

The International Thermodynamic Equation of Seawater – 2010

Introductory lecture slides



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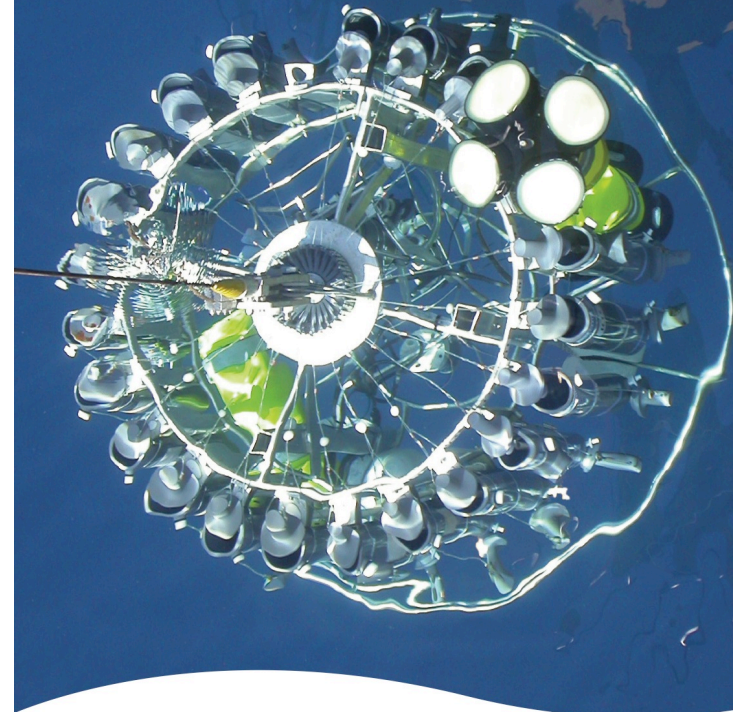
Never Stand Still

Science

Ocean Physics, School of Mathematics and Statistics

The international thermodynamic equation of seawater – 2010:

Calculation and use of thermodynamic properties



These slides provide a short summary of the use of TEOS-10 in oceanography

The official guide to TEOS-10 is IOC *et al.* (2010); the front cover is shown.

The www.TEOS-10.org web site serves the computer software, including algorithms to evaluate all the thermodynamic properties of ice and moist air.



Background to TEOS-10

- The 1980 International Equation of State (EOS-80) has served the community very well for 30 years.
- EOS-80 provides separate algorithms for density, sound speed, heat capacity and freezing temperature.
- However, EOS-80 *does not* provide expressions for entropy, internal energy and most importantly **enthalpy**.
- All such thermodynamic properties are best derived from a single Gibbs function so that the properties are totally consistent with each other.
- The TEOS-10 (**T**hermodynamic **E**quation **O**f **S**eawater – 2010) Gibbs function incorporates the most recent laboratory data, making the algorithms more accurate, e. g.
 - the properties of pure water are more accurate than in EOS-80,
 - the temperature scale has been updated from IPTS-68 to ITS-90.
 - the density of very cold brackish water is significantly improved.



Features of the new International Thermodynamic Equation of Seawater – 2010

- SCOR/IAPSO Working Group 127 settled on a definition of the Reference Composition of seawater. This was a necessary first step in order to define the Gibbs function at very low salinities. This Reference Composition, consisting of the major components of Standard Seawater, was determined from earlier analytical measurements.
- The definition of the Reference Composition enabled the calculation of the Absolute Salinity of seawater that has this Reference Composition (making use of modern atomic weights).
- The properties of seawater have been defined up to higher temperatures (80°C; useful for desalination plant design) and to higher Absolute Salinities (120 g kg⁻¹; useful for special places such as Shark Bay, Western Australia).



Chemical Composition of Standard Seawater – the Reference Composition

Using the available information and 2005 atomic weight estimates, mole fractions of standard seawater can be determined.

The Na^+ contribution is determined by the requirement to achieve exact charge balance.

The resulting “**Reference Composition**” is shown to the right.

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

Solute	Mole fraction	Mass fraction
Na^+	.4188071	.3065958
Mg^{2+}	.0471678	.0365055
Ca^{2+}	.0091823	.0117186
K^+	.0091159	.0113495
Sr^{2+}	.0000810	.0002260
Cl^-	.4874839	.5503396
SO_4^{2-}	.0252152	.0771319
HCO_3^-	.0015340	.0029805
Br^-	.0007520	.0019130
CO_3^{2-}	.0002134	.0004078
B(OH)_4^-	.0000900	.0002259
F^-	.0000610	.0000369
OH^-	.0000071	.0000038
B(OH)_3	.0002807	.0005527
CO_2	.0000086	.0000121
Sum	1.0000000	1.0000000

Reference Salinity as a stepping stone to Absolute Salinity

- Practical Salinity is calculated from the conductivity of seawater, and is not the mass fraction of salt in seawater.
- The thermodynamic properties of seawater are more closely dependent on the mass fraction (Absolute Salinity S_A) of dissolved material, not the conductivity or Practical Salinity S_P .
- In particular, the density of seawater is a function of S_A not of S_P . Hence we need to use Absolute Salinity in order to accurately determine the horizontal density gradients (for use in the “thermal wind” equation).
- The horizontal density gradient is used via the “thermal wind” equation to deduce the mean ocean circulation.
- Hence an accurate evaluation of the ocean’s role in heat transport and in climate change requires the use of Absolute Salinity.



Reference Salinity as a stepping stone to Absolute Salinity

- Reference Salinity S_R is defined to provide the best available estimate of the Absolute Salinity S_A of both
 - (i) seawater of Reference Composition,
 - (ii) Standard Seawater (North Atlantic surface seawater).
- S_R can be related to Practical Salinity S_P (which is based on conductivity ratio) by
$$S_R = (35.165\ 04/35) \text{ g kg}^{-1} \times S_P.$$
- The difference between the new and old salinities of $\sim 0.165\ 04 \text{ g kg}^{-1}$ ($\sim 0.47\%$) is about 80 times as large as the accuracy with which we can measure S_P at sea.



How is the TEOS-10 Gibbs Function used?

From a Gibbs function, all of the thermodynamic properties of seawater can be determined by simple differentiation and algebraic manipulation.

Formulas for properties of seawater and ice expressed in terms of the Gibbs functions $g(S_A, T, p)$ for seawater and $g(T, p)$ for ice.

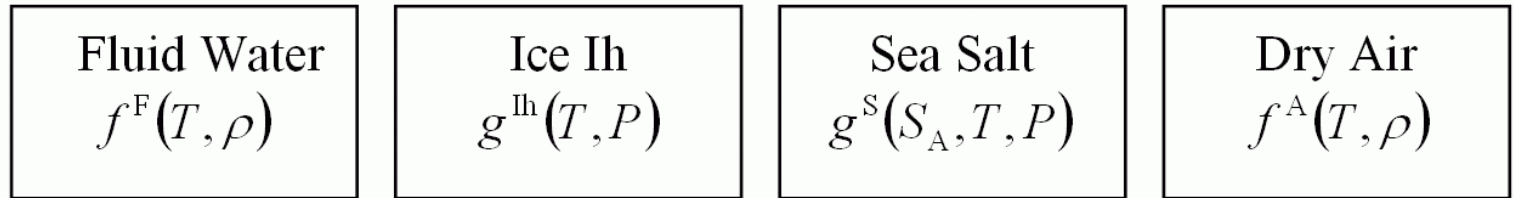
Property	Symbol	Expression in $g(S, T, p)$ of seawater	Expression in $g(T, p)$ of ice
specific Gibbs energy	g	g	g
specific enthalpy	h	$g - T g_T$	$g - T g_T$
specific Helmholtz energy	f	$g - p g_p$	$g - p g_p$
specific internal energy	u	$g - T g_T - p g_p$	$g - T g_T - p g_p$
Specific entropy	s	$-g_T$	$-g_T$
pressure	p	p	p
density	ρ	$1 / g_p$	$1 / g_p$
specific isobaric heat capacity	c_p	$-T g_{TT}$	$-T g_{TT}$
thermal expansion	α	g_{Tp} / g_p	g_{Tp} / g_p
isothermal compressibility	κ_T	$-g_{pp} / g_p$	$-g_{pp} / g_p$
isentropic compressibility	κ_s	$(g_{ip}^2 - g_{ii} g_{pp}) / (g_p g_{ii})$	$(g_{ip}^2 - g_{ii} g_{pp}) / (g_p g_{ii})$
Sound speed	w	$g_p \sqrt{g_{ii} / (g_{ip}^2 - g_{ii} g_{pp})}$	—
chemical potential of water	μ_w	$g - S_A g_S$	g
pressure coefficient for ice	β	—	$-g_{Tp} / g_{pp}$

