

Aquatic Chemistry Exercises 13-22

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Exercise 13

Previous exercises have examined the carbonate system in ideal waters. However natural waters contain other ions and compounds that interact with the carbonate system, thus changing it's characteristics and responses to environmental changes. The ability to model natural waters requires a thorough understanding of these interactions. Carbonate salts are commonly geologically occurring and are a good example of solutes that interact with the carbonate systems already examined, affecting water pH. Application of carbonate salts to natural waters, in the form of $CaCO_3$, is also of great importance to the efforts to counteract the negative effects of acid rain. Performing such pollution mitigation efforts requires robust modelling of the effects and thus a good understanding of how solutes affect water systems. The aim of this exercise is to model the affect of Sodium bicarbonate, $NaHCO_3$, on water pH.

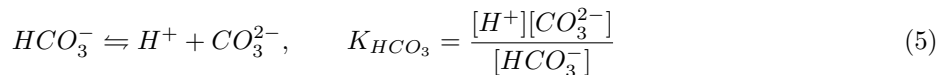
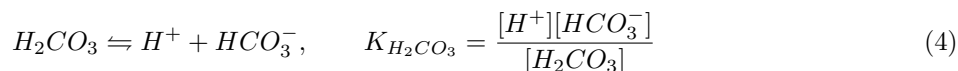
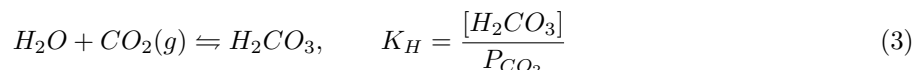
When dissolved in water $NaHCO_3$ disassociates according to (1).



This changes the charge balance which now becomes:

$$0 = [H^+] + [Na^+] - [OH^-] - [HCO_3^-] - 2 \cdot [CO_3^{2-}] \quad (2)$$

Given the following equilibrium equations describing the carbonate system:



Substituting in (3)-(6) to the charge balance and simplifying yields

$$0 = [H^+] + [Na^+] - \frac{K_W}{[H^+]} - \frac{K_{H_2CO_3} \cdot K_H \cdot P_{CO_2}}{[H^+]} - 2 \cdot \frac{K_{H_2CO_3} \cdot K_{HCO_3} \cdot K_H \cdot P_{CO_2}}{[H^+]^2} \quad (7)$$

Which when written in the form of a polynomial takes the form of

$$0 = [H^+]^3 + [Na^+][H^+]^2 - [H^+](K_W + K_{H_2CO_3} \cdot K_H \cdot P_{CO_2}) - 2 \cdot K_{HCO_3} \cdot K_{HCO_3} \cdot K_H \cdot P_{CO_2} \quad (8)$$

The pH can then be calculated by solving the polynomial equation above for $[H^+]$ using the `roots` function in matlab.

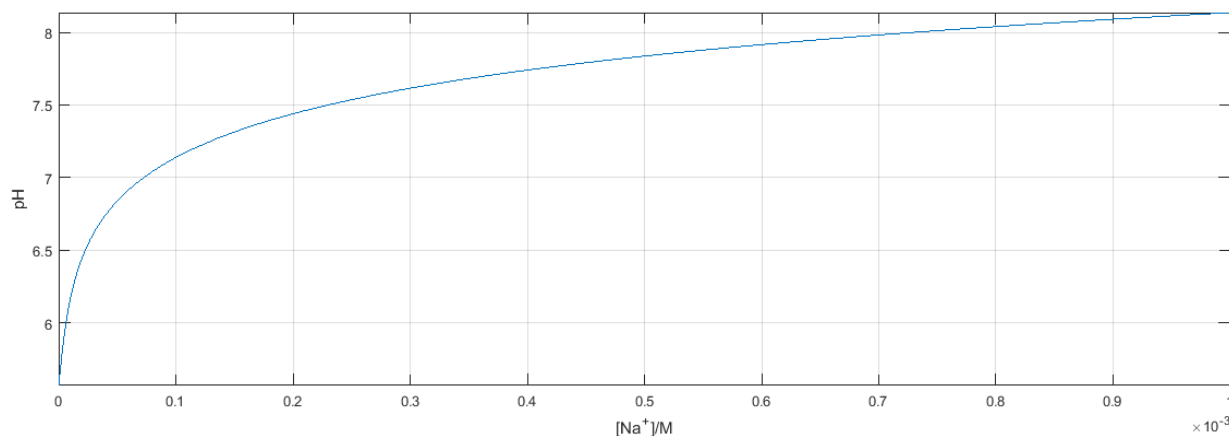


Figure 1: Figure showing how the pH of an ideal water system in equilibrium with the atmosphere ($P_{CO_2} = 400 \cdot 10^{-6}$ atm) varies with $[Na^+]$.

Figure 1 was generated using matlab and the function `phna.m` and the script `e13.m` (see below). It shows the pH increasing with the addition of Na^+ ions.

The results of this modelling exercise appear to be reasonable and correspond to what would be expected given the charge balance equation (7). The results also show why addition of carbonate salts can be an effective measure to increase the pH in acidified natural water systems.

File: `phna.m`

```
function phres=phna(na)
% Constants at 10 degC
kw = 10^(-14.540);
kh2co3 = 10^(-6.482);
khco3 = 10^(-10.471);
kh = 10^(-1.260);
pco2 = 4*10^-4; % atm

a(1) = 1 ; a(2) = na ; a(3) = -(kw + kh2co3 * kh * pco2) ; a(4) = -2 * kh2co3 * khco3 * kh * pco2;

X = roots([a]);
x = max(X(find(imag(X) == 0))); % conc. h+
phres = -log10(x);
end
```

File: e13.m

```
fplot(@phna, [0 10-3])  
xlabel(' [Na+]/M')  
ylabel('pH')  
grid on
```

Exercise 14

Different natural water systems will have different buffering properties based on their composition and environment (P_{CO_2}). One way of observing the buffering properties of a water system is to perform an acid-base titration and produce a titration curve. The titration curve can also be used to determine how much acid or base is required to change the pH of a water system to a specific value. This is valuable eg. when determining the amount of $CaCO_3$ to add to a lake to counteract anthropogenic acidification. This exercise aims model an acid-base titration in an ideal water system and explain the change in buffering capacity observed at higher P_{CO_2} .

As explored in Exercise 13 the charge balance when adding Na^+ ions in the form of $NaHCO_3$ becomes as follows:

$$0 = [H^+] + [Na^+] - [OH^-] - [HCO_3^-] - 2 \cdot [CO_3^{2-}] \quad (9)$$

Here it can be seen that the same charge balance holds true if Na^+ ions are added in the form of $NaOH$. It can further be seen that if, after the addition of Na^+ ions, Cl^- ions are added in the form of HCl the charge balance will become:

$$0 = [H^+] + [Na^+] - [Cl^-] - [OH^-] - [HCO_3^-] - 2 \cdot [CO_3^{2-}] \quad (10)$$

Substituting in (3) - (6) and rewriting in its polynomial form it becomes:

$$0 = [H^+]^3 + [Na^+][H^+]^2 - [Cl^-][H^+]^2 - [H^+](K_W + K_{H_2CO_3} \cdot K_H \cdot P_{CO_2}) - 2 \cdot K_{HCO_3} \cdot K_{HCO_3} \cdot K_H \cdot P_{CO_2} \quad (11)$$

From (10) it can be seen that from a calculation standpoint addition of Cl^- ions can be viewed as a subtraction of Na^+ ions.

