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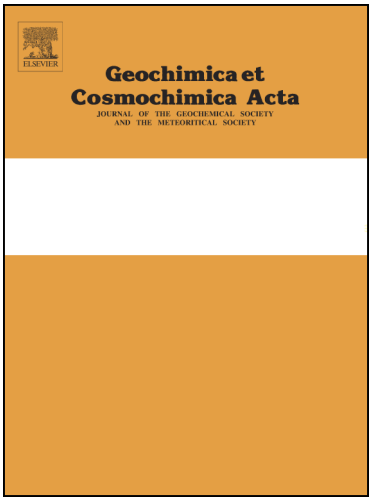

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Generalised expressions for the response of pH to changes in ocean chemistry

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Abstract

The extent to which oceans are capable of buffering chemical changes resulting from the uptake of carbon dioxide (CO_2) or other acidifying processes can be quantified using buffer factors. Here, we present general expressions describing the sensitivity of pH, CO_2 and other acid-base species to a change in ocean chemistry. These expressions can include as many acid-base systems as desirable, making them suitable for application to, e.g., upwelling regions or nutrient-rich coastal waters. We show that these expressions are fully consistent with previously derived expressions for the Revelle factor and other buffer factors, which only included the carbonate and borate acid-base systems, and provide more accurate values.

We apply our general expressions to contemporary global ocean surface water and possible changes therein by the end of the 21st century. These results show that most sensitivities describing a change in pH are of greater magnitude in a warmer, high-CO_2 ocean, indicating a decreased seawater buffering capacity. This trend is driven by the increase in CO_2 and slightly moderated by the warming. Respiration-derived carbon dioxide may amplify or attenuate ocean acidification due to rising atmospheric CO_2, depending on their relative importance. Our work highlights that, to gain further insight into current and future pH dynamics, it is crucial to properly quantify the various concurrently acting buffering mechanisms.

1. Introduction

The ocean provides an important service to mankind by absorbing 25-30% of the anthropogenic CO_2 released. This oceanic carbon uptake not only limits global warming, but

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also causes changes in ocean chemistry, collectively referred to as ocean acidification. These changes include increases in CO_2, dissolved inorganic carbon (DIC) and proton (H^+) concentrations and decreases in carbonate ion (CO_3^{2-}) concentration, calcium carbonate saturation states and the efficiency of ocean CO_2 uptake. The latter results from a decrease in the ocean CO_2 buffer capacity due to diminished CO_3^{2-} concentrations (Sundquist et al., 1979; Frankignoulle, 1994).

Long-term observations on the inorganic carbon system and pH at a number of sites revealed systematic decreases in pH and increases in DIC (Dore et al., 2009; Bates et al., 2014), consistent with model simulations showing declining open-ocean surface-water pH since the industrial revolution (Orr et al., 2005). Moreover, model projections indicate that pH in the future ocean will be more sensitive to biogeochemical processes (Caldeira and Wickett, 2003; Egleston et al., 2010; Hofmann et al., 2010a; Orr, 2011). The response of pH to these processes not only depends on the sensitivity of seawater, but also on the number of protons involved (reaction stoichiometry) and the process rate (Hofmann et al., 2010a; Hagens et al., 2014). Seawater sensitivity additionally displays spatial differences: polar regions for example, are known to be relatively vulnerable to a change in pH due to their naturally low CO_3^{2-} concentrations, and the temperature dependency of CO_2 solubility and acid-base dissociation constants, while the reverse holds for warmer tropical regions (Orr et al., 2005; Fabry et al., 2009; Orr, 2011). This temporal and regional variability in the sensitivity of pH implies that we need to advance our understanding of the factors governing pH in the ocean.

The sensitivity of pH to a change in driving factors is usually expressed in terms of buffering capacity or buffer factors. Traditionally, the buffering capacity of a solution is defined as its ability to neutralise changes in pH or $[H^+]$ upon the addition of a strong acid or base (Van Slyke, 1922) and is calculated from the inverse slope of a titration curve (Morel and Hering, 1993; Stumm and Morgan, 1996):

$$\beta = \left(\frac{\partial pH}{\partial ANC} \right)^{-1} \tag{1}$$

where ANC, or acid neutralisation capacity, represents the difference between base and acid concentrations of a solution relative to a predefined zero level of protons (Stumm and Morgan, 1996). For natural waters, ANC is usually replaced by total alkalinity (A_T), which is defined as the ANC with a zero level of protons at the CO_2 equivalence point or a pH of 4.5,

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a temperature of 25ºC, standard atmospheric pressure, and zero ionic strength (Dickson, 1981):

$$\beta = \left(\frac{\partial pH}{\partial A_T} \right)^{-1} \tag{2}$$

The increasing awareness that ocean chemistry is changing has stimulated theoretical work on pH buffering and two related buffer factors have been introduced. Similar to the pioneering work of Frankignoulle (1994), Egleston et al. (2010) presented and derived an explicit equation for β_{A_T}:

$$\beta_{A_T} = \left(\frac{\partial \ln[H^+]}{\partial A_T} \right)^{-1} \tag{3}$$

and Hofmann et al. (2010a) introduced a proton concentration buffer factor β_H:

$$\beta_H = \left(\frac{\partial [H^+]}{\partial A_T} \right)^{-1} \tag{4}$$

Note that the partial derivatives in Eq. (1-4) indicate that other chemical water properties, e.g., DIC and other total concentrations of acid-base species, are kept constant when determining this buffering capacity (Morel and Hering, 1993). Equations (2-4) represent the most general way of describing the resistance of natural waters to changes in pH. Depending on the context, however, one may be interested in the way a particular biogeochemical process (Zhang, 2000; Soetaert et al., 2007) or a specific acid-base system, rather than A_T, influences the change in pH.

Inspired by the work of Frankignoulle (1994), we present explicit equations for calculating the sensitivity of protons to changes in ocean chemistry and apply them to several case studies. These sensitivities are required if we are to better understand pH dynamics in a changing world or the impact of biogeochemical processes on pH. The sensitivity $\frac{\partial [H^+]}{\partial A_T}$ as presented in this paper is identical to the inverse of the buffer factor (Eq. (4)) of Hofmann et al. (2010a), and conceptually equivalent to the inverse of the buffer capacity (Morel and Hering, 1993) and the buffer factor β_{A_T} of Egleston et al. (2010). We first derive general explicit equations for the sensitivity of protons and acid-base species to changes in ocean chemistry. Secondly, we show how the derived relationships relate to previous studies that

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excluded acid-base systems other than borate (Frankignoulle, 1994; Egleston et al., 2010) and we show that a similar approach applies to the well-known Revelle factor. We compare our analytical approach to numerical estimates for a selection of sensitivities. Then, we show how much more sensitive the pH will be in the year 2100 given projected atmospheric carbon dioxide levels. Finally, we apply the sensitivities to explore ocean acidification due to the combined effects of atmospheric CO_2 uptake and eutrophication-stimulated organic matter respiration.

