



Salinity – a measure of total dissolved salt concentration in seawater

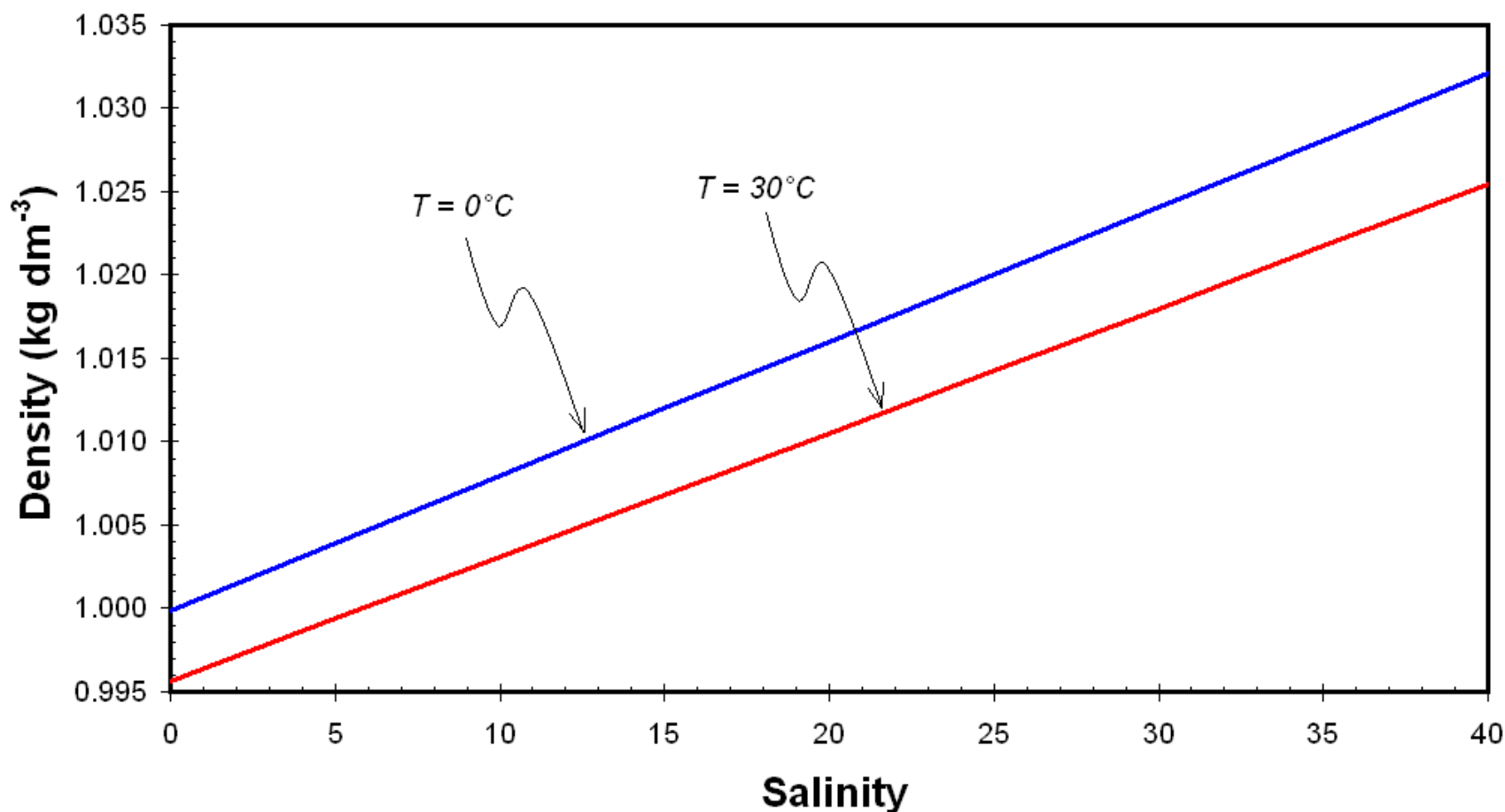
Salinity matters because it...

- controls the freezing point of seawater (previous lecture);
- allows major ion concentrations to be calculated (previous lecture);
- can be related to ionic strength (for chemical speciation calculations) \Rightarrow affects activity coefficients



Salinity matters because it...

