

Modelling pH in natural waters

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Prerequisites: This paper is for students attending classes in general physical chemistry. Most of the theory in this paper is covered by references [1], [2] and [3]. It is suggested that the fundamentals of biochemical reactions, chemical equilibrium and kinetics are studied in advance. Knowledge of Mathcad is required, but the more specific features of Mathcad necessary to the model will be introduced to the student in this document.

Goals: This document will show how simple equilibrium considerations can be used for modelling the behaviour of pH in natural rivers. The project can be extended by adding actual water analysis into the model, and furthermore, by measuring photosynthetic and respirational rates. The latter is described in detail in reference [4].

Performance objectives: After completing the project described here you should be able to:

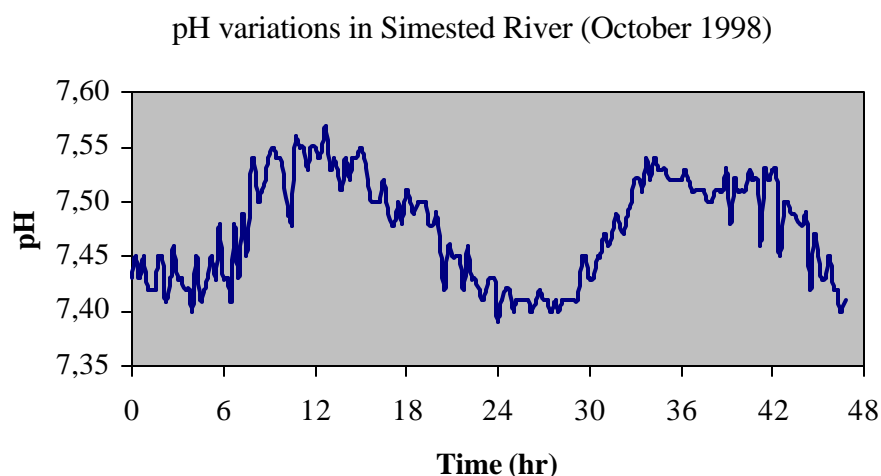
1. Understand the carbonate system in open, closed and natural systems
2. Write and solve equilibrium equations in Mathcad
3. Understand and write iterative procedures in Mathcad
4. Model pH changes in natural rivers using Mathcad
5. Account for temperature and ionic strength effects on chemical equilibrium by using the model

Introduction: For most natural rivers pH is determined almost solely by the species contained in the so-called carbonate system. Other acid-base systems may interfere, but they are usually of minor importance. One of the species in the carbonate system, dissolved CO_2 , is also involved in the respiration and photosynthesis of plants and animals. The concentration of dissolved CO_2 will oscillate during the day, which means that the pH in most natural rivers will also oscillate. This pH-oscillation can be modelled by using simple acid-base and kinetic considerations, which this paper will show.

The extent of this project can be varied depending on the level of the chemistry course. A simple model will teach the student to write and solve equilibrium equations and differential equations iteratively. In the advanced model the student will also learn how to make corrections taking temperature and ionic strength into account. Eventually it would also be necessary to measure the ionic concentrations by using different analytical methods.

The basic equations are described in section 1 and can be seen in further detail in [4]. Equilibrium constants are taken from [2,5]. For treatment of the carbonate system, the reader is referred to [1,2]. Finally, it must be stressed that all experimental data in this paper is either measured or calculated for a specific river in Denmark.

The river: We have measured pH in the river Simested in the course of a month, from early October to early November. The graph below shows pH as a function of time during two days in October, starting at midnight. These pH variations are what we want to model. As can be seen the oscillations are almost sinusoidal, with amplitude of 0.07 pH units and a period of approximately 24 hours.



Helpful Hints: This section can be used to refresh your Mathcad skills.

Solving equations by using Mathcad's built-in FIND routine can be difficult, since this routine requires suitable guess values before it can solve the equations. Since it is essential when solving chemical equilibrium equations that the concentrations are positive, it is important to ensure that the solutions that Mathcad finds are indeed positive. This can be solved by specifying that the results should be above zero. The following example will show how to solve two simultaneous equations giving only positive results.

Guess values: $x := 0$ $y := 0$ (Pressing $\langle \Rightarrow \rangle$ produces the ':= ' which is Mathcad's way of defining a variable)

Given (Tells Mathcad that you are writing some equations for it to solve)

$2 \cdot x - 3 \cdot y = 4$ (Use $\langle \text{CTRL} \rangle$ and $\langle + \rangle$ or the Boolean Equal sign in the Evaluation and Boolean Palette to write the bold equal sign used in equations)

$$x^2 + 2 \cdot y^2 = 9$$

$x \geq 0$ (Here we tell Mathcad that the solution we are looking for must be above zero concerning both the x and the y variable)

$$y \geq 0$$

Result := Find(x, y) (The resulting x and y variable will be stored in the new variable Result, which will be a vector. The x and y values can be brought forward by using an index. This can be done with the $\langle \text{ALT GR} \rangle$ and $\langle 8 \rangle$ or the subscript button in the Arithmetic Palette.)

Resulting x value: $\text{Result}_0 = 2.882$

Resulting y value: $\text{Result}_1 = 0.588$

Solving differential equations is possible by using the build-in Mathcad solver. However it is often more easy and just as reliable to use the simple Euler method. An example is given below. In this example the equation to solve is:

$$\frac{dy}{dx} = y \quad x_0 = 0 \quad y_0 = 1$$

and according to Euler the solution is given by

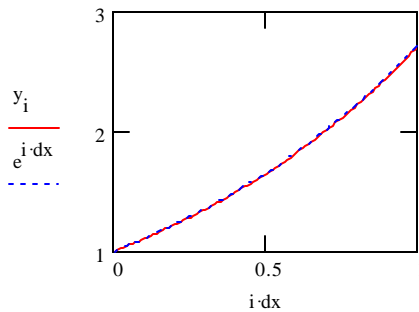
$$y_{i+1} = y_i + \frac{dy_i}{dx_i} \cdot \Delta x \quad \text{or simply} \quad y_{i+1} = y_i + y_i \cdot dx \quad \text{provided } \Delta x \text{ is significantly small}$$

With a quick guess on the size of dx and the total number of iterations, MathCad is able to perform the iterations and place y1, y2, y3 ect. in a result vector.

$$y_0 := 1 \quad dx := 0.01 \quad i := 0, 1, \dots, 100$$

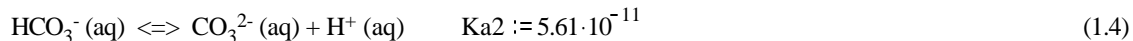
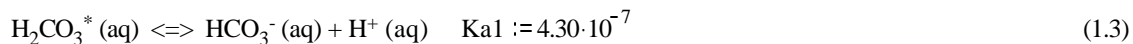
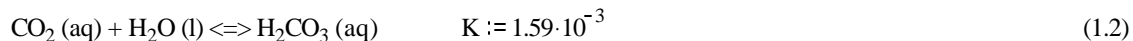
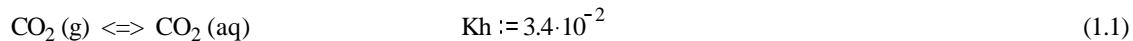
$$y_{i+1} := y_i + y_i \cdot dx$$

The content of the result vector is shown in the figure on the right together with the analytical solution, $y = e^x$, for comparison.



