Review on SolveSAPHE-r2: revisiting and extending the Solver Suite for Alkalinity-pH Equations for usage with CO_2, HCO_3^- or CO_3^{2-} input data by Guy Munhoven

Guy Munhoven has investigated the number of solutions (pH values) of the carbonate system for the pairs Alk_T-CO_2, Alk_T-HCO_3^-, and Alk_T-CO_3^{2-}. Using detailed mathematical analysis he has shown that for reasonable values for the variables in the first two pairs one obtains a unique (one and only) physically sensible solution (positive concentration of all compounds). In contrast, the pair Alk_T-CO_3^{2-} is more of a challenge: (1) Depending on the concentration of CO_3^{2-} three cases have to been discerned; although all three cases have been properly analyzed by Munhoven, the third one (with $\gamma > 0$) is the most relevant (the only relevant in the ocean). (2) For CO_3^{2-} concentrations > 1 μmol kg^{-1} (implying $\gamma > 0$) either two or no physically sensible solution exists.

Based on his detailed mathematical insight, Munhoven has developed algorithms to solve the various equations (in order to be efficient, good bounds and initial values are useful). The algorithms were coded in FORTRAN-90 and extensively tested.

After Munhoven (2013) this is another outstanding contribution by Guy Munhoven. It is clearly written, however, not 'easy reading'. With respect to mathematical analysis, the work can be considered as the capstone (a heavy one!) to the arc of all 15 possible pairs of carbonate system parameters.

I have only one major comment (which is beyond mathematics) and a few minor points.

When calculating pH from alkalinity and carbonate ion concentration in typical seawater (let's say at Alk_T = 2300 μmol kg^{-1} and 100 μmol kg^{-1} $<$ [CO_3^{2-}] $<$ 600 μmol kg^{-1}) one obtains two solutions and the question is 'Which one to take?'. In order to shed some light on this problem I have calculated the concentrations of all carbonate system parameters for a fixed alkalinity (Alk_T = 2300 μmol kg^{-1}) as a function of pH (Fig. 1). For [CO_3^{2-}] = 500 μmol kg^{-1} one obtains two solutions: pH_1 = 8.70 and

pH_2 = 10.75 with quite different DIC values. The higher pH value is discarded because the DIC is 'unrealistically' low and that pH = 8.70 would be the chosen answer. This chioce has been taken, for example, by Zeebe & Wolf-Gladrow (2001, p. 277, 'use the larger one'): they recommend using the real solution with the largest H^+ concentration (lowest pH). Although this choice works out fine in common seawater, it has not been properly justified. And the justification is actually beyond mathematics.

