

**Subject:** Re: Conversion of specific conductance and calculation of brine volume fraction for NaCl Solution & NaCl Ice

**From:** Soenke Maus <sonke.maus@ntnu.no>

**Date:** 9/19/17, 12:54 AM

**To:** Megan O'Sadnick <megan@tek.norut.no>, Marc Oggier <moggier@alaska.edu>, Christian Petrich <christian@tek.norut.no>, Martina Lan Salomon <martina.salomon@ntnu.no>

Dear all,

I did a calibration of literature data, fitting the residuals of the "simple" CSIRO/Unesco rescaling I suggested earlier. Compared to Christians fit, it is a double fit then, as the CSIRO makes the first job followed by residual fitting. The enclosed Matlab file now contains the polynomials. Results are compared in the enclosed figures to literature data - of which I only fitted the values tabulated by Kaufmann and Vanysek at 25°C. Other data were not included in the fit (also the CRC data that I think Christian had fitted), as they are given with less precision, which is indicated with larger symbols in the figures. One is linear scale just focusing on a narrow regime, one log scale to extend from 0.02 to 200 g/kg salt content.

As you see, the relative deviation has a slight drift, but now remains below 0.3% for the range 0.06-60 g/kg.

Note the m-file is forced to give NAN below a conductivity of 0.06 S/cm at 25°C (about 0.03 g/kg), as in this regime the UNESCO equations are giving increasingly deviating values. Not surprising - they are claimed to be valid between 2 and 40 psu for seawater. However, they apparently perform reasonably well from 0.03 to even 200 g/kg (just 3% error). Closer to infinite dilution, if one once should measure there (we don't at the moment), one would have to design a different formula.

I will use this m-file + CSIRO toolbox in all my computations, as it makes use of temperature and temperature-concentration cross terms that have been derived with extreme precision for seawater. So there is a lot of work behind that one does not need to do. More accurate would of course be to deal with temperature dependence specifically for NaCl only, yet there is little data available. The existing data (20° and 0°C in the figure) are scattered and do not clearly show that one would have to modify. In any case do they indicate that the prediction is valid to +/- 1% relative.

This formula is also easily citable (CSIRO + polynomial) and reproducible by others via the CSIRO toolbox, which is also important, as we are dealing with chemistry

territory we are not extremely familiar with.

Hope this is useful for you

Best,

Sönke

Hi Megan,

thank you for your comment. I was busy the last week yet like to answer before I leave to holidays:

1) Your statement that seawater and aqueous NaCl solutions have "substantially different" atomic weights is not correct. This would indeed be a surprise, considering the dominance of NaCl in seawater. The value 31.4038 g/mol you mention is the "average atomic weight" of ions in seawater. For NaCl the corresponding value is not 58.44 but  $58.44/2 = 29.22$  g/mol and the difference to seawater is thus not that big. It is of the same order as the difference in electric conductivity.

2) What you suggest to compile into a code is a bit incomplete. The reference values that you sent (table of conductances) are valid up to brackish water concentration ( $\sim 0.1$  mol). Your suggestion that these "could be altered based on estimated concentration" means you need the concentration to compute the concentration. In my experience it is not trivial to extrapolate conductance data to compute seawater-like solute content of NaCl. Also, a temperature dependence is lacking in your proposal, and hence you need to measure always at 25 deg C. The values are not at all capable to compute for example salinity from conductivity data near the freezing point to estimate the latter.