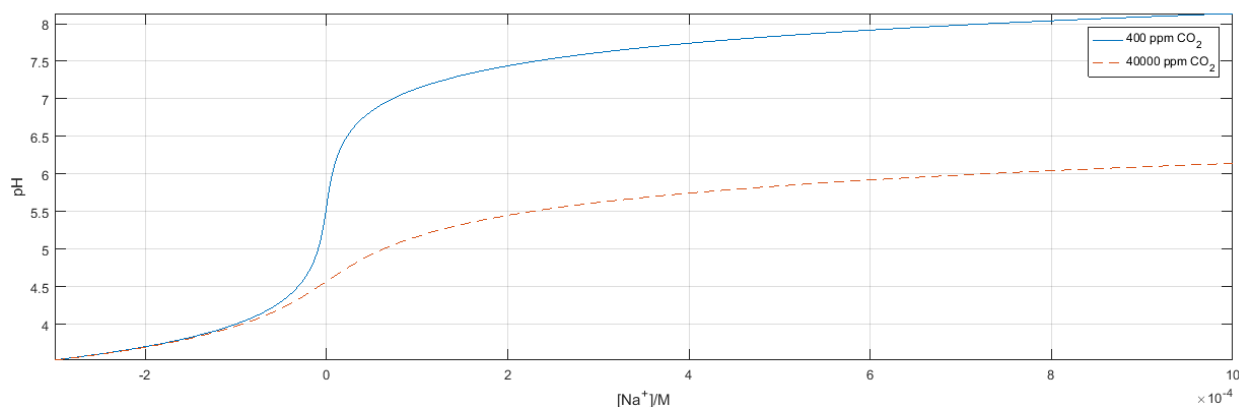


Figure 2: Figure showing a modelled titration curve of Cl^- (depicted as negative concentrations of Na^+) and Na^+ added to an ideal water system at partial pressures of CO_2 of $4 \cdot 10^{-4}$ and $4 \cdot 10^{-2}$ atm.

Figure 2 was generated using matlab and the function `phna.m` described in Exercise 13 (see above) as well as the function `phna2.m`, identical to `phna.m` apart from having a different constant set for P_{CO_2} (see

below), and the script `e14.m` (see below). The calculations treat concentrations of Cl^- ions as negative concentrations of Na^+ ions and calculates the pH by solving the polynomial charge balance (8) for $[H^+]$ using matlabs `roots` function.

As can be seen from Figure 2 the water system in an environment with a P_{CO_2} of $4 \cdot 10^{-2}$ atm has a much larger ability to buffer the addition of a base. This is most prominent when the pH is above 4. The increased base-buffering capacity is consistent with that increased P_{CO_2} leads to increased $[H_2CO_3]$ which will then deprotonate to $[HCO_3^-]$ and $[CO_3^{2-}]$ - leading to an increase in $[H^+]$ and thus a lower pH.

File: phna2.m

```
function phres=phna2(na)
    % Constants at 10 degC
    kw = 10^(-14.540);
    kh2co3 = 10^(-6.482);
    khco3 = 10^(-10.471);
    kh = 10^(-1.260);
    pco2 = 4*10^-2; % atm

    a(1) = 1 ; a(2) = na ; a(3) = -(kw + kh2co3 * kh * pco2) ; a(4) = -2 * kh2co3 * khco3 * kh * pco2;

    X = roots([a]);
    x = max(X(find(imag(X) == 0))); % conc. h+
    phres = -log10(x);
end
```

File: e14.m

```
fplot(@phna, [-3*10^-4 10^-3])
xlabel(' [Na^+]/M')
ylabel('pH')
grid on
hold on
fplot(@phna2, [-3*10^-4 10^-3], '--')
legend('400 ppm CO_2', '40000 ppm CO_2')
```

Exercise 15

A useful application of the water pH models that have been developed in earlier exercises is calculating the amount of an acid or base to add to a water system to change the pH from a known value to a desired value. This is highly relevant for example when adding $CaCO_3$ to lakes to counteract anthropogenic acidification. This exercise aims to calculate the amount of HCl , H_2SO_4 and $NaOH$ that are required to adjust the pH of a known quantity of an ideal water system by a specified amount.

Assuming the same water system as has been examined in Exercise 14, an expression for the $[Na^+]$ as a function of $[H^+]$ can be constructed from the charge balance (2):

$$[Na^+] = [H^+] - [OH^-] - [HCO_3^-] - 2 \cdot [CO_3^{2-}] \quad (12)$$

Substituting in (3)-(6) to the charge balance and simplifying yields

$$[Na^+] = 10^{-pH} - \frac{K_W}{10^{-pH}} - \frac{K_{H_2CO_3} \cdot K_H \cdot P_{CO_2}}{10^{-pH}} - 2 \cdot \frac{K_{H_2CO_3} \cdot K_{HCO_3} \cdot K_H \cdot P_{CO_2}}{(10^{-pH})^2} \quad (13)$$

This model works with $[Na^+]$ as the ion coming from the base $NaOH$. As was examined in Exercise 14, $[Na^+]$ is calculationally equivalent to $-[Cl^-]$ when dealing with the acid HCl . H_2SO_4 is a diprotic acid, however as can be seen from the charge balance it can calculationally be considered equivalent to $-3[Na^+]$:

$$0 = [H^+] - [OH^-] - [HSO_4^-] - 2 \cdot [SO_4^{2-}] - [HCO_3^-] - 2 \cdot [CO_3^{2-}] \quad (14)$$

The difference in $[Na^+]$ between two solutions at different pH, $\Delta[Na^+]$, can be found by taking the difference of (13) calculated at each pH.

Given the total volume of the solution (assumed here to be constant), V_w , the number of moles necessary to bring about such a change in pH, n , can be calculated as $n = \Delta[Na^+] \cdot V_w$. Given the molarity M of an acid/base and the factor f being the number of $[Na^+]$ equivalents, the volume of acid/base required to achieve the desired change in pH, V , can be calculated as $V = \frac{n}{M} \cdot \frac{1}{f}$.

One central assumption in these calculations is that the volume will remain constant as the acid/base is added. For small additions this would appear to be a reasonable assumption. However the assumption can also be checked by viewing the process of addition as two steps. The first step being an addition of the acid/base with no increase in volume and the second being an increase in volume of pure water which changes $[H^+]$ and thus the pH. If the initial volume is denoted V_1 , the final volume V_2 , the $[H^+]$ after addition of volume-less acid/base is $[H^+]_1$, the $[H^+]$ after the pure water volume addition $[H^+]_2$ and the corresponding pHs pH_1 and pH_2 then the error in pH can be calculated as follows:

$$pH \text{ error} = -\log\left(\frac{[H^+]_1 \cdot V_1}{V_2}\right) - pH_1 \quad (15)$$

These calculations were performed using matlab and the function `nafunc.m` and the script `e15.m`. The conditions, calculated results and calculated error due to the assumption of constant volume can be seen in Table 1.

The error in pH due to the assumption of constant volume is insignificant for all of the conditions and the assumption is therefore considered valid. The calculated volume of acid/base to add appear to be reasonable given the small initial volumes.

Table 1: Table modeled conditions, calculated volume needed to affect the desired change in pH and the calculated error in pH due to assumption of constant volume.

| | Condition 1 | Condition 2 | Condition 3 |
|---------------------------|---------------------|------------------------------------|---------------------|
| Acid/base | <i>HCl</i> | <i>H₂SO₄</i> | <i>NaOH</i> |
| Initial volume /L | 0.1 | 0.1 | 0.3 |
| Initial pH | 8.0 | 6.0 | 4.5 |
| Final pH | 6.0 | 4.0 | 7.5 |
| Volume acid/base added /L | $7.2 \cdot 10^{-3}$ | $3.5 \cdot 10^{-4}$ | $3.9 \cdot 10^{-3}$ |
| pH error | 0.0303 | 0.0015 | 0.0056 |

File: nafunc.m

```
function naconc=nafunc(ph)
    kw = 10^(-14.540);
    kh2co3 = 10^(-6.482);
    khco3 = 10^(-10.471);
    kh = 10^(-1.260);
    pco2 = 4*10^-4; % atm
    hconc = 10^(-ph);
    naconc = ((kw+(kh2co3*kh*pco2))/hconc) + ((2*kh2co3*khco3*kh*pco2)/hconc^2) - hconc;
end
```