Section 1: Carbon dioxide in open and closed systems

The carbonate system consists of all the species involved in the dissociation of carbonic acid, that is: CO_2 , H_2CO_3 , HCO_3^- , CO_3^{2-} . The reactions involved are:



Hypothetical carbonic acid: Before proceeding to investigate open and closed systems, we must define an entity called hypothetical carbonic acid, H_2CO_3^* which is given by: $[\text{H}_2\text{CO}_3^*] = [\text{CO}_2] + [\text{H}_2\text{CO}_3]$ (mol/l). This is basically the total amount of potential carbonic acid. The reason for introducing this measure is that it is difficult to distinguish between dissolved CO_2 and carbonic acid by using analytical methods (an acid-base titration, for example, would reveal H_2CO_3^*).

Exercise 1: The equilibrium constant for the reaction: $\text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq})$ is given above. Use this to show, that $[\text{CO}_2] \approx [\text{H}_2\text{CO}_3^]$.*

Carbon dioxide in an open system: In an open system, carbon dioxide can be exchanged freely between water and the atmosphere. When this system is in equilibrium, the concentration of dissolved carbon dioxide is determined by Henry's law. In order to find pH and the concentration of all the remaining carbonate species, the charge balance must be used. In a simple system containing only carbonate species, the charge balance can be written as:

$$[\text{H}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \quad (1.5)$$

If we were to calculate pH for pure water in an open system, we would proceed like this:

Known values (from eq. 1.3 and 1.4):

$$K_h := 0.034 \quad p\text{CO}_2 := 3.2 \cdot 10^{-4} \quad K_w := 10^{-14} \quad K_{a1} := 4.30 \cdot 10^{-7} \quad K_{a2} := 5.61 \cdot 10^{-11}$$

In an open system, the amount of carbon dioxide is constant, given by Henry's law (eq. 1.1):

$$[\text{CO}_2] = K_h \cdot p\text{CO}_2$$

Next, we use the approximation from Exercise 1: $[\text{H}_2\text{CO}_3^*] \approx [\text{CO}_2]$:

$$[\text{H}_2\text{CO}_3^*] := K_h \cdot p\text{CO}_2$$

Then we use the charge balance given above by inserting the acid dissociation constants and substituting $[\text{HCO}_3^-]$ and $[\text{CO}_3^{2-}]$ with $[\text{H}_2\text{CO}_3^*]$ as well as substituting $[\text{OH}^-]$ with $[\text{H}^+]$. The equation system now looks like this in Mathcad:

Guess value:

$$H := 10^{-7}$$

Given

$$H = \frac{K_w}{H} + \frac{H_2CO_3^* \cdot K_{a1}}{H} + 2 \cdot \frac{H_2CO_3^* \cdot K_{a1} \cdot K_{a2}}{H^2}$$

Note the use of the equilibrium constant expression from equations 1.3 and 1.4.

$$H \geq 0$$

Solving:

$$\text{Find}(H) = 2.165 \cdot 10^{-6}$$

Which gives a pH value of $-\log(2.165 \cdot 10^{-6}) = 5.665$

Exercise 2: What if the water contained 0.001 mol/L of NaHCO₃?

Carbon dioxide in a closed system: In a closed system, the total amount of carbonate species is constant and Henry's law can no longer be used to find the concentration of dissolved carbon dioxide. However, if the total amount of carbonate species is known, the mass balance:

$$C_{\text{tot}} = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] \quad (1.6)$$

describes the system adequately.

Exercise 3: Using the mass balance (eq. 1.6) and the expressions for the acid-dissociation constants, write $[H_2CO_3^]$ as a function of C_{tot} and $[H^+]$.*

Exercise 4: Find pH in a solution of 0.001 mol/L of NaHCO₃ in a closed system. Compare with the pH value you found in exercise 2 for an open system.

Section 2: Carbon dioxide dynamics in natural rivers

By now you should be familiar with the concept of open and closed systems in equilibrium. The chemical reactions used to describe these systems are generally considered to be fast, except the hydration of carbonic acid, which is relatively slow [2]. In natural systems we also need to take biological transformation and diffusion of CO₂ into account.

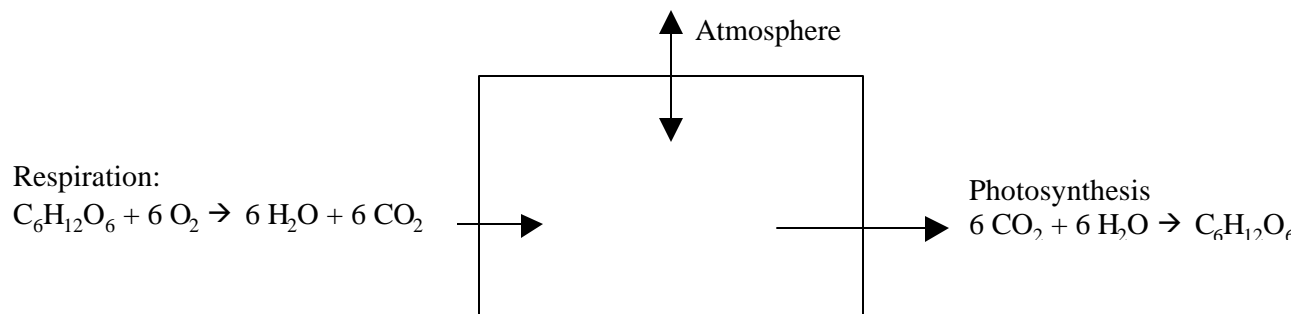


Figure showing the exchange of carbon dioxide in a river. Both photosynthesis and respiration are si

CO₂ is produced in the respiration process and consumed during photosynthesis, where it is used for building carbohydrates. If the system is supersaturated with CO₂, some will diffuse into the atmosphere and the other way around if it is undersaturated. This process is often called reaeration. Other processes such as nitrification where carbon dioxide is also produced, are not considered here.