3) The approach I use to convert from conductivity to salinity is certainly not exact, but it is easy to use and based on values from textbook data on conductivity of NaCl near standard seawater concentration (Eg. Falckenhagen, Robinson and Stokes, Int. Critical Tables, etc...). Textbook values differ slightly from source to source yet appear to have a relative precision of 0.2% near the salinity of standard seawater (about 35). My original intension was to use this approach to effectively compute the freezing point of seawater-like aqueous NaCl solutions when measuring electric conductivity. So, it is optimized near  $S=35$ . However, as seawater is so strongly dominated by NaCl I think that assuming the same temperature and relative concentration behaviour is not a big problem. I checked some values and found that it still has only an 1.4 % relative error (underestimation) at an NaCl mass fraction of 5 g/kg (sea

attached table). Also 10.161 g/kg (converted from grams per liter) for 18.000 S/cm is given by Hach as Standard: <https://www.hach.com/conductivity-standard-18-000-s-cm-10-246-mg-l-nacl-100-ml>, and here the deviation is 1.5%. As I do not measure ice salinity with more than one digit, I regarded this so far as somehow acceptable.

4) Note that seawater equations in the Csiro toolbox are only valid down to 2 g/kg salinity. Therefore I did another check based on the book "Chemical Oceanography" of Millero+Sohn (my print is from 1992):

Conductance  $G$  at infinite dilution:

$G_{sw} = 127.85 \text{ S/cm/mol}$

$G_{NaCl} = 126.45 \text{ S/cm/mol}$

Atomic mass, kg per mol:

$M_{sw} = 62.8076$

$M_{NaCl} = 58.443$

Then one get  $S/\text{cm}/\text{kg}$  by dividing  $G_{sw}/M_{sw}$  and may get the ratio of per kg conductances of NaCl and seawater

$(G_{NaCl}/M_{NaCl})/(G_{sw}/M_{sw}) = 1.0621$

Note that (your attached Millero file) that a 35 psu seawater solution corresponds to 1.0047 times larger salinity in g/kg (35.165 g/kg).

This gives the number  $1.0621/1.0047 = 1.0571$

This number means that, at infinite dilution, a 35 g/kg NaCl solution would have a 1.0571 larger conductivity than a 35 psu seawater. However, it might be useful to correct this.

Note that this value is close to the factor 1.056 I suggested at 35 psu.

To conclude, the ratio of conductances for seawater and NaCl seems similar at infinite dilution and near 35 psu. However, as mentioned above (file attached, and standards given by Hach), using the toolbox from Csiro approach apparently underestimates the salinity for typical sea ice values of 5 and 15 g/kg by (relative) 1-2 %. It seems that NaCl and seawater behave differently in this regime. But I feel uncertain, from where to get the best standards. Here one probably should do some more calibration work, and modify the Csiro approach.

So far, any further is welcome, would be good if we can agree upon a conversion...

Sönke

Hi Sönke,

Thank you for this feedback. A few comments/questions...

1. The CSIRO seawater equations/toolbox is certainly very helpful when working with seawater however I would actually view its use as more complicated given the number of variables and equations included. Such variables may be estimated for seawater but not for NaCl, simply substituting in  $\text{NaCl}$  will not necessarily compensate for these differences. For instance, the atomic mass of seawater = 31.4038 g/mol (Millero et al., 2008; attached here as maybe Marc and Martina have not seen it? I found it interesting J ) is used which is substantially different than atomic mass of NaCl = 58.44 g/mol . In all honesty however, I am not overly familiar with the Thermodynamic Equations of seawater 2010 used in the CISERO toolbox so, again, I may be misunderstanding and would appreciate a little more explanation if so (and possible...I know it is a bit complicated!).

My argument would be that using the approach I outlined, we can simply be more certain of the calculation and where error is introduced. Either way, think we all agree that the same method should be used throughout all our calculations (NTNU and Norut) so will go along with the group's decision.

2. Thank you for the help on the freezing point as well as brine density. Was looking for something simpler but for some reason was not having much luck. I am fine using these in the final calculation of brine value fraction unless others take issue.

Thanks again!