2. Methods

2.1 Analytical derivations of buffer factors

To arrive at a general, complete set of buffer factors, we combined and extended several earlier outlined approaches (Frankignoulle, 1994; Soetaert et al., 2007; Egleston et al., 2010). If examples are used for clarification, they will be given for the carbonate system, but similar derivations can be made for any other acid-base system.

Generally speaking, any given change in pH can be split into multiple parts representing multiple processes:

$$dpH = \left(\frac{\partial pH}{\partial T}\right) dT + \left(\frac{\partial pH}{\partial S}\right) dS + \left(\frac{\partial pH}{\partial DIC}\right) dDIC + \left(\frac{\partial pH}{\partial A_T}\right) dA_T + \ldots \quad (5)$$

where T is temperature and S is salinity. The partial derivatives in Eq. (5) indicate that they are only valid if other variables are kept constant within their derivation. The dots indicate that more acid-base systems may be included, depending on the system of interest and the processes taking place. Usually, only carbonate and borate systems are used in the calculations, but in coastal systems, in pore-waters and in ocean oxygen minimum zones, other acid-base systems such as sulphide may impact pH. Following Soetaert et al. (2007), we decided to include the ammonium, phosphate, nitrate, nitrite, sulphide, silicate, fluoride and sulphate acid-base systems in our derivation, and ignore the contribution of other minor acid-base species and organic acids. Although the latter can substantially contribute to A_T in estuarine and other coastal waters (Cai et al., 1998; Kuliński et al., 2014), their acid-base properties are poorly constrained (Muller and Bleie, 2008; Kim and Lee, 2009), making it difficult to include them in this derivation. The selected acid-base systems should be included in the definition of A_T, which then becomes (Dickson, 1981; Wolf-Gladrow et al., 2007):

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$$A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [NH_3] + [HPO_4^{2-}] + 2[PO_4^{3-}] \\ -[H_3PO_4] - [HNO_3] - [HNO_2] + [HS^-] + 2[S^{2-}] + [SiO(OH)_3^-] \\ +2[SiO_2(OH)_2^{2-}] - [HF] - 2[H_2SO_4] - [HSO_4^-] + [OH^-] - [H^+] \quad (6)$$

This definition can be rewritten by grouping each acid-base system together:

$$A_T = A_C + A_B + A_{NH_4} + A_P + A_{NO_3} + A_{NO_2} + A_{HS} + A_{Si} + A_F + A_{SO} + A_W \quad (7)$$

Here, A_C, A_B, A_{NH_4}, A_P, A_{NO_3}, A_{NO_2}, A_{HS}, A_{Si}, A_F and A_{SO} refer to the contributions of the carbonate, borate, ammonium, phosphate, nitrate, nitrite, sulphide, silicate, fluoride and sulphate acid-base systems to A_T respectively, while A_W refers to the contribution due to the auto-dissociation of water. So, taking the carbonate system as an example, we can see that $A_C = [HCO_3^-] + 2[CO_3^{2-}]$. Equation (7) can be differentiated with respect to $[H^+]$:

$$\frac{\partial A_T}{\partial [H^+]} = \frac{\partial A_C}{\partial [H^+]} + \frac{\partial A_B}{\partial [H^+]} + \frac{\partial A_{NH_4}}{\partial [H^+]} + \frac{\partial A_P}{\partial [H^+]} + \frac{\partial A_{NO_3}}{\partial [H^+]} + \frac{\partial A_{NO_2}}{\partial [H^+]} + \frac{\partial A_{HS}}{\partial [H^+]} \\ + \frac{\partial A_{Si}}{\partial [H^+]} + \frac{\partial A_F}{\partial [H^+]} + \frac{\partial A_{SO}}{\partial [H^+]} + \frac{\partial A_W}{\partial [H^+]} \quad (8)$$

It is important to realise that the subscripts in Eq. (8) simply represent terms belonging together being grouped (as for Eq. (7)) and do not imply that total concentrations of all acid-base species remain constant. However, if we also assume that A_T changes only due to addition or removal of $[H^+]$, then Eq. (8) is directly linked to the inverse of the well-known acid-base buffering capacity (Eq. (2)) sensu Morel and Hering (1993) and identical to the inverse of proton concentration buffer factor (Eq. (4)) as defined by Hofmann et al. (2010a):

$$\beta_H = \sum_{i=1}^{k} \left(\frac{\partial A_i}{\partial [H^+]} \right)_i \quad (9)$$

Here, *i* represents the total concentration of an acid-base system, A_i represents the contribution of that acid-base system to A_T, and *k* represents the total number of acid-base systems present in the system.

Since we are interested in the effect of the change in the total concentration of a certain acid-base species (TotX) on $[H^+]$, we differentiate both TotX and A_T with respect to changes in proton concentration and the concentration of an acid-base species X that makes up part of TotX:

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$$dTotX = \left(\frac{\partial TotX}{\partial [X]}\right)_{H^+} d[X] + \left(\frac{\partial TotX}{\partial [H^+]}\right)_X d[H^+] \tag{10a}$$

$$dA_T = \left(\frac{\partial A_T}{\partial [X]}\right)_{H^+} d[X] + \left(\frac{\partial A_T}{\partial [H^+]}\right)_X d[H^+] \tag{10b}$$

We can convert these expressions to describe the sensitivity of $[H^+]$ to a change in TotX by making use of the matrix inversion method (Egleston et al., 2010):

$$\begin{pmatrix} dTotX \\ dA_T \end{pmatrix} = J \begin{pmatrix} d[X] \\ d[H^+] \end{pmatrix} \tag{11}$$

The Jacobian J is defined as

$$J = \begin{pmatrix} a & b \\ c & d \end{pmatrix} = \begin{pmatrix} \left(\frac{\partial TotX}{\partial [X]}\right)_{H^+} & \left(\frac{\partial TotX}{\partial [H^+]}\right)_X \\ \left(\frac{\partial A_T}{\partial [X]}\right)_{H^+} & \left(\frac{\partial A_T}{\partial [H^+]}\right)_X \end{pmatrix} \tag{12}$$

From matrix algebra, we know that

$$\begin{pmatrix} d[X] \\ d[H^+] \end{pmatrix} = J^{-1} \begin{pmatrix} dTotX \\ dA_T \end{pmatrix} \tag{13}$$

The inverse Jacobian J^{-1} can then be defined as

$$J^{-1} = \begin{pmatrix} \frac{\partial [X]}{\partial TotX} & \frac{\partial [X]}{\partial A_T} \\ \frac{\partial [H^+]}{\partial TotX} & \frac{\partial [H^+]}{\partial A_T} \end{pmatrix} = \begin{pmatrix} \frac{-d}{bc-ad} & \frac{b}{bc-ad} \\ \frac{c}{bc-ad} & \frac{-a}{bc-ad} \end{pmatrix} \tag{14}$$

where a, b, c and d refer to the corresponding partial derivatives of Eq. (12).