File: e15.m

```
% volume hcl added:
deltahcl = nafunc(8) - nafunc(6); % difference in concentration of hcl between pH 8 and 6
nhcl = deltahcl / 10; % amount of hcl in moles (assuming total volume constant)
Mhcl = 0.01; % molarity of hcl solution
volhcl = nhcl/Mhcl; % volume of hcl needed to change pH from 8 to 6 in L
totVolHcl = volhcl + 0.1; % total volume (not assuming constant volume)
hconcHcl = 10^(-6); % H+ concentration assuming constant volume
hconc2Hcl = (hconcHcl * 0.1) / totVolHcl; % H+ concentration not assuming constant volume
ph2Hcl = -log10(hconc2Hcl); % pH not assuming constant volume
pherrorHcl = ph2Hcl - 6; % difference in pH due to assuming constant volume

% volume h2so4 added:
deltah2so4=nafunc(6) - nafunc(4); % difference in concentration of h2so4 between pH 6 and 4
nh2so4 = deltah2so4/10; % amount of h2so4 in moles (assuming total volume constant)
Mh2so4 = 0.01; % molarity of h2so4 solution
volh2so4 = ((nh2so4 / Mh2so4)/3) % volume of h2so4 needed to change pH from 6 to 4 in L
totVolh2so4 = 0.1 + volh2so4;
hconch2so4 = 10^(-4);
hconc2h2so4 = (hconch2so4 * 0.1) / totVolh2so4;
ph2h2so4 = -log10(hconc2h2so4);
pherrorh2so4 = ph2h2so4 - 4;

% volume of naoh added to raise ph from 4.5 to 7.5
deltanaoh = nafunc(7.5) - nafunc(4.5);
nnaoh = (deltanaoh / 10) * 3;
Mnaoh = 0.02;
volnaoh = nnaoh / Mnaoh
totVolnaoh = volnaoh + 0.3;
```

```
hconcnaoh = 10^(-7.5);  
hconc2naoh = (hconcnaoh * 0.3) / totVolnaoh;  
ph2naoh = -log10(hconc2naoh);  
pherrornaoh = ph2naoh - 7.5;
```


Exercise 16

Alkalinity is a term used to describe the buffering capacity of water and is defined as the sum of equivalence sum of all bases that can be titrated with a strong acid. Alkalinity is an important measure used in environmental monitoring and water treatment as it contains much information about how the water will react to environmental changes and treatment measures. This exercise aims to calculate the Gran-alkalinity of two natural waters from Zimbabwe using Gran-titration data.

Gran-titration is an exact method for determining the alkalinity of water. It is based on measuring how the pH of a water sample changes as it is titrated with an acid of known concentration. The resulting data can then be analysed to determine how many moles of acid is required to exhaust the buffering basic anions in the water sample, measured as the added amount of acid at which the pH starts to increase linearly with additional added acid.

The first step in calculating the Gran-alkalinity is to calculate the Gran function. It is defined as

$$\begin{cases} \text{y-axis} = (V + V_0) \cdot 10^{-\text{pH}} \\ \text{x-axis} = \frac{C_a \cdot V}{V_0} \end{cases} \quad (16)$$

Where V is the volume of added acid, V_0 is the volume of the water sample and C_a is the concentration of the titration acid. Analysing the units yields that the y-axis shows the number of moles of $[H^+]$ in the solution and the x-axis is the number of moles of added acid per volume original sample. Graphing the Gran-function will yield an initial horizontal part in which all the added H^+ are buffered and a linear part in which all H^+ contributes to decreasing pH. Between these two parts is transition region. Performing linear regression on the linear part of the Gran-function and extrapolating the x-intercept yields the theoretical value at which all buffering anions are exhausted - which is the Gran-alkalinity.

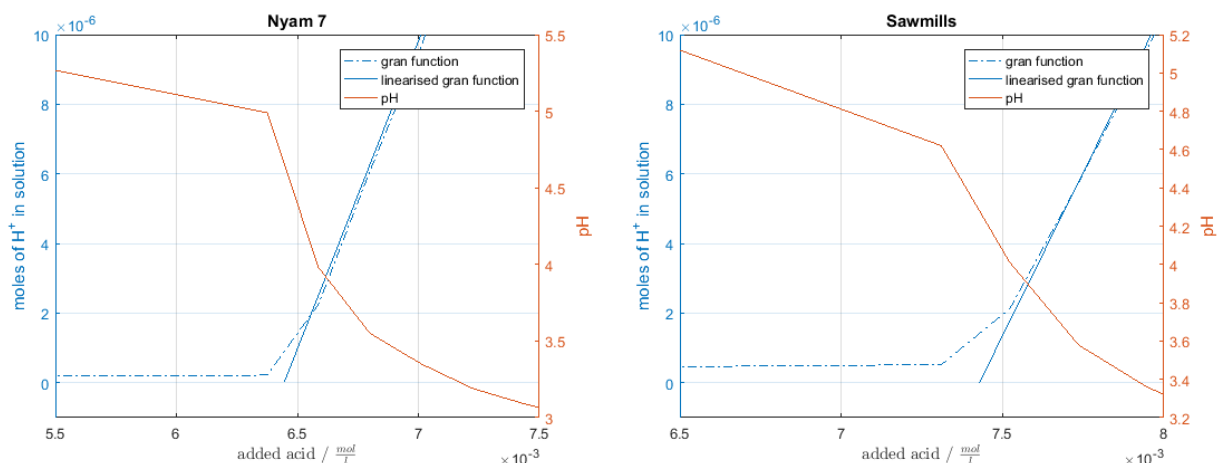


Figure 3: Figure showing the Gran-function and linearised and extrapolated Gran-function as well as the pH for two natural waters in Zimbabwe.

This exercise calculated the Gran-alkalinity of two natural waters, Nyam 7 and Sawmills, in Zimbabwe based of titration data by David Wallin and Lars Aspelin (1999), see Table . The calculations were performed

Table 2: Table showing titration data for two the Nyam 7 and Sawmills natural waters in Zimbabwe. Data by David Wallin and Lars Aspelin, 1999

| Point # | <i>Nyam 7</i> | | <i>Sawmills</i> | |
|---------|-----------------|-----------|-----------------|-----------|
| | Added acid / ml | Sample pH | Added acid / ml | Sample pH |
| 1 | 0 | 7.01 | 0 | 9.12 |
| 2 | 1.50 | 4.99 | 1.72 | 4.62 |
| 3 | 1.55 | 3.98 | 1.77 | 4.01 |
| 4 | 1.60 | 3.55 | 1.82 | 3.58 |
| 5 | 1.65 | 3.35 | 1.87 | 3.36 |
| 6 | 1.70 | 3.19 | 1.92 | 3.2 |
| 7 | 1.75 | 3.09 | 1.97 | 3.09 |
| 8 | 1.80 | 3.01 | 2.02 | 3.01 |
| 9 | 1.85 | 2.94 | 2.07 | 2.93 |
| 10 | 1.90 | 2.88 | 2.12 | 2.87 |
| 11 | 1.95 | 2.82 | 2.17 | 2.82 |
| 12 | 2.00 | 2.78 | 2.22 | 2.77 |
| 13 | 2.05 | 2.75 | 2.27 | 2.73 |

in matlab using the script e16.m (see below). The Gran-alkalinity was performed based on linear regression analysis of points #4-13 for both samples.

The Gran-alkalinity of Nyam 7 was calculated to $6.4 \cdot 10^{-3} \frac{\text{eq}}{\text{l}}$ and for Sawmills to $7.4 \cdot 10^{-3} \frac{\text{eq}}{\text{l}}$. The full Gran-functions for the two waters as well as the extrapolated linear regression lines can be seen in Figure 3.

