023)

$$439 \quad J_W = -D_f(u) \ln \frac{\psi_f}{x_W}. \quad (6)$$

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

$$442 \quad x_W = \frac{53.556\ 514\ 4}{54.676\ 283\ 8} = 0.979\ 52, \quad \ln x_W = -0.0206926. \quad (7)$$

443 In eq. (6),  $D_f(u)$ , the *Dalton coefficient*, is an empirical transfer coefficient as a function of the wind  
 444 speed,  $u$ , as a parameterisation of the turbulent transport processes of water in the vicinity of the  
 445 interface. Applications of the *Monin-Obukhov Similarity Theory* (MOST) in order to estimate the  
 446 Dalton coefficient are reviewed by Liu et al. (1979), Foken and Richter (1991), Foken (2004, 2016) and  
 447 in the Digital Supplement of Feistel and Hellmuth (2024). A review of empirical Dalton coefficients is  
 448 given by Debski (1966); historical evaporation experiments are summarised by Biswas (1969).

449 In eq. (6), the sea-surface humidity is expressed by the *relative fugacity* (RF),  $\psi_f$ , defined by the ratio  
 450 of the water-vapour fugacity in humid air,  $f_V$ , to that fugacity at saturation,  $f_V^{\text{sat}}$  (Feistel and Lovell-  
 451 Smith 2017), see eq. (49). In ideal-gas approximation, RF equals conventional RH (Lovell-Smith et al.  
 452 2016)

$$453 \quad \psi_f \equiv \frac{f_V}{f_V^{\text{sat}}} \approx \psi_x \equiv \frac{x}{x^{\text{sat}}}. \quad (8)$$

454 Here, the mole fraction of water vapour in humid air is  $x$ , and its value at saturation is  $x^{\text{sat}}$ . Further,  
 455  $\psi_x$  is the conventional definition of RF in metrology and meteorology which, however, is inconsistent  
 456 with alternative definitions such as the one employed in climatology (Lovell-Smith et al. 2016).  
 457 Independent of ideal-gas conditions, but sufficiently close to saturation, such as near the sea surface,  
 458 RF can be estimated in excellent approximation from the Clausius-Clapeyron formula (Feistel et al.  
 459 2022),

$$460 \quad \psi_f \approx \exp \left\{ \frac{L(T_{\text{dp}}, p)}{R_W} \left( \frac{1}{T} - \frac{1}{T_{\text{dp}}} \right) \right\}. \quad (9)$$

461 The evaporation enthalpy of pure water (IAPWS SR1-86 1992) at the dewpoint  $T_{\text{dp}}$  is  $L$ , and  $R_W =$   
 462  $461.523 \text{ J kg}^{-1} \text{ K}^{-1}$  is the specific gas constant of water. The typical marine RF is

$$463 \quad \psi_f \approx 80 \text{ \%rh}, \quad (10)$$

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

474 Various empirical evaporation equations, commonly known as *Dalton equations*, are found in the  
 475 literature (Wüst 1920, Sverdrup 1936, 1937, Montgomery 1940, Debski 1966, Biswas 1969,  
 476 Baumgartner and Reichel 1975). Several numerical climate models estimate evaporation from the  
 477 formula (Stewart 2008, Pinker et al. 2014),

$$478 \quad J_W = D_q(u)(q_0 - q_{10}), \quad (11)$$

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

$$481 \quad J_W = D_q(u)(0.98 q^{\text{sat}} - q). \quad (12)$$

482 Here,  $q$  is the near-surface specific humidity, and  $q^{\text{sat}}$  is the saturation value at the same  
 483 temperature and pressure. The factor 0.98 accounts for the salinity, see eq. (7). After a few

484 approximation steps (Feistel and Hellmuth 2023), these Dalton equations can be derived from the  
 485 TEOS-version, eq. (6), however, there is an important qualitative difference. At constant RH, due to  
 486 global warming, specific humidities such as  $q$  and  $q^{\text{sat}}$ , as well as their difference, are increasing  
 487 following the Clausius-Clapeyron saturation formula. Accordingly, eq. (12) implies that also the  
 488 evaporation rate  $J_W$  is growing this way, by contrast to eq. (6). This virtual acceleration of the  
 489 hydrological cycle is evidently inconsistent with the prediction of Held and Soden (2006). This  
 490 parameterisation-caused additional latent heat flux implies a spurious ocean cooling that may  
 491 contribute to the finding that many numerical climate models tend to underestimate the observed  
 492 ocean warming (Weller et al. 2022).

493 From eq. (6), the sensitivity of the latent heat flux,  $LJ_W$ , with respect to RH variations is easily  
 494 estimated. For a mean evaporation rate of 1200 mm per year, the corresponding mass flux is about  
 495  $J_W \approx 3.8 \times 10^{-5} \text{ kg m}^{-2} \text{ s}^{-1}$  and the related heat flux is  $LJ_W \approx 95 \text{ W m}^{-2}$  with respect to the ocean  
 496 surface area and a specific evaporation enthalpy of  $L = 2501 \text{ kJ kg}^{-1}$ . At a surface humidity of  $\psi_f =$   
 497 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,  
 498 and of  $LD_f(u) \approx 468 \text{ W m}^{-2}$  for that of latent heat. Then, from

$$499 \quad \Delta(LJ_W) = L \frac{\partial J_W}{\partial \psi_f} \Delta\psi_f = -LD_f(u) \frac{\Delta\psi_f}{\psi_f} \quad (13)$$

500 it follows that an increase by  $\Delta\psi_f = 1 \text{ \%rh}$  results in a heat flux reduction by  $\Delta(LJ_W) =$   
 501  $5.85 \text{ W m}^{-2}$ . So, the currently observed ocean warming (Cheng et al. 2024) of  $1.3 \text{ W m}^{-2}$  could  
 502 theoretically be caused already by a minor marine humidity increase of  $\Delta\psi_f = 0.2 \text{ \%rh}$ , a value far  
 503 below the present measurement uncertainty between 1 and 5 %rh of relative humidity. The  
 504 resolution of climate models and observation seems to be insufficient yet to identify the possible role  
 505 of RH for the unclear explanation of the warming ocean.

506

## 507 **5 Sea Air as a Two-Phase Composite**

508 Gibbs' (1873) method of using potential functions can be applied to any systems possessing stable  
 509 thermodynamic equilibria and obeying energy conservation, without being restricted to merely  
 510 homogeneous or single-phase samples. The intentionally strict mutual consistency of the different  
 511 TEOS-10 potential functions permits a mathematical description of multi-phase composites such as  
 512 sea ice, consisting of ice with included brine pockets (Feistel and Hagen 1998, Feistel and Wagner  
 513 2005), or clouds, where liquid water or ice is floating in saturated humid air (Hellmuth et al. 2021).  
 514 Another important model is that of *sea air*, a sample consisting of a mass  $m^{\text{SW}}$  of seawater in  
 515 thermodynamic equilibrium with a mass  $m^{\text{AV}}$  of humid air (Feistel et al. 2010d, Feistel and Hellmuth  
 516 2023). Such a model may serve as a mathematical description for certain thermodynamic properties  
 517 of ocean-atmosphere interaction.