The sensitivities $\left(\frac{\partial A_T}{\partial [X]}\right)_{H^+}$, $\left(\frac{\partial TotX}{\partial [X]}\right)_{H^+}$ and $\left(\frac{\partial TotX}{\partial [H^+]}\right)_X$ (Eq. (12)) can be analytically derived using simple differentiation (Table 3a). Combined with $\left(\frac{\partial A_T}{\partial [H^+]}\right)_X$, one can insert these partial derivatives into Eq. 14 to obtain the analytical expressions for the sensitivities

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$\frac{\partial[X]}{\partial A_T}$, $\frac{\partial[X]}{\partial TotX}$, and the two sensitivities which are of most interest to this study, $\frac{\partial[H^+]}{\partial TotX}$ and $\frac{\partial[H^+]}{\partial A_T}$. As first identified by Frankignoulle (1994), the remaining challenge is thus to obtain a general expression for the term $\left(\frac{\partial A_T}{\partial[H^+]}\right)_X$, which is the change in A_T due to the change in $[H^+]$ under the assumption that species X is kept constant. It is therefore not equal to β_H, which implies that all total concentrations are constant, but it is tightly linked to it. Specifically:

$$\left(\frac{\partial A_T}{\partial[H^+]}\right)_X = \beta_H - \left(\frac{\partial A_X}{\partial[H^+]}\right)_{TotX} + \left(\frac{\partial A_X}{\partial[H^+]}\right)_X \tag{15}$$

i.e., the sought-after $\left(\frac{\partial A_T}{\partial[H^+]}\right)_X$ equals the buffer factor (β_H) for the condition that the total concentrations of all acid-base species remain constant, minus the term describing the contribution of the acid-base system to which species X belongs, plus a term accounting for the change in A_X due to a change in $[H^+]$ under the assumption that X remains constant.

To illustrate the procedure, we select the carbonate system as the system of interest. As an example we take the addition of CO_2, meaning that DIC changes while the total concentrations of the other acid-base systems and A_T remain constant, i.e. ocean acidification. For this purpose, we define CO_2^* as the sum of aqueous CO_2 and carbonic acid (H_2CO_3), such that an addition of CO_2 equals an increase in CO_2^*. In this case, CO_2^* is our species of interest X and DIC is our independent state variable TotX, while the other total concentrations are reaction invariant, i.e., they are not affected by the chemical transformations in the systems (Waller and Makila, 1981). Nevertheless, the addition of CO_2^* affects $[H^+]$ and thus will change the speciation of these acid-base systems. Therefore, to analytically derive the partial derivatives of Eq. (8) that belong to the reaction invariant, it is necessary to express the corresponding species of Eq. (6) in terms of their total concentration, $[H^+]$ and equilibrium constants only (Park, 1969; Soetaert et al., 2007) (Table 1b). The corresponding analytical expressions for the partial derivatives can be found in Table 2b. In our example, DIC is not invariant, and $\left(\frac{\partial A_T}{\partial[H^+]}\right)_{CO_2^*}$ cannot be equal to β_H. Therefore, to analytically represent

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$\left(\frac{\partial A_T}{\partial[H^+]}\right)_{CO_2^*}$ we have to remove the term $\left(\frac{\partial A_C}{\partial[H^+]}\right)_{DIC}$ from the definition of β_H, but recall that the addition of CO_2 does not affect A_T. Thus, to implement the contribution of the carbonate system to A_T when DIC is not invariant, we can express A_C, as well as its partial derivative with respect to $[H^+]$ (Eq. (8)), in terms of equilibrium constants, $[H^+]$ and $[CO_2^*]$ (Tables 1a and 2a) and add $\left(\frac{\partial A_C}{\partial[H^+]}\right)_{CO_2^*}$ to the analytical representation of $\left(\frac{\partial A_T}{\partial[H^+]}\right)_{CO_2^*}$. In more general terms, $\left(\frac{\partial A_C}{\partial[H^+]}\right)_{CO_2^*}$ can be expressed as $\left(\frac{\partial A_X}{\partial[H^+]}\right)_X$, where A_X represents the contribution of the acid-base system associated with TotX to A_T. Since β_H is explicitly defined under the assumption that A_T changes only due to changes in $[H^+]$, i.e., all total concentrations are reaction invariant, we can find the analytical expression for β_H by summing all the terms from Table 2b. Then, taking again the addition of CO_2 as example, we can find the analytical expression for $\left(\frac{\partial A_T}{\partial[H^+]}\right)_{CO_2^*}$ by subtracting $\left(\frac{\partial A_C}{\partial[H^+]}\right)_{DIC}$ (also from Table 2b) from β_H and adding $\left(\frac{\partial A_C}{\partial[H^+]}\right)_{CO_2^*}$ (Table 2a). This yields

$$\left(\frac{\partial A_T}{\partial[H^+]}\right)_{CO_2^*} = \beta_H - \left(\frac{\partial A_C}{\partial[H^+]}\right)_{DIC} + \left(\frac{\partial A_C}{\partial[H^+]}\right)_{CO_2^*} \tag{16}$$

where

$$\left(\frac{\partial A_C}{\partial[H^+]}\right)_{DIC} = \frac{-1}{[H^+]}\left(\begin{array}{l}[HCO_3^-]\left(\frac{[CO_2^*]-[CO_3^{2-}]}{DIC}\right)\\ +2[CO_3^{2-}]\left(\frac{2[CO_2^*]+[HCO_3^-]}{DIC}\right)\end{array}\right) \tag{17, T.2b}$$

and

$$\left(\frac{\partial A_C}{\partial[H^+]}\right)_{CO_2^*} = \frac{-1}{[H^+]}\left(-nA_C + \left([HCO_3^-]+4[CO_3^{2-}]\right)\right) \tag{18,T.2a}$$

where n stands for the charge contribution to alkalinity (Soetaert et al., 2007). In the case of the carbonate system, adding or removing CO_2 changes DIC but not A_T, i.e. n equals 0, such

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that Eq. (18) simplifies. Addition or removal of bicarbonate (HCO_3^-) or CO_3^{2-} changes A_T and *n* is 1 and 2, respectively. As a result, Eq. (16) can also be applied to the addition or removal of HCO_3^- or CO_3^{2-}, with the same expression but a different result for Eq. (18). The relation between $\left(\frac{\partial A_C}{\partial [H^+]}\right)_{CO_2^*}$ and either of the terms $\left(\frac{\partial A_C}{\partial [H^+]}\right)_{HCO_3^-}$ or $\left(\frac{\partial A_C}{\partial [H^+]}\right)_{CO_3^{2-}}$ can be generalised into:

$$\left(\frac{\partial A_X}{\partial [H^+]}\right)_X = \left(\frac{\partial A_X}{\partial [H^+]}\right)_{X_{ref}} + \frac{nA_X}{[H^+]} \tag{19}$$

Here, X_{ref} is the reference species of the acid-base system associated with TotX for the total alkalinity expression. This reference species is also referred to as the zero level of protons (Wolf-Gladrow et al., 2007). Similarly as for CO_2, a change in any X_{ref} is equivalent to a change in its corresponding TotX when other properties are held constant (MacIntyre, 1978).