Compared to the chemical reactions in the carbonate system, biological and diffusion processes are relatively slow. This means that at a certain point in time it is possible to have chemical equilibrium and yet supersaturated or undersaturated conditions.

It is possible to formulate the changes in CO₂ mathematically in a differential equation including both biological and diffusion processes:

$$\frac{d[\text{CO}_2]}{dt} = -P(t) + R + K_{\text{CO}_2} \cdot ([\text{CO}_2]_{\text{sat}} - [\text{CO}_2]) \quad (2.1)$$

$P(t)$ describes the photosynthesis as a function of time. The negative sign arises because it actually models oxygen production (one oxygen molecule produced consumes one carbon dioxide molecule if a carbohydrate is formed). The function is given in reference [4]:

$$P(t) = \begin{cases} P_{\max} \cdot \cos\left(\frac{2 \cdot \pi \cdot t}{T \cdot \alpha}\right), & -\frac{\alpha}{4} \leq \frac{t}{T} \leq \frac{\alpha}{4} \\ 0 & \end{cases} \quad (2.2)$$

The function $P(t)$ in equation 2.2 can be written in Mathcad thus:

$$P(t) := \text{if} \left[\left\{ \frac{t}{T} < \frac{-\alpha}{4} \right\} + \left\{ \frac{t}{T} > \frac{\alpha}{4} \right\}, 0, P_{\max} \cdot \cos \left\{ \frac{2 \cdot \pi \cdot t}{\alpha \cdot T} \right\} \right] \quad (2.3)$$

where P_{\max} is the maximum oxygen level at noon (mol/L/hr), t is the time of day (hr), T is the period (24 hrs) and α is the relative daylength. With noon at $t=0$, α the relative daylength can be calculated on any day by using $\alpha=1$ at equinox and $\alpha=1.5$ at summer solstice and $\alpha=0.5$ at winter solstice.

R is the respiration (mol/L/hr), which is approximately constant during the modelling period.

The time of year determines the magnitude of the photosynthesis and respiration with photosynthesis being very large during the summer because of the longer daytime and higher light intensity.

Exercise 5: Create a function $P(t)$ in Mathcad like the one above. Using $\alpha=0.5$ and $T=24$ and with $P_{\max}=1$, plot it versus time (t), where t goes from -12 to 12. You can do this by using the Graph Palette or the @ key. What if you use $\alpha=1$? What role does P_{\max} play?

Finally, the reaeration term given by:

$$\frac{d[\text{CO}_2]}{dt} = -K_{\text{CO}_2} \cdot ([\text{CO}_2] - [\text{CO}_2]_{\text{sat}}) \quad (2.4)$$

where K_{CO_2} is the reaeration constant (1/hr), $[\text{CO}_2]_{\text{sat}}$ is the saturation concentration given by Henry's law and $[\text{CO}_2]$ is the actual concentration of dissolved CO_2 (both in mol/L).

By solving the differential equation we can actually model the CO_2 level at any time during the day. Combining this with the equilibrium calculations in the previous section, we should therefore be able to find pH as a function of time. Even though this sounds simple, several parameters and conditions need to be known before we can proceed.

A closer look at the differential equation shows that it is actually a first order equation which can easily be solved analytically. However, an analytical solution ignores the reactions of CO_2 in the carbonate system. To take these reactions into consideration we have to solve it numerically by using an iterative procedure.

The dynamics of the system become irrelevant in a strictly open system where $[\text{CO}_2]$ is determined solely by the atmospheric concentration of CO_2 . However the system isn't strictly closed either since we allow reaeration to take place. To solve this problem we have to break the problem into two parts, one where the system is considered closed (constant C_{tot}) to make dynamic calculations possible, and one where the system is considered open (constant $[\text{CO}_2]$) to introduce reaeration.

Exercise 6: To give an idea of how to solve a differential equation iteratively in Mathcad, use the equation below to make a plot of the CO_2 concentration vs. time for a 24 hour period.

$$\frac{d[\text{CO}_2]}{dt} = -K_{\text{CO}_2} \cdot ([\text{CO}_2] - [\text{CO}_2]_{\text{sat}})$$

using the following conditions:

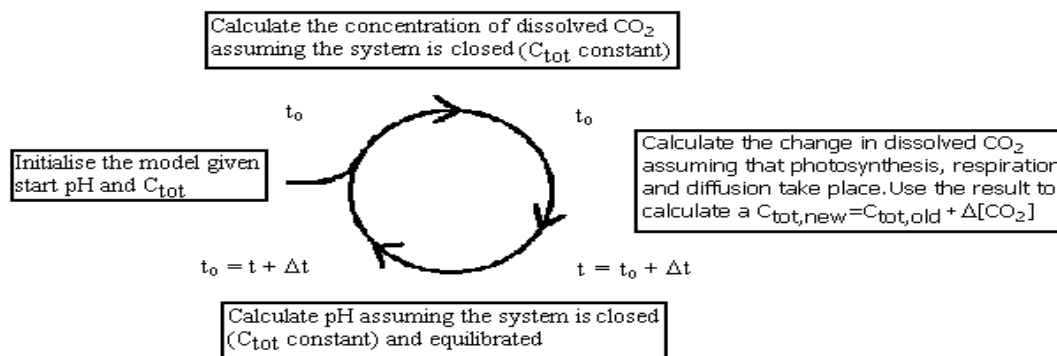
$$K_{\text{CO}_2} := 1 \quad \text{CO}_2_{\text{sat}} := 10^{-3} \quad \text{CO}_2_{\text{Start}} := 0$$

Section 3: Setting up the model

In this section we focus more directly on making a suitable model in Mathcad. We assume that the total carbon content is known (closed system). Based on this, the pH and CO₂ concentration is calculated as if the system was in equilibrium (t₀). These initial conditions are used in the differential equation to calculate the rate of CO₂ change in the system. After a period Δt, a new C_{tot} can be calculated (t=t₀+Δt) assuming:

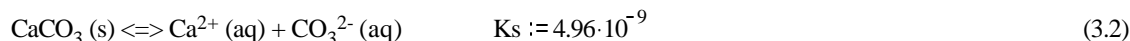
$$C_{\text{tot}} = C_{\text{tot,old}} + \frac{d[\text{CO}_2]}{dt} \cdot \Delta t \quad (3.1)$$

The situation is now the same as when the initial conditions were given (t₀). Combining the steps above results in the following model algorithm of an iterative procedure:



The equation that determines pH in our model is the charge balance equation. Ideally, we would have to measure the concentration of all the ions in the river, but even with a limited information about the ion content it is still possible to use the model. The philosophy behind this is that if the ions present in the river don't interfere with the carbonate system, they will simply be added to either side of the charge balance equation and tend to be cancelled out. The sodium ion is a good example of that. It does not react with species in the carbonate system and it has no acid-base abilities. Calcium, however, forms an insoluble compound with the carbonate ion, and since calcium is usually present in considerable quantities in rivers [6], we need to include calcium in the charge balance. The same could be said about magnesium, but magnesium is usually present in smaller quantities than calcium and will not be considered here.