Hard water is defined as water having a $[Ca^{2+}] + [Mg^{2+}]$ of 3500 - 7000 $\mu\text{eq} / \text{l}$ and very hard as having a combined concentration grater than 7000 $\mu\text{eq}/\text{l}$. The samples examined in this exercise have a Gran-alkalinity of 6400 and 7400 $\mu\text{eq}/\text{l}$ respectively. If we assume that $[HCO_3^-] \gg [H^+], [OH^-], [CO_3^{2-}]$, which is reasonable assuming the pHes of 7.01 and 9.12 (see Exercise 4, 5 & 6) and that the samples contain little or no DOC, which is reasonable given that the samples are groundwater, then the charge balance can be approximated as follows:

$$\begin{cases} [HCO_3^-] = 6400, 7400 \mu\text{eq l}^{-1} \\ [HCO_3^-] = \sum \text{eq concentrations of cations} \end{cases} \quad (17)$$

The hardness of the water will depend on the species and concentrations of cations present in the water. However given that Ca^{2+} and Mg^{2+} are frequently among the most abundant cations in groundwater it appears reasonable that their combined equivalent concentration will be grater than 3500 $\mu\text{eq} / \text{l}$ and for the Sawmills sample, possibly grater than 7000 $\mu\text{eq} / \text{l}$ meaning that it likely that the water samples are hard and possibly very hard.

File: e16.m

```
%% added acid in ml and corresponding pH for nyam7 and sawmill
nyam7=[0 7.01
1.50 4.99
1.55 3.98
1.60 3.55
1.65 3.35
1.70 3.19
```

```

1.75 3.09
1.80 3.01
1.85 2.94
1.90 2.88
1.95 2.82
2.00 2.78
2.05 2.75];

sawmills=[0 9.12
1.72 4.62
1.77 4.01
1.82 3.58
1.87 3.36
1.92 3.20
1.97 3.09
2.02 3.01
2.07 2.93
2.12 2.87
2.17 2.82
2.22 2.77
2.27 2.73];

%% Calculate gran alkalinity
v=20;
Mhcl=0.085;

granNyam7(:,1) = (nyam7(:,1).*Mhcl)./v;
granNyam7(:,2) = ((nyam7(:,1)+v)/1000).*10.^(-nyam7(:,2));
granSawmills(:,1) = (sawmills(:,1).*Mhcl)./v;
granSawmills(:,2) = ((sawmills(:,1)+v)/1000).*10.^(-sawmills(:,2));

polyfitNyam7x = polyfit(granNyam7(4:end,2), granNyam7(4:end,1),1);
nyam7granalkalinity = polyfitNyam7x(2)
polyfitNyam7y = polyfit(granNyam7(4:end,1),granNyam7(4:end,2),1);
nyam7px=linspace(nyam7granalkalinity,(nyam7granalkalinity + 2*10^-3));
nyam7py=nyam7px.*polyfitNyam7y(1) + polyfitNyam7y(2);

polyfitSawmillsx = polyfit(granSawmills(4:end,2), granSawmills(4:end,1),1);
sawmillsgranalkalinity = polyfitSawmillsx(2);
polyfitSawmillsy = polyfit(granSawmills(4:end,1), granSawmills(4:end,2),1);
sawmillspx=linspace(sawmillsgranalkalinity, (sawmillsgranalkalinity + 2*10^-3));
sawmillspy=sawmillspx.*polyfitSawmillsy(1) + polyfitSawmillsy(2);

%% Plots
figure(2)
yyaxis left
xlabel('added acid /  $\frac{\text{mol}}{\text{l}}$ ','interpreter','latex')
nyamplot_gran = plot(granNyam7(:,1), granNyam7(:,2), '-.');
ylabel('moles of H+ in solution')
hold on
plot(nyam7px,nyam7py,'-')

```

```

axis([5.5*10^-3 7.5*10^-3 -0.1*10^-5 1*10^-5])
yyaxis right
nyamplot_ph = plot(granNyam7(:,1), nyam7(:,2));
ylabel('pH')
grid on
legend('gran function', 'linearised gran function', 'pH')
title('Nyam 7')

figure(3)
yyaxis left
xlabel('added acid /  $\frac{\text{mol}}{\text{l}}$ ', 'interpreter', 'latex')
sawmillsplot_gran = plot(granSawmills(:,1), granSawmills(:,2), '-.');
ylabel('moles of H+ in solution')
hold on
plot(sawmillspx,sawmillspx,'-')
axis([6.5*10^-3 8*10^-3 -0.1*10^-5 1*10^-5])
yyaxis right
sawmills_ph = plot(granSawmills(:,1), sawmills(:,2));
ylabel('pH')
grid on
legend('gran function', 'linearised gran function', 'pH')
title('Sawmills')

```

Exercise 17

An organic acid dissociation fraction was created for this exercise. It assumes that all organic acids are monoprotic and shows the percentage of the concentration of humic acids dissociated at a specific pH-value. The organic acid dissociation fraction is expressed as $\frac{[R^-]}{[R^-] + [RH]}$ and is created by utilizing equations 7.2 and 7.3 found in the textbook:

$$\frac{[R^-]}{[R^-] + [RH]} = \frac{[R^-]}{7 \cdot 10^{-6} \cdot [DOC]} = \frac{7 \cdot 10^{-6} [DOC]}{7 \cdot 10^{-6} [DOC]} \cdot \frac{K_R}{K_R + [H^+]} = \frac{K_R}{K_R + 10^{-pH}}$$

The rate of dissociation of organic acids, K_R , is dependent on the pH-value of the solution. K_R is also dependent on what type of organic acids that exists in the system. Different organic acids are found in different environments, so K_R may need to be adjusted depending on the location. For purposes of calculation, the value of K_R may sometimes need to be set constant. In fig. 4 we can see the acid dissociation fraction plotted with both a constant and pH-dependent K_R for the interval $4 < pH < 8$.

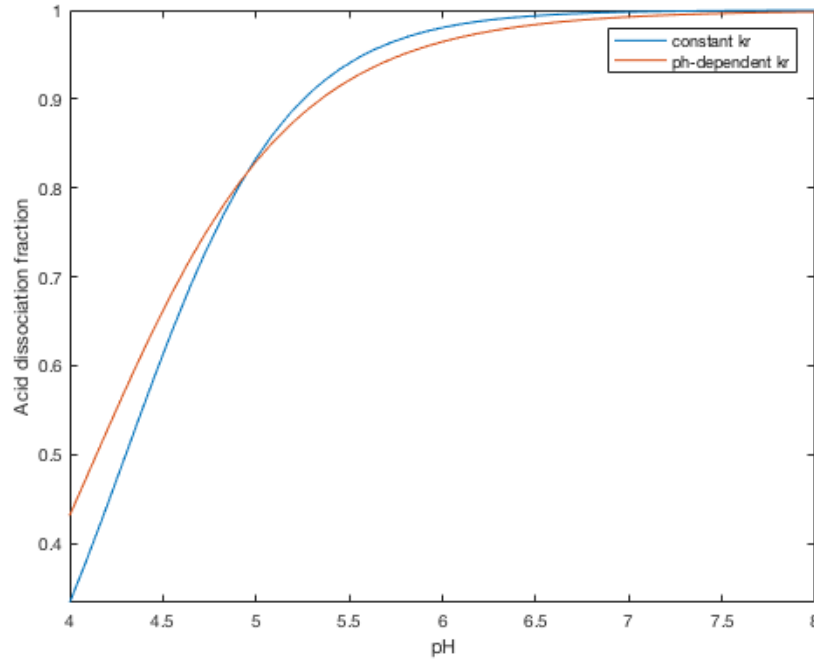


Figure 4: An organic acid dissociation fraction for different pH-values.

For this interval, it depends on what the purpose of analysis is if a constant K_R could be utilised. For example, in a rougher estimation of the concentration of organic acids it may be applied.

