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## Buffering, stoichiometry, and the sensitivity of pH to biogeochemical and physical processes: a proton-based model perspective (AGGREGATION CH 5)

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# Buffering, stoichiometry, and the sensitivity of pH to biogeochemical processes: a proton-based model perspective

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## Abstract

Against the background of global ocean acidification, mechanistic understanding of pH changes is essential. In this publication, a tool to quantify the influences of kinetic processes on the pH is presented. This is done by taking the traditional pH modelling approach one step further: instead of calculating influences of modelled biogeochemical processes on the pH via the detour of alkalinity, those influences are calculated directly. The process specific rate of change of the proton concentration can be calculated via the *sensitivity* of the pH to the respective process. This sensitivity is a function of the stoichiometric coefficient for the proton in the introduced *fractional reaction equation at current pH* of the process in question. The concept of fractional stoichiometry at current pH can be linked to the well known marine chemical concepts of ionization fractions and buffer capacity. By creating a link between stoichiometry and the process specific rate of change of the proton concentration, the presented approach does not remain a mere mathematical recipe, but provides a chemical interpretation of the mechanisms underlying pH changes in aquatic models. Applying the concept of buffer capacity and pH sensitivities to an averaged global ocean shows that towards the end of the century the oceans will be around four times less buffered than today and the order of processes according to pH sensitivities will change.

## 1 Introduction

The antropogenic release of carbon dioxide to the atmosphere leads to acidification of the global surface waters (IPCC, 2007; Zeebe et al., 2008) which is likely to have an adverse effect on aquatic ecosystems (Orr et al., 2005; Gazeau et al., 2007; Guinotte and Fabry, 2008). In response, there is currently a large effort by the scientific community to better understand past, present and future changes in the pH. A crucial task within this program is to quantify how large those changes are and to better understand first how biogeochemical processes are driving or modulating these pH changes. Therefore, over the last few years, a range of modelling approaches have been advanced that describe the pH evolution of open waters (e.g. Follows et al., 2006; Soetaert et al., 2007; Wolf-Gladrow et al., 2007; Hofmann et al., 2008b) as well as interstitial pore water in sediments. (e.g. Marinelli and Boudreau, 1996; Boudreau, 1996; Gehlen et al., 1999; Luff et al., 2001; Jourabchi et al., 2005)

The classical approach to carbonate chemistry and pH calculations in natural waters is centred around the alkalinity concept (Morel and Hering, 1993; Stumm and Morgan, 1996;

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Zeebe and Wolf-Gladrow, 2001). To quantify or model pH changes one essentially uses a two-step approach. First, one quantifies the influence of biogeochemical processes on the alkalinity, which then results in a suitable alkalinity change for the system at hand. In a second step, one translates this alkalinity change into a corresponding pH change using a procedure that typically involves a pH equilibration algorithm. In essence, one uses the alkalinity as a mediator between biogeochemical processes and the observed or modelled pH changes. However, because of this two-step process, there is no direct link between the biogeochemical processes on the one hand, and pH changes on the other hand. In other words, the current approach to pH modelling does not allow for a direct quantification of the influences of individual biogeochemical processes on the proton concentration.

In this paper, we propose an extension of the current alkalinity centered approach, which puts protons at the center of attention, and which enables a direct quantification of the effects of biogeochemical processes on pH. The central idea is that we can derive a *sensitivity* of the pH to each biogeochemical process, which determines how strongly this biogeochemical process will influence the pH. This practise allows for a quantification and therefore an intercomparison of the influences of different processes on the pH.

The current paper is an extension and generalization of the pH modelling methodology detailed in Hofmann et al. (2008b), which itself was based on earlier work by Jourabchi et al. (2005), Soetaert et al. (2007) and Wolf-Gladrow et al. (2007). In Hofmann et al. (2008b), we primarily concentrated on the numerical aspects of pH modelling, while here, we will principally focus on concepts and chemical interpretation. To promote understanding, and to keep the mathematical expressions within reasonable limits, we will outline our approach by means of a simple example, which only incorporates a restricted number of processes (CaCO<sub>3</sub> precipitation, CO<sub>2</sub> exchange across the air-water interface, and the carbonate acid-base system). The approach is however entirely general, and can be extended to any set of reaction and transport processes, and any number of acid-base systems. These generalizations are discussed in the Appendices.

## 2 Two pH modelling approaches

### 2.1 Problem statement

Assume that on a given day, a water reservoir is sampled and total alkalinity (TA), dissolved inorganic carbon (DIC) as well as the pH are measured. Twenty days later, the reservoir is sampled again, and the measurements are repeated. The acquired data are given in Table (1).

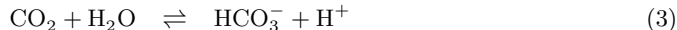
	t = 0 d	t = 20 d	$\Delta$
TA	2200	1963	-237
DIC	2000	1864	-136
pH	8.165	7.923	-0.242

Table 1: Parameters of the example water reservoir at t = 0 d and t = 20 d; Concentrations are in  $\mu\text{mol kg}^{-1}$ . Note that throughout this paper, the term "proton concentration" will refer to the concentration of the free hydrogen ion, and hence, the  $\text{pH} = -\log([\text{H}^+])$  is defined on the free hydrogen ion concentration scale (Dickson, 1981; Zeebe and Wolf-Gladrow, 2001).

The water management body responsible for the reservoir would like to better understand the observed pH changes. Therefore, they request that a model should be developed which describes the pH evolution over the 20 day observational period. From previous studies, it is known that the pH chemistry of the reservoir is mainly influenced by CaCO<sub>3</sub> precipitation and CO<sub>2</sub> exchange across the air-water interface. These are the two dominant "slow" kinetic processes that drive the biogeochemical changes in the reservoir over a time scale of days, and they can be represented by the reaction equations



where  $\text{CO}_2(g)$  represents gaseous  $\text{CO}_2$  in the atmosphere. In addition, the pH chemistry will also depend on a number of "fast" acid-base dissociation reactions, with characteristic time scales of less than a minute (Zeebe and Wolf-Gladrow, 2001). To keep the model suitably simple, only the carbonate system is accounted for



This conceptual model of the water chemistry inside the reservoir needs to be translated into a concrete implementation via a suitable set of differential equations, that not only reproduces the measured values at the end of the 20 day period, but also can answer two research questions:

1. How did the pH evolve in between the sampling times?
2. Which slow kinetic "driving" process (calcite precipitation or  $\text{CO}_2$  exchange across the air-water interface) affected the pH change the most and how did the effects of both processes on the pH change over time?

Clearly, the primary goal of this model is to predict the evolution of the pH, or equally the proton concentration, as a function of time. Accordingly, the model should somehow include an equation of the form

$$\frac{d[\text{H}^+]}{dt} = f(\mathbf{R}_P, \mathbf{R}_C) \quad (5)$$

where  $\mathbf{R}_P$  is the net forward rate of carbonate precipitation and  $\mathbf{R}_C$  denotes the rate of  $\text{CO}_2$  exchange. The pH evolution equation (5) expresses the rate of change of the proton concentration as a function of the rates of the "driving" processes. It is important to note that the right hand side of this equation only depends on the rates of the slow kinetic processes. This is because, on the relatively long time-scale of the model, i.e., days, only carbonate precipitation and  $\text{CO}_2$  exchange are "driving" the concentration changes within the reservoir. The fast dissociation reactions can be assumed in thermodynamic equilibrium at all times, and as a result, their net forward rates become implicitly dependent on the rates of the slow kinetic processes. A more general and detailed discussion of this important aspect is given in Appendix A.

When available, the pH evolution equation (5) would certainly be a valuable tool to analyze pH changes in natural systems. It directly links the pH change (the left hand side) to the biogeochemical processes that drive this pH change (the right hand side). However, a key problem with the current approaches to pH modelling is that an equation like (5) is not made available in an explicit form. This is because the conventional approach to carbonate chemistry and pH calculations in natural waters is focused on alkalinity rather than protons. In other words, one explicitly quantifies the effect of biogeochemical processes on alkalinity, but their concomitant effect on protons is only indirectly accounted for. In the next section, we show how a pH model for our reservoir is constructed following the conventional alkalinity centered procedure. In a subsequent section, we will show how this conventional modelling approach can be extended, so that an explicit pH evolution equation like Eq. (5) is obtained.

## 2.2 The implicit pH modelling approach

The construction of a biogeochemical model traditionally starts by listing the mass balance equations for the relevant chemical species in the system. In our example, we will track the concentrations of one<sup>1</sup> kinetic species (i.e., species that only participate in slow kinetic processes:  $[\text{CaCO}_3]$ ) and four equilibrium species (i.e., species that participate in one of the fast equilibrium reactions:  $[\text{CO}_2]$ ,  $[\text{HCO}_3^-]$ ,  $[\text{CO}_3^{2-}]$ , and  $[\text{H}^+]$ ). The differential mass balance equations for those species are listed in sections a1 and a2 of Table (2).

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<sup>1</sup>Note that  $[\text{Ca}^{2+}]$  is assumed constant, but if it was dynamically modelled it would be a kinetic species as well since it does not participate in any equilibrium reactions.