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

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

$$528 \quad G^{SA} = G^{SW} + G^{AV} = mg^{SA}, \quad (14)$$

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

$$532 \quad g^{SA}(S, A, w^{SW}, T, p) = w^{SW}g^{SW}(S, T, p) + (1 - w^{SW})g^{AV}(A, T, p). \quad (15)$$

533 If the two phases are assumed to be at mutual equilibrium, they possess the same temperature,  
 534 pressure and chemical potentials, see eq. (B.11) in Appendix B,  $\mu_W^{SW} = \mu_V^{AV}$ , namely that of water in  
 535 seawater,

$$536 \quad \mu_W^{SW}(S, T, p) = g^{SW} - S \left( \frac{\partial g^{SW}}{\partial S} \right)_{T,p}, \quad (15)$$

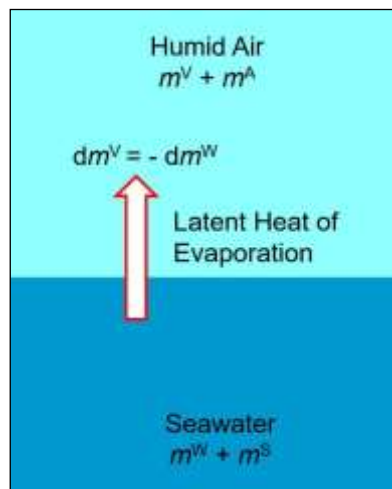
537 equalling that of water vapour in humid air,

$$538 \quad \mu_V^{AV}(A, T, p) = g^{AV} - A \left( \frac{\partial g^{AV}}{\partial A} \right)_{T,p}. \quad (16)$$

539

#### 540 *5.1 Sea Air as a Model for Latent Heat of Evaporation*

541 Water evaporated from the ocean surface drives the climate system. “The by far largest part of heat  
 542 conveyed to the air is in the form of latent heat during subsequent condensation along with cloud  
 543 formation. The heat budget over the sea is mainly controlled by the latent heat released to the air”  
 544 (Albrecht 1940). It is the “*heat source for a gigantic steam engine*”, as Heinrich Hertz had put it in his  
 545 1885 inaugural lecture at Karlsruhe (Mulligan and Hertz 1997). The latent heat of evaporation of pure  
 546 liquid water into pure water vapour is numerically well known from experiments (IAPWS SR1-86  
 547 1992, Harvey 1998, Wagner and Pruß 2002). Slightly differing values are reported in various  
 548 textbooks on hydrology (Debski 1966: p. 332), meteorology (Linke and Baur 1970) or geophysics (Gill  
 549 1982, Kraus and Businger 1994). TEOS-10, however, permits the computation of evaporation  
 550 properties from seawater into humid air, based on the first-time availability of standard equations  
 551 for enthalpies and chemical potentials of those non-ideal mixtures.



552

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

555

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

$$562 \quad L^{SA} \equiv \left( \frac{\partial H^{SA}}{\partial m^V} \right)_{T,p,m^S,m^A,m^{WV}} \quad (17)$$

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

$$565 \quad \frac{\partial m^V}{\partial T} = - \frac{\partial m^W}{\partial T}. \quad (18)$$

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

$$567 \quad H^{SA} \equiv m^{SW}h^{SW} + m^{AV}h^{AV}. \quad (19)$$

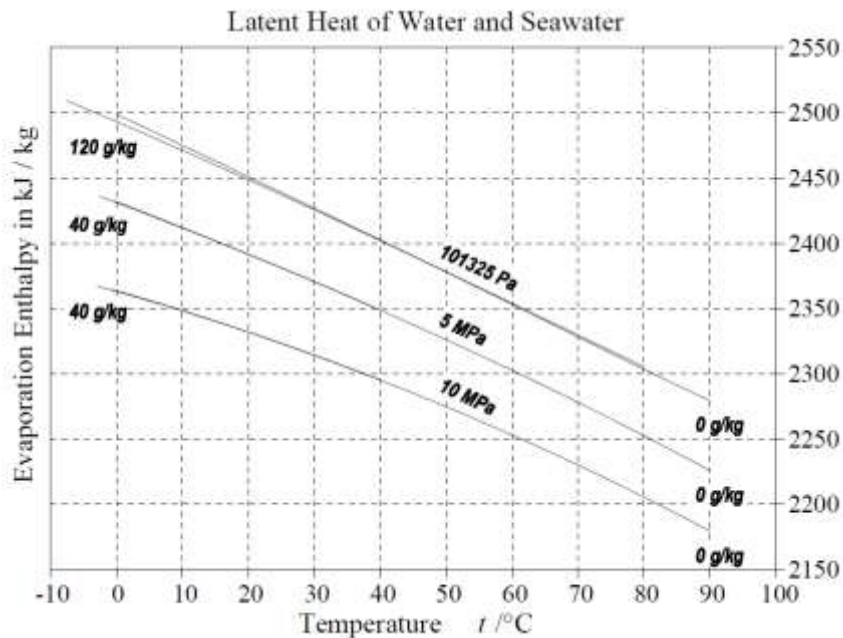
568 Here, the specific enthalpies of seawater,

$$569 \quad h^{SW} = g^{SW} - T \left( \frac{\partial g^{SW}}{\partial T} \right)_{S,p}, \quad (20)$$

570 and of humid air,

$$571 \quad h^{AV} = g^{AV} - T \left( \frac{\partial g^{AV}}{\partial T} \right)_{A,p}, \quad (21)$$

572 are defined in terms of the related Gibbs functions.



573

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



578

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

$$580 \quad L^{SA} = -h^{SW} - m^{SW} \left( \frac{\partial h^{SW}}{\partial S} \right)_{T,p} \left( \frac{\partial S}{\partial m^V} \right)_{m^S, m^{WV}} + h^{AV} + m^{AV} \left( \frac{\partial h^{AV}}{\partial A} \right)_{T,p} \left( \frac{\partial A}{\partial m^V} \right)_{m^A}, \quad (22)$$

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

$$582 \quad L^{SA} = h^{AV} - A \left( \frac{\partial h^{AV}}{\partial A} \right)_{T,p} - h^{SW} + S \left( \frac{\partial h^{SW}}{\partial S} \right)_{T,p}, \quad (23)$$

583 with typical values shown in Fig. 9. If seawater is in mutual equilibrium with humid air at given  
 584 temperature and pressure, salinity and humidity of the parts of sea air satisfy the condition  $\mu_W^{SW} =$   
 585  $\mu_V^{AV}$ , given by eqs. (15) and (16),

$$586 \quad \Delta\mu \equiv g^{SW} - S \left( \frac{\partial g^{SW}}{\partial S} \right)_{T,p} - g^{AV} + A \left( \frac{\partial g^{AV}}{\partial A} \right)_{T,p} = 0 \quad (24)$$

587 At given masses of salt,  $m^S$ , of dry air,  $m^A$ , and of total water,  $m^{WV} = m^W + m^V$ , eq. (24) controls  
 588 the value of either  $m^W$  or  $m^V$ , and this way also of  $S$  and  $A$  as functions of  $T$ ,  $p$ ,  $m^S$ ,  $m^A$  and  $m^{WV}$ .  
 589 Related numerical solutions are readily implemented in the TEOS-10 SIA library; the latent heat of  
 590 sea air can be computed by calling the function `sea_air_enthalpy_evap_si()`, see Wright et al.  
 591 (2010).

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

594

## 595 *5.2 Sea Air as a Model of Sea Spray*

596 As a special form of air-sea interaction, sea spray is typically ejected from the crest of a breaking  
 597 wave, which may happen all along oceanic coasts but also wherever whitecaps are produced from  
 598 swell or stormy sea state, see Fig. 10. In contrast to fresh-water haze, droplets of sea spray cannot  
 599 completely evaporate for the salt they contain, and rather develop into a floating persistent Köhler  
 600 (1936) equilibrium between droplet size, droplet salinity and ambient relative fugacity (Hellmuth and  
 601 Shchekin 2015, Pöhlker et al. 2023). This equilibrium can be described by the TEOS-10 model of sea  
 602 air if the additional Kelvin pressure caused by the surface tension is allowed for.