In our system calcium carbonate is present in the river sediment and it is assumed that it is in equilibrium with the river water at all times. The calcium ion can therefore be determined by [CO₃²⁻] according to the solubility product of the reaction:



The initial value of C_{tot} is not essential to the model, but in order for the model to be stable within the 24 hour modelling period, a reasonable value must be given. You can experiment with different C_{tot} values later on to see the effects.

Exercise 7: Follow the instructions written in red on the right side and insert the relevant information, if necessary.

Starting values:

$$C_{tot_0} \equiv 6.3 \cdot 10^{-3} \quad \text{mol/L} \quad t_0 \equiv -12 \quad \text{hour} \quad pCO_2 \equiv 3.2 \cdot 10^{-4} \quad \text{atm}$$

Known constants:

$$K_{a1} \equiv \blacksquare \quad K_{a2} \equiv \blacksquare \quad K_w \equiv \blacksquare \quad \text{Insert values at marked places.}$$

$$K_h \equiv \blacksquare \quad K_s \equiv \blacksquare \quad K_{CO_2} \equiv \blacksquare \quad \text{hour}^{-1} \quad \text{Make sure that the units are consistent.}$$

$$R_{sp} \equiv \blacksquare \quad \text{mol/L/hour} \quad P_{max} \equiv \blacksquare \quad \text{mol/L/hour}$$

$$T := 24 \quad \text{hours}$$

Calculated constants:

$$\alpha \equiv \blacksquare \quad CO_2_Sat \equiv \blacksquare \quad \text{Calculate } \alpha \text{ on the 15th of October and insert the value. Then insert the saturation concentration of carbon dioxide.}$$

Function describing the photosynthesis:

$$P(t) := \text{if} \left[\left\{ \frac{t}{T} < \frac{-\alpha}{4} \right\} + \left\{ \frac{t}{T} > \frac{\alpha}{4} \right\}, 0, P_{max} \cdot \cos \left\{ \frac{2 \cdot \pi \cdot t}{\alpha \cdot T} \right\} \right] \quad \text{This is the solution to exercise 5.}$$

Function returning CO₂ concentration as a function of C_{tot}:

$$CO_2(C_t, H) := \frac{C_t}{\left\{ 1 + \frac{K_{a1}}{H} + \frac{K_{a1} \cdot K_{a2}}{H^2} \right\}} \quad \text{This is the solution to exercise 3, with } C_{tot} \text{ and } [H^+] \text{ as input variables.}$$

$$\text{Solving variable: } H := 10^{-7}$$

Given

$$2 \cdot \frac{K_s \cdot \left\{ \frac{H^2}{K_{a1} \cdot K_{a2}} + \frac{H}{K_{a2}} + 1 \right\}}{C_t} + H \frac{K_w}{H} + \frac{C_t}{\left\{ \frac{H}{K_{a1}} + 1 + \frac{K_{a2}}{H} \right\}} + 2 \cdot \frac{C_t}{\left\{ \frac{H^2}{K_{a1} \cdot K_{a2}} + \frac{H}{K_{a2}} + 1 \right\}}$$

$$H \geq 0$$

$$HResult(C_t) := \text{Find}(H)$$

Finally the iterative procedure:

$$i := 0..95 \quad dt := 0.25 \quad \text{hour}$$

Use C_{tot} as input. This solving routine finds [H⁺] by using the charge balance.

By using increments of 0.25 hours one day is divided into 96 intervals.

The iterative procedure consists of three equations. The first equation increases the time variable by dt after each iteration. The second equation calculates the change in CO₂ concentration after one iteration and adds it to C_{tot}. Notice that

$$\frac{d[\text{CO}_2]}{dt} = -P(t) + R + K_{\text{CO}_2} \cdot ([\text{CO}_2]_{\text{sat}} - [\text{CO}_2])$$

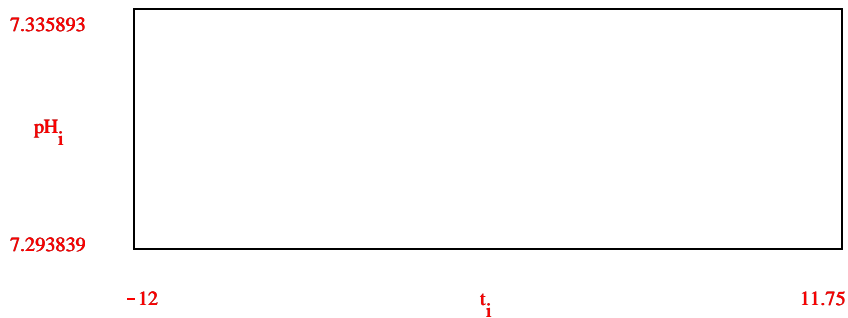
The third equation simply returns the pH value given C_{tot}.

$$t_{i+1} := t_i + dt$$

$$C_{\text{tot},i+1} := C_{\text{tot},i} + \left[-P(t_i) + \text{Resp} + K_{\text{CO}_2} \cdot (\text{CO}_2_{\text{Sat}} - \text{CO}_2(C_{\text{tot},i}, \text{HResult}(C_{\text{tot},i}))) \right] \cdot dt$$

$$\text{pH}_i := -\log(\text{HResult}(C_{\text{tot},i}))$$

After we have pressed F9, the iteration proceeds, and the result will be shown below:



Compare this result with the measured data in section 1 (see also table 2 in Appendix A).

Section 4: Model evaluation

If you plot the calculated pH from the model versus time, and then compare it with the experimental data, you will see that the oscillations and curve shape fit very nicely with those found in the river. The level of the oscillations are, however, some 0.2 pH units lower than expected. This is not surprising considering the numerous assumptions made. We will evaluate some of these assumptions in this section.

Photosynthesis and respiration: The measured photosynthetic and respirational rates are usually difficult to produce accurately and they contribute heavily to the accuracy of the model. The same goes for the reaeration constant, which depends on the flow of the river among other things. Generally the measurements can only represent the period in which they are measured.