Generally, using the appropriate combination of terms expressing A_T from Table 1a and 1b for the state variable of interest, we can write the analytical expression for Eq. (7) that is applicable to the situation. Thus, with the carbonate system as the acid-base system of interest, one would take A_C from Table 1a and the other terms of Eq. (7) from Table 1b. For each of the terms in Table 1a and 1b, the derivatives with respect to $[H^+]$ (Eq. (8)) are given in Table 2. The derivatives of Table 2a, which are valid in case of an independent state variable TotX, are written in such a general way that they can also be applied whenever a change in any of the species contributing to TotX is specified.

2.2 Linking generalised expressions to prior work limited to the carbonate and borate acid-base systems

The expressions presented in Tables 1 and 2 are generally applicable to any combination of acid-base systems, any number of state variables, and for any total concentration or any of species contributing to the total concentration as independent state variable. The expressions in Table 3a are also generally applicable, as long as the conditions under which $\left(\frac{\partial A_T}{\partial [H^+]}\right)_X$ is valid are correctly taken into account for the specific situation. As Egleston et al. (2010) pointed out, more than one acid-base system can be added as an independent state variable, yielding an *m* by *m* Jacobian matrix (Eq. (12)) where *m* equals the number of acid-base

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systems of interest plus 1 (due to the inclusion of A_T). In such cases, $\left(\frac{\partial A_T}{\partial [H^+]}\right)_{X_1,X_2...X_m}$ (Eq. (15)) is built up from (m-1) parts of Table 2a.

The resulting expressions in Table 3b are valid for any combination of acid-base systems and any total concentration, or any species contributing to the total concentration, as independent state variable. The main difference with the expressions in Tables 2 and 3a is that the former are only valid in the case of two independent state variables: A_T and the total concentration, or either of its species, of the acid-base system of interest. That is simply because the matrix inversion given in Eq. (13) is only valid for a 2 x 2 matrix. As the number of state variables increases, the inverse of the Jacobian matrix becomes significantly more complex, meaning that it is difficult to analytically derive the sensitivities $\left(\frac{\partial [H^+]}{\partial A_T}\right)_{X_1,X_2...X_{m-1},X_m}$, $\left(\frac{\partial [H^+]}{\partial TotX_m}\right)_{X_1,X_2...X_{m-1},X_m}$, $\left(\frac{\partial [X_m]}{\partial TotX_m}\right)_{H^+,X_1,X_2...X_{m-1}}$ and $\left(\frac{\partial [X_m]}{\partial A_T}\right)_{H^+,X_1,X_2...X_{m-1}}$. In such cases it is recommended to numerically perform the matrix inversion. One might question how useful the expressions in Table 3b may be as they only have a limited validity. However, often such partial derivatives are used to partition the contributions of separate processes to the total change in pH sensu Eq. (5), both in modelling studies (McNeil and Matear, 2007; Hauri et al., 2013) and when analysing time series (Takahashi et al., 2014). For such analyses, the buffer factors of Table 3b are very well suited as each property is purportedly individually studied while the other properties are kept constant.

The implicit assumption that the partial derivatives in Table 3b are homogeneous, i.e., they are only valid when all other properties are kept constant, has another consequence. A careful comparison of Eq. (19) with $\frac{\partial [H^+]}{\partial TotX}$ in Table 3b shows that, in case of a change in DIC, the factor $\frac{\partial [H^+]}{\partial DIC}$ will be the same irrespective of whether $\left(\frac{\partial A_T}{\partial [H^+]}\right)_X$ is defined with X being CO_2^*, HCO_3^- or CO_3^{2-}. Conceptually this makes sense, as this is implied in the definition of $\frac{\partial [H^+]}{\partial DIC}$. In other words, for the analytical derivation of $\frac{\partial [H^+]}{\partial TotX}$ it is only of importance to

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specify TotX; the choice for X is free and will not affect the outcome of $\frac{\partial[H^+]}{\partial TotX}$. Since a change in TotX is equivalent to a change in X_{ref}, $\frac{\partial[H^+]}{\partial TotX}$ in fact describes the response of $[H^+]$ to a change in either TotX or X_{ref}. Similarly, the factor $\frac{\partial[H^+]}{\partial A_T}$ will produce the same value irrespective of which total concentration, or even which species, is used in its calculation. So as long as X is defined as a species contributing to TotX, $\frac{\partial[H^+]}{\partial A_T}$ can be calculated. These generalisations can, for obvious reasons, not be made for the sensitivities describing a change in X. As a result, the subscripts presented in Table 3a have been dropped in Table 3b.

Finally, all buffer factors presented so far consider the change in $[H^+]$. Since we usually work with pH, rather than $[H^+]$, it is convenient to convert them to factors describing the change in pH. To convert the factors in Table 3a from $[H^+]$ to pH, we use Eq. (20) (Frankignoulle, 1994; Stumm and Morgan, 1996):

$$\left(\frac{\partial Y}{\partial pH}\right)_X = \frac{\partial[H^+]}{\partial pH}\left(\frac{\partial Y}{\partial[H^+]}\right)_X = -\ln(10)[H^+]\left(\frac{\partial Y}{\partial[H^+]}\right)_X \tag{20}$$

where Y may refer to either TotX or A_T.

Similarly, for the factors in Table 3b,

$$\frac{\partial pH}{\partial Y} = \frac{\partial pH}{\partial[H^+]}\frac{\partial[H^+]}{\partial Y} = \frac{-1}{\ln(10)[H^+]}\frac{\partial[H^+]}{\partial Y} \tag{21}$$

The generalised expressions for the buffer factors presented in this paper are fully consistent with those presented by Frankignoulle (1994) and Egleston et al. (2010), where $\frac{\partial[H^+]}{\partial A_T}$ was determined with DIC as state variable, while assuming that total borate was invariant and neglecting the contribution of other acid-base systems except the auto-dissociation of water. For example, the equation given by Egleston et al. (2010) for β_{A_T} is as follows:

$$\beta_{A_T} = \left(\frac{\partial \ln[H^+]}{\partial A_T}\right)^{-1} = \frac{A_C^2}{DIC} - \sigma \tag{22}$$

with, taking into account the correction identified by Álvarez et al. (2014),

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$$\sigma = [HCO_3^-] + 4[CO_3^{2-}] + \frac{[H^+][B(OH)_4^-]}{K_B + [H^+]} + [H^+] + [OH^-] \tag{23}$$

This equation is equivalent to our expression for $\frac{\partial[H^+]}{\partial A_T}$ under the conditions defined in their paper. Egleston et al. (2010) only included the carbonate and borate acid-base systems and auto-dissociation of water in their definition of A_T. The proton concentration buffer factor β_H is thus also only built up from these three components:

$$\beta_H = \left(\frac{\partial A_C}{\partial[H^+]}\right)_{DIC} + \left(\frac{\partial A_B}{\partial[H^+]}\right)_{TotB} + \left(\frac{\partial A_W}{\partial[H^+]}\right)_{H_2O} \tag{24}$$