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



612

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

615

616 The terrestrial atmosphere is dominated by the two-atomic gases  $N_2$  and  $O_2$  with heat capacities  
617 about  $3.5 R$  which prevent the putative radiative vertical instability to occur. This situation may  
618 change, however, in the presence of haze or sea spray. To investigate this effect theoretically, in this  
619 section a TEOS-10 equation for the heat capacity of equilibrium sea air is derived from the definition

$$620 \quad c_p^{SA} \equiv \frac{1}{m} \left( \frac{\partial H^{SA}}{\partial T} \right)_{p, m^S, m^A, m^{WV}}. \quad (25)$$

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

$$623 \quad \frac{\partial m^V}{\partial T} = - \frac{\partial m^W}{\partial T}, \quad (26)$$

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

$$625 \quad c_p^{SA} = w^{SW} c_p^{SW} + w^{AV} c_p^{AV} + L^{SA} \frac{1}{m} \frac{\partial m^V}{\partial T}. \quad (27)$$

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

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

$$631 \quad \left( \frac{\partial \Delta \mu}{\partial T} \right)_{p, m^S, m^A, m^{WV}} = 0. \quad (28)$$

632 Carrying out the derivative, this condition reads

$$633 \quad \left( \frac{\partial g^{SW}}{\partial T} \right)_{S,p} - S \left( \frac{\partial^2 g^{SW}}{\partial S \partial T} \right)_p - S \left( \frac{\partial^2 g^{SW}}{\partial S^2} \right)_{T,p} \left( \frac{\partial S}{\partial T} \right)_{m^S}$$

$$634 \quad = \left( \frac{\partial g^{AV}}{\partial T} \right)_{A,p} - A \left( \frac{\partial^2 g^{AV}}{\partial A \partial T} \right)_p - A \left( \frac{\partial^2 g^{AV}}{\partial A^2} \right)_{T,p} \left( \frac{\partial A}{\partial T} \right)_{m^A}. \quad (29)$$

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

$$637 \quad L^{SA} = T \left\{ \left( \frac{\partial g^{SW}}{\partial T} \right)_{S,p} - S \left( \frac{\partial^2 g^{SW}}{\partial S \partial T} \right)_p - \left( \frac{\partial g^{AV}}{\partial T} \right)_{A,p} + A \left( \frac{\partial^2 g^{AV}}{\partial A \partial T} \right)_p \right\}, \quad (30)$$

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

$$639 \quad L^{SA} = T \left\{ S \left( \frac{\partial^2 g^{SW}}{\partial S^2} \right)_{T,p} \left( \frac{\partial S}{\partial T} \right)_{m^S} - A \left( \frac{\partial^2 g^{AV}}{\partial A^2} \right)_{T,p} \left( \frac{\partial A}{\partial T} \right)_{m^A} \right\}. \quad (31)$$

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

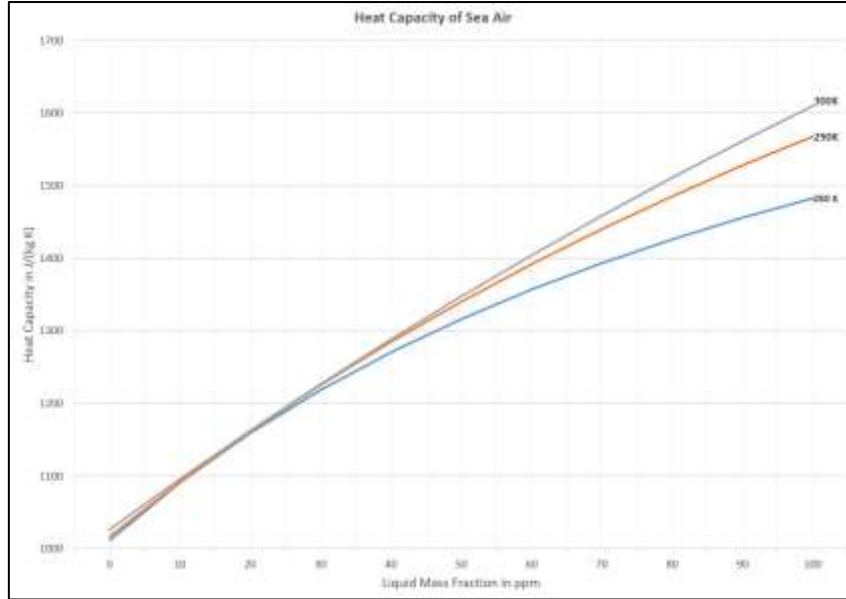
$$641 \quad \left( \frac{\partial S}{\partial T} \right)_{m^S} = \left( \frac{\partial S}{\partial m^W} \right)_{m^S} \frac{\partial m^W}{\partial T} = \frac{S}{m^{SW}} \frac{\partial m^W}{\partial T}, \quad (32)$$

642 and similarly,

$$643 \quad \left( \frac{\partial A}{\partial T} \right)_{m^A} = \left( \frac{\partial A}{\partial m^V} \right)_{m^A} \frac{\partial m^V}{\partial T} = - \frac{A}{m^{AV}} \frac{\partial m^V}{\partial T}. \quad (33)$$

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

$$645 \quad \frac{\partial m^V}{\partial T} = \frac{L^{evap}}{T} \left\{ \frac{S^2}{m^{SW}} \left( \frac{\partial^2 g^{SW}}{\partial S^2} \right)_{T,p} + \frac{A^2}{m^{AV}} \left( \frac{\partial^2 g^{AV}}{\partial A^2} \right)_{T,p} \right\}^{-1}. \quad (34)$$



646

647 Fig. 11: TEOS-10 values for the isobaric specific heat capacity, eq. (35), of sea air at atmospheric  
648 pressure and sea-spray standard-ocean salinity,  $S = 35.16504 \text{ g kg}^{-1}$ , at temperatures of 280 K (lower  
649 curve), 290 K (middle curve) and 300 K (upper curve) as functions of the liquid mass fraction,  $w^{SW}$ ,  
650 up to 100 ppm.

651

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

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

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

659

### 660 5.3 Sea Air as a Model for Irreversible Evaporation

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

By definition, if a volume at equilibrium is divided into partial volumes, each of those parts is at equilibrium itself, and each pair of those is at mutual equilibrium also. By contrast, the combination of several local-equilibrium elements forms a non-equilibrium state if pairs of elements exist that are out of mutual equilibrium. Extensive properties such as mass, energy, entropy or enthalpy can be added up to give correct values of the entire system. When exchange processes between those elements occur, gains and losses of masses, energies or enthalpies are mutually balanced by conservation laws, however, this is not the case for entropy.

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

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

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

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

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

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

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

the change is given by

$$693 \quad \frac{dN^{SA}}{dt} = \left( \frac{\partial N^{SA}}{\partial m^V} \right)_{T,p,m^S,m^A,m^{wV}} \frac{dm^V}{dt}. \quad (39)$$

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

$$695 \quad \frac{dN^{SA}}{dt} = \left[ \eta^{AV} - A \left( \frac{\partial \eta^{AV}}{\partial A} \right)_{T,p} - \eta^{SW} + S \left( \frac{\partial \eta^{SW}}{\partial S} \right)_{T,p} \right] J_m. \quad (40)$$

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

$$699 \quad \eta = \frac{h-g}{T}, \quad (41)$$

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

$$701 \quad T \frac{dN^{SA}}{dt} = (L^{SA} + \Delta\mu) J_m. \quad (42)$$

702 Here, the latent heat,  $L^{SA}$ , is given by eq. (23), and the distance from mutual equilibrium,  $\Delta\mu$ , by eq.  
703 (24).

704 The first term,

$$705 \quad T \frac{d_e N^{SA}}{dt} \equiv L^{SA} J_m, \quad (43)$$

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

709 The second term,

$$710 \quad T \frac{d_i N^{SA}}{dt} \equiv J_m \Delta\mu. \quad (44)$$

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

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

$$720 \quad \frac{dH^{SA}}{dt} = -T \frac{d_e N^{SA}}{dt} + V^{SA} \frac{dp}{dt} + \sum_i \mu_i \frac{dm_i}{dt} > -T \frac{dN^{SA}}{dt} + V^{SA} \frac{dp}{dt} + \sum_i \mu_i \frac{dm_i}{dt}, \quad (45)$$

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

$$723 \quad dh = -T d\eta + v dp + \sum_{i=1}^{n-1} (\mu_i - \mu_0) dw_i. \quad (46)$$

724 Entropy production appears wherever a flux is passing its driving gradient. Near equilibrium, this flux  
725 is proportional to its driving force (Glansdorff and Prigogine 1971, Landau and Lifschitz 1974, Kraus