Charge balance: As mentioned in section 3 we would expect some difficulties fulfilling the charge balance due to the lack of complete ion analysis. It is easy to check such inconsistency by calculating the conductivity of the ions included and comparing it to an experimentally measured conductivity:

Molar conductivity ($S \cdot \text{cm}^2/\text{mol}$)

$$\lambda_{\text{Ca}} \equiv 118.94 \quad \lambda_{\text{H}} \equiv 349.65 \quad \lambda_{\text{HCO}_3} \equiv 44.5 \quad \lambda_{\text{CO}_3} \equiv 138.60 \quad \lambda_{\text{OH}} \equiv 198.0$$

From table 1:

$$\text{H} := 10^{-7.25} \quad \text{OH} := \frac{10^{-14}}{\text{H}} \quad \text{HCO}_3 := 2.041 \cdot 10^{-3} \quad \text{CO}_3 := \frac{K_{a2} \cdot \text{HCO}_3}{\text{H}} \quad \text{Ca} := 9.7 \cdot 10^{-4}$$

This gives a theoretical conductivity of:

$$(\text{H} \cdot \lambda_{\text{H}} + \text{Ca} \cdot \lambda_{\text{Ca}} + \text{OH} \cdot \lambda_{\text{OH}} + \text{HCO}_3 \cdot \lambda_{\text{HCO}_3} + \text{CO}_3 \cdot \lambda_{\text{CO}_3}) \cdot 1000 = 206.533 \quad (\mu\text{S}/\text{cm})$$

Which is $\frac{207}{323} = 64.087\%$ of the value measured in the river.

This may seem like a huge difference, but the remaining ions don't contribute to pH and don't play any significant role in the carbonate system. Examples of such ions are sodium, potassium, chloride and sulphate. They will all tend to cancel each other out in the charge balance without affecting the model, assuming that they have been introduced as pairs (e.g. Na and Cl).

Section 5: Altering the parameters

Although this model is a simplification, it can still be used to monitor the effects of several parameters in the pH of a river. In this section we shall add some more realism to our model. This includes temperature and ion effects. By now, you should have a working model so that changing any of the parameters of the model should be easy.

Exercise 8: So far we have worked with equilibrium constants defined at 25°C. Using the Van't Hoff equation corrects the constants for temperature to 5°C (a more realistic temperature in autumn). Insert the new constants along with the corresponding P_{max} , R_{sp} and K_{CO_2} from table 1. The initial C_{tot} input should be 2.6×10^{-3} M. What happens to pH?

Exercise 9: We have neglected ion-strength effects so far, and though they are of minor importance in a river you can still examine their effects on the pH. Correcting the equilibrium constants for ion-strength by using $\mu = 5 \cdot 10^{-3}$ M, what are the effects on the pH model? (still assuming 5°C). Use an initial C_{tot} value of 3.0×10^{-3} M

Exercise 10: As discussed in section 4, the charge balance equation should contain all of the ions in the river. The best would be if you made a complete analysis of the water. You can however examine the effects of added ions by simply adding a quantity to either side of the charge balance equation in your model. What happens to the model if there was an additional anion concentration of $[An^-] = 2 \cdot 10^{-3}$ M? What if there was an additional cation concentration $[Cat^+] = 2 \cdot 10^{-3}$ M? (Use $C_{tot} = 2.5 \times 10^{-3}$ M and $C_{tot} = 3.9 \times 10^{-3}$ M respectively)

Mastery Exercise: So far we have simply given the starting values for C_{tot} , so that the model is stable within the 24 hours being modelled. If you extend the model to more than 24 hours, you can see how the model behaves if the starting value for C_{tot} is overestimated or underestimated. The difficult part here is to allow the P(t) function to extend to more than 24 hours. This can be done by using Mathcad's if function.

Solution to exercises:

Exercise 1: The equilibrium constant for the reaction: $\text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq})$

is $K = [\text{H}_2\text{CO}_3] / [\text{CO}_2]$. Therefore,

$[\text{H}_2\text{CO}_3] = K \cdot [\text{CO}_2]$, or almost a thousand times smaller than $[\text{CO}_2]$. Therefore:

$$[\text{H}_2\text{CO}_3^*] = [\text{H}_2\text{CO}_3] + [\text{CO}_2] \approx [\text{CO}_2]$$

Exercise 2:

$[\text{H}_2\text{CO}_3^*]$ is still approximately given by Henry's law, and with $[\text{Na}^+] = 0.1 \text{ mol/L}$ we get:

Known values:

$$\text{H}_2\text{CO}_3^* := K_h \cdot p\text{CO}_2 \quad \text{Na} := 0.001$$

Guess value:

$$\text{H} := 10^{-7}$$

Given

$$\text{Na} + \text{H} = \frac{K_w}{\text{H}} + \text{H}_2\text{CO}_3^* \cdot \left\{ \frac{K_{a1}}{\text{H}} + 2 \cdot \frac{K_{a1} \cdot K_{a2}}{\text{H}^2} \right\}$$

$$\text{H} \geq 0$$

$$\text{Find}(\text{H}) = 4.798 \cdot 10^{-9}$$

$$\text{This gives a pH value } -\log(4.798 \cdot 10^{-9}) = 8.319$$

Exercise 3: The mass balance is given by: $C_{tot} := H_2CO_3^* + HCO_3^- + CO_3^{2-}$

Now we insert the equilibrium constants in place of HCO_3^- and CO_3^{2-} :

$$C_{tot} := H_2CO_3^* + \frac{K_{a1} \cdot H_2CO_3^*}{H} + \frac{K_{a1} \cdot K_{a2} \cdot H_2CO_3^*}{H^2}$$

Then we insert the equilibrium constant in place of HCO_3^- once again and isolate $H_2CO_3^*$:

$$C_{tot} := H_2CO_3^* \cdot \left\{ 1 + \frac{K_{a1}}{H} + \frac{K_{a1} \cdot K_{a2}}{H^2} \right\} \quad \text{and therefore:}$$

$$H_2CO_3^* := \frac{C_{tot}}{\left\{ 1 + \frac{K_{a1}}{H} + \frac{K_{a1} \cdot K_{a2}}{H^2} \right\}} \quad \text{or more properly:}$$

$$H_2CO_3^*(C_{tot}, H) := \frac{C_{tot}}{\left\{ 1 + \frac{K_{a1}}{H} + \frac{K_{a1} \cdot K_{a2}}{H^2} \right\}} \quad \text{In this way you can call the function by using } C_{tot} \text{ and } H \text{ as input.}$$