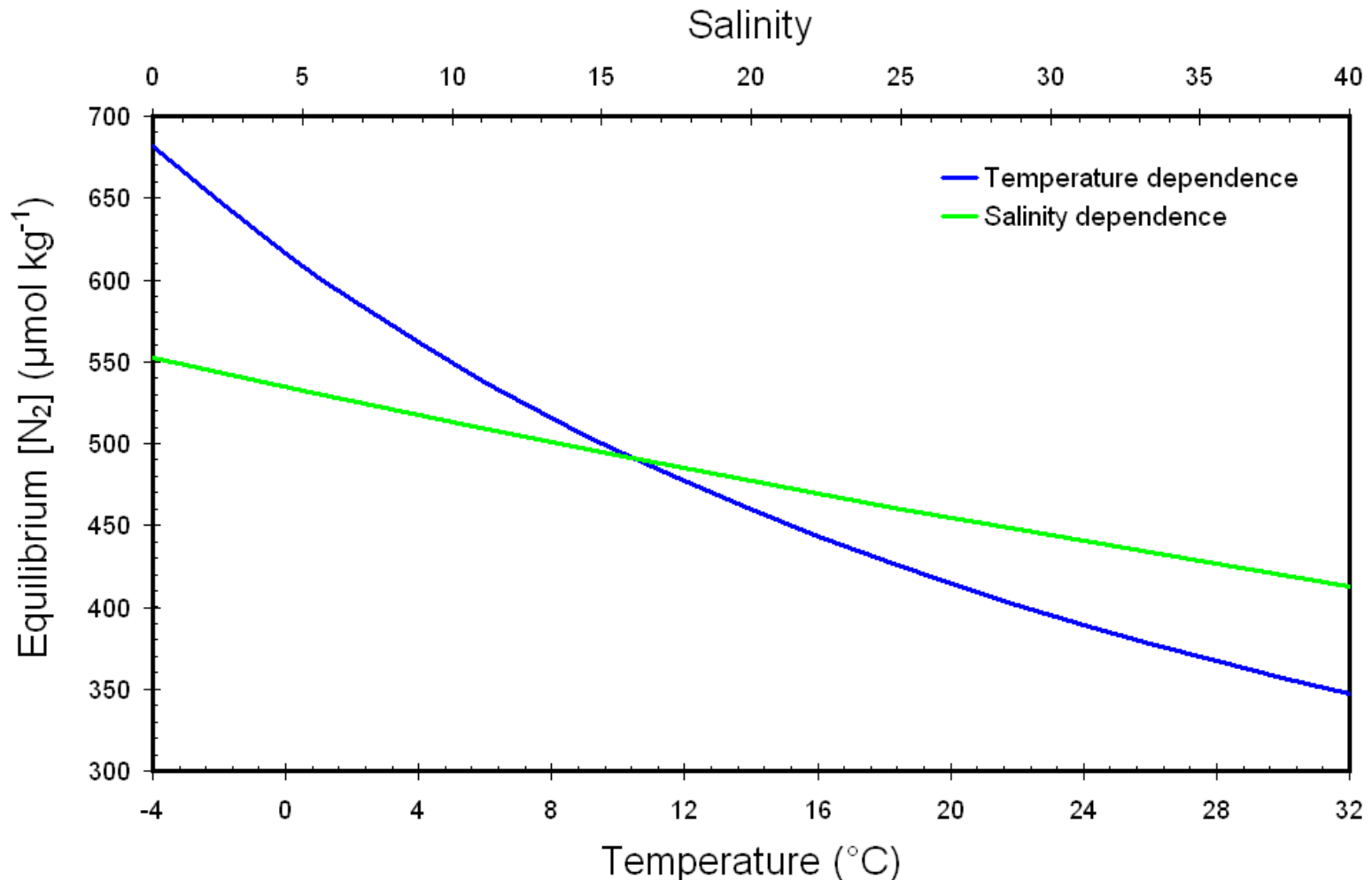
- controls the DENSITY of seawater (together with temperature + pressure): affects circulation of the ocean





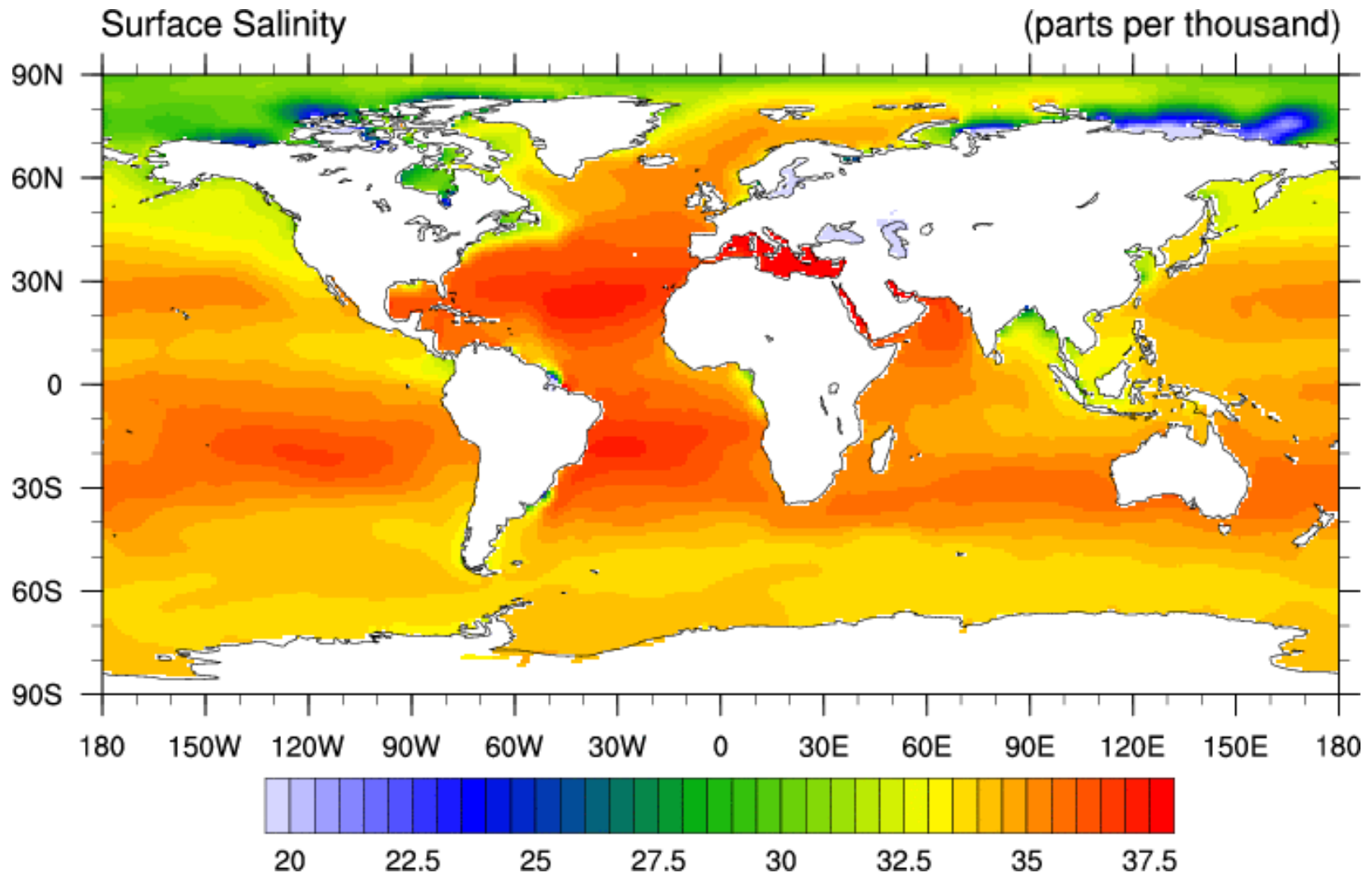
Salinity matters because it...