Modular nature of TEOS-10

Pure-Water Phases

Additives: Natural Mixtures

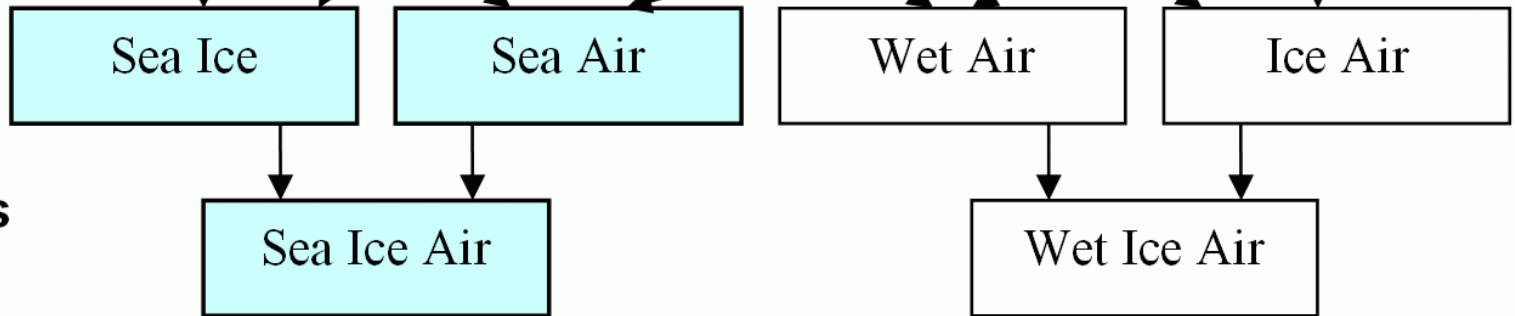
Primary
Standard
(IAPWS)



Single-
Phase
Mixtures



Phase
Equilibria,
Composites



Absolute Salinity Anomaly

- Practical Salinity S_p reflects the conductivity of seawater whereas the thermodynamic properties are more accurately expressed in terms of the concentrations of all the components of sea salt. For example, non-ionic species contribute to density but not to conductivity.
- The Gibbs function is expressed in terms of the Absolute Salinity S_A (mass fraction of dissolved material) rather than the Practical Salinity S_p of seawater.
- $$S_A = (35.165\ 04/35) \text{ g kg}^{-1} \times S_p + \delta S_A(x, y, p)$$

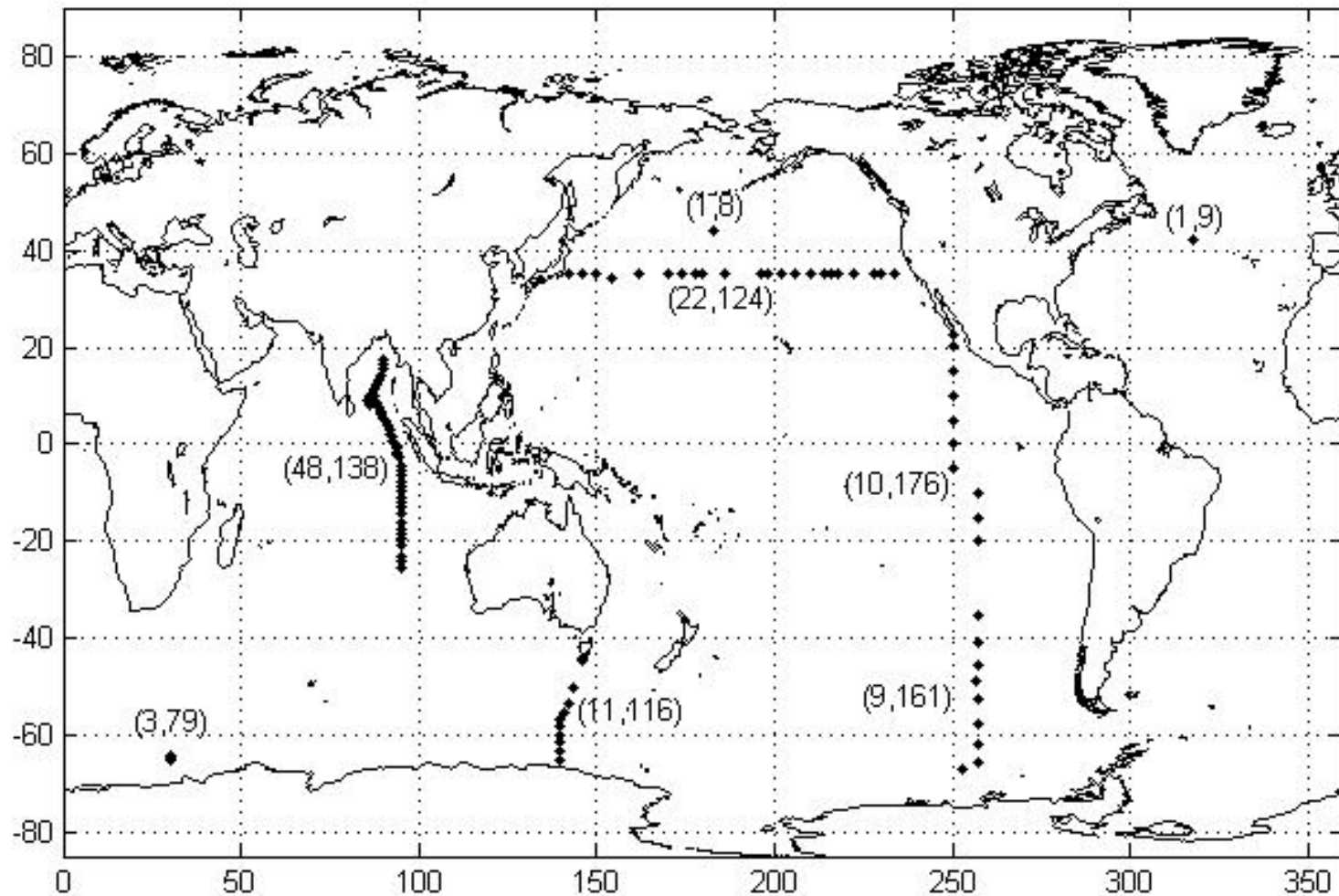


How can we calculate δS_A ?

- The Absolute Salinity Anomaly δS_A is determined by accurately measuring the density of a seawater sample in the laboratory using a vibrating beam densimeter.
- This density is compared to the density calculated from the sample's Practical Salinity to give an estimate of δS_A
- We have done this to date on 811 seawater samples from around the global ocean.
- We exploit a correlation between δS_A and the silicate concentration of seawater to arrive at a computer algorithm, a look-up table, to estimate $\delta S_A = \delta S_A(x, y, p)$.