Cheers,

Megan

**From:** Sönke Maus [<mailto:sonke.maus@ntnu.no>]  
**Sent:** Wednesday, June 21, 2017 5:34 PM  
**To:** Megan O'Sadnick <[megan@tek.norut.no](mailto:megan@tek.norut.no)>; Marc Oggier <[moggier@alaska.edu](mailto:moggier@alaska.edu)>; Christian Petrich <[christian@tek.norut.no](mailto:christian@tek.norut.no)>; Martina Lan Salomon <[martina.salomon@ntnu.no](mailto:martina.salomon@ntnu.no)>  
**Subject:** Re: Conversion of specific conductance and calculation of brine volume fraction for NaCl Solution & NaCl Ice

Hi,

thanks Megan for your effort. In my opinion this looks more complicated as it should be. My approach is:

1. To use the CSIRO seawater toolbox with an additional m-file `swnacl_c3515.m`, which is essentially the conductivity of aqueous NaCl solution at  $S_{\text{NaCl}} = 35 \text{ g/kg}$  and  $T = 15^\circ\text{C}$  (45.317 mS/cm).

In the enclosed csiro toolbox you find this file as well as `nacl_sw_con2sal.m`

which gives you, upon input of conductivity and temperature:

1.  $S$  in psu for seawater (original computation)
2.  $S$  in g/kg solution for NaCl solution

Check values:

$\text{Cond} = 30.0$

$T = -2.0$

$P = 0$

-->  $S_w = 38.7880$ ,  $S_{\text{NaCl}} = 36.5213$

The advantage of this approach is that you retain all nonlinear terms from seawater equations, temperature dependence etc, as derived to high accuracy for seawater. You only change the reference value at 35 g/kg and  $15^\circ\text{C}$ . There are certainly some errors related to that you ignore the other seawater ions, but I think it is of minor relevance, as these ions will have a similar temperature and concentration dependence.

2. Regarding the freezing point of NaCl I have done some effort 10 years ago - you can have a look on p-339 ff in:

[http://sea-ice.no/publications/dr/Maus\\_seaice\\_phd.pdf](http://sea-ice.no/publications/dr/Maus_seaice_phd.pdf)

Summarised: Freezing point as you propose based on *cryoscopic* constant ('cryosperic' is something different) is only valid for dilute solutions, otherwise there are ion interactions (not every ion then suppresses the freezing point ideally, as the ions share the water molecules...) etc. For 30

ppt one needs to use empirical data or advanced thermodynamic models to estimate the freezing point. The enclosed `nacl_sbrine.m` is a fit to data from R. Cohen-Adad and J. W. Lorimer (1991). Alkali Metal and Ammonium Chlorides in Water and Heavy Water (Binary Systems), Volume 47, 1st Edition. eBook ISBN: 9781483285573  
I checked other freezing point datasets, and found this is the best one I know.

3. Finally, for brine volume  $v_b(T, S_i)$ , same equation as you give:

$v_b = 1 / (1 + (S_b / S_i - 1) \cdot \rho_{hob} / \rho_{hof})$ ;

with

- $S_i$  bulk ice salinity: measured
- $S_b$  brine salinity (attached `nacl_sbrine_f.m`)
- $\rho_{hof}$  pure ice density:  $916.7 \cdot (1 - 0.00014 \cdot T)$
- $\rho_{hob}$  NaCl brine density:  $999.843 + 0.764 \cdot S_b + 1.43 \cdot 10^{-4} S_b^2 + 6.82 \cdot 10^{-7} S_b^3$

The equation for brine density is also from my thesis and based on sources described therein.

For  $\rho_{hob}$  a simpler approximation  $\rho_{hob} = 999.843 \cdot (1 + 0.802 \cdot 10^{-3} \cdot S_b)$  suffices, if you are confident with a uncertainty of 0.0002 in the brine volume. If you use  $1000 + 0.8 \cdot 10^{-3} \cdot S_b$  as known from most literature you also end up with 0.0002 uncertainty in brine volume. This is good enough for most purposes - I did the more precise estimates at that time to figure out possible error sources.