726 and Businger 1994, Feistel and Hellmuth 2024a), usually termed *Onsager force*. For example, the  
 727 evaporation mass flux of water, eq. (6),

$$728 \quad J_m = C \Delta\mu \quad (47)$$

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

$$732 \quad \frac{d_i N^{SA}}{dt} = C (\Delta\mu)^2 \geq 0, \quad (48)$$

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

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

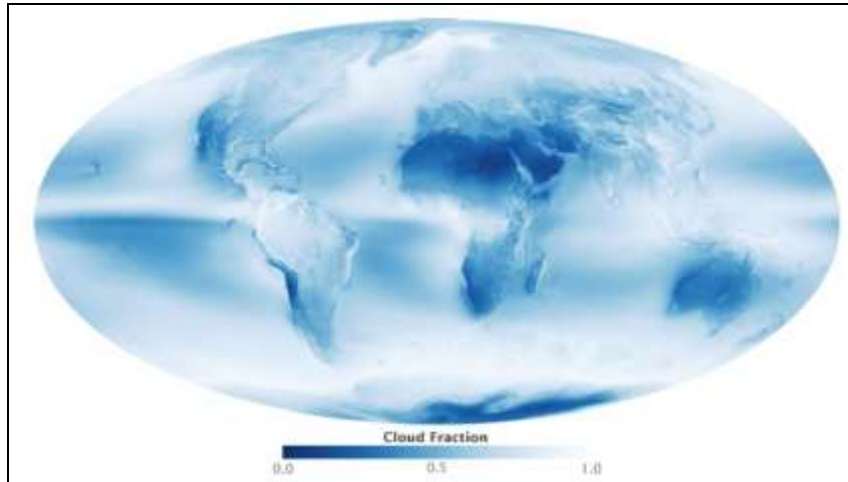
742 Under typical marine circumstances, the entropy production density of ocean evaporation can be  
 743 estimated to about 4 mW K<sup>-1</sup> m<sup>-2</sup>, contributing roughly 0.4 % to the global entropy production  
 744 (Feistel and Ebeling 2011, Feistel and Hellmuth 2024a).

745

746

## 747 **6 Cloudiness and Ocean Warming**

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



761

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

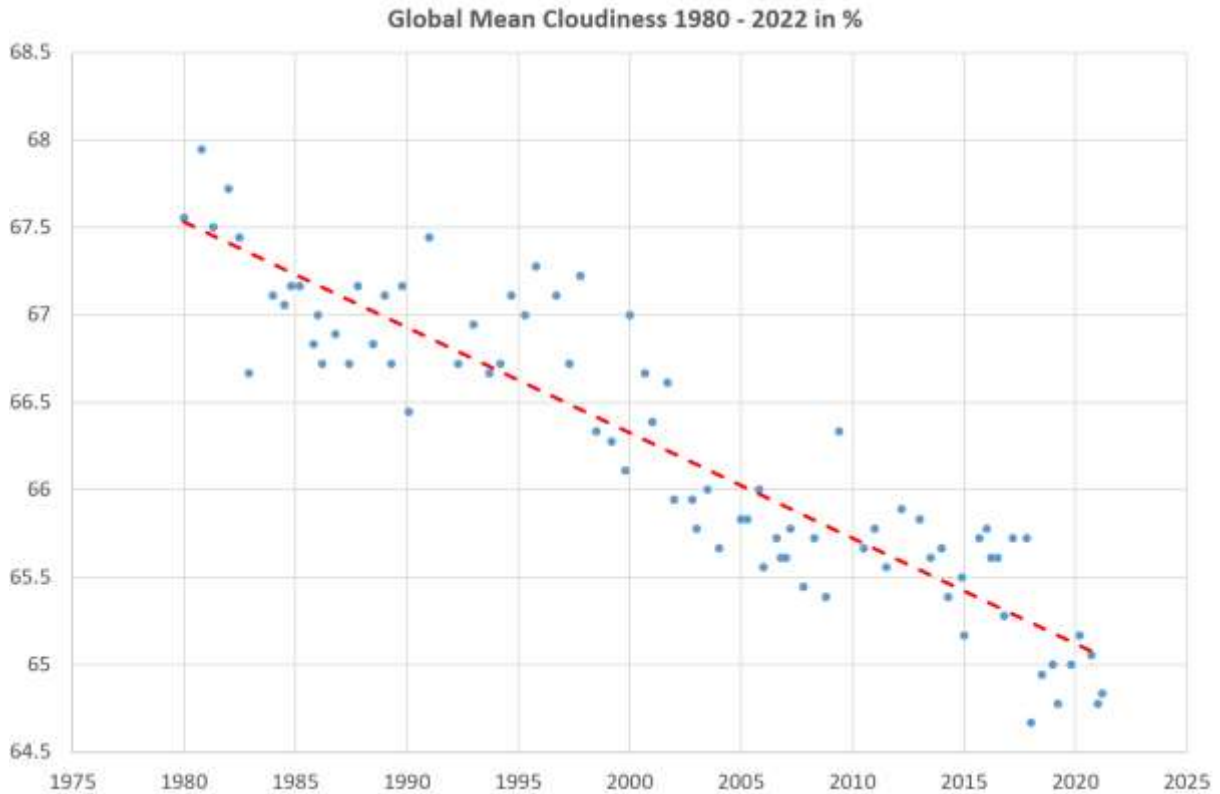
764

### 765 6.1 Cloudiness Trend

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

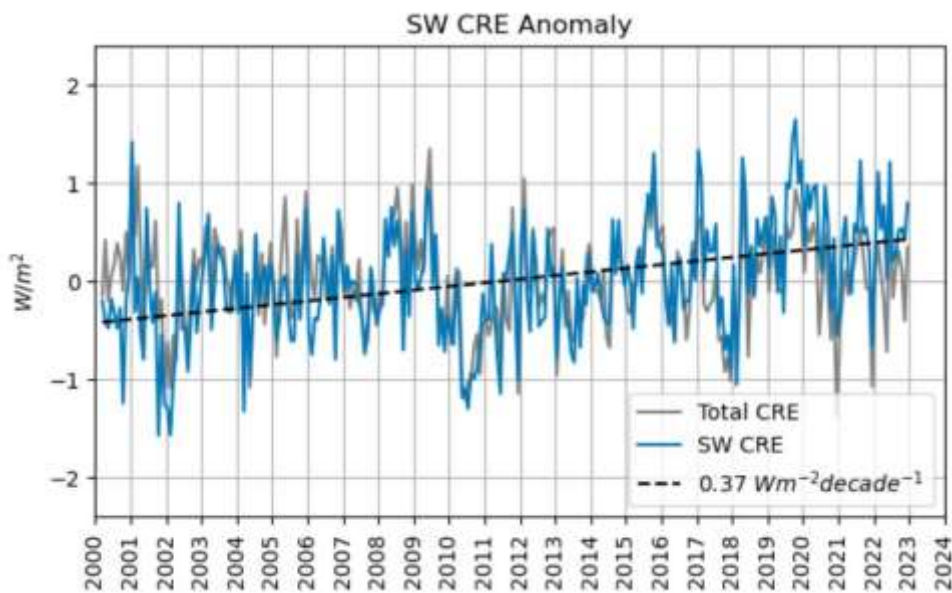
773 Assuming that this shrinking occurred in a similar way above both land and sea, the ocean is  
 774 expected to receive increasingly more solar irradiation. This phenomenon is known as the *short-wave*  
 775 *cloud radiative effect* (SW CRE), see Fig. 14.

776 On the other hand, clouds are opaque with respect to oceanic upward thermal radiation and emit  
 777 themselves downward infrared radiation. This phenomenon is known as the *long-wave cloud*  
 778 *radiative effect* (LW CRE), see Fig. 15. Radiation models show that on the global average these two  
 779 effects cancel each other almost completely up to minor residual of  $-1 \text{ mW m}^{-2} \text{ yr}^{-1}$ , so that the  
 780 continuously shrinking cloudiness may be assumed to have practically no net effect on the ocean's  
 781 radiation balance (Phillips and Foster 2023, Feistel and Hellmuth 2024b). However, more detailed  
 782 investigations in the future may reveal more rigorous results for the ocean than this simplified  
 783 picture.