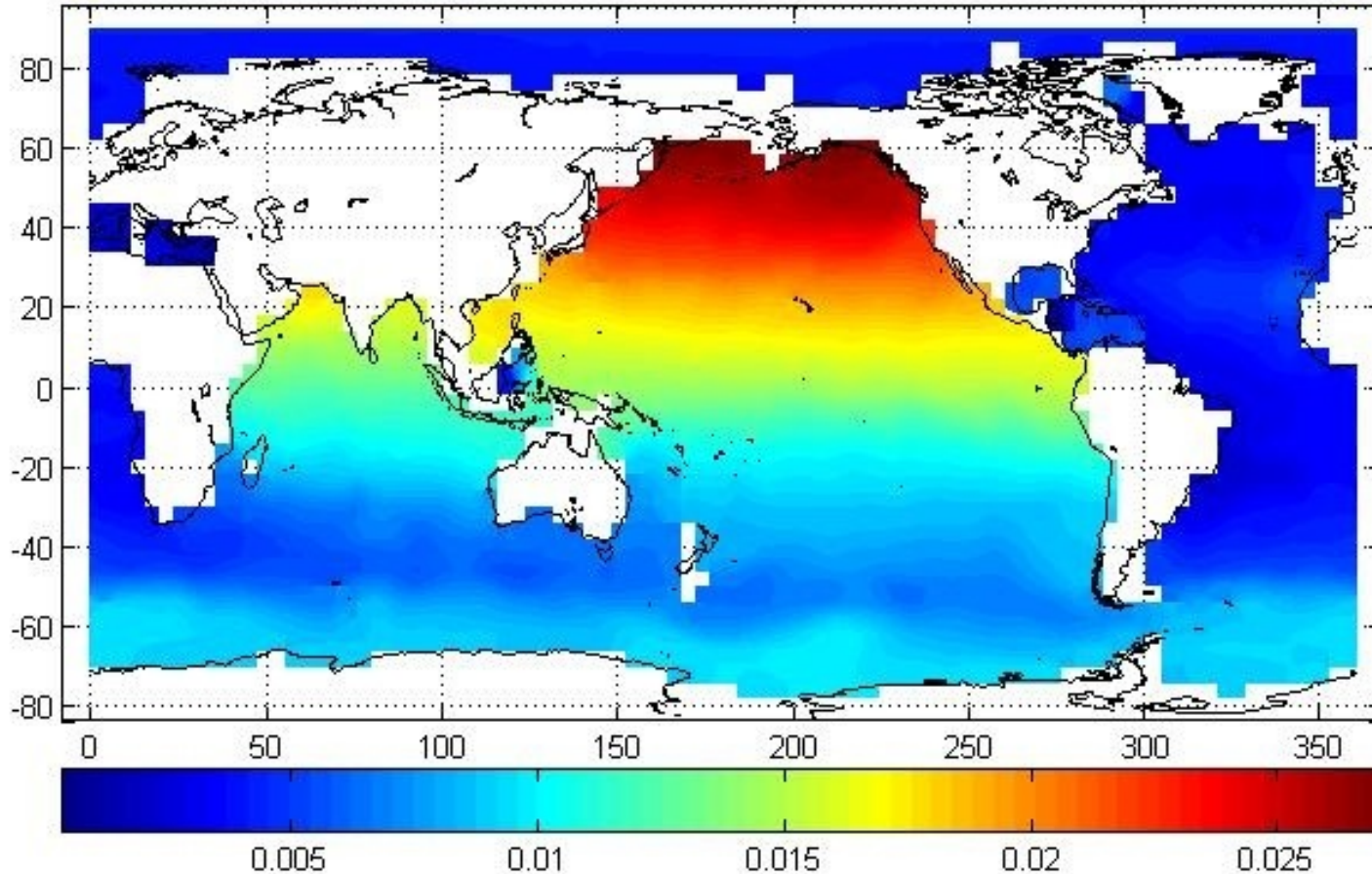
$$S_A = (35.165\ 04/35) \text{ g kg}^{-1} \times S_P + \delta S_A(x, y, p)$$

Where have the 811 samples come from?

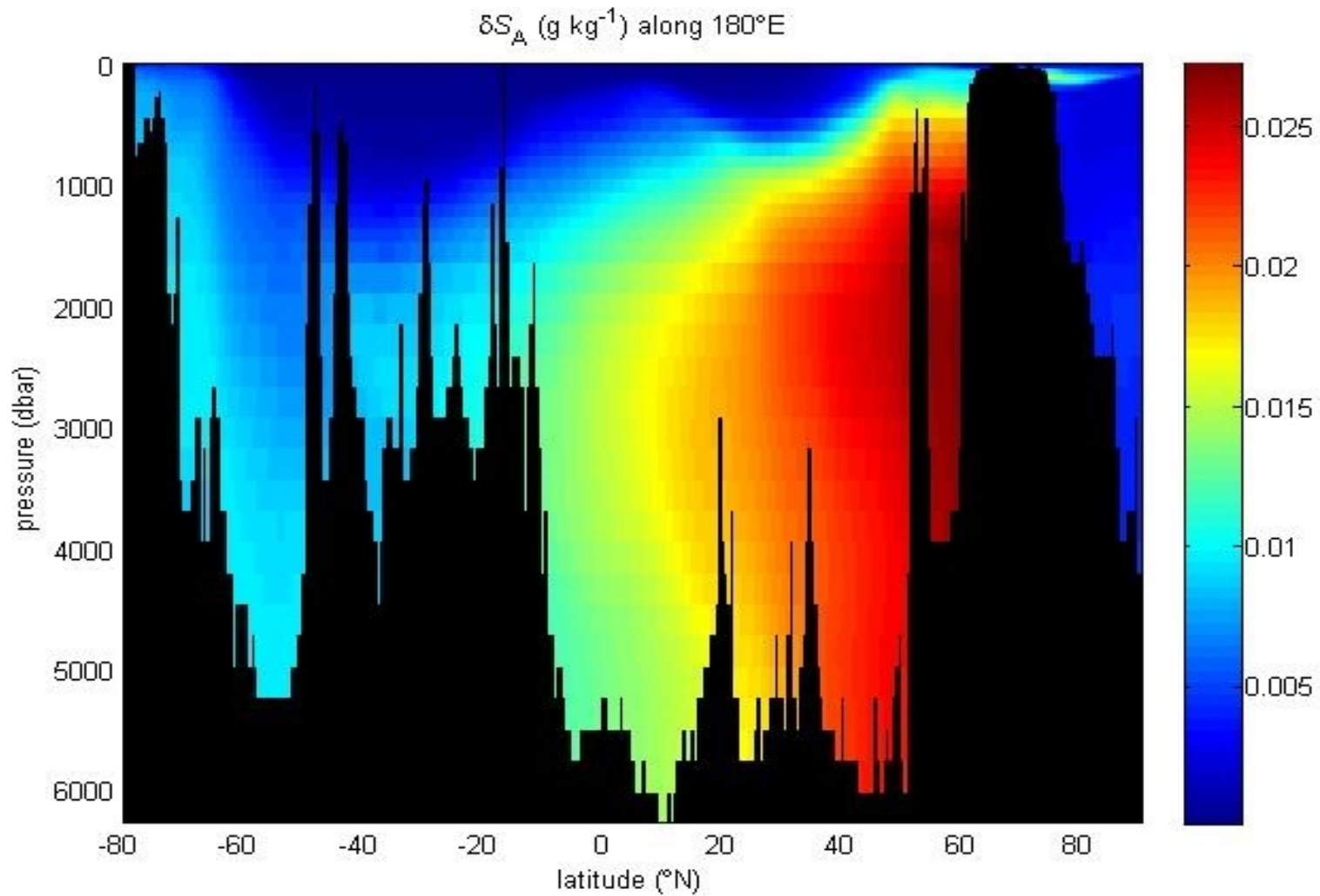


What is the spatial distribution of δS_A ?

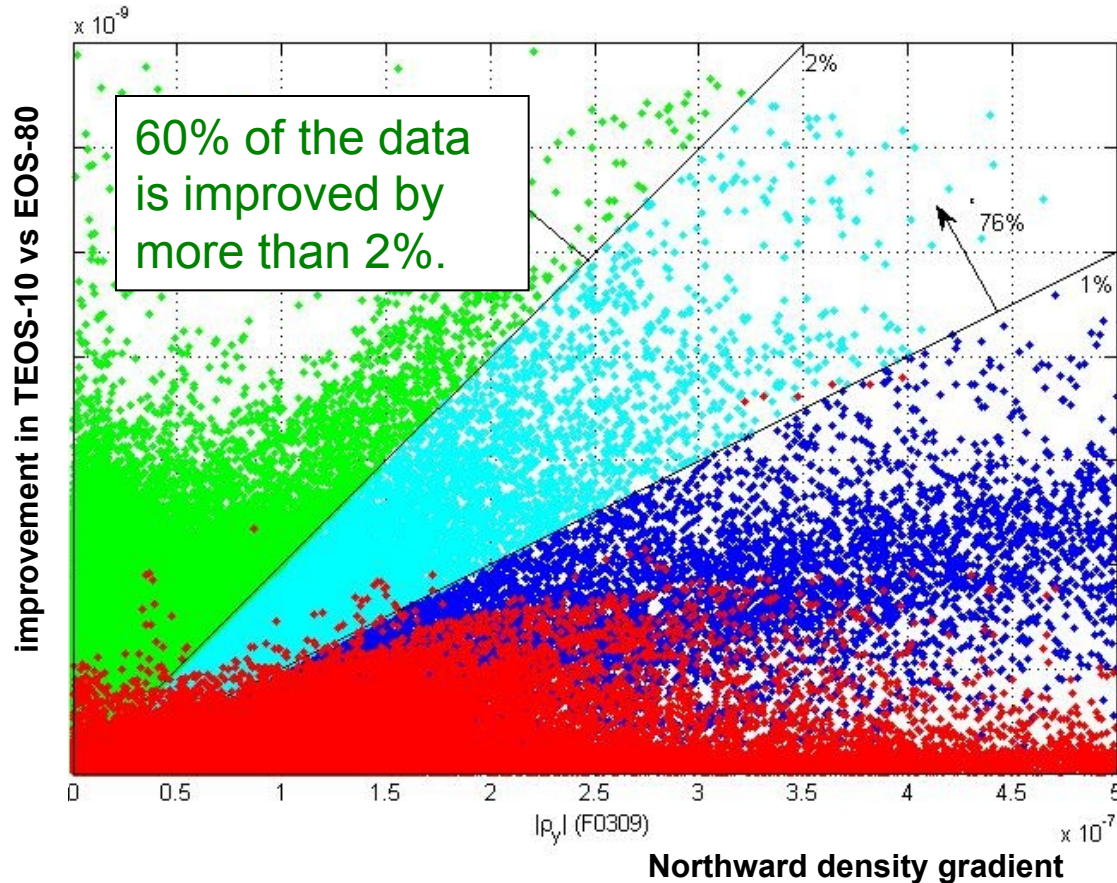
δS_A (g kg^{-1}) at $\rho = 2000$ dbar



What is the spatial distribution of δS_A ?