For the calculations of the concentration of DOC in Lake Öresjön, a function was set up through the expression of the concentration of organic anions 7.3 in the textbook

$$[R^-] = 7 \cdot 10^{-6} \cdot [DOC] \cdot \frac{K_R}{K_R + [H^+]} \Leftrightarrow [DOC] = \frac{[R^-] \cdot (K_R + [H^+])}{7 \cdot 10^{-6} \cdot K_R}$$

The concentrations of organic anions was hydrogen put into the function. The pH dependent K_R was used. The concentrations were calculated to be

$$[DOC]_{85} = 3.6745 \frac{mg}{L}$$

$$[DOC]_{05} = 5.3668 \frac{mg}{L}$$

This increase of dissolved organic carbon can be explained from the decreased acidity, concentrations of hydrogen going from 20 to 6 $\frac{mg}{L}$ from 85 to 05. The organic humus particles functions as cement for soil particles. This cementation is stronger for lower pH-values, and so when the pH increases the humus particles will let loose from the soil particles and spread in the water, adding to brownification.

File: e17.m

```
%% 2.
fplot(@(ph) adf(ph, 0), [4, 8]);
hold on
fplot(@(ph) adf(ph, 1), [4, 8]);
legend('constant kr', 'ph-dependent kr')

%% 3.
doc85 = doc(-log10(20*10^-6), 19*10^-6, 1) % answers in mg/L
doc05 = doc(-log10(6*10^-6), 33*10^-6, 1)
```

File: doc.m

```
function docres=doc(pH,R, bool)
if bool == 0
    kr=5*10^-5
elseif bool == 1
    kr = 10^-(3.972 - 0.087 * pH + 0.031 * pH^2);
end
docres=R/(7 * 10^-6 * (kr/(kr + 10^-pH)));
end
```

File: adf.m

```
function adfres=adf(pH, bool)
if bool == 0
    kr = 5*10^-5;
elseif bool == 1
    kr = 10^-(3.972 - 0.087 * pH + 0.031 * pH^2);
end
adfres=kr/(kr + 10^-pH);
end
```

Exercise 18

This exercise aims to look at the concentrations of aluminium species in surface water, and how they differ at different pH-values. In order to plot the concentrations on a graph, three functions were created that give the concentrations of the aluminium species $[Al^{3+}]$, $[Al(OH)^{2+}]$ and $[Al(OH)_2^+]$. The origin of these three aluminium species come from the dissolution of the solid $Al(OH)_3$ by H^+ ions. The reactions for the creation of the three aluminium species are found in the compendium. The equilibrium constants used for calculations for these reaction are as follows

$$K_G = \frac{[Al^{3+}]}{[H^+]^3} = 10^{8.5}$$

$$K_{Al(OH)} = \frac{[Al(OH)^{2+}][H^+]}{[Al^{3+}]} = 1 \cdot 10^{-5}$$

$$K_{Al(OH)_2} = \frac{[Al(OH)_2^+][H^+]}{[Al(OH)^{2+}]} = 5 \cdot 10^{-10}$$

These expressions were then rearranged to create functions that calculate the concentrations.

$$\begin{aligned} [Al^{3+}] &= K_G \cdot 10^{-3pH} \\ [Al(OH)^{2+}] &= K_G \cdot K_{Al(OH)} \cdot 10^{-2pH} \\ [Al(OH)_2^+] &= K_G \cdot K_{Al(OH)} \cdot K_{Al(OH)_2} \cdot 10^{-pH} \end{aligned}$$

The concentrations of the different species, as well as the total concentration of species were then plotted for the interval $4 < pH < 7$, seen in fig. 5.

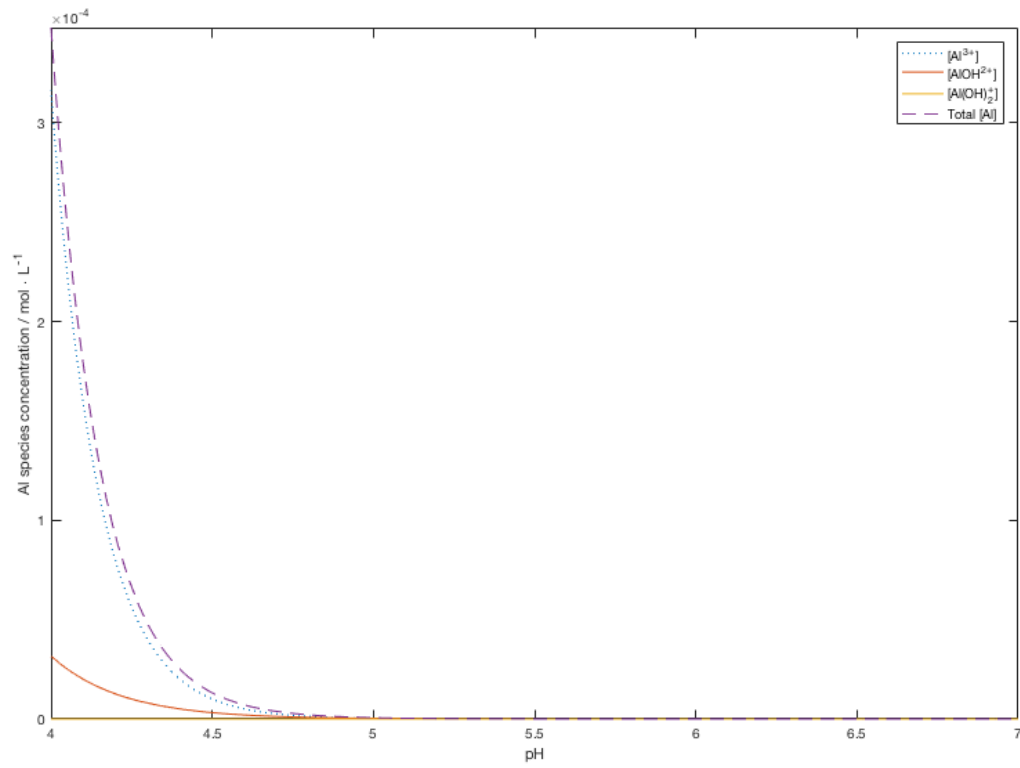


Figure 5: Concentrations of different aluminium species and the total concentration of aluminium species at different pH-values

Fig. 5 shows an exponential growth of the total concentration of aluminum species for pH- values < 5 . The decrease of aluminium species is a consequence of the decreased dissolution of $Al(OH)_3$ with increasing pH. To see more clearly how the concentrations relate to each other a molar fraction diagram (such as in exercise 12) was created, it can be seen in fig. 6.