784

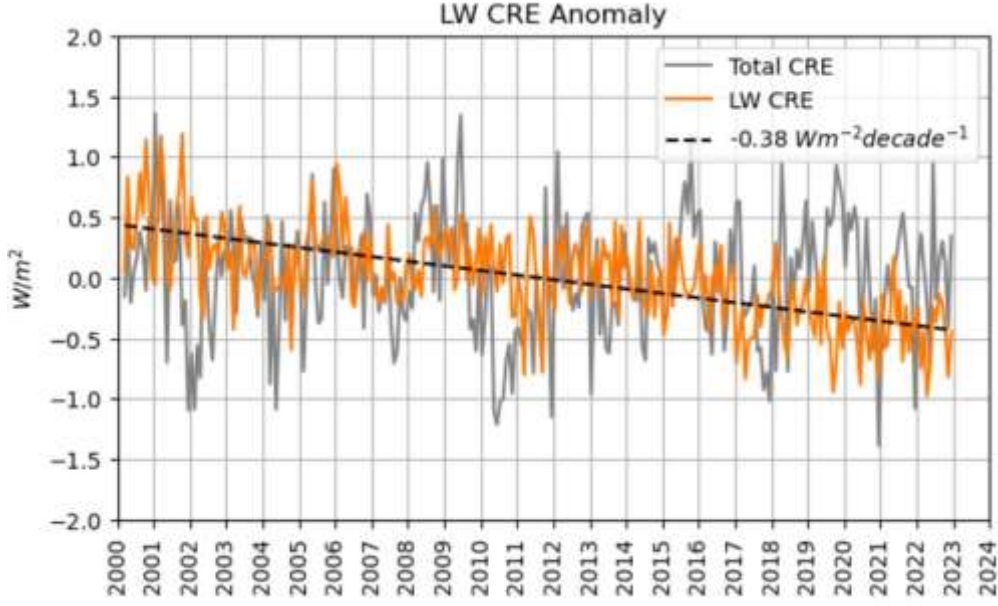
785 Fig. 13: Dots: satellite-derived global mean cloud area fractions 1980-2022 in percent. Data from  
 786 Foster et al. (2023). Dashed line: present cloudiness is 65 % with a climatological linear shrinking  
 787 trend of  $-6.2\%$  per century.



788

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





792

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

796

797

## 6.2 Cumulus Clouds

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

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

$$808 \quad R_W T_{SS} \ln \psi_f = \mu_V^{AV}(A, T_{SS}, p_{SS}) - \mu_W(T_{SS}, p_{SS}). \quad (49)$$

809 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  
 810 mass fraction of the parcel, to be determined from  $\psi_f$  by this condition.

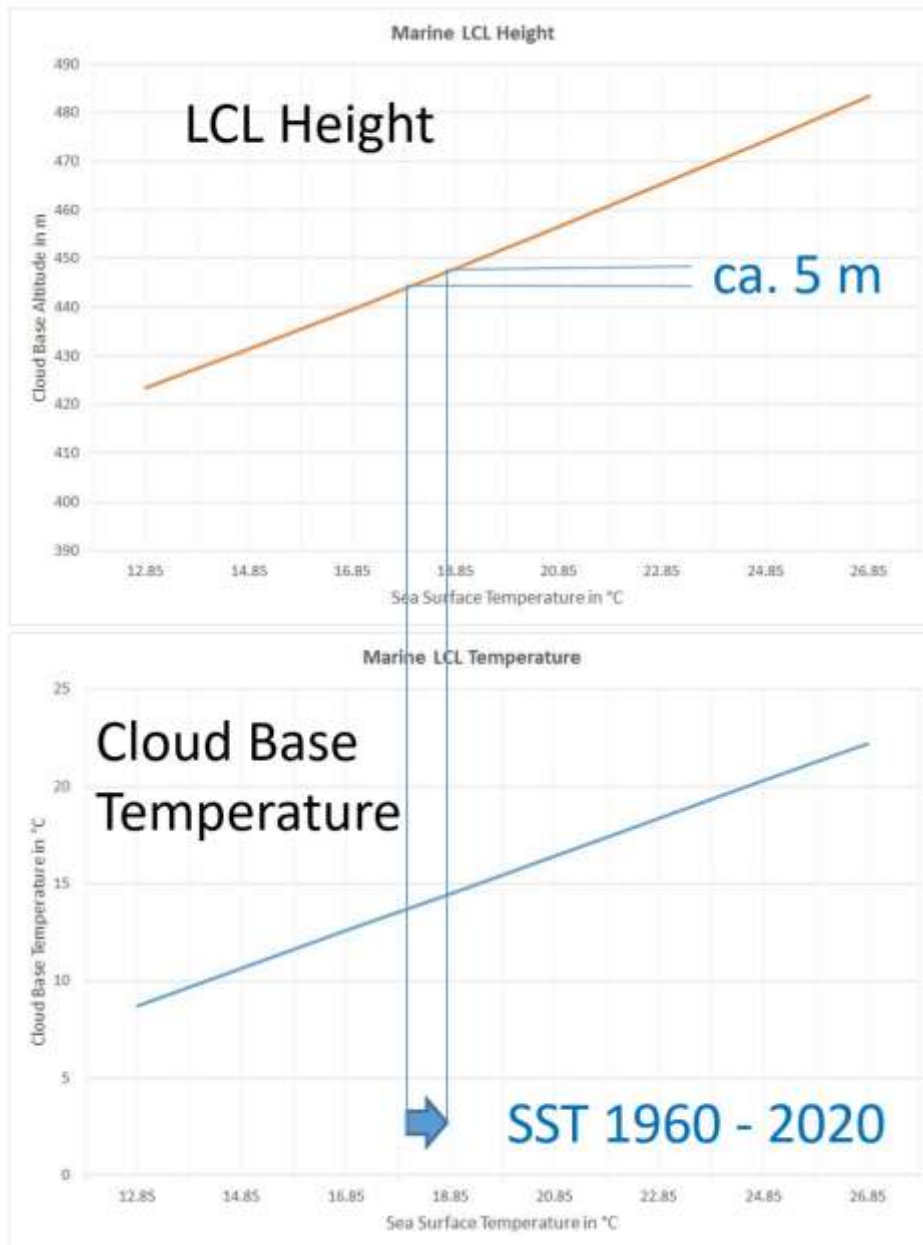
811 At the LCL, the parcel is saturated at  $\psi_f = 1$ , i.e.,

$$812 \quad 0 = \mu_V^{AV}(A, T_{LCL}, p_{LCL}) - \mu_W(T_{LCL}, p_{LCL}). \quad (50)$$

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

$$814 \quad \eta^{AV}(A, T_{SS}, p_{SS}) = \eta^{AV}(A, T_{LCL}, p_{LCL}). \quad (51)$$