Since a change in DIC is equivalent to a change in CO_2^*, we define DIC as the independent state variable TotX, so that the contribution of the independent state variable to A_T is A_C and the species of interest is CO_2^*. The expression for $\left(\frac{\partial A_T}{\partial[H^+]}\right)_{CO_2^*}$ (Eq. (16)) then becomes:

$$\left(\frac{\partial A_T}{\partial[H^+]}\right)_{CO_2^*} = \left(\frac{\partial A_C}{\partial[H^+]}\right)_{CO_2^*} + \left(\frac{\partial A_B}{\partial[H^+]}\right)_{TotB} + \left(\frac{\partial A_W}{\partial[H^+]}\right)_{H_2O} \tag{25}$$

Taking the relevant factors of Tables 2a and 2b, and recalling that *n* equals 0 in the case of a DIC addition, with some rearranging we define

$$\left(\frac{\partial A_T}{\partial[H^+]}\right)_{CO_2^*} = \frac{-1}{[H^+]}\left(\begin{array}{l}[HCO_3^-] + 4[CO_3^{2-}] + [B(OH)_4^-]\frac{[B(OH)_3]}{TotB} \\ +[OH^-] + [H^+]\end{array}\right) \tag{26}$$

It can mathematically be shown that $\frac{[H^+][B(OH)_4^-]}{K_B + [H^+]}$ is equal to $[B(OH)_4^-]\frac{[B(OH)_3]}{TotB}$, from which it follows that:

$$\left(\frac{\partial A_T}{\partial[H^+]}\right)_{CO_2^*} = \frac{-1}{[H^+]}\sigma \tag{27}$$

Now we insert this definition into our expression for $\left(\frac{\partial[H^+]}{\partial A_T}\right)_X$ (Table 3b) and adapt it to include our previously defined parameters X = CO_2^*, n = 0, TotX = DIC and $A_X = A_C$:

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$$\frac{\partial[H^+]}{\partial A_T} = \frac{DIC[H^+]}{A_C^2 + \left([H^+]\left(\frac{-1}{[H^+]}\sigma\right)\right)DIC} \tag{28}$$

This can be rearranged to yield

$$\frac{\partial[H^+]}{\partial A_T} = \frac{DIC[H^+]}{A_C^2 - \sigma \cdot DIC} \tag{29}$$

Dividing both numerator and denominator on the right hand side by DIC and dividing the left and right hand sides by $[H^+]$ gives:

$$\frac{1}{[H^+]}\frac{\partial[H^+]}{\partial A_T} = \frac{1}{\frac{A_C^2}{DIC} - \sigma} \tag{30}$$

from which it can easily be seen that:

$$\left(\frac{1}{[H^+]}\frac{\partial[H^+]}{\partial A_T}\right)^{-1} = \left(\frac{\partial \ln[H^+]}{\partial A_T}\right)^{-1} = \frac{A_C^2}{DIC} - \sigma \tag{31}$$

The factors that Egleston et al. (2010) derived are valid for a change in DIC without taking into account which species of DIC is changed, although they are also applicable in case of a change in the reference species CO_2^*. Thus, their factors β_{A_T} and β_{DIC} are equivalent to our factors $\frac{\partial[H^+]}{\partial A_T}$ and $\frac{\partial[H^+]}{\partial TotX}$, respectively, as presented in Table 3b. Their factors γ_{A_T} and γ_{DIC} are equivalent to our factors $\frac{\partial[X]}{\partial A_T}$ and $\frac{\partial[X]}{\partial TotX}$, but only in the special case where X equals X_{ref}, since their γ_{A_T} and γ_{DIC} are defined for the addition of CO_2^* (which is X_{ref} for the carbonate system) and lack a term describing the charge contribution to alkalinity. Interestingly though, their factors ω_{A_T} and ω_{DIC} are also similar to our factors $\frac{\partial[X]}{\partial A_T}$ and $\frac{\partial[X]}{\partial TotX}$, but with X = CO_3^{2-}. This is further detailed in part A of the Supplementary Information.

The factors β_{DIC} and β_{A_T} of Egleston et al. (2010) are also equivalent to the factors Φ_D and Φ_H derived by Frankignoulle (1994), which describe the change in pH due to change in

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dissolved CO_2 and A_T, respectively. Frankignoulle (1994), however, additionally derived chemical, heterogeneous buffer factors that describe the change in pH resulting from changes in $[HCO_3^-]$ and $[CO_3^{2-}]$. By specifically inducing a change in either of these species, both DIC and A_T are affected. After converting from pH to $[H^+]$, his results can be summarised as:

$$\frac{\partial[H^+]}{\partial X} = \frac{\partial[H^+]}{\partial TotX} + n\frac{\partial[H^+]}{\partial A_T} \tag{32}$$

Thus, if CO_2^* is added or removed, $\frac{\partial[H^+]}{\partial X}$ equals $\frac{\partial[H^+]}{\partial TotX}$, in line with what has been discussed above. Part B of the Supplementary Information shows the derivation of Eq. 32.

The generalised expression for the buffer factors can, in principle, also be used to elucidate and quantify the salinity, temperature and pressure (p) dependencies of pH (Hofmann et al., 2009). However, the resulting expressions are rather complex and it is therefore recommended to calculate the sensitivities numerically (see part C of the Supplementary Information).

The acid-base buffer factor (β_H) and underlying terms are also linked to the well-known Revelle factor (RF) expressing the sensitivity of pCO_2 to changes in DIC (Revelle and Suess, 1957; Bolin and Eriksson, 1959; Sundquist et al., 1979):

$$RF = \frac{\partial \ln[CO_2]}{\partial \ln DIC} = \frac{DIC}{[CO_2]}\left(\frac{\partial[CO_2]}{\partial DIC}\right) \tag{33}$$

From the expression for $\frac{\partial[X]}{\partial TotX}$ in Table 3b, and defining that TotX = DIC, X = CO_2 (from now on denoted CO_2^* for consistency) and, since it is homogeneous, *n* equals 0, we can define $\frac{\partial[CO_2^*]}{\partial DIC}$:

$$\frac{\partial[CO_2^*]}{\partial DIC} = \frac{[CO_2^*][H^+]\left(\frac{\partial A_T}{\partial[H^+]}\right)_{CO_2^*}}{A_C^2 + [H^+]\left(\frac{\partial A_T}{\partial[H^+]}\right)_{CO_2^*} DIC} \tag{34}$$

The factor $\left(\frac{\partial A_T}{\partial[H^+]}\right)_{CO_2^*}$ is defined as in Eq. (16). From Eq. (34) it easily follows that:

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$$RF = \frac{[H^+]\left(\frac{\partial A_T}{\partial [H^+]}\right)_{CO_2^*} DIC}{A_C^2 + [H^+]\left(\frac{\partial A_T}{\partial [H^+]}\right)_{CO_2^*} DIC} \tag{35}$$

This generalised Revelle factor includes all acid-base systems relevant for the system of interest and it can easily be shown that it is fully consistent with the homogeneous RF derived by Sundquist et al. (1979) and Zeebe and Wolf-Gladrow (2001). The work done by Sundquist et al. (1979) only includes the carbonate and borate acid-base systems and neglects the auto-dissociation of water. In this specific case, $\left(\frac{\partial A_T}{\partial [H^+]}\right)_{CO_2^*}$ is defined as:

$$\left(\frac{\partial A_T}{\partial [H^+]}\right)_{CO_2^*} = \left(\frac{\partial A_C}{\partial [H^+]}\right)_{CO_2^*} + \left(\frac{\partial A_B}{\partial [H^+]}\right)_{TotB} \tag{36}$$