[a1] The mass balance for the kinetic species is:

$$\frac{d[\text{CaCO}_3]}{dt} = \mathbf{R}_P \quad (6)$$

(7)

[a2] The mass balances for the equilibrium species are:

$$\frac{d[\text{CO}_2]}{dt} = -\mathbf{R}_{\text{CO}_2\text{diss}} + \mathbf{R}_C \quad (8)$$

$$\frac{d[\text{HCO}_3^-]}{dt} = \mathbf{R}_{\text{CO}_2\text{diss}} - \mathbf{R}_{\text{HCO}_3^-\text{diss}} \quad (9)$$

$$\frac{d[\text{CO}_3^{2-}]}{dt} = \mathbf{R}_{\text{HCO}_3^-\text{diss}} - \mathbf{R}_P \quad (10)$$

$$\frac{d[\text{H}^+]}{dt} = \mathbf{R}_{\text{CO}_2\text{diss}} + \mathbf{R}_{\text{HCO}_3^-\text{diss}} \quad (11)$$

[b] Removing the net forward rates of the fast processes by linear combination provides:

$$(9) + 2(10) - (11) = \frac{d([\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] - [\text{H}^+])}{dt} = -2\mathbf{R}_P \quad (12)$$

$$(8) + (9) + (10) = \frac{d([\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}])}{dt} = \mathbf{R}_C - \mathbf{R}_P \quad (13)$$

(14)

[c] The total quantities or equilibrium invariants are thus defined as:

$$\text{TA} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] - [\text{H}^+] \quad (15)$$

$$\text{DIC} = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (16)$$

[d] The equilibrium mass action equations are:

$$K_1^* = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} \quad (17)$$

$$K_2^* = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (18)$$

[e] The kinetic rate laws are:

$$\mathbf{R}_P = k_P (1 - \Omega)^n \quad (19)$$

$$\mathbf{R}_C = k_C ([\text{CO}_2]_{\text{sat}} - [\text{CO}_2]) \quad (20)$$

Table 2: *The pH model development procedure:*

[a] The mass conservation equations for all relevant chemical species in the example system are listed. A distinction is made between kinetic species and equilibrium species. The mass balances of the equilibrium species contain at least one rate of a fast "equilibrium" reaction.

[b] By a suitable linear combination, the rates of the fast "equilibrium" reactions can be removed from the differential equations of the equilibrium species. We arrive at a reduced equation set where the number of transformed equations (2) always equals the original number of mass balances (4) minus the number of equilibrium reactions (2).

[c] The definition of TA and DIC follows from the transformed equations.

[d] The transformed equations themselves are not sufficient for a complete model statement since the system would be underdetermined. We need to add the equilibrium mass action laws for the fast reactions in order to close the model formulation. The  $K^*$ 's denote stoichiometric equilibrium constants as opposed to thermodynamic or hybrid equilibrium constants; see [Zeebe and Wolf-Gladrow \(2001\)](#) for a discussion of different types of equilibrium constants

[e] Rate laws for the slow "kinetic" reactions.  $\Omega = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_{spc}^*}$  is the saturation state of the water with  $K_{spc}^*$  being the stoichiometric solubility product for calcite.

A first problem that needs resolution is that the mass balances for the equilibrium species still contain the not explicitly known net forward reaction rates of the fast equilibrium reactions. These reactions are not modelled via kinetic expressions, but are assumed to reside in thermodynamic equilibrium at all times making their net forward rates implicit functions of the rates of the slow kinetically modelled processes (see also Appendix A). Yet, through a

suitable linear combination, known as a *transformation into canonical form*, these equilibrium rates can be removed from the equation set (Lichtner, 1996; Meysman, 2001; Hofmann et al., 2008b). As a result, one obtains the reduced equation set (see sections b and c in Table 2 for the derivation of these equations)

$$\frac{dTA}{dt} = -2\mathbf{R}_P \quad (21)$$

$$\frac{dDIC}{dt} = \mathbf{R}_C - \mathbf{R}_P \quad (22)$$

Rather than the dissociated species, these mass balance equations now feature the *total quantities* alkalinity (TA) and the dissolved inorganic carbon (DIC). These equations describe the time evolution of TA and DIC and form the core of the conventional "alkalinity-centred" approach to pH modeling. Both the TA and DIC changes are expressed as a function of the rates of the driving kinetic processes (here  $\mathbf{R}_P$  and  $\mathbf{R}_C$ ). Employing suitable kinetic rate laws for these kinetic processes, these evolution equations can be numerically integrated. Rate expressions for carbonate precipitation and CO<sub>2</sub> exchange for our example are provided in section e of Table (2).

Technically, the total quantities TA and DIC are termed *invariant* with respect to the fast equilibrium reactions, because they are no longer influenced by the underlying acid-base equilibria (and thus they are also invariant to temperature and salinity changes). Note that in the usual model development procedure, one will not explicitly consider the transformation into canonical form. Instead, the evolution equations for TA and DIC (Eqs. 21 and 22) are immediately written down, while the specific form of the alkalinity in Eq. (15) is postulated (see Dickson, 1981; Wolf-Gladrow et al., 2007) rather than derived<sup>2</sup>.

As Table (2) details all necessary information, an attempt to solve the model can now be performed. In theory, the direct integration of the evolution equations for TA and DIC (Eqs. 21 and 22) should allow for a calculation of TA( $t$ ) and DIC( $t$ ) at any future time  $t$  starting from some initial values TA( $t_0$ ) and DIC( $t_0$ ). However, such a direct integration is not possible. The problem is that the kinetic rate expressions are not specified in terms of TA and DIC, but feature the concentrations of the equilibrium species [CO<sub>2</sub>] and [CO<sub>3</sub><sup>2-</sup>].

To overcome this problem, numerical pH modelling procedures typically use a two-step approach (e.g. Ben-Yaakov, 1970; Culberson, 1980; Luff et al., 2001; Follows et al., 2006). This two step procedure includes an additional "equilibration step": during every timestep, the current values of alkalinity and dissolved inorganic carbon, TA( $t$ ) and DIC( $t$ ) (starting with TA( $t_0$ ) and DIC( $t_0$ ) in the first timestep), are used to calculate a full speciation, i.e., to calculate the concentrations of all equilibrium species. For our example, those concentrations are the concentrations of all three carbonate species and the proton concentration. Because of the non-linearity of the equilibrium mass action equations in the proton concentration [H<sup>+</sup>], which is an unknown here, this calculation must be performed using a numerical procedure (e.g. numerical root finding). The concentrations of the equilibrium species are then used to calculate the rates of all kinetically modelled processes (here [CO<sub>2</sub>] is used to calculate  $\mathbf{R}_C$ , and [CO<sub>3</sub><sup>2-</sup>] is used to calculate  $\mathbf{R}_P$ ). Those rates, in turn, are employed for the numerical integration of the evolution equations for TA and DIC (Eqs. 21 and 22) over some time step  $\Delta t$  to arrive at TA( $t + \Delta t$ ) and DIC( $t + \Delta t$ ).

By repeating this two-step procedure for a suitable sequence of time steps, one eventually obtains the evolution of TA, DIC and pH over the desired time interval. The simulated pH

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<sup>2</sup>Here, we explicitly include the transformation into canonical form in Table (2), because it demonstrates the implicit logic that lies behind this procedure. It shows one does not need to postulate the definition of alkalinity as such. The alkalinity is essentially a derived quantity, whose specific form directly follows from the linear combination of the mass balances of the equilibrium species in the biogeochemical model. Obviously, the linear combination is done deliberately in a certain way to obtain a subset of Dickson's (Dickson, 1981) total alkalinity in order to be consistent with other works and alkalinity measurement techniques (Gran, 1952; Hansson and Jagner, 1973; Dickson, 1981; DOE, 1994; Anderson et al., 1999; Dickson et al., 2007), but the specific subset of Dickson's total alkalinity depends on the mass balances of the equilibrium species in the biogeochemical model and is derived during the transformation into canonical form.

evolution is not directly obtained from an evolution equation like Eq. (5). Instead, the pH is implicitly determined from the time evolution of the TA and DIC. Therefore, we call this the *implicit pH modelling approach* (in Hofmann et al. (2008b) this approach was called *operator splitting approach* because of the two-step procedure). Figure (1) shows the results of this implicit modelling procedure for our water reservoir over the 20 day period<sup>3</sup>. The parameter values that were used are summarized in Table (3).

Symbol	Value	Units	Reference
$S$	35	-	
$T$	15	$^{\circ}\text{C}$	
$K_1^*$	9.386	$\mu\text{mol kg-soln}^{-1}$	(Roy et al., 1993)
$K_2^*$	$6.685 \cdot 10^{-4}$	$\mu\text{mol kg-soln}^{-1}$	(Roy et al., 1993)
$[\text{Ca}^{2+}]$	$1.028 \cdot 10^4$	$\mu\text{mol kg-soln}^{-1}$	(DOE, 1994)
$K_{spc}^*$	$4.315 \cdot 10^5$	$(\mu\text{mol kg-soln}^{-1})^2$	(Mucci, 1983)
$k_P$	1.0	$\mu\text{mol kg-soln}^{-1}$	
$n$	2.0	-	
$K_0\text{CO}_2$	$3.746 \cdot 10^4$	$\mu\text{mol kg-soln}^{-1} \text{ atm}^{-1}$	(Weiss, 1974)
$p\text{CO}_2$	383.0	$\mu\text{atm}$	(Guinotte and Fabry, 2008)
$k_C$	0.5	$d^{-1}$	

Table 3: Parameters values used in the example model.