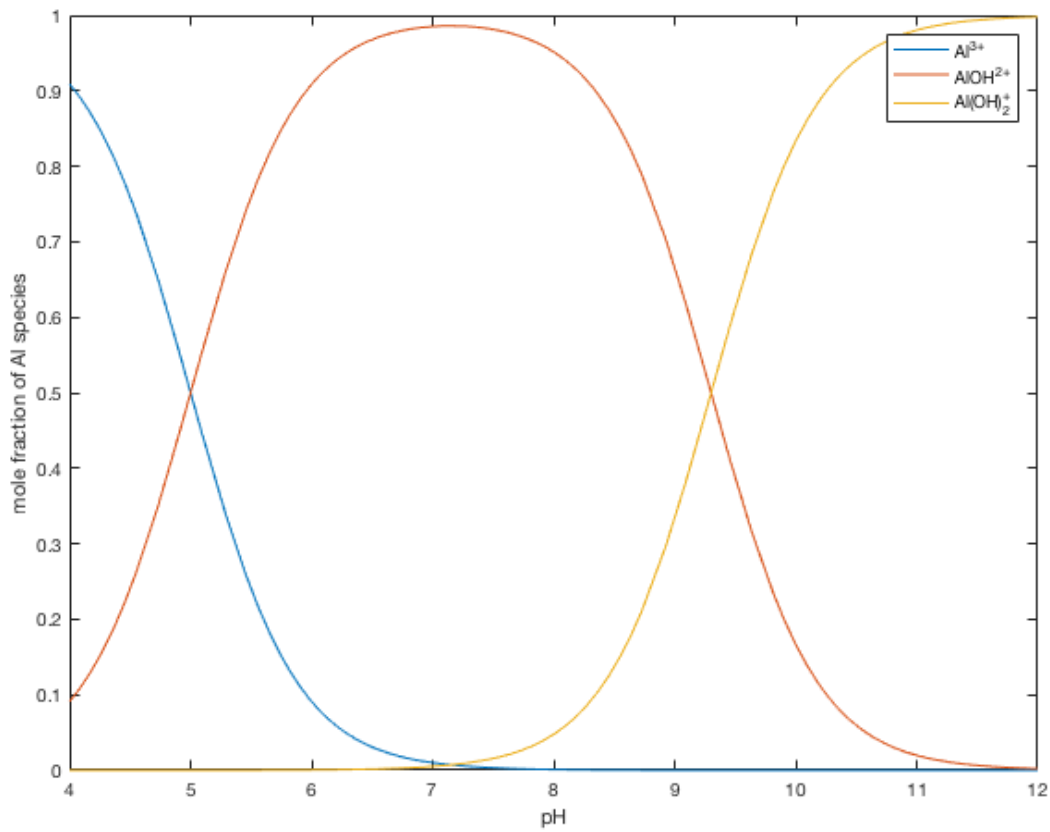


Figure 6: Molar fraction diagram of aluminium species in surface water at different pH-values

Al^{3+} dominates the surface waters at pH-levels below 5, while $Al(OH)^{2+}$ and $Al(OH)_2^+$ dominate at neutral and alkaline conditions, respectively.

Atlantic salmon and perch can stay unaffected below total concentrations of aluminum of $1 \mu mol L^{-1}$ and $10 \mu mol L^{-1}$, respectively. Analysing the graph in fig. 5 we find these concentrations at pH-values 4.9 and 4.55.

File: e18.m

```
%% e18.m
%% 1
figure
fplot(@al3conc, [4 7], ':');
hold on
fplot(@alohconc, [4 7]), '-.';
fplot(@aloh2conc, [4 7]);
fplot(@totalconc, [4 7], '--');
```

```

xlabel('pH');
ylabel('Al species concentration / mol \cdot L^{-1}');
legend('Al^{3+}', 'AlOH^{2+}', 'Al(OH)_2^{+}', 'Total [Al]');

```

```

%% 2
figure
fplot(@molfrac, [4 12]);
xlabel('pH');
ylabel('mole fraction of Al species')
legend('Al^{3+}', 'AlOH^{2+}', 'Al(OH)_2^{+}')
%% 3

```

File: alohconc.m

```

%% alohconc.m
function conc = alohconc(pH)
    kg=10^8.5;
    h=10^-pH;
    kaloh = 10^-5;
    conc = kg*kaloh*h^2;
end

```

File: aloh2conc.m

```

%% aloh2conc.m
function conc = aloh2conc(pH)
    kg=10^8.5;
    h=10^-pH;
    kaloh = 10^-5;
    kaloh2 = 5*10^-10;
    conc = kg*kaloh*kaloh2*h;
end

```

File: molfrac.m

```

function x = molfrac(pH)
    x(1) = al3conc(pH) / totalconc(pH); % mole fraction of Al(3+)
    x(2) = alohconc(pH) / totalconc(pH); % mole fraction of AlOH(2+)
    x(3) = aloh2conc(pH) / totalconc(pH); % mole fraction of Al(OH)2(+)
end

```

File: al3conc.m

```

%% al3conc.m
function conc = al3conc(pH)
    kg=10^8.5;
    h=10^-pH;
    conc = kg*h^3;
end

```

File: totalconc.m

```

%% totalconc.m
function conc = totalconc(pH)
    conc = al3conc(pH) + alohconc(pH) + aloh2conc(pH);
end

```

Exercise 19

Depending on what variables that are known, the acid neutralising capacity (ANC) can be used to analyse the buffer capacity as well as deriving a pH-value for aquatic systems. In this exercise we calculate the ANC of the precipitation from the four locations given in exercise 2 and a corresponding pH value from that ANC calculation.

The ANC was calculated by using the definition that utilises concentrations of cations to strong bases and anions to strong acids.

$$[ANC] = \Sigma_{scb} n C^{n+} - \Sigma_{asa} m C^{m-}$$

The data of the concentrations was gathered from the table in exercise 2 and inserted in the equation above, the results as follows.

$$[ANC]_{Klosterhede} = -84 \mu eq \text{ L}^{-1}$$

$$[ANC]_{Kootwijk} = -21 \mu eq \text{ L}^{-1}$$

$$[ANC]_{Höglwald} = -20 \mu eq \text{ L}^{-1}$$

$$[ANC]_{Ballyhooly} = 16 \mu eq \text{ L}^{-1}$$

The corresponding pH-value was then calculated by creating a function in matlab based on the definition of ANC that includes the anions to weak acids and the cations to weak bases, assuming no DOC or Al in the water and a partial pressure $P_{CO_2} = 4 \cdot 10^{-4} atm$. Using the roots command the function gives a concentration of H^+ which can subsequently be used to calculate the pH-value.

$$\begin{aligned} 0 &= [ANC] - \frac{K_{H_2CO_3} K_H P_{CO_2}}{[H^+]} + [H^+] \\ &\iff \\ 0 &= [H^+]^2 + [ANC] \cdot [H^+] - K_{H_2CO_3} K_H P_{CO_2} \end{aligned}$$

The resulting pH-value for each location was as follows

$$pH_{Klosterhede} = 4.07$$

$$pH_{Kootwijk} = 4.67$$

$$pH_{Höglwald} = 4.69$$

$$pH_{Ballyhooly} = 6.36$$

The small difference between the results given and the pH-value given in the table for exercise 2 could be explained by a difference in value of $K_{H_2CO_3}$, K_H or P_{CO_2} .

File: e19.m

```

%% 1
% (Na(+) K(+) 2*Ca(2+) 2*Mg(2+) NH4(+)) - (NO3(-) 2*SO4(2-) Cl(-))
ANCKlos=(192 + 5 + 15 + 48 + 35) - (50 + 90 + 239);
ANCKoot=(59 + 2 + 6 + 16 + 86) - (38 + 73 + 79);
ANChogl=(11 + 10 + 24 + 9 + 55) - (41 + 75 + 13);
ANCbll=(266 + 7 + 18 + 67 + 28) - (11 + 42 + 317);
%% 2
%solution using fzero
hconc = fzero(@fcalc, 10^-6); % adjust second parameter until reasonable result is reached
ph = -log10(hconc);

%solution using roots
newPh = fcalc2(-2)

```

File: fcalc.m

```

function y=fcalc(h)
kh2co3 = 10^-(6.482);
kh = 10^-(1.260);
pco2=4*10^-4;
anc=59*10^-6; % insert ANC value for any location in eq/L

y=anc-(kh2co3*kh*pco2)/h + h;
end

```

File: fcalc2.m

```

function ph=fcalc2(ancmicro)
kh2co3 = 10^-(6.482);
kh = 10^-(1.260);
pco2=4*10^-4;
anc=ancmicro*10^-6;

a(1)=1; a(2)=anc; a(3)=-(kh2co3*kh*pco2);
X = roots([a]);
x = max(X(find(imag(X) == 0))); % conc. h+;

ph = -log10(x);
end

```

Exercise 20

There is definite practical value of determining the ANC of aquatic systems. Not only does it give a measure of the buffer capacity of a system, or calculate a specific pH-value as in exercise 19, it can also be used as an efficient tool to analyse how the change in pH of a system after the system has been polluted with various ions. In this exercise ANC is used to determine the pH-value of a lake before and after a lake has been accidentally exposed to a discharge of ammonia, as well as the pH after said ammonia has been nitrified to nitrate.