Assuming for this purpose that proton activity and concentration are equal, the expression given by Sundquist et al. (1979) reads:

$$RF = DIC\left([H_2CO_3] + [CO_3^{2-}] + \frac{G[HCO_3^-] - 4[CO_3^{2-}]^2}{[HCO_3^-] + 4[CO_3^{2-}] + G}\right)^{-1} \tag{37}$$

with:

$$G = \frac{TotB \cdot K_B [H^+]}{(K_B + [H^+])^2} \tag{38}$$

The work by Zeebe and Wolf-Gladrow (2001) also includes the auto-dissociation of water. In this case, $\left(\frac{\partial A_T}{\partial [H^+]}\right)_{CO_2^*}$ is defined as in Eq. (25). Their expression for RF reads:

$$RF = \frac{DIC}{[CO_2^*]}\left(\frac{\partial DIC}{\partial [CO_2^*]}\right)^{-1} \tag{39}$$

with:

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$$\frac{\partial DIC}{\partial [CO_2^*]} = \frac{\dfrac{4K_{C_1}K_{C_2}}{[H^+]^2} + \dfrac{K_{C_1}}{[H^+]} + \dfrac{(K_{C_1})^2 K_{C_2}}{[H^+]^3} + \dfrac{[H^+]}{[CO_2^*]} \cdot \left(1 + \dfrac{K_{C_1}K_{C_2}}{[H^+]^2} + \dfrac{K_{C_1}}{[H^+]}\right)\left(1 + \dfrac{K_W}{[H^+]^2} + \dfrac{TotB \cdot K_B}{(K_B + [H^+])^2}\right)}{\dfrac{4K_{C_1}K_{C_2}}{[H^+]^2} + \dfrac{K_{C_1}}{[H^+]} + \dfrac{[H^+]}{[CO_2^*]}\left(1 + \dfrac{K_W}{[H^+]^2} + \dfrac{TotB \cdot K_B}{(K_B + [H^+])^2}\right)} \tag{40}$$

Part D of the Supplementary Information shows that Eqs. (37) and (39) are both equivalent to Eq. (35).

3. Applications

3.1 Sensitivities in contemporary global ocean surface water

We have now derived all partial derivatives of Eq. (5) and are thus able to attribute changes in pH to different factors. To make these buffer factors more tangible, and to get a feeling for the importance of each of the factors, we will take the global ocean surface water as a model system and apply changes in each of the factors discussed in Sect 2.1 and 2.2. Since $\frac{\partial pH}{\partial TotX}$ and $\frac{\partial pH}{\partial A_T}$ are independent of the species of the acid-base system that is added or removed (Table 3b), we will only consider changes in TotX, rather than the individual species. All calculations were performed on the free pH scale (see part C of the Supplementary Information for a discussion on the various pH scales) using the R package *AquaEnv* (Hofmann et al., 2010b). To highlight that the free scale is used in this paper, from now on we will denote pH as pH_F. As carbonate dissociation constants we used those of Lueker et al. (2000) as recommended by Dickson et al. (2007). For the other acid-base dissociation constants and the CO_2 solubility constant, we chose the default settings of *AquaEnv*.

The initial conditions of our model system were chosen to represent the global open-ocean surface-water mean of the year 2000 (Table E.1 of the Supplementary Information). We calculated the sensitivities of pH_F to changes in TotX, A_T, T and S for 2000 and 2100, assuming that temperature and atmospheric pCO_2 ($pCO_{2,atm}$) change according to the highest Representative Concentration Pathway, RCP8.5. The increase in $pCO_{2,atm}$ until 2100 was taken from Meinshausen et al. (2011), thereby assuming that seawater pCO_2 increases by the same magnitude. The increase in global average SST from the 1990s to the 2090s has been

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estimated at 2.73±0.72ºC (Bopp et al., 2013). All other parameters were kept constant. If necessary, nutrient concentrations were converted from µmol L^{-1} to µmol kg^{-1}.

Table 4 shows the sensitivities for the contemporary global open ocean surface water and how these may change by the end of the 21st century. A negative sensitivity, as for DIC, indicates that adding this species to the system leads to a decrease in pH_F, consistent with our general knowledge of the carbonate system. The reverse holds for the positive sensitivities, such as $\frac{\partial pH}{\partial A_T}$, where an increase in A_T leads to an increase in pH_F. The signs of the sensitivities do not change in the range of conditions we consider here and, in fact, do not change over the whole range of pH_F values in oceanic and coastal waters, since the denominator in the sensitivities of Table 3b always has a negative sign, i.e., the term $\left([H^+]\left(\frac{\partial A_T}{\partial [H^+]}\right)_X - nA_X\right)TotX$ is always negative and exceeds A_X^2. Therefore, the sign of $\frac{\partial pH}{\partial TotX}$ depends on the sign of A_X; if the contribution of an acid-base system to TA is positive, then $\frac{\partial pH}{\partial TotX}$ is by definition negative. The magnitude of a sensitivity with respect to a total concentration of an acid-base species mainly depends on two factors: (1) A_X, which controls the numerator in $\frac{\partial pH}{\partial TotX}$, and (2) TotX, which controls the denominator in $\frac{\partial pH}{\partial TotX}$ as it is much more variable than $[H^+]\left(\frac{\partial A_T}{\partial [H^+]}\right)_X - nA_X$ and much larger than A_X^2, the other two terms appearing here. The factor $\left(\frac{\partial A_T}{\partial [H^+]}\right)_X$ only deviates substantially from β_H when A_X contributes substantially to A_T; in these cases, the absolute value of $\left(\frac{\partial A_T}{\partial [H^+]}\right)_X$ exceeds that of β_H by up to 1 order of magnitude (in the case of A_C). It varies per species whether TotX or A_X mainly controls the magnitude of $\frac{\partial pH}{\partial TotX}$. For example, the denominators of $\frac{\partial pH}{\partial DIC}$ and $\frac{\partial pH}{\partial TotB}$ have a similar order of magnitude, but since A_B is 1 order of magnitude smaller than A_C, the absolute value of $\frac{\partial pH}{\partial DIC}$ is much higher than that of $\frac{\partial pH}{\partial TotB}$. In contrast, A_B is 1

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order of magnitude higher than A_{Si}, but due to the much smaller total concentration of silicate in comparison to borate, the absolute value of $\frac{\partial pH}{\partial TotSi}$ is higher.