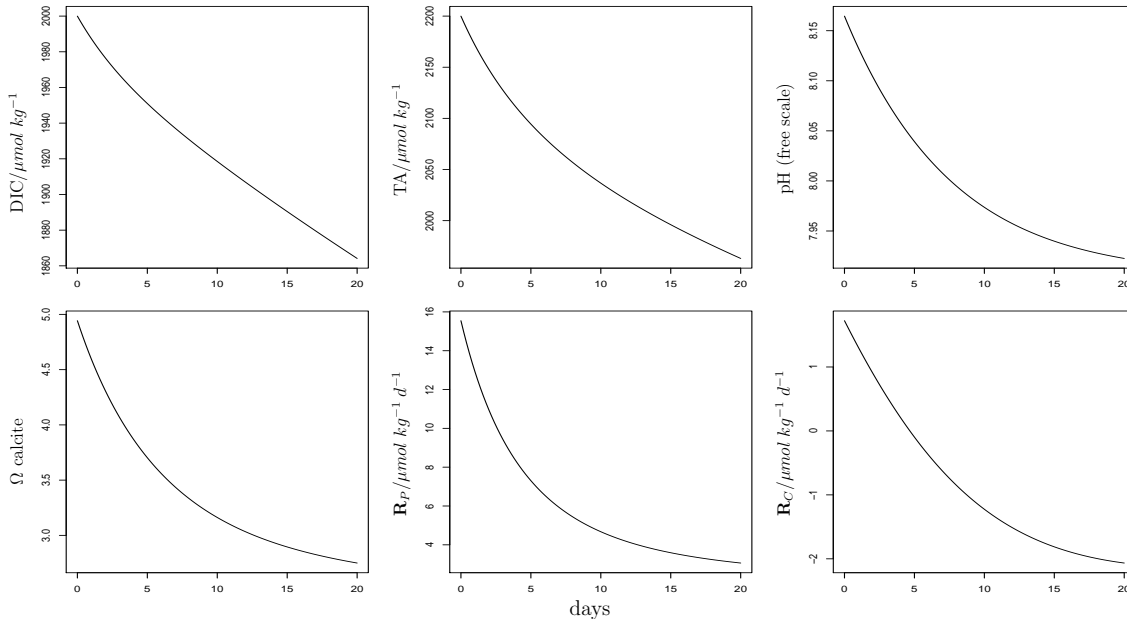


Figure 1: Changes in key variables of the example system over the course of 20 days, calculated with the implicit approach.

As shown by the pH profile in Fig. (1), the implicit modelling procedure is able to predict how the pH changes over time, and so it is able to answer our first research question ("How did the pH evolve in between the sampling times?"). That means, to model the pH dynamics, one does not need an explicit evolution equation like Eq. (5). Yet, the absence of such an evolution equation also has an important consequence: the implicit pH modelling approach is not able to answer our second question ("Which slow kinetic process affected the pH change the most and how did the effects of both processes on the pH change over time?"). We are not able to check whether carbonate precipitation or  $\text{CO}_2$  exchange is the main responsible

<sup>3</sup>Note that all models discussed in this paper have been coded in the statistical programming language R (R Development Core Team, 2005) using the packages deSolve (Soetaert, 2008) and AquaEnv (Hofmann et al., 2008c). The code can be obtained from the corresponding author.

process for the observed pH changes. In the implicit pH modelling approach, the link between kinetic processes and pH changes is obscured by the numerical equilibration step.

### 2.3 The explicit pH modelling approach

As indicated above, an evolution equation of the form of Eq. (5) would be a valuable tool to improve our understanding of pH changes in natural waters. It shows how different kinetic processes separately contribute to the pH change (or better the rate of change of the proton concentration  $\frac{d[\text{H}^+]}{dt}$ ). The derivation of such an equation is rather straightforward. In equilibrium, it is well known that all quantities in the carbonate system (TA, DIC,  $[\text{CO}_2]$ ,  $[\text{HCO}_3^-]$ ,  $[\text{CO}_3^{2-}]$ , and  $[\text{H}^+]$ ) can be calculated from any combination of two components from this list. Taking the proton and DIC concentrations as the primary components, we can hence express the alkalinity TA as a function of these components

$$\text{TA} = \text{TA}(\text{DIC}, [\text{H}^+]) = (\alpha_1[\text{H}^+] + 2\alpha_2[\text{H}^+])\text{DIC} - [\text{H}^+] \quad (23)$$

where we introduced the ionization fractions  $\alpha_i$  as functions of the proton concentration  $[\text{H}^+]$  in the usual way (Skoog and West, 1982; Stumm and Morgan, 1996)

$$\alpha_0 = \frac{[\text{CO}_2]}{\text{DIC}} = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + K_1^*[\text{H}^+] + K_1^*K_2^*} \quad (24)$$

$$\alpha_1 = \frac{[\text{HCO}_3^-]}{\text{DIC}} = \frac{K_1^*[\text{H}^+]}{[\text{H}^+]^2 + K_1^*[\text{H}^+] + K_1^*K_2^*} \quad (25)$$

$$\alpha_2 = \frac{[\text{CO}_3^{2-}]}{\text{DIC}} = \frac{K_1^*K_2^*}{[\text{H}^+]^2 + K_1^*[\text{H}^+] + K_1^*K_2^*} \quad (26)$$

Note that Eq. (23) implies that the equilibrium constants  $K_1^*$  and  $K_2^*$  are constant over time. However, both DIC and  $[\text{H}^+]$  are functions of time, so differentiating both the left and right hand side of Eq. (23) with respect to time by applying the chain rule of differentiation, one immediately arrives at<sup>4</sup>

$$\frac{d\text{TA}}{dt} = \left( \frac{\partial \text{TA}}{\partial [\text{H}^+]} \right) \frac{d[\text{H}^+]}{dt} + \left( \frac{\partial \text{TA}}{\partial \text{DIC}} \right) \frac{d\text{DIC}}{dt} \quad (27)$$

A simple rearrangement of terms directly provides following expression for the rate of change of the proton concentration

$$\frac{d[\text{H}^+]}{dt} = \frac{1}{\left( \frac{\partial \text{TA}}{\partial [\text{H}^+]} \right)} \left( \frac{d\text{TA}}{dt} - \left( \frac{\partial \text{TA}}{\partial \text{DIC}} \right) \frac{d\text{DIC}}{dt} \right) \quad (28)$$

This expression features the rate of change of both alkalinity and DIC. However, these terms were already known from the evolution equations of these quantities (Eqs.(21) and (22)). Accordingly, upon substitution, we finally arrive at

$$\frac{d[\text{H}^+]}{dt} = S_P \mathbf{R}_P + S_C \mathbf{R}_C \quad (29)$$

with

$$S_P = \frac{1}{\left( \frac{\partial \text{TA}}{\partial [\text{H}^+]} \right)} \left( -2 + \frac{\partial \text{TA}}{\partial \text{DIC}} \right) \quad (30)$$

$$S_C = \frac{1}{\left( \frac{\partial \text{TA}}{\partial [\text{H}^+]} \right)} \left( -\frac{\partial \text{TA}}{\partial \text{DIC}} \right) \quad (31)$$

This expression matches the sought after form of the pH evolution (5). The terms  $S_P$  and  $S_C$  will be called the *sensitivity* of pH with respect to  $\text{CaCO}_3$  precipitation and  $\text{CO}_2$  exchange

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<sup>4</sup>Note that this procedure is equivalent to constructing the total differential of TA as function of DIC and  $[\text{H}^+]$  and then dividing it by  $dt$ .



respectively. An important aspect is that these sensitivities can be calculated in a closed analytical form. This is because, although the calculation of  $[\text{H}^+]$  from DIC and TA requires a numerical solution, the partial derivatives in Eqs. (30) and (31) can be analytically calculated from our starting expression for the alkalinity (Eq. (23)).

Eq. (29) provides a true evolution equation for the proton concentration (or equally the pH). This differential equation can be directly integrated together with the evolution equation for DIC (Eq. (22)). This immediately provides the evolution of DIC and pH over the desired time interval.

Direct integration thus allows us to calculate the values of  $[\text{H}^+](t)$  and  $\text{DIC}(t)$  at any future time  $t$  starting from the initial values  $[\text{H}^+](t_0)$  and  $\text{DIC}(t_0)$ . The concentrations for the other components of the carbonate system (that is, TA,  $[\text{CO}_2]$ ,  $[\text{HCO}_3^-]$ ,  $[\text{CO}_3^{2-}]$ ) can be calculated *analytically* from  $[\text{H}^+](t)$  and  $\text{DIC}(t)$ . In other words, one does no longer need the traditional sequential two-step approach: the numerical root finding procedure is obsolete since the variable  $[\text{H}^+]$ , which the equilibrium mass action equations of the acid base systems are non linear in, is not an unknown any more in every timestep.