Similarly to exercise 19, a function to calculate the pH based on the ANC was made for this exercise. Concentrations of DOC and aluminium were not neglected. Assuming the lake is of a relatively ordinary kind and therefore with a pH-value below 9, concentrations of OH^- and CO_3^{2-} were neglected. The function was then created as such

$$\begin{aligned}
 0 &= [ANC] - [HCO_3^-] - [R^-] + [H^+] + 3[Al^{3+}] \\
 &\iff \\
 0 &= [ANC] - \frac{K_{H_2CO_3} \cdot K_H \cdot P_{CO_2}}{[H^+]} - [R^-] + [H^+] + 3K_G \cdot [H^+]^3 \\
 &\iff \\
 0 &= [ANC] - \frac{K_{H_2CO_3} \cdot K_H \cdot P_{CO_2}}{[H^+]} - 7 \cdot 10^{-6} \cdot [DOC] \cdot \frac{K_R}{K_R + [H^+]} + [H^+] + 3K_G [H^+]^3
 \end{aligned}$$

Where values of K_G , P_{CO_2} and $[DOC]$ was set per exercise instructions, K_H and $K_{H_2CO_3}$ was set for 10° C, and a constant $K_R = 5 \cdot 10^{-5}$ was used due to the assumption of a pH below 9 (see exercise 17). The equation was then rearranged to remove all denominator $[H^+]$ so the roots-function in Matlab could be applied.

$$0 = 3 \cdot K_G \cdot [H^+]^5 + 3 \cdot K_R \cdot K_G \cdot [H^+]^4 + [H^+]^3 + ([ANC] + K_R) \cdot [H^+]^2 + ([ANC] \cdot K_R - K_{H_2CO_3} \cdot K_H \cdot P_{CO_2} - 7 \cdot 10^{-6} \cdot [DOC]) \cdot [H^+] + K_{H_2CO_3} \cdot K_H \cdot P_{CO_2} \quad (18)$$

Entering the values for the constants as well as the value of the ANC before the accident in eq. 18 gave the pH-value

$$pH_{pre} = 6.8$$

The addition of ammonia will change the ANC and therefore the pH-value of the lake. The ammonia was assumed be fully protonated into ammonium due to the pH-value. As per definition 7.11 in the textbook, the ANC will increase as the concentration of positive charges, contributed by ammonium, increases. The concentration of positive charges contributed by ammonium in the lake was therefore calculated.

$$\begin{aligned}
 M_{NH_3} &= 17,031 \cdot 10^{-3} \frac{kg}{mol} \\
 m_{NH_3} &= (15 \cdot 10^3 \cdot 0.24) kg \\
 \frac{m_{NH_3}}{M_{NH_3}} &= n_{NH_3} = n_{NH_4^+} = 2.1138 \cdot 10^5 \text{ mol} \\
 V_{lake+discharge} &= (20 \cdot 10^4 \cdot 3 + 15) \cdot 10^3 \text{ l} \\
 [NH_4^+] &= \frac{n_{NH_4}}{V_{lake+discharge}} = 352.29 \frac{\mu eq}{l}
 \end{aligned}$$

$$[ANC]_{post} = [ANC]_{pre} + [NH_4^+] = 472.29 \frac{\mu eq}{l}$$

$[ANC]_{post}$ was then entered into eq. 18 and the pH-value after the incident was calculated to be

$$pH_{post} = 7.49$$

If all the ammonium is nitrified to nitrate the ANC will change accordingly. As nitrate is considered, at this pH, an anion to a strong acid the ANC will decrease and the pH-value of the lake will decrease. This nitrification turns the entire concentration of ammonium into an equal concentration of nitrate. A new ANC value was therefore calculated.

$$[ANC]_{nitrification} = [ANC]_{pre} - [NO_3^-] = [ANC]_{pre} - [NH_4^+] = -232.29 \frac{\mu eq}{l}$$

The new ANC-value was thereafter put into eq. 18 and a new pH-value was given.

$$pH_{nitrification} = 4.23$$

The nitrification can be equated to a spill of nitric acid into the lake. As the acid is strong it will be completely deprotonated. When the ammonium is nitrified into nitrate, the strength of the anion will push the equilibrium of free floating hydrogen to a higher concentration.

File: e20.m

```
%% 1
ANCpre = 120;
preph=ph20(ANCpre)

%% 2
Mnh3 = 17.031*10^-3 % kg/mol
mnh3 = 15*10^3 * 0.24; % kg
nnh3 = mnh3 / Mnh3;
nnh4 = nnh3;

totvol = (20*10^4*3 + 15) * 10^3; % L
cnh4 = (nnh4 / totvol) * 10^6; % ?eq / L
ANCpost = ANCpre + cnh4
postph = ph20(ANCpost)

%% 3
ANCno3 = ANCpre - cnh4;
no3ph = ph20(ANCno3)
```

File: ph20.m

```
function ph = ph20(ancmicro)
    kh2co3 = 10^-(6.482); % constant at 10degC
    kh = 10^-(1.260); % constant at 10degC
    pco2 = 2 * 4*10^-4;
    doc = 4; % mg * L^-1
    kg = 10^8.5;
    kr = 5*10^-5; % OBS this is a simplification, discuss using graph from e17.
    anc=ancmicro*10^-6; %ANC now in eq/L
```

```

a(1)= 3 * kg;
a(2)= 3 * kr * kg;
a(3)= 1;
a(4)= anc + kr;
a(5)= kr * anc - kh2co3 * kh * pco2 - 7*10^-6 * doc * kr;
a(6) = -kr * kh2co3 * kh * pco2;

X = roots([a]);
x = max(X(find(imag(X) == 0))); % conc. h+;

ph = -log10(x);
end

```

Exercise 21

The anthropological process of adding and letting $CaCO_3$ dissolve into aquatic systems, distributing Ca^{2+} and CO_3^{2-} to raise the buffer capacity of the system, is known as liming. The name of the process is taken from limestone, which consists mainly of $CaCO_3$. The process can be applied to lakes that are too acidic and thus contributes to a more ecological environment.

In this exercise, two lakes with the same pH were to be limed, raising their pH value from 4.5 to 6.9. One of the lakes is clear with $[DOC] = 4 \frac{mg}{L}$, the other is humic with $[DOC] = 20 \frac{mg}{L}$. Assuming $K_G = 10^{8.5}$ and P_{CO_2} two times the atmospheric partial pressure, the ANC before adding $CaCO_3$ for both lakes was calculated through use of definition 7.10 in the compendium.

$$[ANC]_{clear}^{pre} = -44.0125 \frac{\mu eq}{L}$$

$$[ANC]_{humic}^{pre} = 24.5958 \frac{\mu eq}{L}$$

Next, the difference in ANC necessary for raising the pH-value to 6.9 for each lake was calculated.

$$\Delta [ANC] = [ANC]^{post} - [ANC]^{pre}$$

$$\Rightarrow$$

$$\Delta [ANC]_{clear} = 186.9201 \frac{\mu eq}{L}$$

$$\Delta [ANC]_{humic} = 230.0305 \frac{\mu eq}{L}$$

The concentration of $CaCO_3$ necessary for the change in ANC could then be calculated through

$$[CaCO_3] = M_{CaCO_3} \cdot \frac{\Delta [ANC]}{2} \cdot 10^{-3}$$

Where $M_{CaCO_3} = 100.09 \frac{g}{mol}$. As ANC is given in $\frac{\mu eq}{L}$ and the charge of carbonate and calcium is 2+, the change in ANC is divided in two to give corresponding concentration in $\frac{mol}{L}$. The results were then calculated to be

$$[CaCO_3]_{clear} = 9.35 \frac{g}{m^3}$$

$$[CaCO_3]_{humic} = 11.51 \frac{g}{m^3}$$

As can be seen from the calculations of the ANC-values of the two lakes before the spill, the clear lake has a lower ANC. This means that the buffer capacity of the clear lake is smaller than that of the humic lake. This in turn makes the clear lake more sensitive to changes in pH, as can be seen by the lesser amount of $CaCO_3$ needed to raise the pH to 6.9 when compared to the humic lake.