Table 4 shows that $\frac{\partial pH}{\partial TotPO_4}$ has the highest absolute value, and for this reason $TotPO_4$, together with TotSi, is by default included in the most common programs for calculating the carbonate chemistry, such as CO2SYS (Lewis and Wallace, 1998), SWCO2 (Hunter, 2007) and seacarb (Lavigne et al., 2014). The units of the sensitivities with respect to changes in the total concentrations are in $(\text{mol kg}^{-1})^{-1}$. This means that adding 1 µmol kg^{-1} $TotPO_4$ to this system leads to a decrease in pH_F of 0.00180, while the addition of 1 µmol kg^{-1} DIC, under these conditions equivalent to a ΔpCO_2 of 1.59 ppmv, lowers pH_F by 0.00175. However, in natural systems DIC changes are about two orders of magnitude higher than those in $TotPO_4$ because of the Redfield ratio. Hence, as displayed in Eq. (5), it is ultimately the combination of the change in TotX combined with the sensitivity that determines the actual change in pH_F.

Increasing T, S and p all lead to a decrease in pH_F. Under constant DIC and A_T, the increase in K_{C_2} resulting from an increase in temperature exceeds that of K_{C_1}, resulting in a shift of the carbonate system towards CO_2^*. A warming of 1ºC lowers pH by 0.0137, while the effect of changing pressure is much smaller; increasing p by 1 bar (which implies an increase in depth of ca. 10 m) leads to a decrease in pH of 0.000417. Our estimate of $\frac{\partial pH_F}{\partial T}$ is in reasonable agreement with the -0.016±0.001 estimated by Takahashi et al. (2014), who use a more extensive data set and report pH on the total scale (from now on denoted as pH_T). Note that Pilson (2014), in contrast to these results, calculated an increase in pH (displayed on the NIST scale, from now on denoted as pH_{NIST}) with an increase in T. This different result can, however, be explained by the different approaches used. In our approach we keep the total concentrations of the acid-base species and A_T constant when calculating the sensitivity of pH with respect to an increase in T. This leads to an increase in pCO_2 while keeping DIC constant, and thus a lowering in pH. Pilson (2014), however, kept the atmospheric $[CO_2]$ and A_T constant when increasing T. Since an increase in T leads to lower CO_2 solubility (Weiss, 1974), less atmospheric CO_2 is absorbed by the water, resulting in a decrease of both DIC and the fugacity of CO_2 (fCO_2), and thus an increase in pH. Increasing S by 1 leads to a lowering in pH of 0.0099. By also including the effect of S on TotB, Takahashi et al. (2014)

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estimated a value for $\frac{\partial pH_T}{\partial S}$ of -0.0125±0.0005. If we assume that an increase in S of 1 units leads to an increase in TotB of 12.358 µmol kg^{-1} (Lee et al., 2010), then we can calculate a combined sensitivity of increasing S and TotB of -0.0142. Taking into account the different pH scale, this is not far from the estimate of Takahashi et al. (2014).

3.2 Sensitivities in the future ocean

When comparing the sensitivities of the contemporary ocean and a warmer, high-CO_2 ocean, it becomes clear that not all sensitivities respond in a similar way to these processes. The majority of sensitivities becomes greater when pCO_2 increases, indicating larger pH change associated with a certain increment of TotX. Taking DIC as an example, an increase of 1 µmol kg^{-1} DIC in a high-CO_2 ocean (pCO_2 = 891 ppmv, DIC increase equivalent to ΔpCO_2 = 6.14 ppmv) lowers pH_F by 0.00270. This is equivalent to an increase in $[H^+]$ that is 3.71 times higher compared to the increase in $[H^+]$ when adding 1 µmol kg^{-1} of DIC to the contemporary ocean. This factor of 3.71 is significantly higher than the ca. 1.4 found by Riebesell et al. (2009), who used a more conservative increase in $pCO_{2,atm}$. Also the sensitivity of pH to a change in A_T increases; an increase of 1 µmol kg^{-1} A_T, caused by e.g. 0.5 µmol kg^{-1} of calcite dissolution, raises pH by 0.00263, equivalent to a 3.93 times higher decrease in $[H^+]$. In addition, the high-CO_2 ocean is less sensitive to changes in S and T, the latter of which is consistent with Riebesell et al. (2009), who found the same trend in both cold and warm surface waters.

In contrast to ocean acidification, ocean warming lowers most sensitivities, because of an increase in buffering capacity due to a higher $[CO_3^{2-}]$ (Sunda and Cai, 2012). Taking DIC as an example, an increase of 1 µmol kg^{-1} DIC in a warmer ocean (equivalent to ΔpCO_2 = 1.54 ppmv) lowers pH_F by 0.00167, i.e., the increase in $[H^+]$ is 93.9% of the increase in the contemporary ocean. Similarly, the decrease in $[H^+]$ in a warmer ocean is 93.1% of the current decrease resulting from an increase in A_T of 1 µmol kg^{-1}. While most sensitivities related to TotX show an opposite response to warming and acidification, this is not the case for the sensitivities related to S and T changes.

When ocean acidification and warming are combined, the response of the sensitivities largely reflects that of ocean acidification alone, but somewhat attenuated because of opposing effects of increases in T and pCO_2. Taking again DIC and A_T as examples, in this scenario a

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1 μmol kg^{-1} addition of DIC (equivalent to ΔpCO_2 = 5.88 ppmv) leads to an increase in $[H^+]$ that is 3.43 times higher compared to the increase in $[H^+]$ when adding 1 μmol kg^{-1} of DIC to the contemporary ocean, while an increase in A_T of 1 μmol kg^{-1} causes a decline in $[H^+]$ that is 3.62 times higher in a warmer, high-CO_2 ocean. Both of these values are lower than the factors mentioned for an increase in pCO_2 only. The values of the sensitivities for warming and acidification combined cannot be calculated by summing the separate changes of a higher T and pCO_2. The reason for this is that our assumption that pCO_2 is the same in both the high and the low T scenarios implies that DIC is slightly lower in the scenario where T is higher. If we had kept DIC, rather than pCO_2, the same in the high and low T scenarios, then this would have been possible.

When comparing the relative changes in sensitivity between the contemporary and a warmer, high-CO_2 ocean, it can be seen that $\frac{\partial pH}{\partial A_T}$ increases more than the absolute value of $\frac{\partial pH}{\partial DIC}$. This is important when considering a process that influences both A_T and DIC, such as calcite dissolution or precipitation where the A_T:DIC production or consumption ratio is 2:1. In the contemporary ocean, the increase in $[H^+]$ by adding 1 μmol kg^{-1} A_T is 91.1% of the decrease in $[H^+]$ by adding 1 μmol kg^{-1} DIC. In a warmer, high-CO_2 ocean, this fraction will increase to 96.0%. Thus, the change in A_T becomes relatively more important for the observed pH_F change.

Future carbon dioxide emission scenarios will determine the direction and magnitude of changes in ocean buffer factors. Figure 1 shows the projected changes in $\frac{\partial pH}{\partial DIC}$, $\frac{\partial pH}{\partial A_T}$, $\frac{\partial pH}{\partial pCO_2}$ and the Revelle factor based on four emission scenarios of the 5th IPCC assessment (2013). The atmospheric CO_2 trajectories of Meinshausen et al. (2011) were combined with average ocean surface water composition (Table E.1) and no temperature increase was assumed because of its limited effect. The impact of biogeochemical processes and ocean acidification on ocean pH will increase in proportion to the projected atmospheric perturbation. The business-as-usual scenario (RCP8.5) will result in an ocean that is less buffered and can take up less carbon dioxide than an ocean subject to the scenario with early measure to reduce carbon emissions (RCP3D). The average Revelle factor will change from 9.9 in the year 2000 to 15.0 for RCP8.5 and 10.5 for RCP3D. These different CO_2 trajectories

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also have a major impact on the sensitivity of ocean pH to biogeochemical processes such as calcification and primary production.