- affects the solubility of dissolved gases.





Surface Salinity Distribution

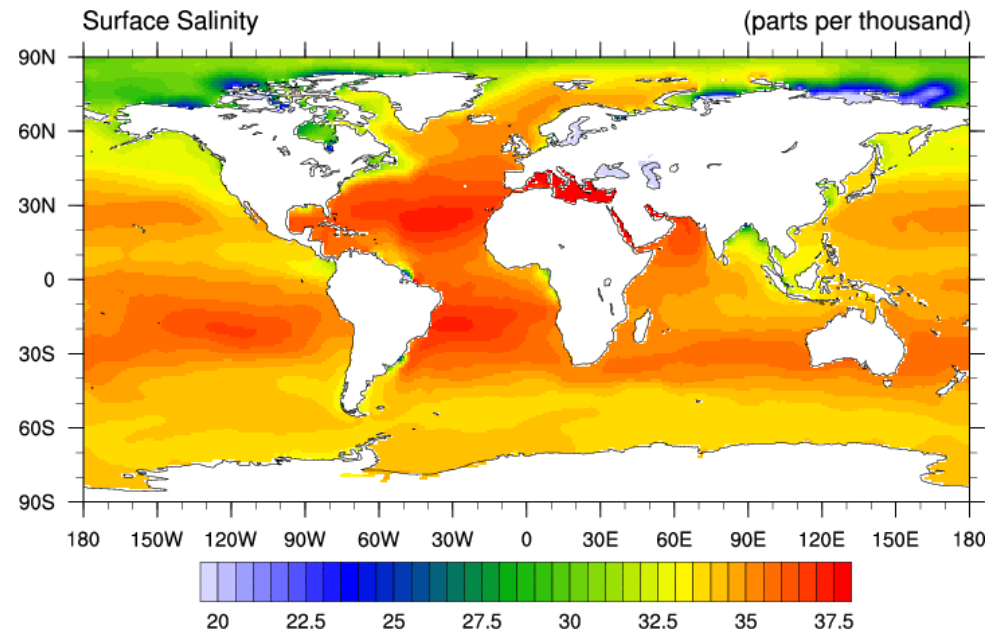




Surface Salinity Distribution

Overall range for surface waters is usually:

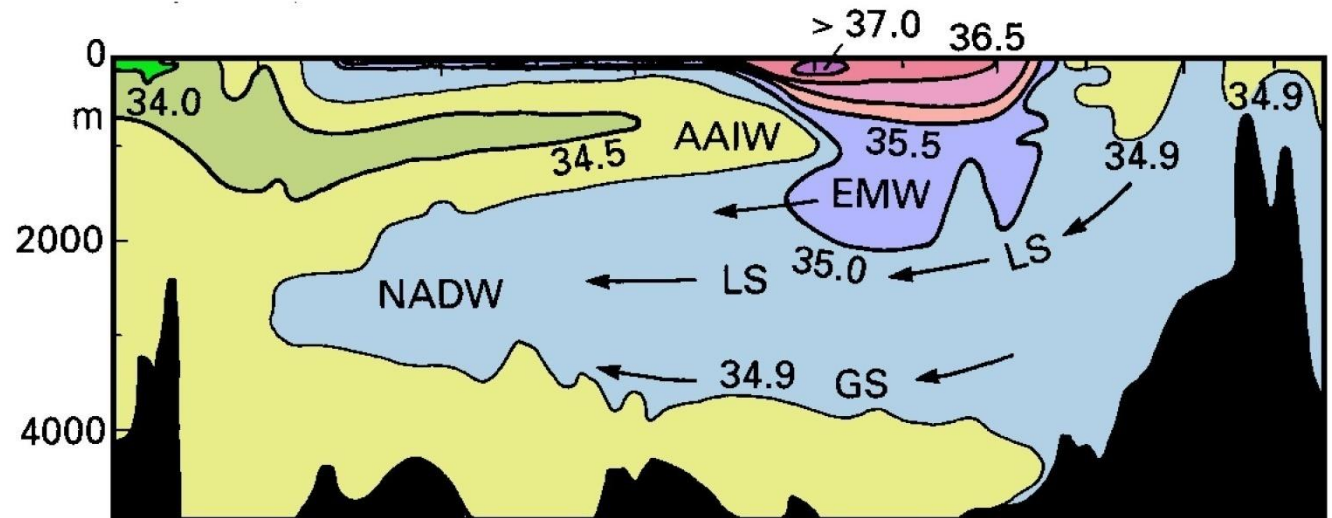
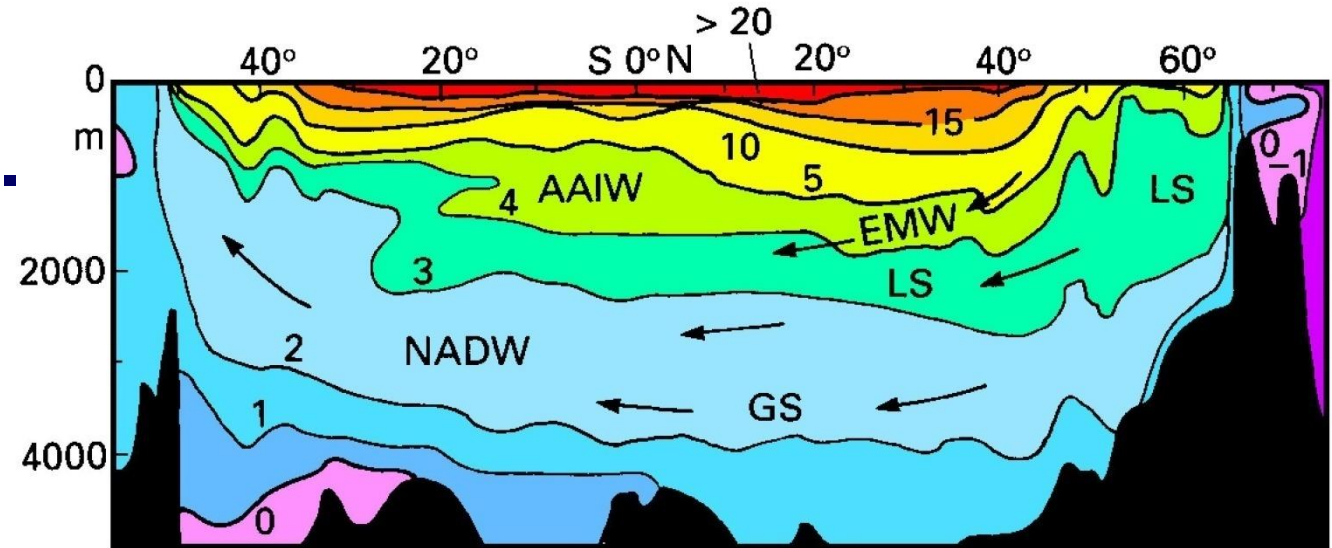
- <34 in high latitude oceans.
- c. 35 at the equator
- up to 38 in the open ocean
- lower in coastal and Arctic waters