Hope this helps  
Cheers  
Sönke

Hi there,

As noted in the meeting at the beginning of the month, Chris and I have spent some time developing a method to convert our measurements of specific conductance to bulk salinity and

subsequently brine volume fraction. The documents attached here include a step-by-step guide ('SpecCond\_Salinity\_BVF', perhaps too many steps!) as well as the two tables, originally from the CRC Handbook of Chemistry, referred to in the summary ('ConcProp\_AqSol', 'EqCond\_AqSol'). I have not written a code yet to accompany this method- Marc, I believe you mentioned you might want to take this on?

Please let me know if you have any thoughts or questions.

Happy Solstice!

Cheers,

Megan

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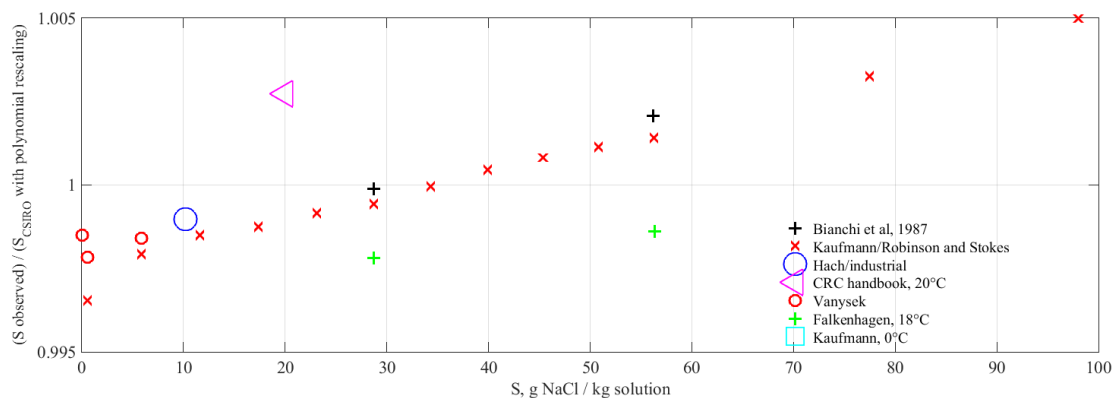
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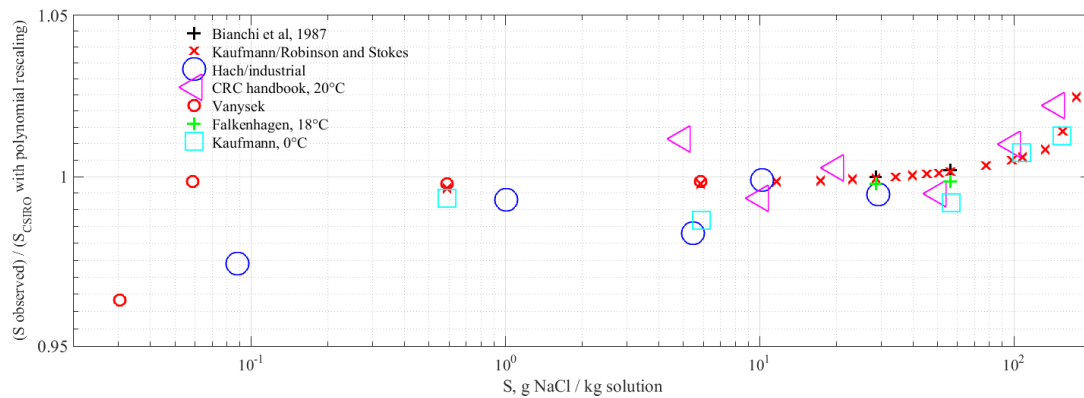
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—NaCl\_S\_Csiro\_kali\_lin.png—