Improvement in calculating the horizontal density gradient



This figure is for data from the world ocean below 1000 m.

This improvement is mainly due to using S_A rather than S_P .

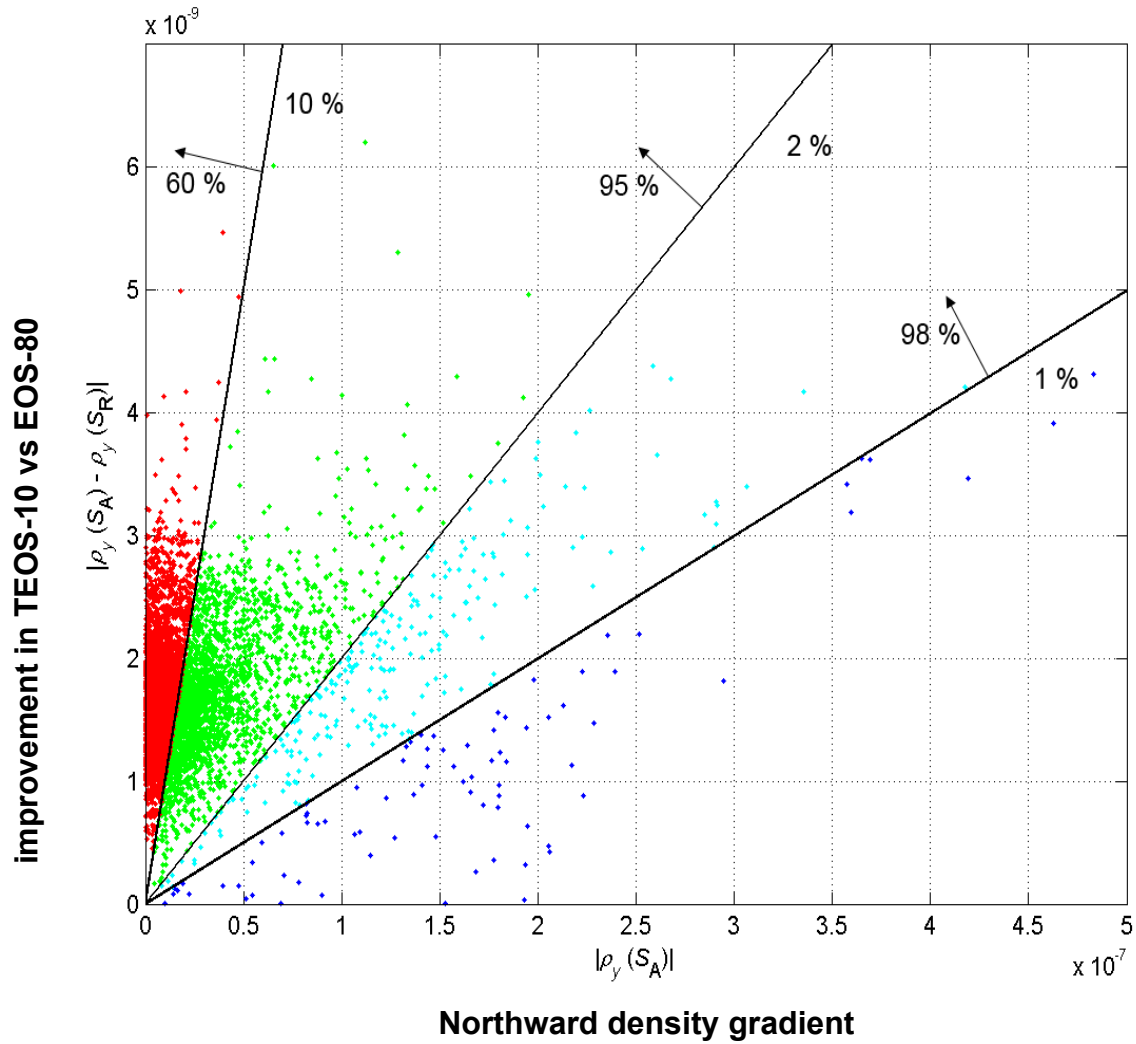
The red data uses S_R in place of S_A .

This shows that for calculating density, the other improvements in TEOS-10 are minor compared with accounting for composition anomalies.

$$\rho^{-1} \nabla_p \rho = \beta \nabla_p S_A - \alpha \nabla_p \Theta$$

$$S_A \rightarrow S_R \uparrow$$

The North Pacific: 10% change in the thermal wind with TEOS-10



Why adopt Absolute Salinity δS_A ?

- The pure water content of seawater is $[1 - 0.001 S_A / (\text{g / kg})]$ not $[1 - 0.001 S_P]$. Since S_A and S_P differ numerically by about 0.47%, there seems no reason for continuing to ignore this difference, for example in ocean models.
- Practical Salinity is not an SI unit of concentration.
- Practical Salinity is limited to the salinity range 2 to 42.
- Density of seawater is a function of S_A not of S_P . Hence we need to use Absolute Salinity in order to accurately determine the horizontal density gradients (for use in the “thermal wind” equation).
- The improved horizontal density gradients will lead to improved heat transports in ocean models.



What is the “heat content” of seawater?

?????

The air-sea heat flux is a well-defined quantity, and it can be measured.

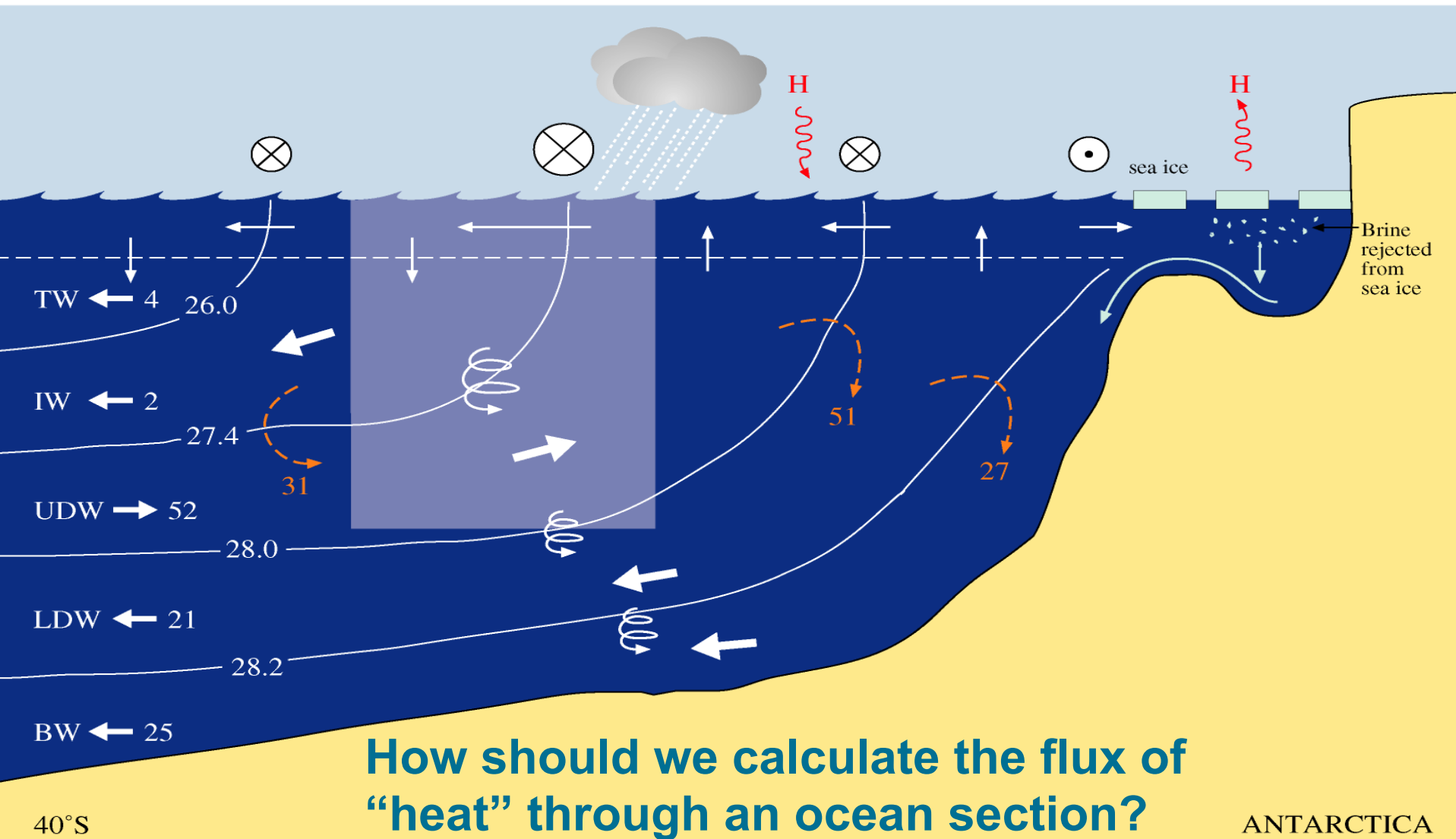
But what is the heat flux carried by seawater? That is, how would we calculate the meridional heat flux carried by the ocean circulation?