815

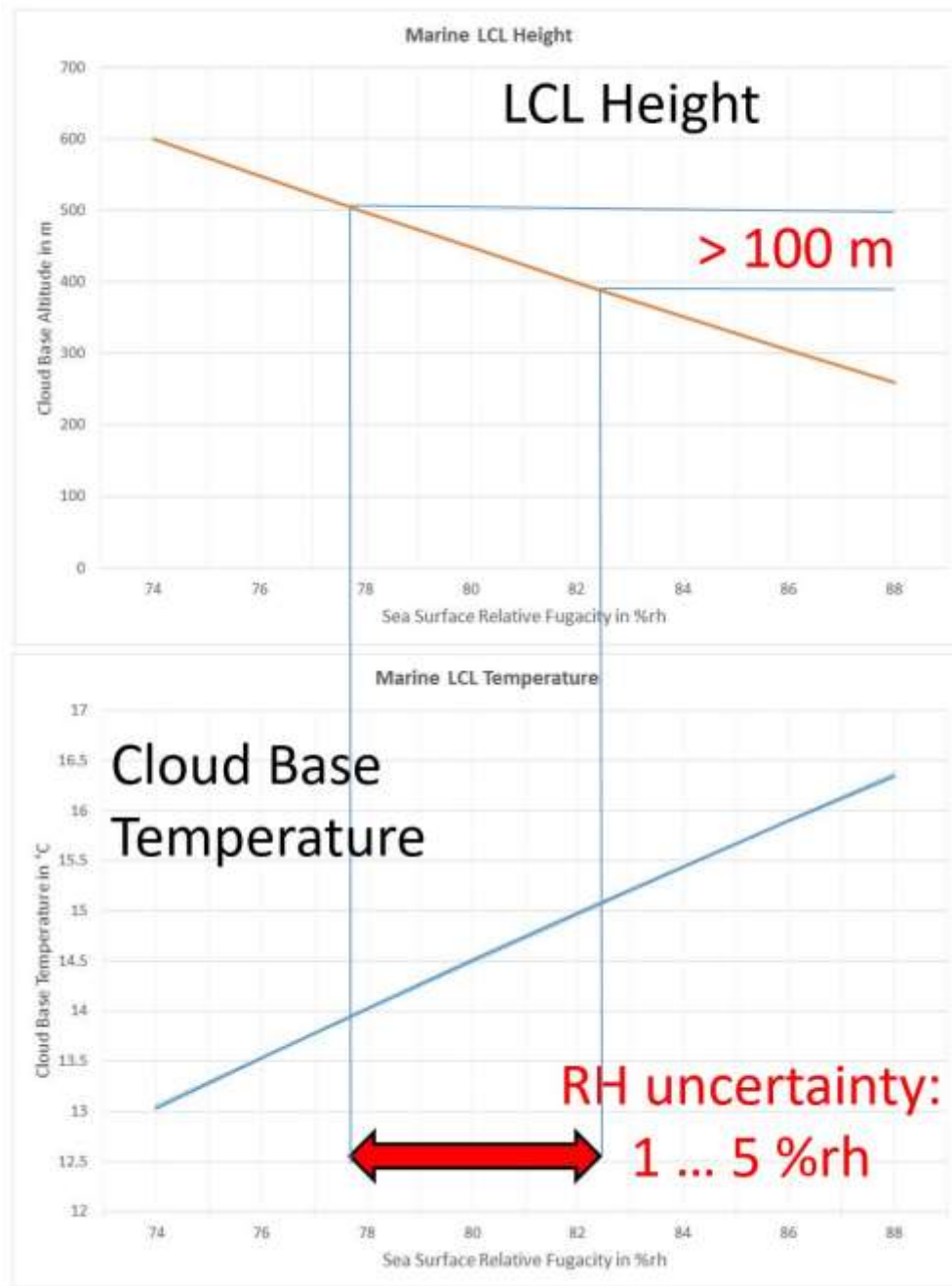


816

817 Fig. 16: As a function of typical low-latitude sea-surface temperatures, LCL height (top) and LCL  
 818 temperature (bottom) are computed from the TEOS-10 equations (49) – (52) at a typical marine  
 819 surface RH of 80 %rh. The added interval indicates the global mean SST change between 1960 and  
 820 2020 which has resulted in an increase of the cloud base altitude by about 5 m.

821

822



823

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

829

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

$$832 \quad z_{LCL} = \frac{1}{g_E} [h^{AV}(A, \eta^{AV}, p_{SS}) - h^{AV}(A, \eta^{AV}, p_{LCL})]. \quad (52)$$

833 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  
 834 by partial derivatives of the TEOS-10 thermodynamic potentials of humid air and liquid water, and

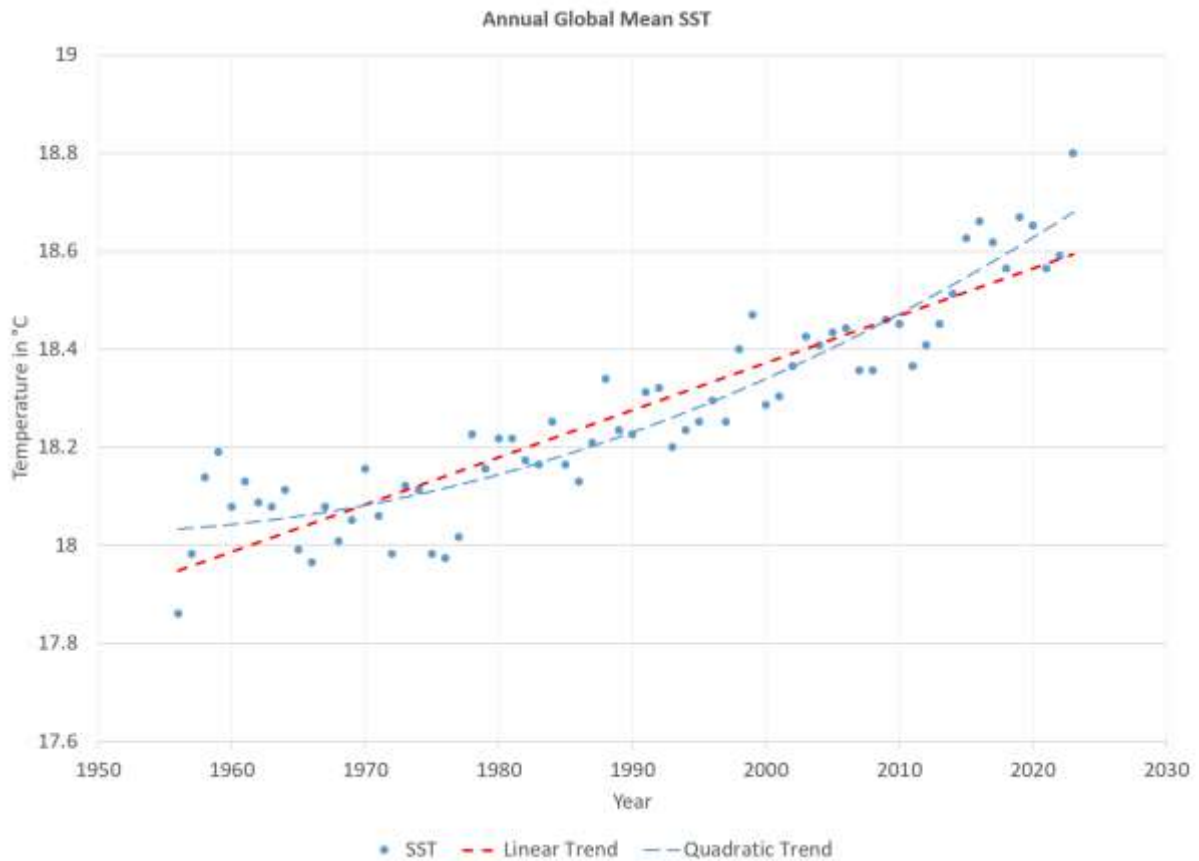
835 are numerically available from the *Sea-Ice-Air (SIA) library* (Feistel et al. 2010d, Wright et al. 2010).  
 836 Solving eqs. (49) – (52) numerically, the LCL properties ( $A, T_{LCL}, p_{LCL}, z_{LCL}$ ) are obtained from the  
 837 given surface properties, ( $\psi_f, T_{SS}, p_{SS}$ ).

838 Table 1: LCL cloud-base temperatures,  $T_{LCL}$ , pressures,  $p_{LCL}$ , and heights,  $z_{LCL}$ , as functions of the  
 839 SST,  $T_{SS}$ , at marine surface relative fugacity of  $\psi_f = 80$  %rh, computed from TEOS-10 eqs. (49) –  
 840 (52), as well as climatic LCL sensitivities,  $\alpha, \beta, \gamma$ , eq. (53), with respect to increasing SST (Feistel and  
 841 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

842

843



844

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

848

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

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

$$861 \quad \alpha \equiv \left( \frac{\partial A}{\partial T_{SS}} \right)_{p_{SS}, \psi_f} = - \left( \frac{\partial q}{\partial T_{SS}} \right)_{p_{SS}, \psi_f}, \quad \beta \equiv \left( \frac{\partial T_{LCL}}{\partial T_{SS}} \right)_{p_{SS}, \psi_f} \quad \text{and} \quad \gamma \equiv \left( \frac{\partial p_{LCL}}{\partial T_{SS}} \right)_{p_{SS}, \psi_f}, \quad (53)$$

862 of the TEOS-10 LCL equations (49) – (52) with respect to the surface temperature while keeping  
 863 surface RH fixed (Feistel and Hellmuth 2024). Selected results for those sensitivities are given in Table  
 864 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>  
 865 describes the rate of increase of specific humidity at the sea surface, often dubbed the “Clausius-  
 866 Clapeyron effect”. The value of  $\beta \approx 0.96$  indicates that the cumulus cloud base warms up slower  
 867 than the ocean by about 4 %, and  $\gamma \approx -0.28$  hPa K<sup>-1</sup> is the LCL pressure lowering caused by ocean  
 868 warming, corresponding to ascending clouds. The value  $\beta < 1$  implies that the thermal downward  
 869 radiation from the cloud base does not keep pace with the ocean upward radiation, so that the net  
 870 climatic feedback of cumulus clouds is negative and acts against ocean warming. These clouds do not  
 871 provide a physical explanation for the observed enhanced ocean warming.