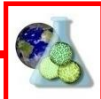




Salinity matters because it...

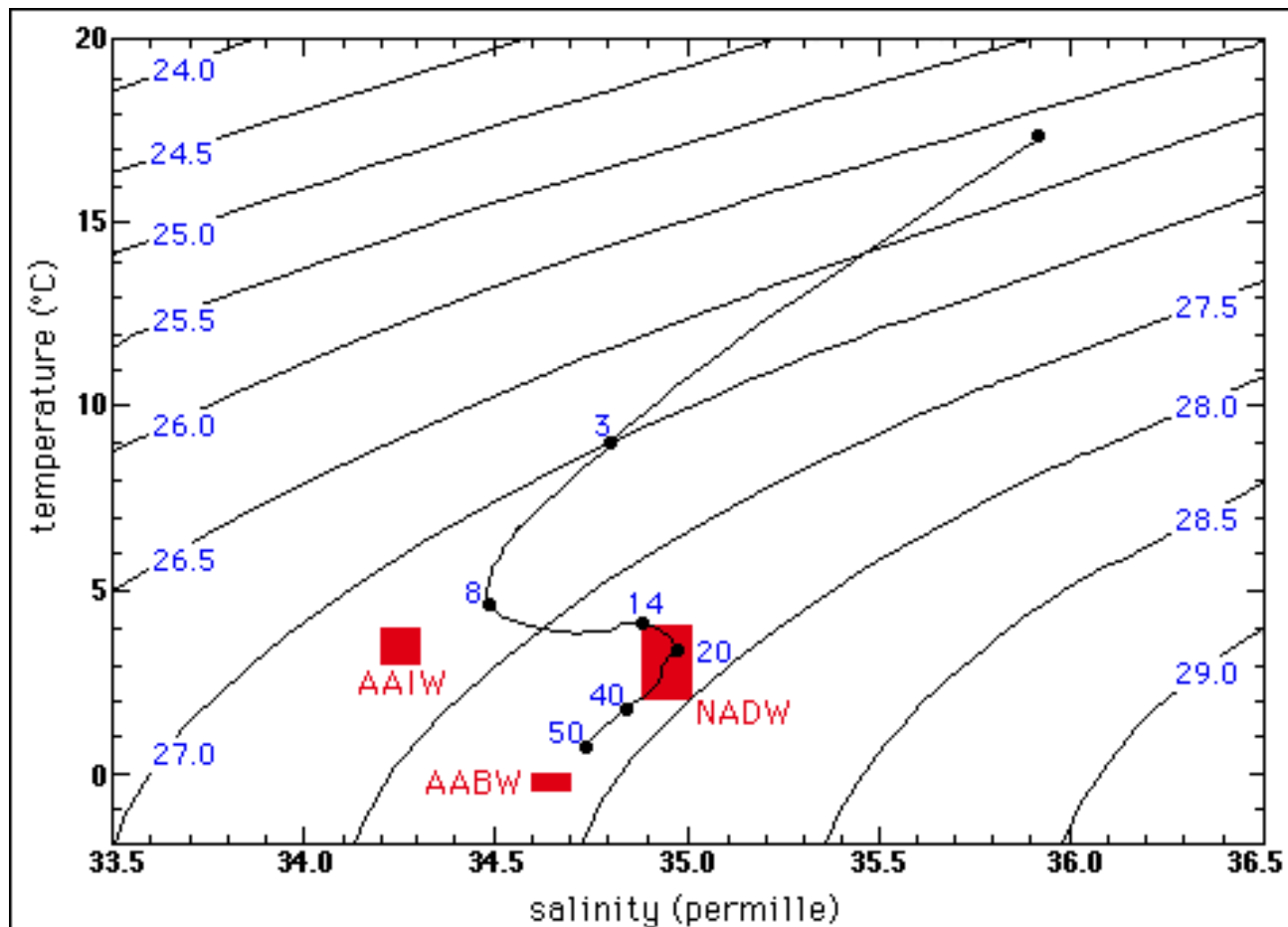
- is a tracer of ocean circulation.