This meridional heat flux is the main role of the ocean in climate and in climate change; but how can we evaluate this heat flux?

?????



The Ocean's role in Climate



The concept of potential temperature

Potential temperature, θ , involves a thought experiment.

You take your seawater sample at pressure p and you mentally put an insulating plastic bag around it, and then you change its pressure. Usually you move the plastic bag to the sea surface where $p_r = 0$ dbar. Once there, you “measure” the temperature and call it “potential temperature”.

In ocean models the air-sea heat flux enters the ocean as a flux of potential temperature, using a constant specific heat capacity.



Present oceanographic practice regarding “heat”

To date we oceanographers have treated potential temperature θ as a conservative variable.

We also mix water masses on $S-\theta$ diagrams as though both salinity and potential temperature are conserved on mixing.

In ocean models, air-sea heat fluxes cause a change in θ using a constant specific heat capacity (whereas in fact c_p varies by 5% at the sea surface).

That is, we treat “heat content” as being proportional to θ .

- How good are these assumptions?
- Can we do better?



The First Law of Thermodynamics in terms of θ

The First Law of Thermodynamics is written in terms of enthalpy h as

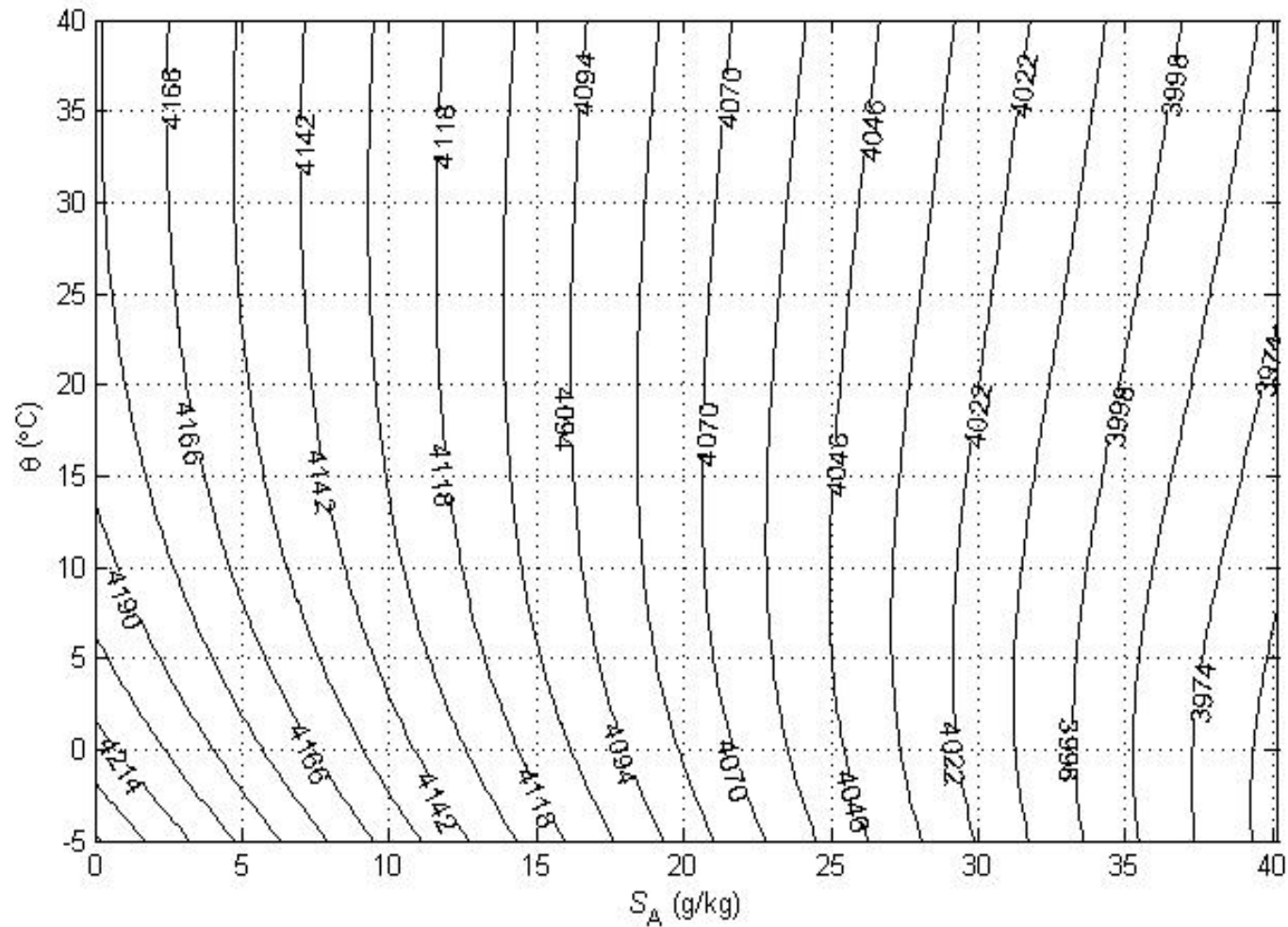
$$\rho \left(\frac{dh}{dt} - \frac{1}{\rho} \frac{dP}{dt} \right) = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon$$

We would like the bracket here to be a total derivative, for then we would have a variable that would be advected and mixed in the ocean as a conservative variable whose surface flux is the air-sea heat flux.

If we take $h = (S_A, \theta, p)$, thermodynamic reasoning leads to

$$\rho \left(\frac{(T_0 + t)}{(T_0 + \theta)} c_p(p_r) \frac{d\theta}{dt} + [\mu(p) - (T_0 + t)\mu_T(p_r)] \frac{dS_A}{dt} \right) = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon$$

Specific heat capacity at constant pressure, c_p , J kg⁻¹ K⁻¹ at $p = 0$ dbar



Potential enthalpy, h^0 , and Conservative Temperature, Θ

Just as θ is the temperature evaluated after an adiabatic change in pressure, so potential enthalpy is the enthalpy of a fluid parcel after the same adiabatic change in pressure.