872

### 873 *6.3 Stratocumulus and Other Clouds*

874 “Marine low clouds strongly cool the planet” (Myers et al. 2021). Over the Atlantic, “the strongest  
 875 surface longwave cloud effects were shown in the presence of low level clouds” (Kalisch and Macke  
 876 2012). “Low-cloud feedbacks are also a leading cause of uncertainty in future climate prediction  
 877 because even small changes in cloud coverage and thickness have a major impact on the radiation  
 878 budget” (Wood 2012: p. 2373).

879 Generally, however, the dominating cloud type over the ocean is stratocumulus (Eastman et al.  
 880 2011). “They are common over the cooler regions of subtropical and midlatitude oceans where their  
 881 coverage can exceed 50% in the annual mean” (Wood 2012: p. 2373) with a typical thickness about  
 882 320 m and “a tendency for thicker clouds (median 420 m) in mid- and high latitudes” (Wood 2012: p.  
 883 2378). “Stratocumuli tend to form under statically stable lower-tropospheric conditions” (Wood  
 884 2012: p. 2374). On the annual average, stratocumulus is particularly frequent (up to 60 % coverage)  
 885 at the subtropical coastal upwelling regions such as the cold Benguela, Humboldt and California  
 886 Currents (Wood 2012: Fig. 4a, Muhlbauer et al. 2014: Fig. 2). However, in those areas there is no  
 887 obvious correlation of cloud cover with ocean warming (Fig. 1). Stratocumulus also forms large cloud  
 888 cover (about 20 % coverage) in the boreal and austral west-wind bands (Wood 2012: Fig. 4a) where  
 889 the ocean is strongly warming up (Fig. 1).

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

892 2374). Marine stratocumulus cloud feedback is still a major challenge and source of uncertainty of  
 893 climate models (Hirota et al. 2021). However, “similar to other low-cloud types in the marine  
 894 boundary layer, the impact of stratocumulus clouds on the outgoing longwave radiation is marginal  
 895 due to the lack of contrast between the temperature of stratocumulus cloud tops and the  
 896 temperature of the sea surface over which they form. Thus, the net radiative effect of stratocumulus  
 897 clouds is primarily controlled by factors influencing their shortwave cloud forcing such as the cloud  
 898 albedo and the cloud coverage” (Muhlbauer et al. 2014: p. 6695).

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

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

915

## 916 **7 Summary**

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

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

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

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

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

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

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

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

962

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

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

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

970 **Table A1:** Metrics of articles in the *Ocean Science* Special Issue #14, “Thermophysical properties of  
 971 seawater” (Feistel et al. 2008a), from February 2013 till March 2024. “SIA” stands for the TEOS-10  
 972 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

973

974 **Table A2:** Metrics published by March 2024 of selected TEOS-10 related articles apart from *Ocean*  
975 *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			

976

977 **Table A3:** IAPWS documents supporting TEOS-10, openly accessible at [www.iapws.org](http://www.iapws.org). IAPWS  
978 documents are independently and painstakingly verified before they may become adopted at an  
979 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

980

981 **Table A4:** Numbers of unique internet downloads 2011-2023 of supporting material from the TEOS-  
982 10 homepage at [www.teos-10.org](http://www.teos-10.org). "GSW" stands for the TEOS-10 Gibbs Seawater open source code  
983 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

984

985 **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
Ji et al. (2021)	Absolute Salinity off China	2 462	856	3
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	
Ji et al. (2024)	Bohai Sea Salinity Anomaly	254	56	
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
Pawlowicz & Yerubandi (2024)	Water as a Substance	4		0

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			

986

987 **Appendix B: Thermodynamic Potentials**

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

993 A key theoretical tool for the physical investigation of the globally warming climate and the related  
 994 energy balances is *thermodynamics*. It is known from experience that there exists a distinguished  
 995 state of various ambient substances that is known as a *thermodynamic equilibrium state*. If a sample  
 996 of matter is in this state, it may never spontaneously alter its measurable macroscopic properties  
 997 unless it becomes disturbed by external contact and exchange of energy or matter with its  
 998 surrounding. Typical properties which characterise a particular equilibrium state are the total mass of  
 999 a sample,  $m$ , its volume,  $V$ , its temperature,  $T$ , or its pressure,  $p$ . Of a given sample, different  
 1000 equilibrium states may exist that differ in those quantities, but there exists a specific relation  
 1001 between those variables, known as an *equation of state*, which is characteristic for the given  
 1002 substance and remains universally valid at any of its possible equilibrium states. The most general  
 1003 and comprehensive equation of state of a given substance is a *thermodynamic potential* of that  
 1004 substance.

1005 Thermodynamics is a mathematical theory for the construction and exploitation of equations of state  
 1006 and of properties derived therefrom for the prediction or verification of observations or experiments.  
 1007 Depending on the properties of interest, equations of state may be formulated in various different  
 1008 mathematical forms. It was discovered by J. Willard Gibbs (1873) that from a suitable thermodynamic  
 1009 potential all thermodynamic properties of a given substance at any of its equilibrium states can be  
 1010 derived by appropriate mathematical methods.

1011 For theoretical reasons (namely, the statistical so-called *canonical ensemble*, Landau and Lifschitz  
 1012 1966: §31; Kittel 1969: Ch. 18), a preferred thermodynamic potential of a pure substance is its  
 1013 *Helmholtz Energy*, or *Free Energy*,  $F(m, T, V)$ , expressed in terms of the sample's mass,  $m$ , its  
 1014 temperature and volume. For mixtures, the single mass must be replaced by the set of partial masses  
 1015 of the species involved. Here, mass is used as a measure for the amount of substance, rather than  
 1016 particle or mole numbers, for the practical reason that in oceanography masses are easier measured  
 1017 than moles, and so TEOS-10 is following that tradition and is a mass-based description. Classical  
 1018 empirical thermodynamics of Clausius and Gibbs was formulated independently of the existence and  
 1019 properties of atoms or molecules which presently define the mole (BIPM 2019).

1020 To the *Internal Energy*  $E$  of the sample, the Helmholtz energy is related by the Helmholtz Differential  
 1021 Equation,

$$1022 \quad E = F - T \left( \frac{\partial F}{\partial T} \right)_{m,V} \quad (\text{B.1})$$

1023 Note that IOC et al. (2010) uses the symbol  $U$  for the Internal Energy rather than  $E$  in eq. (B.1). This  
 1024 replacement is done here for denoting with  $u$  the wind speed, eq. (6), rather than specific internal  
 1025 energy, which is defined here by  $e = E/m$ , eqs. (1) and (B.3). The symbol  $E$  is frequently used in the  
 1026 thermodynamic literature, for example by Gibbs (1873a) and Landau and Lifschitz (1966).