Salinity matters because it...

- Can be used to identify water masses



An example of a T-S diagram for observations at depths from 150 m to 5,000 m at 9°S latitude in the Atlantic Ocean. Dots represent individual seawater samples; numbers indicate depths in hundreds of meters. Red boxes represent the major subsurface Atlantic water masses. **AABW** = Antarctic Bottom Water; **NADW** = North Atlantic Deep Water; **AAIW** = Antarctic Intermediate Water.



Processes that alter Seawater Salinity at ocean boundaries

Major:

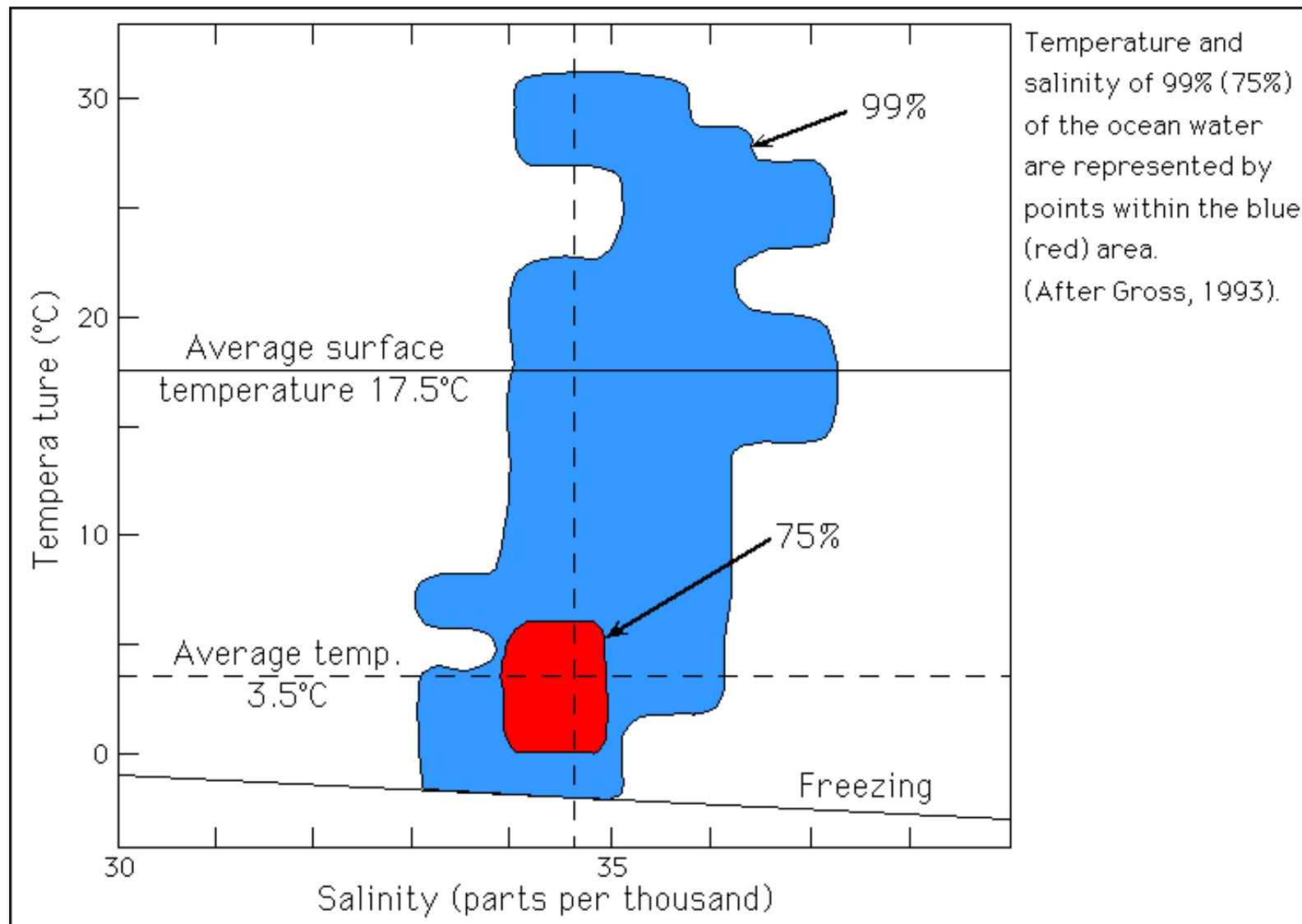
- Evaporation
- Precipitation (direct)
- Runoff (rivers)
- Groundwater flow
- Ice formation, brine-rejection during ice formation
- Ice melting

Minor:

- Precipitation of salts
- Hydrothermal brine injection



Temperature-Salinity Distribution

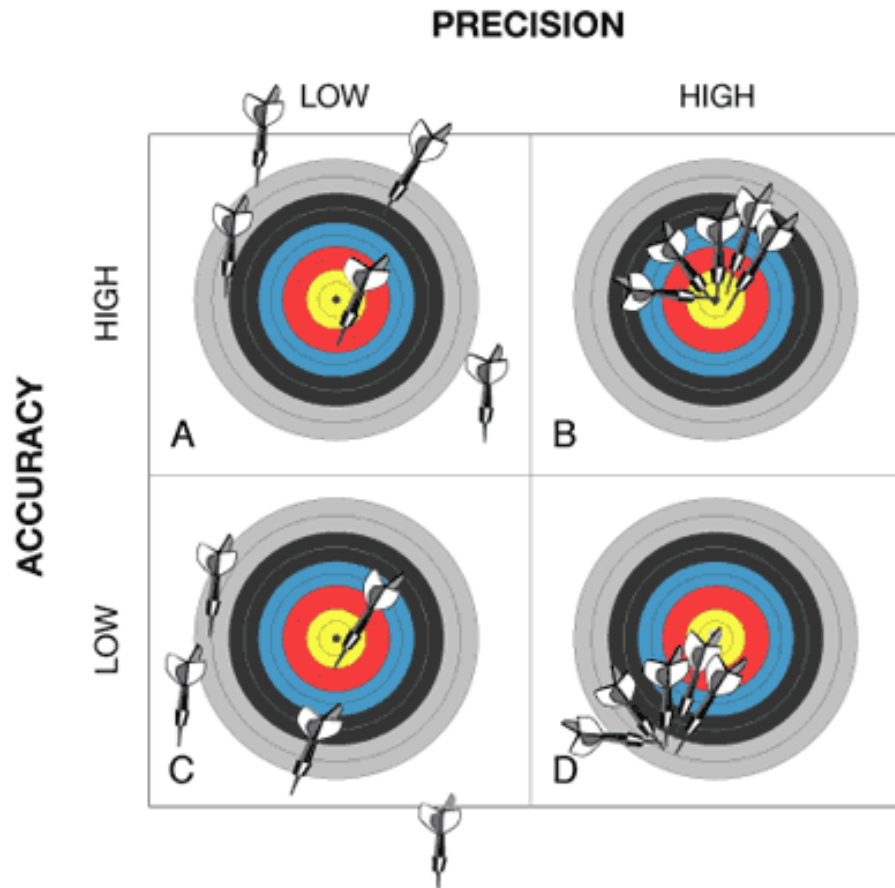




Salinity measurement

Deep Atlantic (>1000m) varies from 34.5 to 35.0, therefore:

- Salinity measurements need to be **accurate** and **precise**.





A Brief (?) History of Salinity Measurement

1. Evaporation to dryness → Weighing

Seems straightforward, but gives variable results because:

Salt in Residue	Effect of heating
NaCl	OK
KCl	OK
K ₂ SO ₄	OK
Na ₂ SO ₄ · xH ₂ O	OK (easily loses water)
MgCl ₂ · xH ₂ O	may decompose to HCl
CaCl ₂ · xH ₂ O	may lose some HCl
MgCO ₃	gives MgO and CO ₂
Ca(HCO ₃) ₂	gives CaCO ₃ + CO ₂ then CaO and CO ₂
Organic matter	gives H ₂ O and CO ₂

- sea salts hold onto water (water of hydration)
- the strong heating required to drive off the water decomposes some salts

Workarounds to these problems were developed by marine chemists in the late 1800's.



First strict definition of SALINITY (Knudsen, 1902):

„Salinity is defined as the weight in grams of the dissolved **inorganic** matter in one kilogram of seawater after all the bromide and iodide have been replaced by the equivalent amount of chloride and all carbonate converted to oxide“ (and therefore lost from the sample as CO_2).

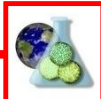
- Units of salinity **were** g (kg-sw)^{-1} or ‰ or parts-per-thousand
- Based on a long and tedious analytical procedure which involved mixing seawater with HCl and saturating with Cl_2 gas, heating to 480°C for 72 h, weighing, etc...
- A ,reference‘ or ,certification‘ method which is not practical for routine work at sea.
- A ,conventional‘ definition (some dissolved substances in seawater are not accounted for, approx. 0.1 g kg^{-1})



2. Chlorinity: The Mohr titration.

Sørensen and Knudsen(1902) noted:

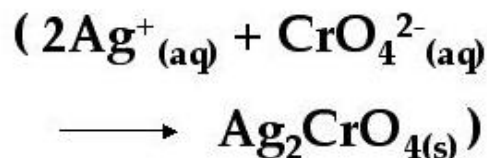
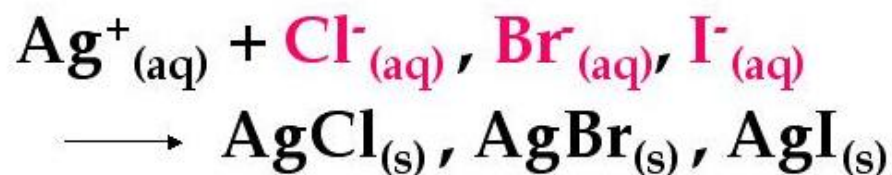
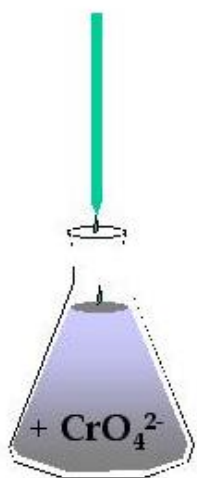
- Constant ratio of major constituents of seawater (e.g. Cl/Na, SO_4/Mg)
- Measuring one constituent allows the total salinity to be estimated.
- 55% of total dissolved solids in seawater is Cl^-
- Cl^- (together with other halide ions) could be determined accurately.



This led to the *empirical* definition of Salinity in terms of “Chlorinity” (Sørensen, 1902):

Sorensen, 1902

Chlorinity: the mass of chlorine equivalent to the total mass of halogens contained in one kilogram of seawater.