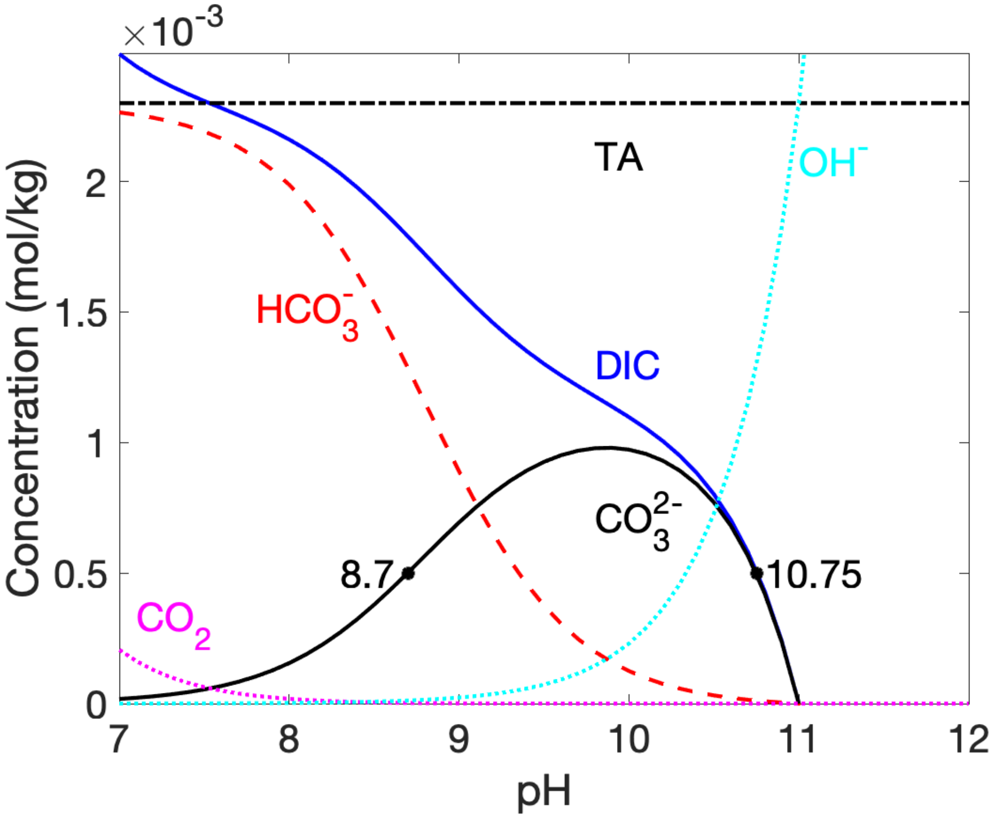

Figure 1: Illustration of varying number of solution for given TA (black dash-dotted line; TA = 2300 μmol kg^{-1} is a typical/characteristic oceanic value)) and carbonate ion concentration, [CO_3^{2-}]. The results are plotted over pH (surface ocean pH ist slightly above 8, lower values can be found in deeper layers, higher values in the surface during algal blooms (up to 9) or in sea ice brines (above 10, however, at different TA values). At pH = 7 most of TA is in the form of bicarbonate whereas [CO_3^{2-}] is relative small. Above pH = pK$_2$ (here = 9.1) the concentration of CO_3^{2-} is larger than that of HCO_3^- and clearly dominates the contribution to TA. However, with further increasing pH the concentration of OH^- becomes larger and larger and at pH $\approx$ 11 is dominating by far the contribution to TA; this is only possible when the concentrations of bicarbonate and carbonate ions go down. Thus whereas the pair TA-CO_3^{2-} possesses always two solutions at pH $<$ 11 (as an example: for TA = 2300 μmol kg^{-1} and [CO_3^{2-}] = 500 μmol kg^{-1} pH = 8.70 and pH = 10.75 are solutions) there does not exist a solution at pH $>$ 11.

Minor points:

Units of alkalinity: I suggest replacing meq (outdated) by mmol (compare, for example, Dickson et al., 2007, Chapter 5, Table 2)

L50 typo: whoe → whose

L51 's is a factor to convert from that scale to the free scale': it might be useful to mention that the value of s is close to 1

Fig. 1: axes labels (quantities & units) missing, same for color bars; remove titles (numbers); y-axes from 1 to 0 to 3 or from -1 to 3 (???); a bit more explanation/discussion might be in order

L174 typo: eq. (12then → eq. (12) then

L193 $[H^+] \gg$: something missing here

L210 $H_1 < H_{\text{min}}$ and $H_2 > H_{\text{min}}$ might be shortened to $H_1 < H_{\text{min}} < H_2$

L229 'exact knowledge determination' ???

L271 API = ???

L275 'In the course of the development s related to ...' ??? something missing here?

L291 'equation function' ???