$$h^0(S_A, \theta, 0) = h(S_A, \theta, p) - \int_0^p v(S_A, \theta, p') dp'.$$

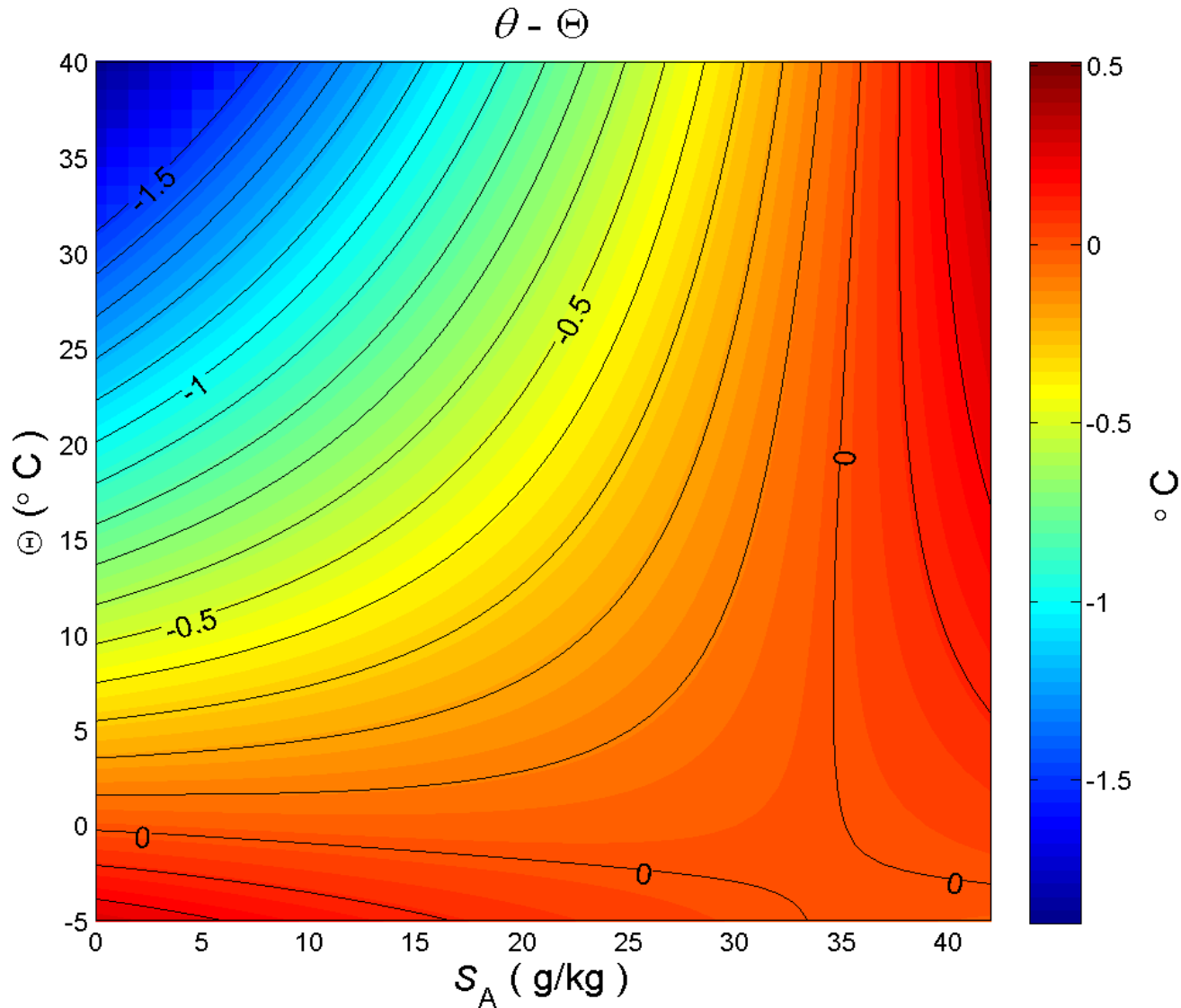
Taking the material derivative of this leads to (with $h^0 = c_p^0 \Theta$)

$$\rho \left(\frac{(T_0 + t)}{(T_0 + \theta)} c_p^0 \frac{d\Theta}{dt} + \left[\mu(p) - \frac{(T_0 + t)}{(T_0 + \theta)} \mu(0) \right] \frac{dS_A}{dt} \right) = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon$$

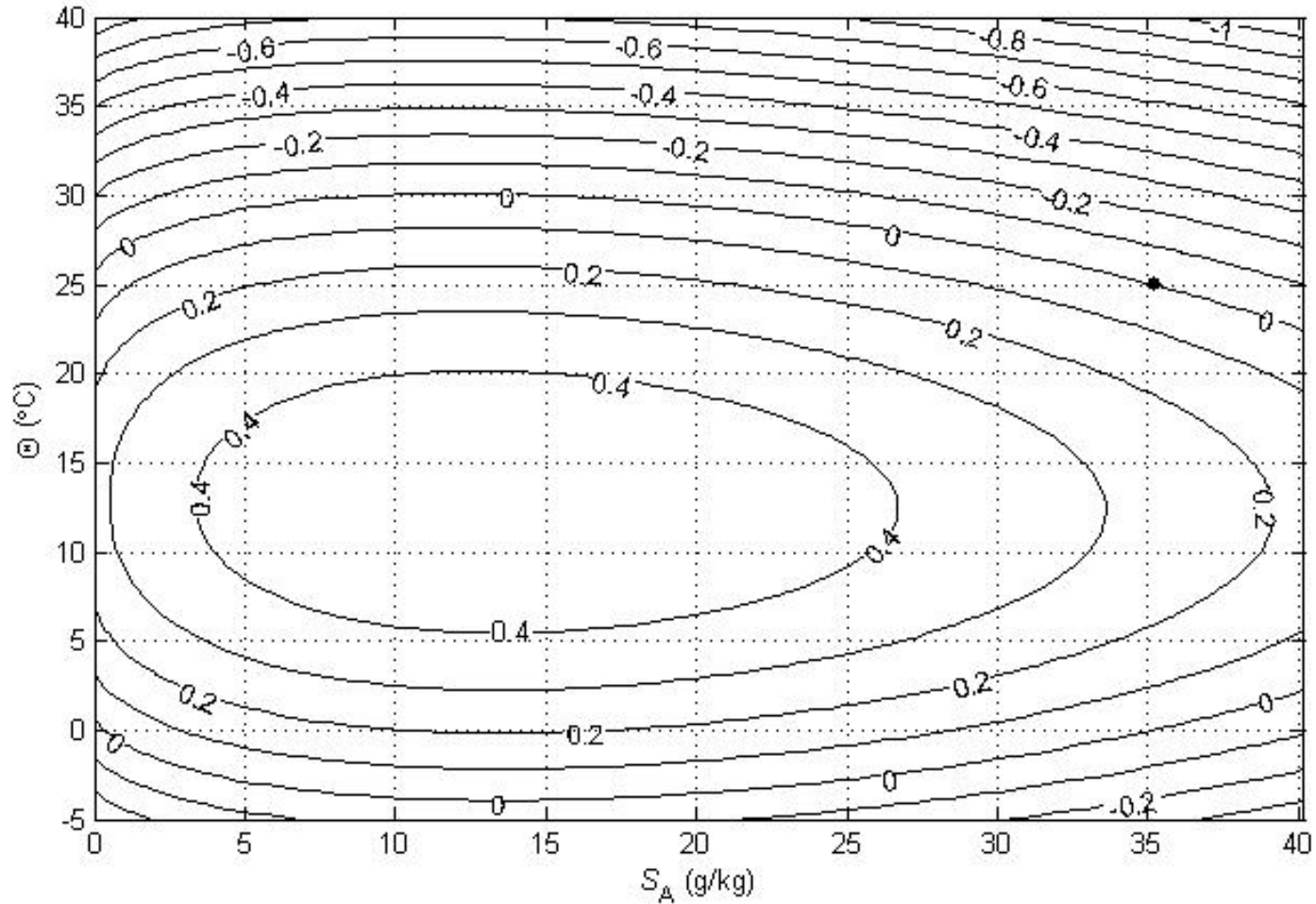
The “specific heat” c_p^0 is a constant, and the square bracket here is very close to zero, even at a pressure of 40 MPa = 4,000 dbar. This means that the First Law of Thermodynamics can be accurately written as

$$\rho \frac{dh^0}{dt} = \rho c_p^0 \frac{d\Theta}{dt} = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon.$$

The difference between potential temperature and and Conservative Temperature, $\theta - \Theta$ ($^{\circ}\text{C}$)