Exercise 4: With a solution of $NaHCO_3$, the charge balance and mass balance would look like this:

$$[H^+] + [Na^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}].$$

$$C_{tot} = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] = 0.1$$

Solving for the system:

Known values:

$$Na := 0.001 \quad K_{a1} := 4.30 \cdot 10^{-7} \quad K_{a2} := 5.61 \cdot 10^{-11} \quad K_w := 10^{-14} \quad C_{tot} := 0.001$$

Guess value:

$$H := 10^{-7} \quad H_2CO_3^* := 10^{-3}$$

Given

$$H + Na = \frac{K_w}{H} + H_2CO_3^* \cdot \left\{ \frac{K_{a1}}{H} + 2 \cdot \frac{K_{a1} \cdot K_{a2}}{H^2} \right\} \quad \text{(The charge balance, rewritten with respect to } [H_2CO_3^*] \text{)}$$

$$H_2CO_3^* = \frac{C_{tot}}{\left\{ 1 + \frac{K_{a1}}{H} + \frac{K_{a1} \cdot K_{a2}}{H^2} \right\}} \quad \text{(The mass balance, rewritten with respect to } [H_2CO_3^*] \text{)}$$

$$H \geq 0$$

$$\text{Find}(H) = 4.959 \cdot 10^{-7}$$

$$\text{And pH is } -\log(4.952 \cdot 10^{-7}) = 6.305 \quad \text{which is much smaller than for the open system.}$$

Exercise 5: We have:

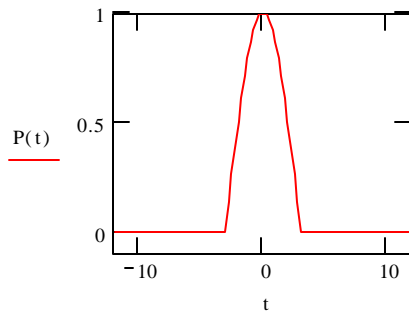
$$\alpha := 0.5 \quad T := 24 \quad P_{\max} := 1$$

$$t := -12, -11.75.. 12 \quad (\text{specifies that } t \text{ goes from } -12 \text{ to } 12 \text{ using steps of } 0.25)$$

The function $P(t)$ can be created using Mathcad's if command:

$$P(t) := \text{if} \left[\left\{ \frac{t}{T} < \frac{-\alpha}{4} \right\} + \left\{ \frac{t}{T} > \frac{\alpha}{4} \right\}, 0, P_{\max} \cdot \cos \left\{ \frac{2 \cdot \pi \cdot t}{\alpha \cdot T} \right\} \right]$$

Plotting the function:



While P_{\max} determines the maximum oxygen production (the peak height), α determines the length and rate at which oxygen is produced.

Exercise 6: There are several ways to solve this in Mathcad. The easiest way is to solve it iteratively by using small increments:

$$\Delta t := 0.25 \quad (\text{hr})$$

$$K_{CO_2} := 1 \quad CO_{2_sat} := 10^{-3} \quad CO_{2_0} := 0 \quad t_0 := 0$$

Next we define the iteration:

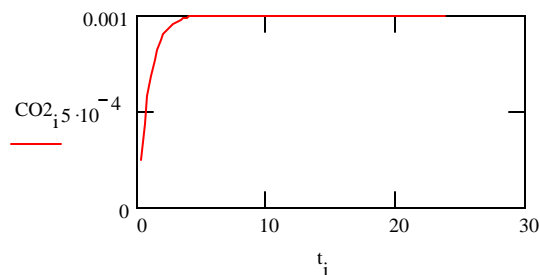
$$N := 95 \quad (\text{Number of iterations}) \quad i := 1.. N \quad (\text{index number})$$

Now for the iteration:

$$CO_{2_i} := CO_{2_{i-1}} - K_{CO_2} \cdot (CO_{2_{i-1}} - CO_{2_sat}) \cdot \Delta t$$

$$t_i := t_{i-1} + \Delta t$$

Now we plot the function:



With no other influence the saturation concentration is reached within 3-4 hours.

Exercise 7: Starting values:

$$C_{tot_0} := 6.3 \cdot 10^{-3} \quad t_0 := -12 \quad CO2_Sat := Kh \cdot pCO2$$

Known constants:

$$Ka1 := 4.30 \cdot 10^{-7} \quad Ka2 := 5.61 \cdot 10^{-11} \quad Kw := 1 \cdot 10^{-14} \quad Kh := 0.034 \quad Ks := 4.96 \cdot 10^{-9}$$

$$Resp_Hour := 1.27 \cdot 10^{-4} \quad Pmax := 2.16 \cdot 10^{-4} \quad KCO2 := 0.044$$

α is defined as the length of the actual day relative to the daylength at equinox. The daylength can be found by using data on sunset and sunrise for the location in question. For Simstedt River in Denmark the following data was found:

15th October: Sunrise at 6.55 - Sunset at 17.20

21st September (equinox): Sunrise at 6.06 - Sunset at 18.24

$$\text{By converting to decimals, we get } \alpha := \frac{(17.33 - 6.92)}{(18.40 - 6.10)} \quad \text{and thus } \alpha = 0.846$$

Guess value:

$$H := 10^{-7}$$

We solve for $[H^+]$ by using C_{tot} as input:

Given

$$2 \cdot \frac{Ks \cdot \left\{ \frac{H^2}{Ka1 \cdot Ka2} + \frac{H}{Ka2} + 1 \right\}}{Ct} + H = \frac{Kw}{H} + \frac{Ct}{\left\{ \frac{H}{Ka1} + 1 + \frac{Ka2}{H} \right\}} + 2 \cdot \frac{Ct}{\left\{ \frac{H^2}{Ka1 \cdot Ka2} + \frac{H}{Ka2} + 1 \right\}}$$

$H \geq 0$

$$HResult(Ct) := \text{Find}(H)$$

Function returning CO_2 concentration as a function of C_{tot} :

$$CO2(Ct, H) := \frac{Ct}{\left\{ 1 + \frac{Ka1}{H} + \frac{Ka1 \cdot Ka2}{H^2} \right\}}$$

Function describing the photosynthesis:

$$P(t) := \text{if} \left[\left\{ \frac{t}{T} < \frac{-\alpha}{4} \right\} + \left\{ \frac{t}{T} > \frac{\alpha}{4} \right\}, 0, Pmax \cdot \cos \left[\frac{2 \cdot \pi \cdot t}{\alpha \cdot T} \right] \right]$$

Finally the iterative procedure:

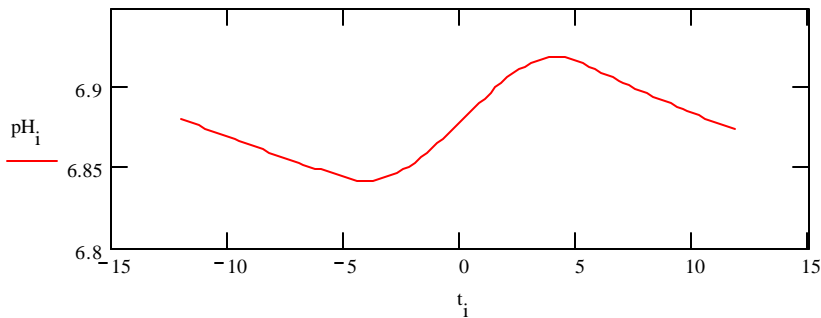
$i := 0.. 95$ $dt := 0.25$ (24 hours with calculations every 15 minutes gives 96 steps)

$t_{i+1} := t_i + dt$

$C_{tot,i+1} := C_{tot,i} + \left[-P(t_i) + \text{Resp_Hour} + K_{CO_2} \cdot \left(CO_{2_Sat} - CO_2(C_{tot,i}, HResult(C_{tot,i})) \right) \right] \cdot dt$

$pH_i := -\log(HResult(C_{tot,i}))$

The iteration gives the result below:



If we compare this result with the measurements in the river, we find that the pH level is about 0.6 pH-units too low and that the amplitude is 0.04 compared with 0.07 measured in the river. Taken the simplicity of the model, this result is quite satisfactory.

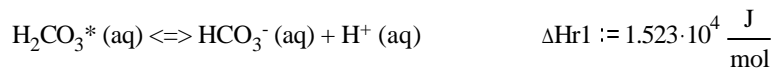
Exercise 8: The Van't Hoff equation is given as:

$$\ln\left(\frac{K_{T2}}{K_{T1}}\right) := \frac{\Delta H_r}{R} \cdot \left\{ \frac{1}{T1} - \frac{1}{T2} \right\}$$

where K_{T2} and K_{T1} are the equilibrium constants at temperatures $T2$ and $T1$ respectively, ΔH_r is the standard enthalpy of reaction (J/mol), R is the gas-constant (J/mol/K) and $T1$ and $T2$ are the temperatures (K). It is assumed that no phase change takes place during the temperature change [2].

This gives the following equilibrium constants at $T2=5^\circ\text{C}$:

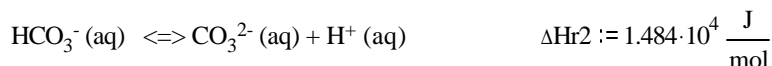
$$R := 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$



$$Ka1_{5C} := \exp\left[\ln(Ka1) + \frac{\Delta H_{r1}}{R} \cdot \left\{ \frac{1}{298 \text{ K}} - \frac{1}{278 \text{ K}} \right\} \right]$$

$$Ka1_{5C} = 2.763 \cdot 10^{-7}$$

Exercise 8 cont.:



$$K_{a2_5C} := \exp \left[\ln(K_{a2}) + \frac{\Delta H_{r2}}{R} \cdot \left\{ \frac{1}{298 \text{ K}} - \frac{1}{278 \text{ K}} \right\} \right]$$

$$K_{a2_5C} = 3.646 \cdot 10^{-11}$$

And so on....

$$K_{h_5C} := 0.059 \quad K_{w_5C} := 1.98 \cdot 10^{-15} \quad K_{s_5C} := 1.24 \cdot 10^{-8}$$

By using the measured and calculated values obtained at 5°C, we can see that the level of the pH oscillations has risen to about pH=7.8 compared to pH=6.9 at 25°C. The level measured in the river was about pH=7.5. The amplitude of the oscillation is about 0.07 compared to 0.04 at 25 °C. The amplitude measured in the river was about 0.07. The effects may not be large, but you can still see how temperature effects pH in a river.

Exercise 9: With an ionic strength of $\mu=5 \cdot 10^{-3}$ M, it is appropriate to use the Güntelberg approximation (applicable to ionic strength below 0.1 mol/l), which is given by:

$$-\ln(\gamma) := \frac{0.51 \cdot z^2 \cdot \sqrt{\mu}}{1 + \sqrt{\mu}}$$

where γ is the activity coefficient of the anion or cation, z is the ioncharge and μ is the ionic strength. The value 0.51 is temperature dependent, but the effect in water is relatively small, so we will neglect it here.

For monovalent and divalent ions we get

$$\gamma_1 := \exp \left\{ - \frac{0.51 \cdot 1 \cdot \sqrt{0.005}}{1 + \sqrt{0.005}} \right\} \quad \gamma_2 := \exp \left\{ - \frac{0.51 \cdot 4 \cdot \sqrt{0.005}}{1 + \sqrt{0.005}} \right\}$$

$$\gamma_1 = 0.967$$

$$\gamma_2 = 0.874$$

The new equilibrium constants corrected for activity can now be found:

$$K_{a1_5C_γ} := \frac{K_{a1_5C}}{\gamma_1^2} \quad K_{a2_5C_γ} := \frac{K_{a2_5C}}{\gamma_2} \quad K_{w_5C_γ} := \frac{K_{w_5C}}{\gamma_1^2}$$

$$K_{s_5C_γ} := \frac{K_{s_5C}}{\gamma_2^2} \quad K_{h_5C_γ} := K_{h_5C}$$

Remembering that the definition of pH is $\text{pH} = -\log(a_{\text{H}})$, where a_{H} is the activity of H^+ , we add this to the model:

$$\text{pH}_i := -\log(\gamma_1 \cdot \text{HResult}(C_{\text{tot}_i}))$$

Exercise 9 cont.:

This addition is the only one needed in the model apart from the corrected equilibrium constants.

Inserting the corrected equilibrium constants into the model reveals, that the level of the pH oscillations is pushed downwards by about 0.05, and that the amplitude of the oscillation is approximately the same. Therefore, unless the ionic strength is large, which we will not expect in a river, this effect is relatively small.