Because of the integration of an explicit evolution equation for the proton concentration, we call this the *explicit pH modelling approach* (in Hofmann et al. (2008b) this approach was called *direct substitution approach* because of the substitution of the alkalinity evolution equation by the proton evolution equation). Obviously, the pH evolution that is arrived at is exactly the same as the one obtained via the implicit modelling approach, which is confirmed in the given example model.

Apart from the direct integration, the explicit modelling approach has also an important conceptual advantage in terms of understanding pH changes. The analytical expressions for  $S_P$  and  $S_C$  allow a systematic investigation of the sensitivity of the pH to the associated biogeochemical processes. Equation (29) specifies that the influence of a given process on the pH can always be decomposed as a modulating factor, which is the sensitivity of the pH with respect that process, times the process rate. Processes may have high rates, but a low sensitivity, and vice versa. Accordingly, to examine the overall influence of a kinetic process on the pH, one must look at the combination of both sensitivity and actual rate.

Figure (2) plots the sensitivities  $S_P$  and  $S_C$  as well as the associated reaction rates  $R_P$  and  $R_C$  for our water reservoir example. Both the sensitivities as well as the reaction rates change over time. However, when averaged over the 20 day period, the sensitivity for carbonate precipitation is roughly the same as that for  $\text{CO}_2$  air-water exchange. However, the rate of carbonate precipitation (expressed per mole of C) is one order of magnitude higher. Accordingly, we can conclude that carbonate precipitation is the dominant process influencing the pH in our water reservoir system over the observed 20 day time period.

In summary, the explicit modelling approach is able to answer our first research question ("How did the pH evolve in between the sampling times?"), as well as the second one ("Which slow kinetic process affected the pH change the most and how did the effects of both processes on the pH change over time?").

Note that App. D details the implicit pH modelling approach for an arbitrary complex system, i.e. featuring an arbitrary number of total quantities and reactions.

### 3 The link between pH sensitivities and buffering capacity

Above, we have derived the explicit pH modelling approach as an extension of the conventional implicit pH modelling approach. From this analysis, it is clear that the explicit pH modelling approach can provide valuable insight into pH dynamics. Yet, until now, our derivation has been a pure mathematical recipe without a clear interpretation in terms of water chemistry.

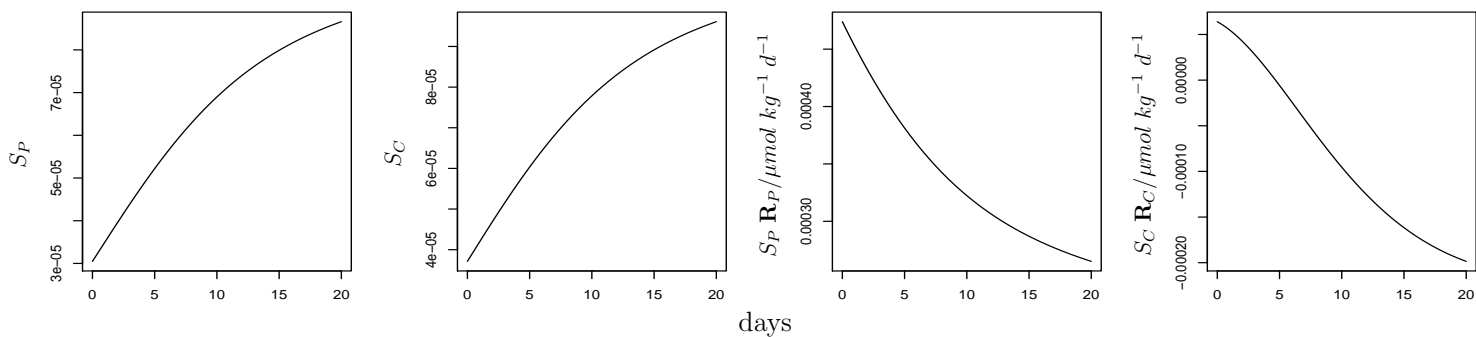


Figure 2: The sensitivities of the pH to and the influences on the pH of calcite precipitation and CO<sub>2</sub> air-water exchange in the example system over the course of 20 days. The sensitivities are dimensionless quantities.

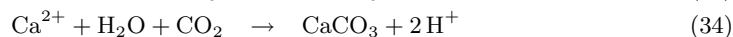
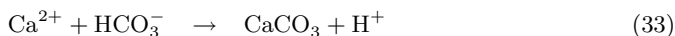
How can we interpret the above sensitivities in terms of the mechanisms that are affecting the pH? What is the role of the "slow" kinetic reactions as opposed to the role of the "fast" acid-base reactions? In the following, we will discuss a method that derives Eq. (29) directly starting from the stoichiometry of the kinetic processes thus providing a direct chemical interpretation of this equation.

### 3.1 Step 1: The proton release rate at current pH

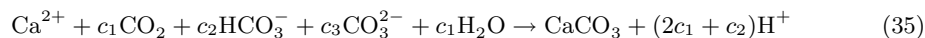
Following the classical textbook definition, the production rate of a particular chemical species due to a given chemical reaction simply equals the reaction rate times the stoichiometric coefficient  $\nu$  of the chemical species in the reaction equation. This also applies to protons, and so in our example, the total release rate of protons would become

$$\nu_{\text{H}^+}^P \mathbf{R}_P + \nu_{\text{H}^+}^C \mathbf{R}_C \quad (32)$$

where  $\nu_{\text{H}^+}^P$  and  $\nu_{\text{H}^+}^C$  represent the stoichiometric coefficients for H<sup>+</sup> in the associated reaction equations for calcite precipitation and CO<sub>2</sub> air-water exchange. However, this is a too simplistic perspective. When literally applying this idea to the specific reaction equations used in our model formulation (i.e., Eqs. (1) and (2)), it would imply that there are no protons released, since  $\nu_{\text{H}^+}^P = \nu_{\text{H}^+}^C = 0$ . Obviously, this cannot be true, and the reason for this discrepancy is the inevitable arbitrariness connected with writing stoichiometric reaction equations. Indeed, instead of Eq. (1), the reaction equation for calcium carbonate precipitation can also be written in the alternative forms



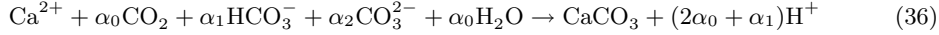
Note that these reaction equations do produce protons, and hence, the stoichiometric coefficient  $\nu_{\text{H}^+}^P$  would become 1 and 2 respectively. We refer to the reaction equations (1), (33) and (34) as *integer reaction equations*, since all stoichiometric coefficients are integers. These integer reaction equations are, however, not the only possible alternatives. Any linear combination of reaction equations (1), (33) and (34) of the form



is valid, provided the coefficients are constrained by  $c_1 + c_2 + c_3 = \nu_{\text{CaCO}_3} = 1$ . Here, the coefficients  $c_1$ ,  $c_2$ , and  $c_3$  are no longer integers but fractions, and so, we call Eq. (35) a *fractional reaction equation*.

Effectively, Eq. (35) provides an infinite number of possibilities to write the reaction equation of carbonate precipitation, with an associated infinite number of possibilities for the stoichiometric coefficient  $\nu_{\text{H}^+}^P = 2c_1 + c_2$ . From this infinite set, there is, however, one set of coefficients  $c_i$  that has a particular chemical meaning. The current pH of the solution induces

a specific partitioning of DIC into  $[\text{CO}_2]$ ,  $[\text{HCO}_3^-]$ , and  $[\text{CO}_3^{2-}]$ . If we substitute the ionization coefficients  $\alpha_i$  as the coefficients  $c_i$  into Eq. (35), we obtain an equation which describes the proton release of calcium carbonate precipitation at the current pH of the system.

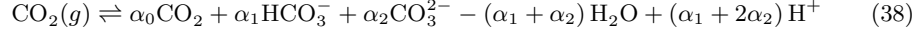


We refer to Eq. (36) as the *fractional reaction equation at current pH* of calcium carbonate precipitation.

When  $\text{CO}_2$  air-water exchange is written in the way of a chemical reaction



we can derive a fractional reaction equation at the current pH for  $\text{CO}_2$  air-water exchange in much the same way



Appendices B and C provide recipes to derive the fractional reaction equation at the current pH for any reaction process, including transport processes.

From Eqs. (36) and (38) the *proton release rate at current pH* for our system is derived as

$$\nu_{\text{H}^+}^P \mathbf{R}_P + \nu_{\text{H}^+}^C \mathbf{R}_C = (2\alpha_0 + \alpha_1)\mathbf{R}_P + (\alpha_1 + 2\alpha_2)\mathbf{R}_C \quad (39)$$

This quantity represents the production rate of protons at a given pH that results from carbonate precipitation and  $\text{CO}_2$  exchange, *without re-equilibration by acid-base reactions*. In other words, it assumes that the water contains an invariant mix of carbonate species, specified by the fixed ionization constants  $\alpha_i$ , which themselves are uniquely determined by the current pH (see Eqs. (24)-(26)).