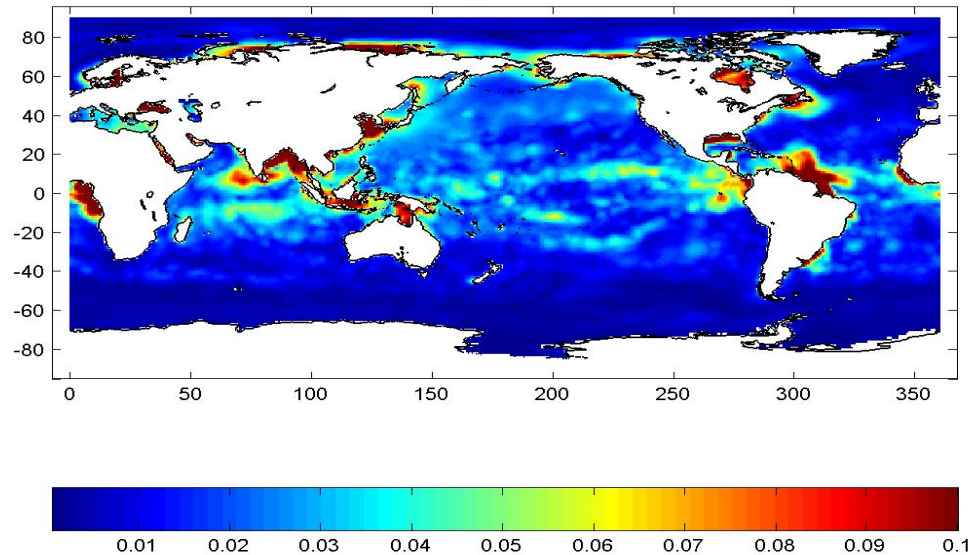
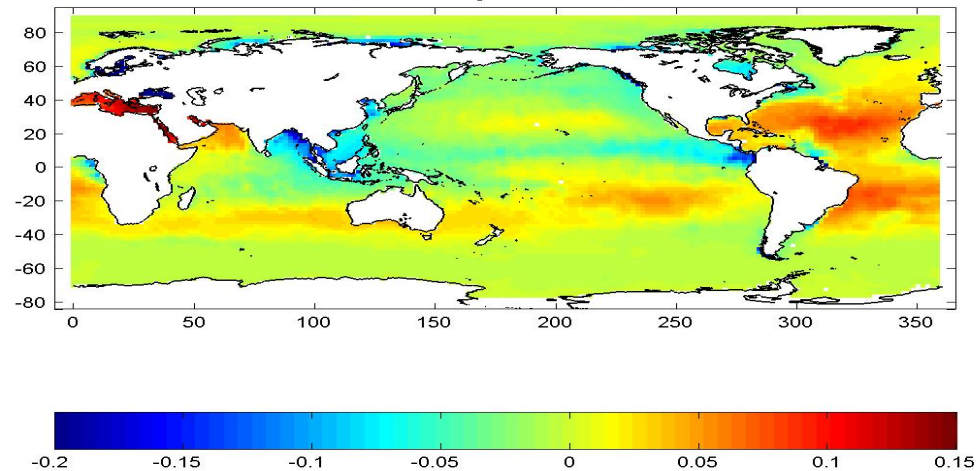


... to be compared with the error in assuming that entropy is a conservative variable; contours in $^{\circ}\text{C}$



Improving “Heat” Conservation in Ocean Models

- Conservative temperature is 100 times closer to being “heat” than is potential temperature.
- The algorithm for conservative temperature has been imported into the MOM4 code and it is available as an option when running the MOM4 code.
- The figures show the expected influence of sea-surface temperature in the annual mean, and seasonally.



Improving “Heat” Conservation in Ocean Models

This improvement in the calculation of the “heat content” of seawater and the “heat flux” carried by the ocean circulation is possible because the TEOS-10 Gibbs function delivers the **enthalpy** of seawater.



The two key changes to oceanographic practice

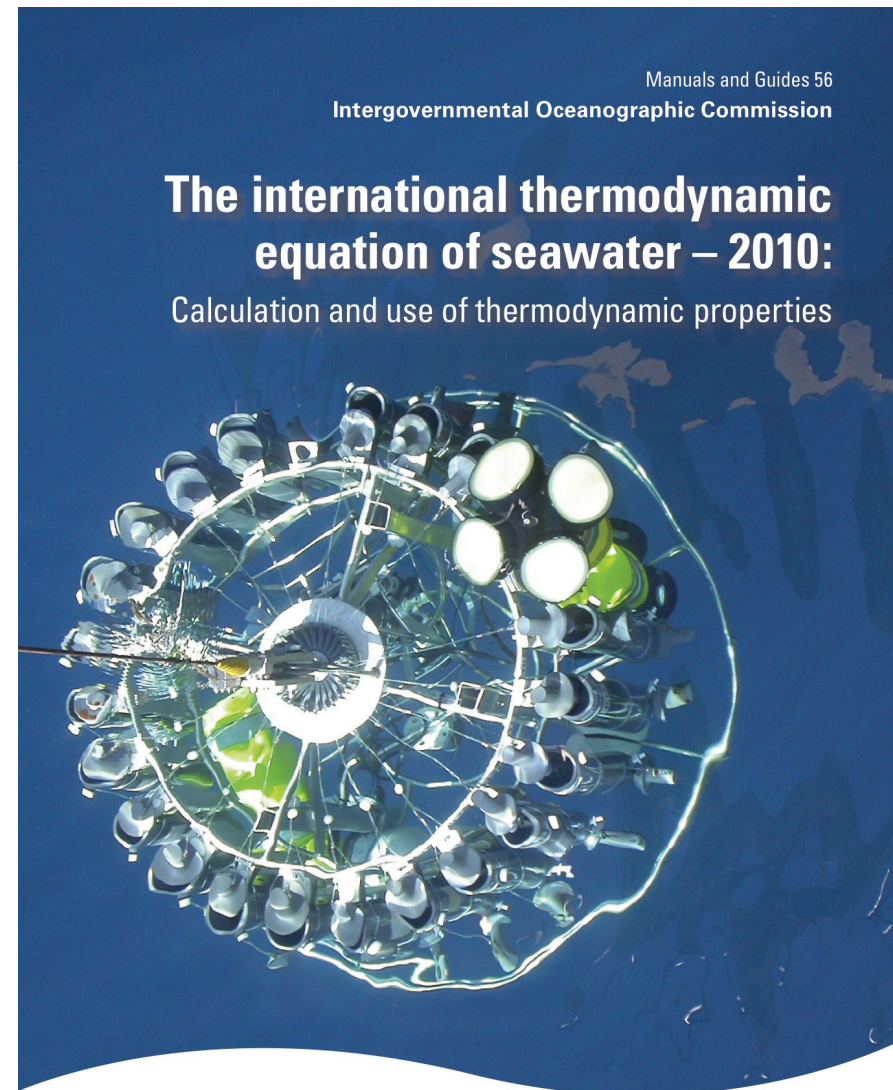
1. Use of a new salinity variable, Absolute Salinity S_A (g/kg) in place of Practical Salinity S_p (ocean models need to also keep track of another salinity variable, called Preformed Salinity S_*).
2. Use of a new temperature variable, Conservative Temperature Θ , replacing potential temperature θ .



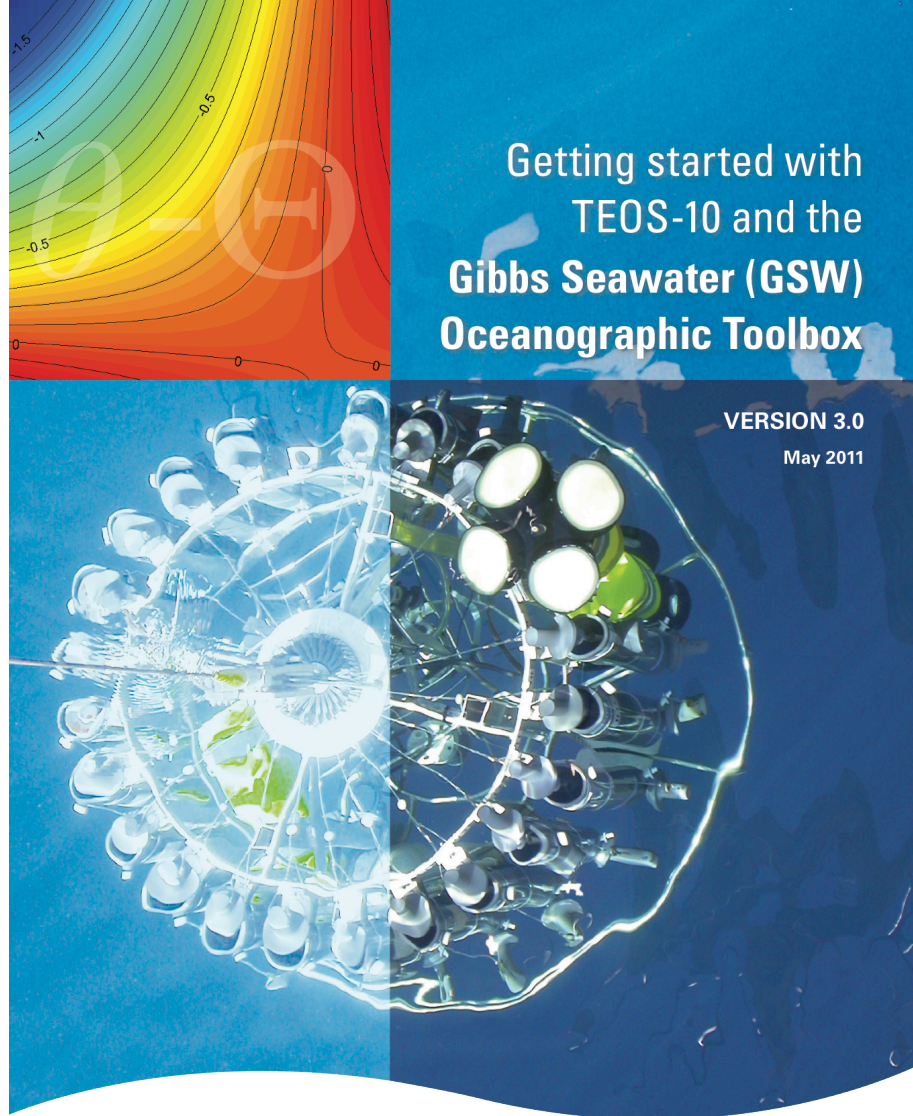
The official guide to TEOS-10 is IOC *et al.* (2010); the front cover is shown.