- Titrate 15 ml of seawater with AgNO_3 solution to a K_2CrO_4 indicator end-point (i.e., until all chloride, iodide and bromide have been precipitated as silver salts).
- This should be ‘halinity’ but was called, simply, ‘chlorinity’.
- Use specialized calibrated glassware (and great care).
- Capable of **precision** of 1 part in 1000 – 3000 (even at sea).
- Standardize the AgNO_3 solution against internationally-accepted ‘Standard Seawater’ of known Chlorinity. (**Accuracy**).



Standard Seawater

- Natural seawater collected in large batches, calibrated against AgNO_3 made from pure Ag, compared with earlier batches, etc.
- From 1908 to 1975 prepared in Knudsen's lab in Copenhagen. 'Copenhagen Water'.
- Since 1975 prepared for IAPSO by the Standard Seawater Service, Wormley, UK (Wormley Water', now marketed by OSIL Ltd).
- International use by oceanographers helped to ensure inter-comparability of salinity data.



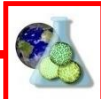


Relation Between Salinity and Chlorinity

Sørensen measured the salinity of 9 seawater samples carefully using a (difficult) reference technique. Also determined the Chlorinity by titration.

Results were: $\longrightarrow \text{Salinity } [‰] = 1.805 \cdot \text{Chlorinity } [‰] + 0.030$

- This relation was the foundation for all salinity measurements for the next 60 years.
- The relationship has never been re-checked.
- Inclusion of low-salinity Baltic Sea samples, with unusual major ion composition, caused the relationship not to extrapolate to zero.



- In 1962, an international panel recommended that the relationship be altered to eliminate the Baltic influence.
- New relationship passed through the origin.
- This was used for next 20 years:

$$\textit{Salinity} [\text{‰}] = 1.80655 \cdot \textit{Chlorinity} [\text{‰}]$$

- Gave the same salinity for ,average‘ ocean values (e.g. 35‰). Gave slightly lower salinity at low chlorinity.



Conductivity and Salinity

- Electrical conductivity is proportional to salinity
- Since the 1960's, the conductivity-based measurement of salinity has replaced titrations

Advantages:

- Conductivity-based measurements are more precise and less prone to operator error.
- Conductivity-based salinity can be *measured in-situ*
- Conductivity measurements are cheaper!



Problem:

- An absolute value of conductivity cannot be measured to sufficient accuracy and precision.

Solution:

- A conductivity ratio relative to 'standard seawater' is measured instead.

Important:

- Accurate **temperature control or measurement** is extremely important as conductivity is strongly affected by temperature:

$0.01^{\circ}\text{C} \Leftrightarrow 0.01\text{‰}$ in salinity



Conductivity-Based Measurements of Salinity

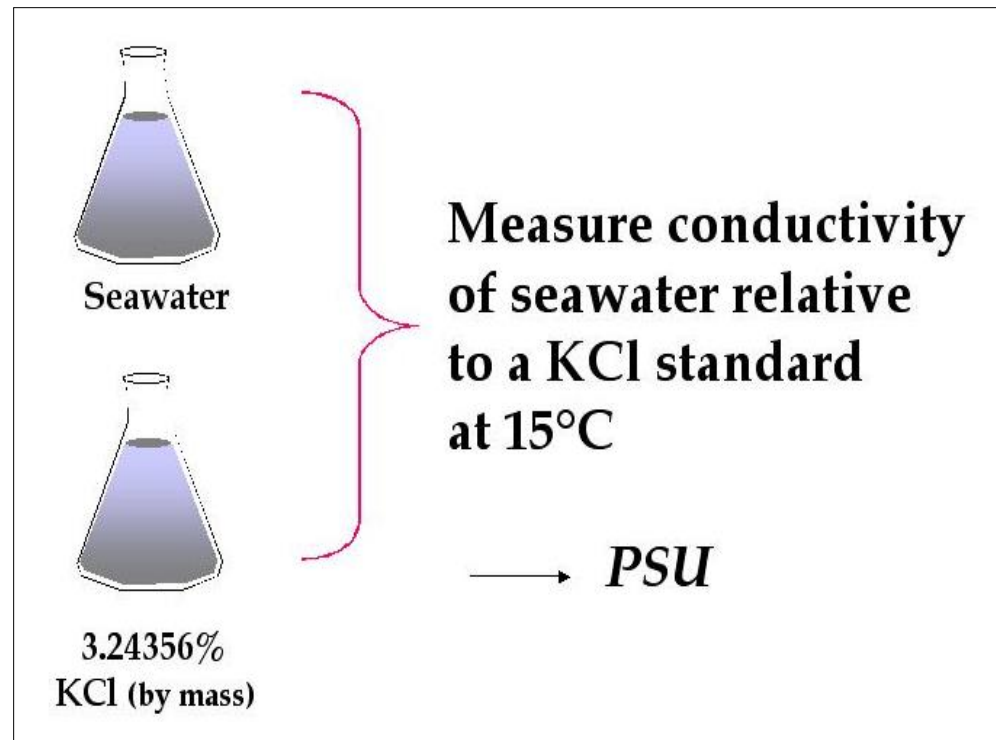
- During the 1960's, experiments found that:
 - Density calculated from conductivity-salinity data was 10x more precise than density calculated from titration-salinity data.
 - The precision of the conductivity data was only 5x better.
- The difference was attributed to:
 - Effect of small variations of seawater composition relative to Cl^- (e.g. non-conservative major ions: $\text{HCO}_3^-/\text{Cl}^-$, $\text{Ca}^{2+}/\text{Cl}^-$).
 - These variations affect the density (but NOT the chlorinity)
 - These variations are measured by conductivity (but NOT by chlorinity titration)
- Conductivity is a better measure for calculating salinity effect on density.
- A new definition and standard for salinity was required.