### 3.2 Step 2: Accounting for re-equilibration

In a non-buffered system (i.e., without "fast" acid-base reactions), the rate of change of protons in solution can be equated to the proton release rate at current pH. However, in a buffered system, this assumption is no longer valid. One needs to account for buffering, i.e., for *re-equilibration* by the acid-base reactions. According to the principle of Le Chatelier-Braun, re-equilibration will always counteract the proton release by kinetic reactions. This implies that the actual rate of change of protons must always be smaller than the non-buffered rate. This can be expressed by

$$\frac{d[\text{H}^+]}{dt} = \frac{\nu_{\text{H}^+}^P}{\beta} \mathbf{R}_P + \frac{\nu_{\text{H}^+}^C}{\beta} \mathbf{R}_C \quad (40)$$

where the newly introduced *buffer factor*  $\beta \geq 1$  implements the modulating influence of buffering. In essence, the presence of  $\beta$  in Eq. (40) will diminish the amplitude of any pH variations induced by the proton release rate at current pH. Starting from the definition of the stoichiometric coefficients  $\nu_{\text{H}^+}^P$  and  $\nu_{\text{H}^+}^C$  in Eq.(39), using the definition of alkalinity Eq.(23), and knowing that  $\alpha_0 + \alpha_1 + \alpha_2 = 1$ , one can easily prove that

$$\nu_{\text{H}^+}^P \equiv 2\alpha_0 + \alpha_1 = 2 - \frac{\partial \text{TA}}{\partial \text{DIC}} \quad (41)$$

$$\nu_{\text{H}^+}^C \equiv \alpha_1 + 2\alpha_2 = \frac{\partial \text{TA}}{\partial \text{DIC}} \quad (42)$$

Comparing the corresponding terms in the evolution equations (40) and (29), this means we can express the pH sensitivities as

$$S_P = \frac{\nu_{\text{H}^+}^P}{\beta} \quad (43)$$

$$S_C = \frac{\nu_{\text{H}^+}^C}{\beta} \quad (44)$$

Accordingly, we immediately find that the buffer factor is defined by

$$\beta \equiv -\frac{\partial \text{TA}}{\partial [\text{H}^+]} \quad (45)$$

This expression is true in general for an arbitrarily complex biogeochemical system. For our example reservoir system, the buffer factor takes on the explicit form

$$\beta = 1 - \left( \frac{\partial \alpha_1}{\partial [\text{H}^+]} + 2 \frac{\partial \alpha_2}{\partial [\text{H}^+]} \right) \text{DIC} \quad (46)$$

A closer examination of this expression confirms that  $\beta$  truly describes chemical buffering. In our reservoir, the only chemical buffering capacity comes from the carbonate system, as represented by the DIC concentration. When there is no carbonate ( $\text{DIC} = 0$ ), the solution has no buffering capacity. In this case, the buffer factor becomes one, and the protons released at current pH will contribute to the pH change in an unmodulated fashion. In contrast, when the carbonate concentration is very large ( $\text{DIC} \mapsto \infty$ ), the solution has an infinite buffering capacity ( $\beta \mapsto \infty$ , because the factor between brackets in front of DIC is always negative). Hence, the rate of change of protons vanishes, and the solution is buffered in such a way that it will no longer experience pH changes.

Figure (3) displays the stoichiometric coefficients for the proton in the fractional reaction equations at current pH of the two kinetic processes and the buffer factor in our example system. Calcium carbonate precipitation produces a little less than one mole of protons per mole of  $\text{CaCO}_3$  precipitated. Similarly,  $\text{CO}_2$  exchange produces a little more than one mole of protons per one mole of  $\text{CO}_2$  taken up by the water. Accordingly, the stoichiometric coefficients for calcite precipitation and  $\text{CO}_2$  exchange are approximately the same. This is not readily obvious from our original reaction equations Eqs. (1) and (2), where neither calcite precipitation nor  $\text{CO}_2$  air-water exchange seem to consume any protons. The buffer factor decreases over the 20 day period, which implies that the system becomes increasingly more sensitive to proton production (or consumption) as the sensitivities increase.

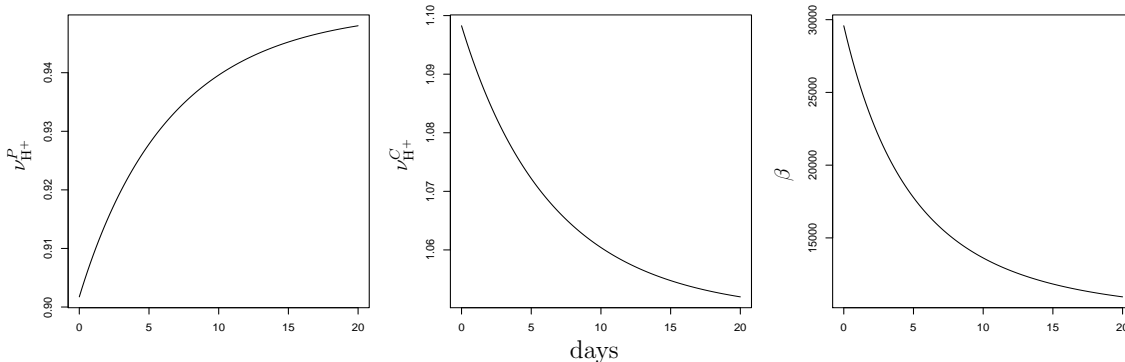


Figure 3: The stoichiometric coefficients for the proton in the fractional stoichiometric equations at current pH of the modelled kinetic processes and the buffer factor for our example system. All three are dimensionless quantities.

Note that App. D details the fractional stoichiometric approach and its connection to the implicit pH modelling approach for an arbitrary complex system, i.e. featuring an arbitrary number of total quantities and reactions.

## 4 Discussion

### 4.1 The buffer factor: generalization

The approach of the previous sections can be readily generalized. When accounting for all relevant acid-base systems in natural seawater (Dickson, 1981) and some more that might

be relevant in samples of extreme aquatic environments (Soetaert et al., 2007), the alkalinity becomes

$$\begin{aligned} \text{TA} = & [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{OH}^-] + [\text{B}(\text{OH})_4^-] + [\text{HPO}_4^{2-}] + 2 [\text{PO}_4^{3-}] + [\text{SiO}(\text{OH})_3^-] \\ & + 2 [\text{SiO}_2(\text{OH})_2^{2-}] + [\text{NH}_3] + [\text{HS}^-] + 2 [\text{S}^{2-}] \\ & - [\text{H}^+] - [\text{H}_3\text{PO}_4] - [\text{HSO}_4^-] - [\text{HF}] - [\text{HNO}_3] - [\text{HNO}_2] - 2 [\text{H}_2\text{SO}_4] \end{aligned} \quad (47)$$

The associated buffer factor can then be derived as

$$\begin{aligned} \beta = -\frac{\partial \text{TA}}{\partial [\text{H}^+]} = & 1 + \frac{K_W^*}{[\text{H}^+]^2} - \left( \frac{\partial \alpha_1^{\text{C}}}{\partial [\text{H}^+]} + 2 \frac{\partial \alpha_2^{\text{C}}}{\partial [\text{H}^+]} \right) \text{DIC} - \frac{\partial \alpha_1^{\text{B}}}{\partial [\text{H}^+]} \left[ \sum \text{B}(\text{OH})_3 \right] \\ & - \left( \frac{\partial \alpha_2^{\text{P}}}{\partial [\text{H}^+]} + 2 \frac{\partial \alpha_3^{\text{P}}}{\partial [\text{H}^+]} - \frac{\partial \alpha_0^{\text{P}}}{\partial [\text{H}^+]} \right) \left[ \sum \text{H}_3\text{PO}_4 \right] - \left( \frac{\partial \alpha_1^{\text{Si}}}{\partial [\text{H}^+]} + 2 \frac{\partial \alpha_2^{\text{Si}}}{\partial [\text{H}^+]} \right) \left[ \sum \text{Si}(\text{OH})_4 \right] \\ & - \frac{\partial \alpha_1^{\text{NH}}}{\partial [\text{H}^+]} \left[ \sum \text{NH}_4^+ \right] - \left( \frac{\partial \alpha_1^{\text{S}}}{\partial [\text{H}^+]} + 2 \frac{\partial \alpha_2^{\text{S}}}{\partial [\text{H}^+]} \right) \left[ \sum \text{H}_2\text{S} \right] + \left( \frac{\partial \alpha_1^{\text{SO}}}{\partial [\text{H}^+]} + 2 \frac{\partial \alpha_0^{\text{SO}}}{\partial [\text{H}^+]} \right) \left[ \sum \text{H}_2\text{SO}_4 \right] \\ & + \frac{\partial \alpha_0^{\text{F}}}{\partial [\text{H}^+]} \left[ \sum \text{HF} \right] + \frac{\partial \alpha_0^{\text{NO}_3}}{\partial [\text{H}^+]} \left[ \sum \text{HNO}_3 \right] + \frac{\partial \alpha_0^{\text{NO}_2}}{\partial [\text{H}^+]} \left[ \sum \text{HNO}_2 \right] \end{aligned} \quad (48)$$

The buffer factor now receives contributions from all acid base systems present and it becomes obvious that our buffer factor is conceptually equal to the *buffer capacity* defined by Morel and Hering (1993) and the *buffer intensity* as given in Stumm and Morgan (1996). The only differences between our buffer factor and the quantities defined by Morel and Hering (1993) and Stumm and Morgan (1996) is that our quantity is defined as derivative with respect to the proton concentration and theirs is defined as derivative with respect to the pH and that we explicitly name our proton balance "total alkalinity".