TEOS-10 is the official thermodynamic description of seawater, ice and of humid air at all pressures in the atmosphere.

Exploiting the thermodynamic equilibrium properties between seawater, ice and humid air, means that we now have very accurate properties such as freezing temperature, latent heat of evaporation etc.



This short 28-page document is an introduction to TEOS-10 and to the Gibbs Seawater Oceanographic Toolbox of computer algorithms.

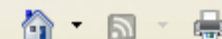


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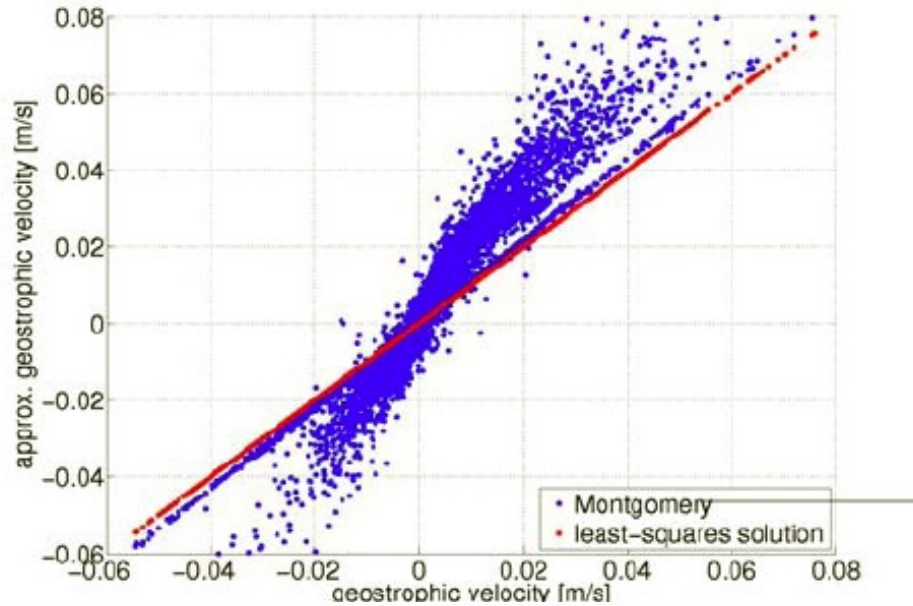
This site is the official source of information about the Thermodynamic Equation Of Seawater - 2010 (TEOS-10), and the way in which it should be used.

TEOS-10 is based on a Gibbs function formulation from which all thermodynamic properties of seawater (density, enthalpy, entropy sound speed, etc.) can be derived in a thermodynamically consistent manner. [TEOS-10 was adopted by the Intergovernmental Oceanographic Commission at its 25th Assembly in June 2009](#) to replace EOS-80 as the official description of seawater and ice properties in marine science.

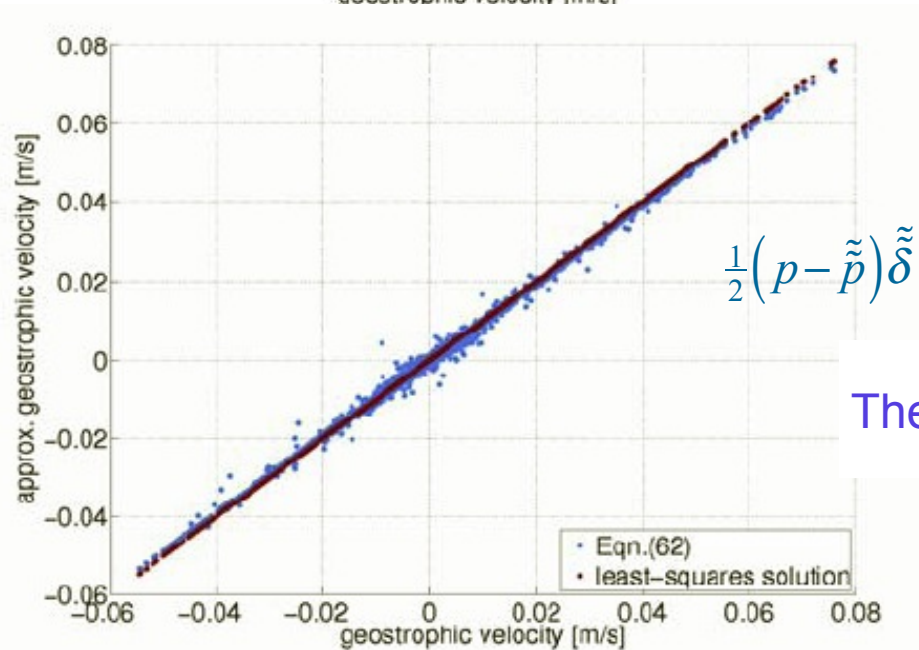
A significant change compared with past practice is that TEOS-10 uses Absolute Salinity S_A (mass fraction of salt in seawater) as opposed to Practical Salinity S_p (which is essentially a measure of the conductivity of seawater) to describe the salt content of seawater. Ocean salinities now have units of g/kg.

Absolute Salinity (g/kg) is an SI unit of concentration. The thermodynamic properties of seawater, such as density and enthalpy, are now correctly expressed as functions of Absolute Salinity rather than being functions of the conductivity of seawater. Spatial variations of the composition of seawater must

Geostrophic Streamfunction for density surfaces



$$p \delta^{35,0} - \int_0^p \delta^{35,0} dp'$$



$$\frac{1}{2}(p - \tilde{p}) \tilde{\delta}(S_A, \Theta, p) - \frac{1}{12} \frac{T_b^\Theta}{\rho} (\Theta - \tilde{\Theta})(p - \tilde{p})^2 - \int_0^p \tilde{\delta} dp'$$

The rms error is improved by a factor of 16.

Implementation of TEOS-10

- In October 2008, the International Association for the Properties of Water and Steam (IAPWS) adopted TEOS-10 as the thermodynamic equation of seawater for industrial and engineering purposes.
- In June 2009, the Intergovernmental Oceanographic Commission adopted TEOS-10 as the new definition of the thermodynamic properties of seawater in oceanography, effective from 1st January 2010.
- The description of TEOS-10 and the TEOS-10 computer software is available at <http://www.TEOS-10.org>
- Oceanographic journals are now encouraging authors to use TEOS-10, including the use of Absolute Salinity. The use of Practical Salinity and EOS-80 in journal articles is being phased out over a transition period (5 years?).



Implementation of TEOS-10

- The thermodynamic properties of seawater are now defined in terms of the TEOS-10 Gibbs function for seawater which is a function of Absolute Salinity.
- Continue to report Practical Salinity S_p to national data bases since
 - (i) S_p is a measured parameter and
 - (ii) we need to maintain continuity in these data bases.
 - Note that this treatment of working scientifically with Absolute Salinity but reporting Practical Salinity to national data bases is exactly what we have been doing for temperature; we store in situ temperature, but we have done our research and published in potential temperature.



TEOS-10 and GSW in a nutshell

In order to analyse oceanographic data under TEOS-10, the observed values of Practical Salinity S_p and *in situ* temperature t need to be converted into Absolute Salinity S_A and Conservative Temperature Θ , as follows,

Step 1. calculate Absolute Salinity, $S_A = \text{gsw_SA_from_SP}(S_p, p, \text{long}, \text{lat})$,

Step 2. calculate Conservative Temperature, $\Theta = \text{gsw_CT_from_t}(S_A, t, p)$.

Having converted (S_p, t, p) to (S_A, Θ, p) , the GSW functions listed on page 14 of this document are then used for analysing the data. The use of these GSW functions ensures consistency between theoretical oceanography, observational oceanography and ocean modelling.