Exercise 10: Assuming that the added anions or cations do not interfere with the other species considered (calcium and the carbonate species) we can simply add their concentration to the charge balance equation in our model. For instance, if we were to add $[An^-] = 2 \cdot 10^{-3}$ mol/L, the charge balance equation would look like this:

$$An := 2 \cdot 10^{-3}$$

Given

$$2 \cdot \frac{K_s \cdot \left\{ \frac{H^2}{Ka1 \cdot Ka2} + \frac{H}{Ka2} + 1 \right\}}{Ct} + H = An + \frac{K_w}{H} + \frac{Ct}{\left\{ \frac{H}{Ka1} + 1 + \frac{Ka2}{H} \right\}} + 2 \cdot \frac{Ct}{\left\{ \frac{H^2}{Ka1 \cdot Ka2} + \frac{H}{Ka2} + 1 \right\}}$$

$H \geq 0$

$HResult(Ct) := Find(H)$

As you can see if you change the model thus, this again does not change the oscillation very much, but it does change the level of the pH oscillations - it lowers it by some 0.1 pH units. If you were to add additional cations, you would raise the level of the oscillations by the same amount. This can certainly explain why our model does not match the experiments with respect to the level of the oscillations and shows the importance of a full water analysis.

References

- [1] W. Stumm, J.J. Morgan, *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters*, John Wiley & Sons, 1981
- [2] V.L. Snoeyink, D. Jenkins, *Water Chemistry*, John Wiley & Sons, 1980
- [3] P.W. Atkins, *Physical Chemistry*, 6th Ed., Oxford University Press, 1998
- [4] J.F. Simonsen, P. Harremoes, *Oxygen and pH Fluctuations in rivers*, *Water Research* **12**, 477-489, (1978)
- [5] *Handbook of Chemistry and Physics*, 73rd Ed., CRC Press, 1992
- [6] E.K. Berner, R.A. Berner, *Global Environment: Water, Air and Geometrical Cycles*, Prentice Hall, 1996
- [7] *Standard Methods for the Examination of Water and Wastewater*, 18th Ed., 1992

Appendix A: Experimental data

Equilibrium constants (25°C) [2]:

$K_{a1} := 4.27 \cdot 10^{-7}$ (first dissociation constant)

$K_{a2} := 4.79 \cdot 10^{-11}$ (second dissociation constant)

$K_h := 3.35 \cdot 10^{-2}$ (Henry's constant)

$K_w := 10^{-14}$ (water dissociation constant)

$K_s := 8.7 \cdot 10^{-9}$ (solubility constant for CaCO_3)

The reation constant for CO_2 at 25°C is:

$K_{\text{CO}_2} := 0.044$ (mol/L/hour)

and at 5°C:

$K_{\text{CO}_2} := 0.027$ (mol/L/hour)

The partial pressure of carbon dioxide is:

$p_{\text{CO}_2} := 3.16 \cdot 10^{-4}$

Experimental data: The first table below shows several analytical parameters from the river Simested in Denmark, measured over the course of a month from early October to early November 1998. Table 2 shows the measured pH values for the modelling period (15-17th October 1998).

	Conductivity ($\mu\text{S}/\text{cm}$)	[Ca ²⁺] (mol/l)	[HCO ₃ ⁻] (mol/l)	Pmax (5°C) (mol/l/hr)	Pmax (25°C) (mol/l/hr)*	Resp (5°C) (mol/l/hr)	Resp (25°C) (mol/l/hr)*	pH
Maximum	500	1.24E-03	---	---	---	---	---	7.54
Minimum	253	2.09E-04	---	---	---	---	---	7.00
Average	360	7.82E-04	---	---	---	---	---	7.21
Model Period	323	9.70E-04	2.04E-03	1.08E-04	2.16E-04	3.29E-05	1.27E-04	7.25

Table 1: Measurements in Simested river from 6th October to 5th November 1998. Maximum, minimum and average values are given. Average values for the model period (15th-17th October) are given in the bottom line of the table. Values marked with '*' are theoretical values based on temperature correction of the measured values at 5°C.

The measurements were conducted as follows:

pH measurements were carried out with two pH data-loggers from Hanna Instruments (HI 92240) with gel-type pH-electrodes (HI 1130B). Before use, and as often as possible, the electrodes were calibrated on location.

For measurement of calcium concentration, conductivity and alkalinity, two samples were taken seven times during the period of the pH measurements. The water samples were analyzed in our laboratory.

Calcium concentration was measured with a Radiometer PHM 220 by using an Orion calcium ion-selective electrode (series 93) with an Orion single junction reference electrode (model 90-01).

Conductivity was measured with a Radiometer conductivity meter (CDM 3) with a CDC 104 conductivity cell.

Alkalinity was measured by titration[7].

t (hr)	pH	t (hr)	pH	t (hr)	pH	t (hr)	pH	t (hr)	pH	t (hr)	pH	t (hr)	pH	t (hr)	pH
-12.00	7.49	-8.75	7.48	-5.50	7.44	-2.25	7.45	1.00	7.53	4.25	7.56	7.50	7.55	10.75	7.54
-11.75	7.50	-8.50	7.47	-5.25	7.43	-2.00	7.45	1.25	7.54	4.50	7.57	7.75	7.54	11.00	7.53
-11.50	7.47	-8.25	7.47	-5.00	7.44	-1.75	7.46	1.50	7.54	4.75	7.56	8.00	7.53	11.25	7.53
-11.25	7.48	-8.00	7.47	-4.75	7.43	-1.50	7.45	1.75	7.53	5.00	7.57	8.25	7.55	11.50	7.53
-11.00	7.49	-7.75	7.48	-4.50	7.45	-1.25	7.46	2.00	7.53	5.25	7.55	8.50	7.54	11.75	7.49
-10.75	7.47	-7.50	7.45	-4.25	7.44	-1.00	7.48	2.25	7.55	5.50	7.56	8.75	7.53	12.00	7.50
-10.50	7.49	-7.25	7.46	-4.00	7.43	-0.75	7.47	2.50	7.55	5.75	7.56	9.00	7.51	12.25	7.48
-10.25	7.51	-7.00	7.46	-3.75	7.43	-0.50	7.48	2.75	7.55	6.00	7.54	9.25	7.51		
-10.00	7.48	-6.75	7.46	-3.50	7.42	-0.25	7.49	3.00	7.55	6.25	7.55	9.50	7.54		
-9.75	7.48	-6.50	7.45	-3.25	7.44	0.00	7.48	3.25	7.56	6.50	7.55	9.75	7.51		
-9.50	7.47	-6.25	7.45	-3.00	7.43	0.25	7.50	3.50	7.56	6.75	7.55	10.00	7.54		
-9.25	7.48	-6.00	7.44	-2.75	7.44	0.50	7.49	3.75	7.56	7.00	7.54	10.25	7.54		
-9.00	7.48	-5.75	7.45	-2.50	7.44	0.75	7.51	4.00	7.57	7.25	7.55	10.50	7.53		

Table 2: pH values measured in the period 15th-17th October 1998. The measurements start at midnight (t = -12) and are given for every 15 minutes.

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