Assuming a mean global ocean surface water composition as given in Tab. 4, and assuming that DIC increases from 2040  $\mu\text{mol/kg-soln}$  to 2260  $\mu\text{mol/kg-soln}$  due to oceanic uptake of antropogenic  $\text{CO}_2$ , one can calculate that the free scale pH drops by around 0.4 pH units from 8.2 to 7.8 (Fig. (4) left hand side). This pH drop is consistent with projected drops in oceanic pH due to the uptake of antropogenic  $\text{CO}_2$  by the end of the 21<sup>st</sup> century (IPCC, 2007; Guinotte and Fabry, 2008). Now, one can plot the average  $\beta$  of the global surface ocean as a function of the free scale pH until the end of the century (Fig. (4)). It becomes obvious that the values at current pH are around 4 times higher than the values at a pH of 7.8. This means, considering  $\text{CO}_2$  input alone, by the end of the century, the global ocean will be around 4 times less buffered than it is now which makes it more susceptible to pH changes by further input of acids ( $\text{CO}_2$  or other acids, e.g., atmospherically deposited ones (Doney et al., 2007)) or bases.

DIC	=	2040.0
TA	=	2400.0
$[\sum \text{B}(\text{OH})_3]$	=	420.0
$[\sum \text{H}_3\text{PO}_4]$	=	2.0
$[\sum \text{Si}(\text{OH})_4]$	=	4.0
$[\sum \text{NH}_4^+]$	=	1.0
$[\sum \text{H}_2\text{S}]$	=	0.1
$[\sum \text{H}_2\text{SO}_4]$	=	28240.0
$[\sum \text{HF}]$	=	70
$[\sum \text{HNO}_3]$	=	31.0
$[\sum \text{HNO}_2]$	=	0.1
pH (free scale)	=	8.2

Table 4: Mean composition of the current global ocean. All values are in  $\mu\text{mol/kg-soln}$ . The values for DIC,  $[\sum \text{B}(\text{OH})_3]$ ,  $[\sum \text{H}_2\text{SO}_4]$ , and  $[\sum \text{HF}]$  have been calculated as functions of salinity  $S=35$  as given in DOE (1994) and Dickson et al. (2007); the value for  $[\sum \text{H}_3\text{PO}_4]$  has been taken from Sarmiento and Gruber (2006); and the values for  $[\sum \text{NH}_4^+]$ ,  $[\sum \text{H}_2\text{S}]$ ,  $[\sum \text{HNO}_3]$ ,  $[\sum \text{HNO}_2]$ , and  $[\sum \text{Si}(\text{OH})_4]$  are values typical for the Atlantic Ocean taken from Soetaert et al. (2007).

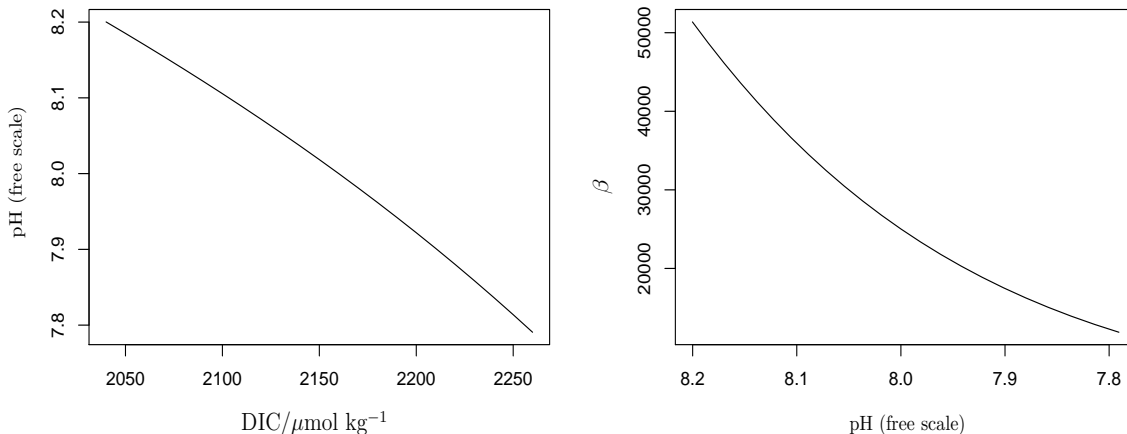


Figure 4: Changes in mean global oceanic free scale pH and  $\beta$  if DIC changes (linearly) from 2040 to 2260  $\mu\text{mol}/\text{kg}\text{-soln}$ . The drop in free scale pH from 8.2 to 7.8 is consistent with projected drops in oceanic pH due to the uptake of antropogenic  $\text{CO}_2$  by the end of the 21st century (IPCC, 2007; Guinotte and Fabry, 2008).

## 4.2 The sensitivity of pH to processes: generalization

For an arbitrary set of biogeochemical process, the evolution equation for the proton concentration becomes

$$\frac{d[\text{H}^+]}{dt} = \sum_X S_X \mathbf{R}_X \quad (49)$$

We can express the sensitivity of the pH to each physical or biogeochemical process as

$$S_X = \frac{\nu_{\text{H}^+}^X}{\beta} \quad (50)$$

This enables a chemical interpretation of the sensitivity. The sensitivity reflects the two-step process: (1) The proton release at current pH (represented by the stoichiometric coefficient of the proton in the fractional reaction equation at current pH in the nominator of sensitivity), which is characteristic for each kinetic process. (2) The subsequent re-equilibration (the buffer factor in the denominator of sensitivity), which is dependent on the acid-base systems that are present.

Note that also the sensitivity of pH to physical transport processes can be expressed in the above way if they are written in the way of a chemical reaction. The manner how  $\text{CO}_2$  air-sea exchange is treated in section (3) is an example for that, and Appendix (C) details how advective-dispersive transport processes over the borders of different water masses, e.g., upwelling, can be treated in the same way.

Considering the given fractional stoichiometric equations at current pH for calcium carbonate precipitation (Eq. (36)), and  $\text{CO}_2$  air water exchange (Eq. (38)), the fractional stoichiometric equations at current pH for primary production (Eq. 62), and oxic mineralisation (Eq. 64) given in Appendix (B), one can express the sensitivities of the pH to those processes (Tab (5)).

With the buffer factor  $\beta$  and all ionization fractions ( $\alpha$  values) calculated with quantities given in Tab (4) one can calculate numerical values for the stoichiometric coefficients  $\nu_{\text{H}^+}$  of the proton in the fractional reaction equations at current pH of the given processes as well as for the sensitivities  $S$  of the pH to those processes for the current state of the global ocean (Tab. (6) left side). The same can be done for the future scenario with the DIC concentration increased to 2260  $\mu\text{mol}/\text{kg}\text{-soln}$  (Tab. (6) right side).

The first striking piece of information is that the pH is around 4 times more sensitive to all of the processes in the future scenarion than in the current situation. However, this is a direct result of the decreasing buffer factor  $\beta$  (see previous section).

calcite precipitation	$S_P$	$= \frac{\nu_{H^+}^P}{\beta}$	$= \frac{2\alpha_0^C + \alpha_1^C}{\beta}$
CO <sub>2</sub> air water exchange	$S_C$	$= \frac{\nu_{H^+}^C}{\beta}$	$= \frac{\alpha_1^C + 2\alpha_2^C}{\beta}$
primary production	$S_{PP}$	$= \frac{\nu_{H^+}^{PP}}{\beta}$	$= \frac{\frac{\alpha_0^{NH}}{\gamma} - \alpha_1^C - 2\alpha_2^C}{\beta}$
oxic mineralisation	$S_{Ox}$	$= \frac{\nu_{H^+}^{Ox}}{\beta}$	$= \frac{\alpha_1^C + 2\alpha_2^C - \frac{\alpha_0^{NH}}{\gamma}}{\beta}$

Table 5: Sensitivities of the pH to a selection of processes relevant in the global ocean. All processes are normalized to 1 mol of carbon processed.  $\gamma = \frac{106}{16}$  is the Redfield  $\frac{C}{N}$  ratio.

	current situation ( $\beta \approx 51374$ )		future scenario ( $\beta \approx 11880$ )	
	$\nu_{H^+}$	$S$	$\nu_{H^+}$	$S$
calcite precipitation	0.88	$1.71 \cdot 10^{-5}$	0.96	$8.09 \cdot 10^{-5}$
CO <sub>2</sub> air water exchange	1.12	$2.19 \cdot 10^{-5}$	1.04	$8.75 \cdot 10^{-5}$
primary production	-0.98	$-1.91 \cdot 10^{-5}$	-0.89	$-7.51 \cdot 10^{-5}$
oxic mineralisation	0.98	$1.91 \cdot 10^{-5}$	0.89	$7.51 \cdot 10^{-5}$

Table 6: Numerical values for the stoichiometric coefficients of the proton in the fractional reaction equations at current pH ( $\nu_{H^+}$ ) for the given processes and the sensitivities of the pH ( $S$ ) to those processes for the current situation (DIC = 2040  $\mu\text{mol/kg-soln}$ ) and a future scenario (DIC = 2260  $\mu\text{mol/kg-soln}$ ).