1027 The potential function  $F$  is extensive, which means that for instance  $F(2m, T, 2V) = 2F(m, T, V)$  is  
 1028 valid for an equilibrium sample of twice the mass. It follows that the mass-specific Helmholtz  
 1029 function,  $F/m \equiv f(T, \rho)$ , depends on two variables only,  $T$  and the mass density,  $\rho \equiv m/V$ , and is  
 1030 mathematically simpler and more convenient than  $F$ , which may always be retrieved from a given  $f$   
 1031 by

$$1032 \quad F(m, T, V) = m \times f\left(T, \frac{m}{V}\right). \quad (\text{B.2})$$

1033 The quantitative description of a substance of interest in the form of a thermodynamic potential such  
 1034 as  $f(T, \rho)$  has axiomatic properties. The description is *complete*, i.e., all thermodynamic properties of  
 1035 that substance are available, it is *consistent*, i.e., for any property one and only one result can be  
 1036 derived, and it is *independent*, i.e., no part of this description may be omitted without losing the  
 1037 completeness. It is obvious that such axiomatic properties are very desirable for the description of  
 1038 geophysical substances, however, such thermodynamic potentials are rarely found in the  
 1039 corresponding literature. In particular in climate research which combines results and data from  
 1040 different disciplines, such as meteorology and oceanography, from research carried out all over the  
 1041 globe and over the years by subsequent generations of specialists, international binding standards  
 1042 such as the International System of Units (SI) are required that ensure mutual consistency and  
 1043 metrological comparability of any involved data produced from experiments, observations and  
 1044 models.

1045 Gibbs' (1873a) original potential function was (internal) energy,  $e = E/m$ . It is known that a sample's  
 1046 energy can be increased by compression,  $-pdv$ , where  $v = 1/\rho$  is the specific volume, or by input of  
 1047 heat,  $Td\eta$ , where  $\eta = N/m$  is the specific entropy. As an extensive quantity, entropy introduced by  
 1048 Clausius (1865, 1976) is denoted here by  $N$  to avoid confusion with seawater salinity,  $S$ . Energy  
 1049 conservation implies that

$$1050 \quad de = Td\eta - pdv. \quad (\text{B.3})$$

1051 Any such change between different equilibrium states of the same sample takes place along a  
 1052 definite, substance-specific surface  $e(\eta, v)$  so that  $de$  in eq. (B.3) is mathematically an exact  
 1053 differential and the partial derivatives of  $e$  possess the physical meanings that

$$1054 \quad T = \left(\frac{\partial e}{\partial \eta}\right)_v, \quad -p = \left(\frac{\partial e}{\partial v}\right)_\eta. \quad (\text{B.4})$$

1055 Gibbs (1873b) also demonstrated that for several equilibrium samples in contact with one another, in  
 1056 absence of gravity or accelerated motion, the samples are in mutual equilibrium only if they have  
 1057 equal values of the coefficients  $T$  and  $p$  of eq. (2.3).

1058 In the geophysical practice, the quantities  $\eta$  and  $v$  are difficult to measure, in contrast to, say,  $T$  or  $p$ .  
 1059 Mathematically equivalent to  $e(\eta, v)$ , thermodynamic potentials in terms of the other three possible  
 1060 pairs of independent variables are formally obtained from so-called Legendre transforms (Alberty  
 1061 2001), namely the *Helmholtz function*  $f(T, v) \equiv e - T\eta$  with the differential

$$1062 \quad df = -\eta dT - pdv, \quad (\text{B.5})$$

1063 the *Gibbs function*  $g(T, p) \equiv f + pv = e - T\eta + pv$  with

1064  $dg = -\eta dT + v dp,$  (B.6)

1065 and the specific *enthalpy*  $h(\eta, p) \equiv g + T\eta = f + T\eta + pv = e + pv$  with

1066  $dh = T d\eta + v dp.$  (B.7)

1067 Depending on the application purpose, each of these potential functions has certain advantages and  
1068 disadvantages, and having all of them optionally at hand in mutually consistent versions is most  
1069 useful.

1070 Gibbs (1874-78) also considered a situation in which a given sample may exchange substance with its  
1071 surrounding. If the exchanged mass of substance  $i$  is  $dm_i$ , the related change of the sample's  
1072 (extensive) energy  $E$  at constant entropy and volume is termed the *chemical potential*  $\mu_i$  of that  
1073 substance,

1074  $dE = T dN - p dV + \sum_i \mu_i dm_i,$  (B.8)

1075 so that this exact differential implies that the chemical potential is obtained from

1076  $\mu_i \equiv \left(\frac{\partial E}{\partial m_i}\right)_{N,V,m_{j \neq i}} = \left(\frac{\partial F}{\partial m_i}\right)_{T,V,m_{j \neq i}} = \left(\frac{\partial G}{\partial m_i}\right)_{T,p,m_{j \neq i}} = \left(\frac{\partial H}{\partial m_i}\right)_{N,p,m_{j \neq i}}.$  (B.9)

1077 Equilibrium of a spatially extended substance, in absence of gravity or accelerated motion, requires  
1078 that in addition to  $T$  and  $p$ , also the chemical potential  $\mu_i$  separately for each present substance  
1079 needs to possess the same value anywhere in the volume. "The potential for each component  
1080 substance must be constant throughout the whole mass" (Gibbs 1874-78: p. 119).

1081 As intensive properties, the specific energies cannot depend on the total mass but only on the mass  
1082 fractions,  $w_i \equiv m_i/m$ . Because by definition  $\sum w_i = 1$ , only  $(n - 1)$  different fractions may be  
1083 independent variables describing the  $n$  components of a mixture. For example, one of the  
1084 components may be chosen as a master species, "0", such as a solvent, and the remaining ones,  $i =$   
1085  $1, \dots, n - 1$ , may denote the solutes.

1086 In terms of  $T$  and  $p$ , chemical potentials are computed from the Gibbs function,  $g$ , through the Gibbs  
1087 energy,  $G$ , of eq. (B.9). Because the Gibbs function depends only on the independent intensive  
1088 variables,  $g(w_1, \dots, w_{n-1}, T, p)$ , the solutes' chemical potentials,  $i > 0$ , are

1089  $\mu_i = \left(\frac{\partial G}{\partial m_i}\right)_{T,p,m_{j \neq i}} = \left(\frac{\partial(mg)}{\partial m_i}\right)_{T,p,m_{j \neq i}} = g + \left(\frac{\partial g}{\partial w_i}\right)_{T,p,w_{j \neq i}} - \sum_{j=1}^{n-1} w_j \left(\frac{\partial g}{\partial w_j}\right)_{T,p,w_{k \neq j}}$  (B.10)

1090 Similarly, the solvent's chemical potential is

1091  $\mu_0 = \left(\frac{\partial G}{\partial m_0}\right)_{T,p,m_{j>0}} = \left(\frac{\partial(mg)}{\partial m_0}\right)_{T,p,m_{j>0}} = g - \sum_{j=1}^{n-1} w_j \left(\frac{\partial g}{\partial w_j}\right)_{T,p,w_{k \neq j}}.$  (B.11)

1092 Therefore, the *relative chemical potentials* of the solutes are simply the partial derivatives,

1093  $\mu_i - \mu_0 = \left(\frac{\partial g}{\partial w_i}\right)_{T,p,w_{j \neq i}}.$  (B.12)

1094 For mixtures,  $n > 1$ , the differential (B.6) of the Gibbs function takes the more general form

1095  $dg = -\eta dT + v dp + \sum_{i=1}^{n-1} (\mu_i - \mu_0) dw_i.$  (B.13)

1096 It follows straightforwardly from (B.10), (B.11) that the sum,

1097  $\sum_{i=0}^{n-1} \mu_i m_i = m g = G,$  (B.14)

1098 equals the Gibbs energy itself (Gibbs 1874-78: eq. (96) therein, Guggenheim 1949, Landau and  
 1099 Lifschitz 1966, Kittel 1969). In particular, if  $n = 1$ , the Gibbs function  $g$  of a pure substance  
 1100 represents its chemical potential,

$$1101 \quad g = \mu. \quad (B.15)$$

1102 Where two phases of a pure substance are in contact at mutual equilibrium, such as saturated water  
 1103 vapour at the liquid water surface, the mathematically distinct Gibbs functions of those phases take  
 1104 equal values. This indispensable condition for mutual consistency between the thermodynamic  
 1105 potentials of TEOS-10 is rigorously obeyed by virtue of appropriate reference-state conditions (Feistel  
 1106 et al. 2008b).

1107 *Code/Data availability.* TEOS-10 library code used for this paper is available from [www.teos-10.org](http://www.teos-10.org)

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