—NaCl\_S\_Csiro\_kali\_log.png—



—sw\_nacl\_con2sal\_cal.m—

```

function [Sw, Snacl] = sw_nacl_con2sal_cal(con,T,P)
cndrsw=con/sw_c3515;

trat=sw_salrt(T)./sw_salrt(25);
con25=con./trat;
% polynom p1 valid below 1.2 mS/cm at 25 °C (S~0.6)
p1=[-1.247514714105395    1.888558315644160    0.476651642658910];
% polynom p2 valid below above 1.2 mS/cm at 35 (S~0.6)
p2=[0.000014549965652   -0.000441051717178    0.004858369979778   -0.028387627621333
1.080106358899861];
%p2=[0.000000444674765   -0.000000328079146   -0.000258730864556    0.003866314378343
-0.026120134008223  1.078558989088485];

crat1=polyval(p1,con25.^5);
crat2=polyval(p2,con25.^5);

crat=crat2;
crat(con25 < 0.6)=crat1(con25 < 0.6);
crat(con25 < 0.06)=nan;

cndrna=con.*crat./swnacl_c3515;
%1.0560 higher conductivity is assumed for NaCl (g/kg) compared to seawater
%(psu)
% Hence at 35 psu, 15°C: 1.056 = NACL_C3515/SW_C3515
% uses otherwise all csiro seawater toolbox functions as input

% Note this translates conductivity at certain temperature and pressure
% to psu for seawater yet to g/kg of an NaCl solution;

% SW_SALT    Salinity from cndr, T, P
%=====
% SW_SALT $Revision: 1.3 $ $Date: 1994/10/10 05:49:53 $
%          Copyright (C) CSIRO, Phil Morgan 1993.
%
% USAGE: S = sw_salt(cndr,T,P)
%
```

```
% DESCRIPTION:
%   Calculates Salinity from conductivity ratio. UNESCO 1983 polynomial.
%
% INPUT:
%   cndr = Conductivity ratio      R = C(S,T,P)/C(35,15,0) [no units]
%   T    = temperature [degree C (ITS-68)]
%   P    = pressure      [db]
%
% OUTPUT:
%   S    = salinity      [psu      (PSS-78)]
%
% AUTHOR:  Phil Morgan 93-04-17  (morgan@ml.csiro.au)
%
% DISCLAIMER:
%   This software is provided "as is" without warranty of any kind.
%   See the file sw_copy.m for conditions of use and licence.
%
% REFERENCES:
%   Fofonoff, P. and Millard, R.C. Jr
%   Unesco 1983. Algorithms for computation of fundamental properties of
%   seawater, 1983. _Unesco Tech. Pap. in Mar. Sci._, No. 44, 53 pp.
%=====

% CALLER: general purpose
% CALLEE: sw_sals.m sw_salrt.m sw_salrp.m

%-----
% CHECK INPUTS ARE SAME DIMENSIONS
%-----
[mc,nc] = size(cndrsw);
[mt,nt] = size(T);
[mp,np] = size(P);

if ~(mc==mt | mc==mp | nc==nt | nc==np)
    error('sw_salt.m: cndr,T,P must all have the same dimensions')
end %if

%-----
% BEGIN
%-----

%R  = cndrsw;
%Rna = cndrna;
%rt = sw_salrt(T);
%Rp  = sw_salrp(R,T,P);
%Rt  = R./(Rp.*rt);
%Sw  = sw_sals(Rt,T);
%Rpna = sw_salrp(Rna,T,P);
%Rtna = Rna./(Rpna.*rt);
%Snac1 = sw_sals(Rtna,T);
R  = cndrsw;
rt = sw_salrt(T);
Rp = sw_salrp(R,T,P);
Rt = R./(Rp.*rt);
```

```
Sw = sw_sals(Rt,T);

Rna = cndrna;
rt = sw_salrt(T);
Rpna = sw_salrp(Rna,T,P);
Rtna = Rna./(Rpna.*rt);
Snacl = sw_sals(Rtna,T);

return
%-----
```

—Attachments:—

NaCl_S_Csiro_kali_lin.png	48.2 KB
NaCl_S_Csiro_kali_log.png	59.6 KB
sw_nacl_con2sal_cal.m	2.8 KB