Additionally, as all processes are normalized to one mole of carbon processed (i.e. to one mole of inorganic carbon precipitated or exchanged and one mole of organic carbon produced or mineralized respectively) the sensitivities of the pH with respect to the four mentioned processes can be directly compared. In the current situation the pH is most sensitive to the exchange of one mole of carbon with the atmosphere, and the least sensitive to one mole of carbon precipitated. The sensitivity of the pH to one mole of carbon produced or mineralized lies between the two other sensitivities. In the future scenario, however, the situation has changed. While the pH is still most sensitive to the exchange of one mole of carbon with the atmosphere, it is now least sensitive to the production or mineralisation of one mole of organic carbon. The pH's sensitivity to calcite precipitation is now larger than its sensitivity to primary production and oxic mineralisation.

## 5 Summary and conclusions

In the present paper, we have identified the main drawback of the classical implicit alkalinity centered pH modelling approach (Ben-Yaakov, 1970; Culberson, 1980; Luff et al., 2001; Follows et al., 2006): it does not allow for a quantification of the influences of different kinetically modelled processes on the pH. By employing the presented explicit pH modelling approach (generalized from the approach detailed in Hofmann et al. (2008b) which is based on earlier work by Jourabchi et al. (2005), Soetaert et al. (2007) and Wolf-Gladrow et al. (2007)), this problem can be overcome: a rate of change for the proton concentration is calculated which is an explicit function of the rates of the kinetically modelled processes modulated by a process specific sensitivity of the pH.

We have also shown that these sensitivities aggregate both, the influence of the slow kinetic process in question, and the influences of the fast equilibrium reactions in the system. This can be understood by considering a two step process where one quantifies the amount of protons produced by the kinetic processes directly, as in an unbuffered system, and only subsequently considers re-equilibration due to the equilibrium reactions. As a result, the sensitivity of the pH with respect to a certain kinetic process can be expressed as a quotient of the stoichiometric coefficient  $\nu_{H^+}$  for the proton in the fractional reaction equation of the process in question in the numerator and the buffer factor  $\beta$  in the nominator.  $\nu_{H^+}$  is a quantity that represents the direct proton production by the kinetic process, without re-equilibration and  $\beta$  is a quantity that depends on the set of equilibrium reactions considered.

By generalization, we showed that the buffer factor  $\beta$  is conceptually equal to the buffer capacity as defined by [Morel and Hering \(1993\)](#) and [Stumm and Morgan \(1996\)](#), while the definition for  $\nu_{H^+}$  contains the well-known ionization fractions ([Skoog and West, 1982](#); [Stumm and Morgan, 1996](#)). These facts firmly root our approach within known aquatic chemical concepts.

Applying the concept of buffer factor and pH sensitivities to an average global surface ocean water composition, we showed that the global surface ocean will be about four times less buffered against the addition of any acid or base at the end of the century than it is now. Furthermore, we showed that the order of the list of processes sorted with respect to how sensitive the pH is to those processes will change towards the end of the century.

Against the background of global ocean acidification and the associated importance of understanding mechanism of pH changes, we have thus presented a logical and straightforward extension of classical pH modelling approaches, which is deeply rooted in existing marine chemical concepts, and which provides further insights and understanding of pH changes - something that the scientific community and humanity as a whole is in desperate need of in the coming decades and centuries of global change.

## A Time scales and the equilibrium assumption

The pH chemistry of natural waters is influenced by processes that act on very different time scales. Based on relaxation time, one can distinguish two groups of processes. On the one hand, there are the various acid-base dissociation systems (carbonate, borate, silicate, etc.) that relax to equilibrium on time scales of less than seconds ([Zeebe and Wolf-Gladrow, 2001](#)). The net forward rate of these fast processes is denoted as  $\mathbf{R}_i^{fast}$ . On the other hand, biogeochemical models will typically include a set of comparatively slow kinetic processes that have much greater relaxation times, ranging from hours to years. These could include chemical reactions, such as calcium carbonate precipitation, as well as physical transport, for example the air-water exchange of  $\text{CO}_2$ . The net forward rate of these slow processes is referred to as  $\mathbf{R}_i^{slow}$ .

This difference in characteristic time scales has an important consequence in terms of model development. Depending on the time and length scales considered, the formulation of the associated pH model will be different. For small time scales ( $< 1$  min), the disequilibrium of the carbonate and other acid-base systems has to be taken into account. This is for example the case when modelling biogeochemical transformations within the diffusive boundary layer at the ocean-atmosphere interface or in the micro-environment surrounding marine plankton (e.g. [Zeebe, 2007](#)). On these small time scales, both the slow and the fast processes need to be modelled via suitable kinetic expressions (unless the slow rates can be assumed zero, which depends on the problem at hand). As a consequence, the evolution of the proton concentration (or equally the pH) will depend on all the process rates and can be described by

$$\frac{d[\text{H}^+]}{dt} = f(\mathbf{R}_1^{fast}, \mathbf{R}_2^{fast}, \dots, \mathbf{R}_1^{slow}, \mathbf{R}_2^{slow}, \dots) \quad (51)$$

Often, however, the time scales of interest are considerably larger: hourly, daily, seasonal, yearly or even or multi-decadal changes in pH need to be investigated. These are the situations we will focus upon here. Examples include ocean biogeochemical models, water quality models of lakes and rivers, hydrogeochemical groundwater models, and diagenetic models of sediments. In such cases, the acid-base reactions are "sufficiently" faster than the model time scale, so that these fast reactions can be considered to instantaneously attain thermodynamic equilibrium. In a biogeochemical modelling context, this is known as the *equilibrium assumption*, which basically implies that the forward and backward kinetic rate constants are assumed to be infinitely large (e.g. [Olander, 1960](#); [Aris and Mah, 1963](#); [DiToro, 1976](#); [Saaltink et al., 1998](#)). The resulting models are called *mixed kinetic-equilibrium* models, because they include two types of process descriptions. The fast reactions are described via the algebraic mass action laws of thermodynamic equilibrium, while the slow processes are modelled via suitable



differential kinetic rate laws.

An important feature of mixed kinetic-equilibrium models is that the temporal evolution of the system (and hence any pH change) is exclusively driven by the rates of the slow kinetic processes. If concentrations are changed by the slow processes, the fast reactions will respond instantaneously according to the principle of Le Chatelier-Braun. This implies that the net forward rate of the fast reactions must be implicitly dependent on the slow kinetic rates, i.e.

$$\mathbf{R}_i^{fast} = f(\mathbf{R}_j^{slow}) \quad (52)$$

as the amount of molecules passing the chemical "pathway" that is presented by the fast equilibrium reaction only depends on the supply or consumption rates of its reactants and products by the slow kinetic reactions, since the reaction step of the fast equilibrium reaction itself is considered to be infinitely fast. Stated alternatively, if all rates  $\mathbf{R}_i^{slow}$  were zero, then the pH would not change, i.e., only the slow kinetic processes are driving changes to the system which means for the proton concentration

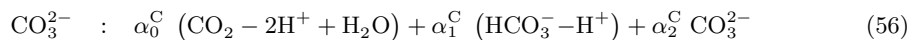
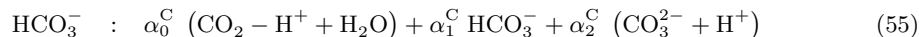
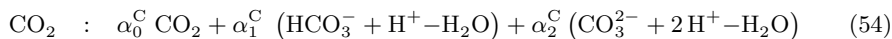
$$\frac{d[\text{H}^+]}{dt} = f(\mathbf{R}_1^{slow}, \mathbf{R}_2^{slow}, \dots) \quad (53)$$

## B A recipe for fractional reaction equations at current pH

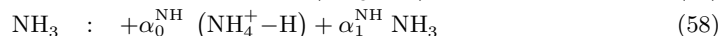
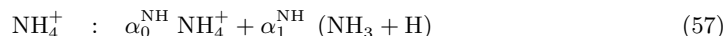
Here we describe a procedure to derive the fractional stoichiometric equation at current pH starting from an arbitrary integer reaction equation, without the need to enumerate all possible integer reaction equations.

In general, the integer reaction equation will feature two types of chemical species. *Kinetic species* are species that do not feature in the acid-base reaction equations. In contrast, *equilibrium species* will feature in one or more reaction equations of the acid-base systems. To arrive at the fractional reaction equation at current pH one must substitute all equilibrium species except for  $\text{H}^+$  in the integer equation. This substitution basically involves a replacement of a given equilibrium species by a collection of ionized counterparts in fractions given by the ionization fractions of the respective acid-base system. These ionized counterparts are accompanied by water molecules and protons to balance masses and charge in the reaction equation. The respective amount of water and proton molecules can be found by considering the respective dissociation or association reactions involved.