The Practical Salinity Scale (1982)

Recommended that:

- The absolute standard should **not** be subject to variations of ionic composition of seawater.
- Should be able to be made in any high-quality laboratory.
- Should be useful for calculation of density to acceptable limits of accuracy and precision.
- Standard concentration should be such that the conductivity would precisely equal that of Wormley Water at a Chlorinity of 19.374 which, by definition, has a salinity of 35.000.





Note:

- Salinity is now defined in terms of a **conductivity ratio**. It is NOT a concentration.

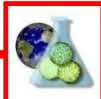
Practical Salinity Scale (1981)

$$\begin{aligned} S = & 0.0080 - 0.1692 K_{15}^{0.5} \\ & + 25.3851 K_{15} + 14.0941 K_{15}^{3/2} \\ & + 7.0261 K_{15}^2 + 2.7081 K_{15}^{5/2} \end{aligned}$$

Basis:

$$K_{15} = 1 \text{ (exactly) for 35 PSU}$$

- Therefore it is DIMENSIONLESS (no units).
- Many people still refer to salinity (wrongly) with units of ,‰' (which is no unit, strictly) or as ,practical salinity units'.

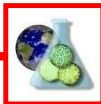


Update!! TEOS-10

- The Intergovernmental Oceanographic Commission (IOC), with the endorsement of the Scientific Committee on Oceanic Research (SCOR) and the International Association for the Physical Sciences of the Oceans (IAPSO), has adopted the International Thermodynamic Equation Of Seawater - 2010 (TEOS-10) as the official description of seawater and ice properties in marine science. All oceanographers are now urged to use the new TEOS-10 algorithms and variables to report their work.
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- Notable differences of TEOS-10 compared with EOS-80 are:
-
- Absolute Salinity S_A is used to describe the salinity of seawater. S_A incorporates the spatially varying composition of seawater.
- Conservative Temperature to replace potential temperature.
- TEOS-10 thermodynamic quantities are totally consistent with each other.
-
- While Absolute Salinity is the TEOS-10 salinity variable for research purposes and for publications, the salinity that is reported to national databases remain Practical Salinity as determined on the Practical Salinity Scale of 1978.



- Notable differences of TEOS-10 compared with EOS-80 are :
- (1) the use of Absolute Salinity S_A to describe the salinity of seawater; Absolute Salinity takes into account the spatially varying composition of seawater. In the open ocean, the use of this new salinity has a non-trivial effect on the horizontal density gradient, and thereby on the ocean velocities calculated via the “thermal wind” relation.
- (2) the use of Conservative Temperature to replace potential temperature. Both of these temperatures are calculated quantities that result from an artificial thought experiment (namely, adiabatic and isohaline change in pressure to the sea surface). Conservative Temperature has the advantage that it better represents the “heat content” of seawater by two orders of magnitude.
- (3) the TEOS-10 properties of seawater are all derived from a Gibbs function (by mathematical processes such as differentiation) and so are totally consistent with each other (in contrast to the now obsolete EOS-80 approach where separate polynomials were provided for each thermodynamic variable and they were not mutually consistent).
- To enable oceanographers to implement TEOS-10, two software packages are available,
 - (i) the Gibbs SeaWater (GSW) Oceanographic Toolbox (MATLAB and FORTRAN) and,
 - (ii) the Sea-Ice-Air (SIA) (FORTRAN and Visual Basic).
- Both are freely available from www.TEOS-10.org.



Salinity Measure	Definition	value	difference from S_R
S_P (Practical Salinity)	Conductivity with temperature and pressure-dependence removed (PSS78)	34.836	-0.164
S_R (Reference Salinity)	Mass fraction of solute in SSW with the same conductivity as the sample	35.000 g kg ⁻¹	-
S_* (Preformed Salinity)	Mass fraction of solute in SSW of the same chlorinity as the sample ^a	34.993 g kg ⁻¹	-0.007
S_A^{dens} (Density Salinity), also S_A (Absolute Salinity)	Mass fraction of solute in SSW of the same density as the sample	35.020 g kg ⁻¹	+0.020

$$S_R / (\text{g kg}^{-1}) = \frac{35.16504}{35} \times S_P$$

$$S_A = S_R + \delta S_A$$



$$S_R / (\text{g kg}^{-1}) = \frac{35.16504}{35} \times S_P$$

$$S_A = S_R + \delta S_A$$

There are several possible ways to estimate the correction factor δS_A . In order from simplest to most complex:

- (a) One can simply assume, in the absence of other information, that $\delta S_A = 0$.

This approach is probably the appropriate choice when working in coastal regions (that is, on the continental shelf and inshore) and/or in marginal seas, especially shallow seas, that have had no direct anomaly measurements (Red Sea, Mediterranean, perhaps Arctic).

- (b) In the open ocean (Atlantic, Pacific, Indian, Southern Oceans, also Baltic), there exists a global atlas of δS_A . As described by McDougall et al., (2012), existing measurements were extrapolated over the whole basin by using spatially-varying correlations with concentrations of silicic acid ($Si(OH)_4$). This is possible because the actual composition variations arising from biogeochemical processes are themselves correlated.

- (c) If measurements of carbon system parameters (two of DIC , TA , pH , or fCO_2), as well as measurements of silicate and nitrate are available, then δS_A can be estimated from a simple equation, linear in $[TA]$, DIC , $[NO_3^-]$, and $[Si(OH)_4]$. The coefficients of this equation (and the theoretical basis of the numerical model from whose calculations they are derived) are described in Pawlowicz et al., (2011).