Fig. legend: 'two roots The' dot missing after roots

Sup. Mathematical and Technical Details

Typos:

2.3.1 $B(OH_3) \rightarrow B(OH)_3$

2.3.3 $H_3(PO)_4 \rightarrow H_3PO_4$

2.3.4 $H_4(SiO)_4 \rightarrow H_4SiO_4$

MATLAB code for Fig. 1:

```
K1 = 1.1e-6; K2 = 7.8e-10; KW = 2.3e-14; KB = 1.9e-9; % use rounded values
bor = 0;  % contribution by borate ignored
alk = 2300e-6; % (mol/kg) typical sea water value
pHa = 7:0.1:12; L = length(pHa);
for i = 1:L
    pH = pHa(i); h = 10^(-pH);
    % Zeebe & Wolf-Gladrow (2001):
s = (alk-KW./h+h-KB*bor./(KB+h)) / (K1./h+2.*K1*K2./h./h); % [CO2]
dic = s*(1.+K1/h+K1*K2./h./h);
hco3 = dic./(1+h./K1+K2./h);
co3 = dic./(1+h/K2+h*h/K1/K2);
CO2(i) = s; HCO3(i) = hco3; CO3(i) = co3; DIC(i) = dic;
Hp(i) = h; OH(i) = KW/h;
end
% 2 solutions for a single CO3: example
CO3ex = 500e-6;
% ------------ CO3 and ALK given ------------------
co3 = CO3ex;
p5  = -co3/K2+1.;
p4  = alk - co3*(K1/K2+(KB+2.*K2)/K2) + KB + K1;
p3  = alk*(KB+K1)-co3*(K1+K1*(KB+2.*K2)/K2+2.*KB) ...
    + (-KB*bor-KW+K1*KB+K1*K2);
p2  = alk*(KB*K1+K1*K2)-co3*(K1*(KB+2.*K2)+2.*KB*K1) ...
    + (-KW*KB-K1*KB*bor-K1*KW+K1*K2*KB);
p1  = alk*KB*K1*K2-co3*2.*KB*K1*K2-K1*KW*KB ...
    + (-K1*K2*KB*bor-K1*K2*KW);
p0  = -K1*K2*KW*KB;
p   = [p5 p4 p3 p2 p1 p0];
r   = roots(p);
% 2 real solutions?
isol = 0;
for j = 1:5
   if (real(r(j)) > 0) \&\& (imag(r(j)) == 0)
    isol = isol+1; pHsol(isol) = round(-log10(r(j)),2)
   end
end
```

```
xp = [min(pHa) max(pHa)]; yp = [alk alk];
plot(pHa,DIC,'b',xp,yp,'k-.',pHa,HCO3,'r--',pHa,CO3,'k', ...
    pHa,CO2,'m:',pHa,OH,'c:', ...
    pHsol(1),CO3ex,'k*',pHsol(2),CO3ex,'k*','LineWidth',2)
text(9.8,2100e-6,'TA','Color','black','Fontsize',fs)
text(9.8,1300e-6,'DIC','Color','blue','Fontsize',fs)
text(9.8,700e-6,'CO_3^{2-}','Color','black','Fontsize',fs)
text(7.8,1500e-6,'HCO_3^-','Color','red','Fontsize',fs)
text(7.1,300e-6,'CO_2','Color','magenta','Fontsize',fs)
text(11,2100e-6,'OH^-','Color','cyan','Fontsize',fs)
text(8.3,500e-6,[num2str(pHsol(1))],'Color','black','Fontsize',fs)
text(10.8,500e-6,[num2str(pHsol(2))],'Color','black','Fontsize',fs)
axis([min(pHa) max(pHa) 0 max(DIC)])
xlabel('pH','Fontsize',fs)
ylabel('Concentration (mol/kg)','Fontsize',fs)
set(gca,'Fontsize',fs)
% print('-dpng','MunhovenTAoverpH.png')
```

References

[1] Dickson, A.G., C.L. Sabine, and J.R. Christian. *Guide to best practices for ocean* CO_2 *measurements*. North Pacific Marine Science Organization, 2007.

[2] Munhoven, Guy. Mathematics of the total alkalinity – pH equation – pathway to robust and universal solution algorithms: the SolveSAPHE package v1. 0.1. *Geoscientific Model Development*, 6(4):1367–1388, 2013.

[3] Zeebe, R.E. and D. Wolf-Gladrow. CO_2 in Seawater: Equilibrium, Kinetics, Isotopes: Equilibrium, Kinetics, Isotopes. 346 pp, Elsevier, 2001.