For the carbonate system, the substitution list is given by:



For the ammonia system, the substitution list is given by:



For the water auto dissociation<sup>5</sup>, the substitution list is given by:



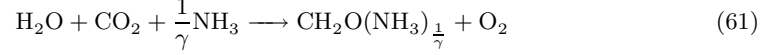

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<sup>5</sup>Note that the substitution for water auto-dissociation given here is only valid if the ion product of water ( $K_W^* = [\text{H}^+][\text{OH}^-]$ ) is considered and  $[\text{H}_2\text{O}]$  is assumed constant. If the true dissociation constant of water ( $K_{\text{H}_2\text{O}}^* = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$ ) is considered and  $[\text{H}_2\text{O}]$  is modelled dynamically, the substitution list has to be derived analogously to the other acid base systems considering the ionization fractions for  $\text{H}_2\text{O}$  and  $\text{OH}^-$ .

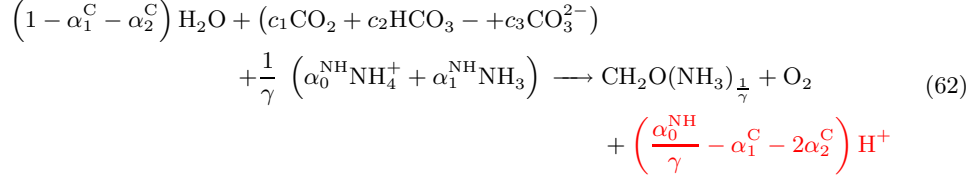
The substitution list of other acid-base equilibria can be derived by analogy.

Note that  $H^+$  is the only equilibrium species that does not need to be substituted.

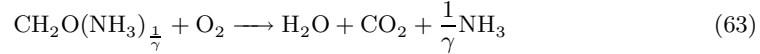
The use of these substitutions lists can be illustrated by means of simple examples. Assuming a  $\frac{C}{N}$  ratio of  $\gamma$ , one can devise a simple integer reaction equation for primary production



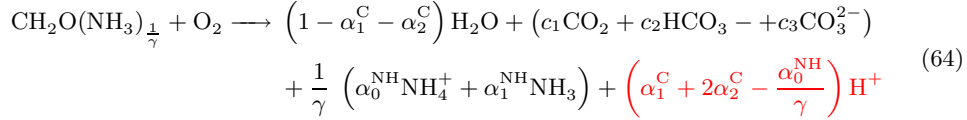
This reaction equation contains two equilibrium species,  $CO_2$  and  $NH_3$ , which need to be substituted using Eqs. (54) and (58) respectively to arrive at the fractional reaction equation at current pH for primary production



Similarly, one can express oxic mineralisation as



and substitute  $CO_2$  and  $NH_3$  to arrive at the fractional reaction equation at current pH for oxic mineralisation



## C Transport processes

Physical transport processes can be treated in the same way as biogeochemical reactions by writing them in a way that resembles a chemical reaction. This has been done for  $CO_2$  air-water exchange in Eq. (37) and will be demonstrated here for transport (e.g., in an advective-diffusive manner) across compartments or water mass boundaries, e.g., due to oceanic mixing.

Assume that the example system described in Sec. (2.1) is in contact with another compartment of water, e.g. via an inflow and an outflow similar to a chemostat. Then, the chemical species<sup>6</sup>  $[CO_2]$ ,  $[HCO_3^-]$ ,  $[CO_3^{2-}]$ , and  $[H^+]$  need to be advectively transported in the model (e.g., by using suitable kinetic expressions of the form  $\mathbf{T}_X = Q ([X]_{in} - [X])$  with  $Q$  being the advective flow and  $[X]_{in}$  the concentration of species X in the inflowing water).

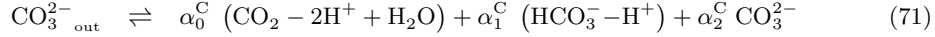
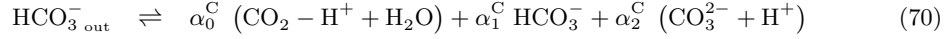
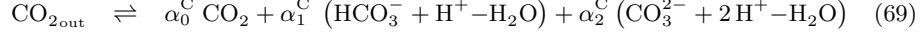
In the same way as done for  $CO_2$  air-water exchange in Eq. (37) these four transport processes can be written in the form of chemical reactions, where the rightwards arrow symbolizes the inflow of the respective species and the leftwards arrow the outflow. The net forward rate of the given "reaction" for species X is the net inflow of X and is calculated as  $\mathbf{T}_X$  as given above.




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<sup>6</sup>Note that if water auto-dissociation would be considered in the model,  $OH^-$  needs to be transported as well.

These integer "reaction" equations can be substituted



Which gives the sensitivities of the pH with respect to the four transport processes

$$S_{\mathbf{T}_{\text{CO}_2}} = \frac{\alpha_1^{\text{C}} + 2\alpha_2^{\text{C}}}{\beta} \quad (73)$$

$$S_{\mathbf{T}_{\text{HCO}_3^-}} = \frac{-\alpha_0^{\text{C}} + \alpha_2^{\text{C}}}{\beta} \quad (74)$$

$$S_{\mathbf{T}_{\text{CO}_3^{2-}}} = \frac{-2\alpha_0^{\text{C}} + \alpha_1^{\text{C}}}{\beta} \quad (75)$$

$$S_{\mathbf{T}_{\text{H}^+}} = \frac{1}{\beta} \quad (76)$$

Note that, since the transport of every chemical species is considered separately, this approach allows for differential transport in a model, i.e. diffusive transport with different molecular diffusion constants.

However, in a model without differential transport, the total quantities (here DIC and TA) can be transported directly

$$\mathbf{T}_{\text{DIC}} = \mathbf{T}_{\text{CO}_2} + \mathbf{T}_{\text{HCO}_3^-} + \mathbf{T}_{\text{CO}_3^{2-}} = Q (\text{DIC}_{\text{in}} - \text{DIC}) \quad (77)$$

$$\mathbf{T}_{\text{TA}} = \mathbf{T}_{\text{HCO}_3^-} + 2\mathbf{T}_{\text{CO}_3^{2-}} - \mathbf{T}_{\text{H}^+} = Q (\text{TA}_{\text{in}} - \text{TA}) \quad (78)$$

In this case, an equation analogous to Eq. (28) can be used to directly calculate the combined influence of all transport processes on the pH (see also Hofmann et al., 2008b,a)

$$\frac{d[\text{H}^+]}{dt} \text{ (due to transport)} = \frac{1}{\left(\frac{\partial \text{TA}}{\partial [\text{H}^+]}\right)} \left( \mathbf{T}_{\text{TA}} - \left(\frac{\partial \text{TA}}{\partial \text{DIC}}\right) \mathbf{T}_{\text{DIC}} \right) \quad (79)$$

## D Treatment of an arbitrary complex biogeochemical system

Consider a system with  $i$  kinetically modelled processes, and  $j$  total quantities (reaction invariants) other than alkalinity. The resulting evolution equations for this system can be written in the general form

$$\frac{d\text{TA}}{dt} = \sum_i \nu_{\text{TA}}^i \mathbf{R}_i \quad (80)$$

$$\frac{dX_j}{dt} = \sum_i \nu_{X_j}^i \mathbf{R}_i \quad (81)$$

where  $\nu_{\text{TA}}^i$  is the stoichiometric coefficient for the alkalinity associated with process  $i$  and  $\nu_{X_j}^i$  is the stoichiometric coefficient for  $X_j$  associated with process  $i$ . According to fractional stoichiometry, the resulting total rate of change of the proton concentration becomes

$$\frac{d[\text{H}^+]}{dt} = \frac{1}{\left(-\frac{\partial \text{TA}}{\partial [\text{H}^+]}\right)} \sum_i \nu_{\text{H}^+}^i \mathbf{R}_i \quad (82)$$

According to the explicit pH modelling approach (see also Hofmann et al., 2008b) the total rate of change of proton concentration is derived as

$$\frac{d[\text{H}^+]}{dt} = \frac{1}{\left(\frac{\partial \text{TA}}{\partial [\text{H}^+]}\right)} \left( \frac{d\text{TA}}{dt} - \sum_j \left(\frac{\partial \text{TA}}{\partial X_j}\right) \frac{dX_j}{dt} \right) \quad (83)$$

Upon substitution of the evolution equations for the total quantities (in our example system Eqs. (21) and (22)) into this equation one finds

$$\frac{d[\text{H}^+]}{dt} = \frac{1}{\left(\frac{\partial \text{TA}}{\partial [\text{H}^+]}\right)} \sum_i \left( \nu_{\text{TA}}^i - \sum_j \left( \frac{\partial \text{TA}}{\partial X_j} \right) \nu_{X_j}^i \right) \mathbf{R}_i \quad (84)$$

Knowing that the sum of all ionization fractions for each total quantity  $X_j$  is 1, it can be shown in general that

$$\nu_{\text{TA}}^i - \sum_j \left( \frac{\partial \text{TA}}{\partial X_j} \right) \nu_{X_j}^i = -\nu_{\text{H}^+}^i \quad (85)$$

for all processes  $i$ . This provides a direct link between the stoichiometric coefficients of total quantities and the stoichiometric coefficient of protons in the fractional reaction equation at current pH: for any process, the negative of the stoichiometric coefficient for protons in the fractional reaction equation at current pH is the stoichiometric coefficient of total alkalinity minus the sum of the stoichiometric coefficients of all other total quantities each weighted with the partial derivatives of total alkalinity with respect to the respective other total quantity.

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