File: e21.m

```
Mcaco3 = 100.09; % g/mol
```

```
%% lake clear
```

```
ancclear = anc(4.5, 4) * 10^6 % \mueq/L
```

```
dancclear = (anc(6.9, 4) - anc(4.5, 4)) * 10^6 % ?eq/L
```



```
ccaco3clear = Mcaco3 * (dancclear/2) * 10-3 % g/m3
```

```
%% lake humic
```

```
anchumic = anc(4.5, 20) * 10-6 % \mueq/L
```

```
danchumic = (anc(6.9, 20) - anc(4.5, 20)) * 10-6 % ?eq/L
```

```
ccaco3humic=Mcaco3 * (danchumic/2) * 10-3 % g/m3
```

File: anc.m

```
function ances=anc(pH,doc)
```

```
kh2co3 = 10-(6.482); % constant at 10degC
```

```
kh = 10-(1.260); % constant at 10degC
```

```
pco2 = 2 * 4*10-4;
```

```
kg = 108.5;
```

```
kr = 5*10-5; % OBS this is a simplification, discuss using graph from e17.
```

```
h=10-pH;
```

```
ances = (kh2co3 * kh * pco2) / h + (7*10-6*doc*kr) / (kr + h) - h - 3 * kg * h3;  
end
```

Exercise 22

In different lakes different buffering systems can be found. Depending on the concentrations of ions in the waters, different buffering systems dominate. In this exercise the ANC for the lakes Härsvatten, Vemmarsjön and Sövdesjön, and the shallow and deep groundwater in southern Sweden was calculated and compared. The accuracy of the ANC model used throughout these exercises was also analysed by measuring the pH through the ANC model and then compared to measured data.

The ANC for each lake/groundwater was calculated through use of the “anions to weak acids and cations to weak bases”-definition (definition 7.10 in the compendium). The data for each location was found in table 3.2 in the compendium. The resulting ANC for each lake/groundwater was as follows.

$$[ANC]_{H\ddot{a}rsvatten} = -35.62 \frac{\mu eq}{L}$$

$$[ANC]_{Vemmarsj\ddot{o}n} = 87.21 \frac{\mu eq}{L}$$

$$[ANC]_{S\ddot{o}vdesj\ddot{o}n} = 2217.99 \frac{\mu eq}{L}$$

$$[ANC]_{Shallow} = 310.97 \frac{\mu eq}{L}$$

$$[ANC]_{Deep} = 3171.37 \frac{\mu eq}{L}$$

Next, a function similar to eq. 18 was created in Matlab. This new function, however, plots the pH as a function of partial pressure CO_2 of the lake/groundwater with their specific ANC. The pH was then plotted for Vemmarsjön and Sövdesjön, as can be seen in fig. 7

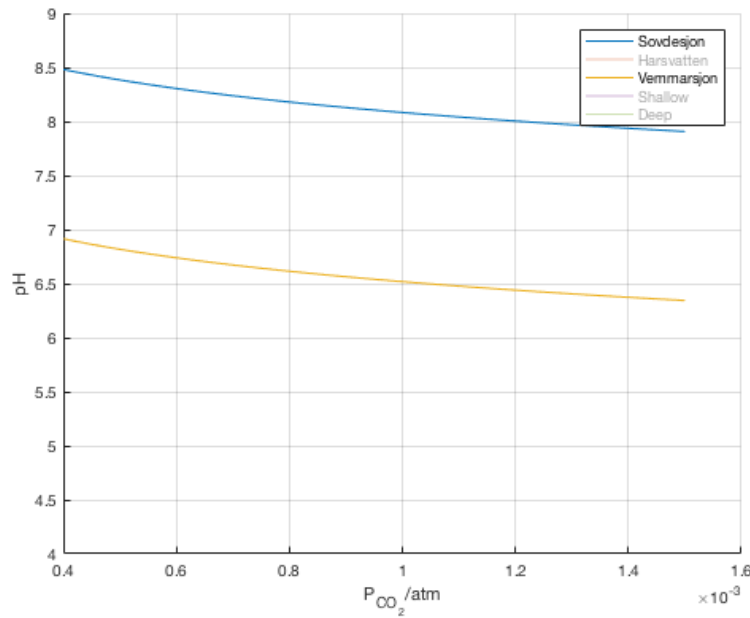


Figure 7: pH-values at different partial pressures of CO_2 for lake Sövdesjön and Härsvatten at their specific ANC

When comparing the resulting ANC-values while looking at concentrations of dissolved species given in table 3.2 a strong correlation between concentrations of HCO_3^- and ANC can be observed. The higher the concentration of HCO_3^- , the higher ANC.

The measured pH, given by table 3.2, for Sövdesjön and Vemmarsjön are 8.16 and 6.1, respectively. Locating these values in fig. 7 gives partial pressures of more than double that of a normal atmosphere, this suggests that the two lakes are supersaturated with CO_2 .

The most important buffering systems of lakes Härsvatten, Vemmarsjön and Sövdesjön is the carbonate system, with bicarbonate being the most significant proton acceptor. This can, as stated above, be observed in the ANC-value of the three lakes.

File: e22.m

```
%% 1
% Concentration of ions in \mu eq / L in the order of, DOC in mg / L
% % Cl(-), SO4(2-), NO3(-), HCO3(-), Na(+), Ca(2+), Mg(2+), K(+), NH4(+), Al(3+), DOC, pH
data = [
    243 102 30 0 240 29 58 11 3 4 3.5 4.5;          % härsvatten
    18 29 2 88 53 78 38 8 2 0 8.5 6.1;             % vemmarsjön
    454 503 5 2218 479 2656 346 72 18 0 10.6 8.16; % sövdesjön
    704 500 16 3172 1196 2525 568 97 6 0 0 6.2;    % deep
    338 332 125 311 287 561 200 56 2 0 0 7.5;     % shallow
];

harsAnc = data(1,4) + r(data(1,11), data(1,12)) - 10^-data(1, 12) * 10^6 - data(1, 10);
vemmAnc = data(2,4) + r(data(2,11), data(2,12)) - 10^-data(2, 12) * 10^6 - data(2, 10);
sovdAnc = data(3,4) + r(data(3,11), data(3,12)) - 10^-data(3, 12) * 10^6 - data(3, 10);
```

```

deepAnc = data(4,4) + r(data(4,11), data(4,12)) - 10^-data(4, 12) * 10^6 - data(4, 10);
shalAnc = data(5,4) + r(data(5,11), data(5,12)) - 10^-data(5, 12) * 10^6 - data(5, 10);

%% 2
%pco2hars = fzero(@getpco2, 4*10^-4)
% hold on
% plot(linspace(4*10^-4, 15*10^-4), 8.16)
hold on
fplot(@ph22sovd, [4*10^-4 15*10^-4])
fplot(@ph22hars, [4*10^-4 15*10^-4])
fplot(@ph22vemm, [4*10^-4 15*10^-4])
fplot(@ph22shal, [4*10^-4 15*10^-4])
fplot(@ph22deep, [4*10^-4 15*10^-4])
grid on
legend('Sovdesjon', 'Harsvatten', 'Vemmarsjon', 'Shallow', 'Deep')
xlabel('P_{CO_2}/atm')
ylabel('pH')
hold off

```

File: ph22vemm.m

```

function ph=ph22vemm(pco2)
    ancmicro= 87.205729462406540; % insert specific ANC for location in \mueq/L here
    kh2co3 = 10^-(6.482); % constant at 10degC
    kh = 10^-(1.260); % constant at 10degC
    doc = 4; % mg * L^-1
    kg = 10^8.5;
    kr = 5*10^-5; % OBS this is a simplification, discuss using graph from e17.
    anc=ancmicro*10^-6; %ANC in eq/L

    a(1)= 3 * kg;
    a(2)= 3 * kr * kg;
    a(3)= 1;
    a(4)= anc + kr;
    a(5)= kr * anc - kh2co3 * kh * pco2 - 7*10^-6 * doc * kr;
    a(6) = -kr * kh2co3 * kh * pco2;

```