In the context of ocean acidification due to atmospheric pCO_2 it instructive to separate the changes in pH with respect to pCO_2 and DIC (Orr, 2011):

$$\frac{\partial pH}{\partial DIC} = \frac{\partial pH}{\partial pCO_2}\frac{\partial pCO_2}{\partial DIC} \tag{41}$$

To analytically calculate $\frac{\partial pH}{\partial pCO_2}$, we take the quotient of $\frac{\partial pH}{\partial DIC}$ and $\frac{\partial pCO_2}{\partial DIC}$. The latter term is derived from Eq. (34):

$$\frac{\partial pCO_2}{\partial DIC} = \frac{1}{K_0}\frac{\partial [CO_2^*]}{\partial DIC} = \frac{pCO_2[H^+]\left(\frac{\partial A_T}{\partial [H^+]}\right)_{CO_2^*}}{A_C^2 + [H^+]\left(\frac{\partial A_T}{\partial [H^+]}\right)_{CO_2^*} DIC} \tag{42}$$

where $[CO_2^*] = K_0 pCO_2$ and assuming that K_0 does not change as temperature remains constant during these calculations. The resulting expression then becomes:

$$\frac{\partial pH}{\partial pCO_2} = \frac{\frac{A_c}{\ln(10)}}{pCO_2[H^+]\left(\frac{\partial A_T}{\partial [H^+]}\right)_{CO_2^*}} \tag{43}$$

As can be seen in Figs. 1a-c, the increased sensitivity $\frac{\partial pH}{\partial DIC}$ is affected by changes in both $\frac{\partial pH}{\partial pCO_2}$ and $\frac{\partial pCO_2}{\partial DIC}$. Throughout the 21st century, the latter term increases by factors of 3.84 and 1.21 for RCP8.5 and RCP3D, respectively, while $\frac{\partial pH}{\partial pCO_2}$ increases from -0.00110 in the year 2000 to -0.000442 for RCP8.5 and -0.000966 for RCP3D, respectively. Under these conditions, an increment of 1 ppmv pCO_2 leads however to $[H^+]$ increases which are only marginally smaller than that of the contemporary ocean (96.3 and 99.1% for RCP8.5 and RCP3D, respectively). These small differences indicate, in line with Orr (2011), that the response of $\frac{\partial pH}{\partial DIC}$ to ocean acidification is largely due to the $\frac{\partial pCO_2}{\partial DIC}$ term.

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3.3 Elucidating interactions between ocean pH perturbations

The future ocean, and in particular the coastal zone, is subject to multiple stressors including ocean acidification, global warming, atmospheric deposition of sulphur and nitrogen, and eutrophication. The combined effects of these human perturbations on ocean pH have not yet been fully explored. In the previous section, we showed that ocean acidification has a much stronger effect on future pH than global warming. Doney et al. (2007), Hunter et al. (2011) and Hagens et al. (2014) showed that acid generation due to deposition of atmospheric sulphur and nitrogen adds to ocean acidification, but that its impact on ocean pH depends on the buffer capacity. Eutrophication, the excess production of organic matter, due to human nutrient inputs can lead to enhanced respiration and eventually to oxygen depletion in coastal waters. Respiration of organic matter also leads to an increase in DIC and thus might eventually lead to a decrease in pH (Frankignoulle et al., 1998; Cai et al., 2011; Mucci et al., 2011). The combined effect of ocean acidification due to dissolution of atmospheric carbon dioxide and that due to eutrophication-induced respiration might be additive and result in highly corrosive waters (Cai et al., 2011; Mucci et al., 2011; Melzner et al., 2013; Wallace et al., 2014).

Figure 2 shows the relationships between pH and dissolved oxygen in seawater subjected to both DIC additions from respiration and atmospheric carbon dioxide. Mean ocean surface water was subjected to the four carbon dioxide trajectories of the 5th IPCC assessment and respiration of Redfield organic matter. The figure also shows the relationship in the pre-industrial ocean when $pCO_{2,atm}$ was 285 ppm. The DIC generated during respiration adds to the ocean acidification due to increasing atmospheric carbon dioxide levels, but the additional pH decline is not constant, consistent with earlier work (Cai et al., 2011; Sunda and Cai, 2012). Comparing year 2100 projections based on RCP8.5 with the pre-industrial ocean shows that without respiration the pH decline would be 0.486 unit (equivalent to $\Delta[H^+]$ = 0.0100 µmol kg^{-1}), while it would be maximally 0.622 unit (equivalent to $\Delta[H^+]$ = 0.0274 µmol kg^{-1}) at an oxygen concentration of 114 µmol kg^{-1} At very low oxygen levels, the additional pH decline due to respiration would be only 0.376 unit; however, the equivalent $\Delta[H^+]$ (0.0293 µmol kg^{-1}) is higher than at the point of maximum pH difference. At O_2 = 49 µmol kg^{-1}, the absolute $[H^+]$ change is highest (0.0335 µmol kg^{-1}); here, the pH difference between both simulations is 0.539. This non-linear behaviour relates directly to changes in

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the sensitivities of pH and [H^+] to DIC changes under altered ambient conditions. Moreover, since both sensitivities are related through $-\ln(10)[H^+]$ (Eq. (21)), it is the ambient [H^+] that controls their different responses to respiration. The decrease in both sensitivities at lower oxygen levels can be attributed to an increase in buffering at these lower pH values (e.g. Egleston et al., 2010), but this response is system-specific and depends on the initial conditions. Therefore, the results of Figure 2 agree in pattern with those of Cai et al. (2011) and Sunda and Cai (2012) but show different points of minimum buffering capacity. Waters that currently have a high buffering capacity, such as the Gulf of Mexico, require a higher pCO_2 increase before their maximum sensitivity to respiration is reached than poorly buffered waters such as the Baltic Sea (Sunda and Cai, 2012). Accordingly, DIC added by respiration will lower pH in the future ocean but not necessarily more than it does now and the other eutrophication problem (Wallace et al., 2014) will thus either stimulate or attenuate pH decline depending both on the intensity of oxygen depletion and the current buffering capacity.

3.4 Analytical versus numerical calculation of buffer factors

It has recently been pointed out that differences between analytical expressions for the Revelle factor that only include the carbonate system and treat the borate system as invariant (Sundquist et al., 1979; Frankignoulle, 1994; Zeebe and Wolf-Gladrow, 2001), and the numerical approximation of CO2SYS and mocsy 2.0, which use the full definition of A_T as given by Dickson (1981), are highest when nutrients contribute significantly to A_T (Orr and Epitalon, 2015). We can use the generic expressions from this paper to show that the analytical and numerical solutions yield similar results when the approach of Frankignoulle (1994) is expanded to include all relevant acid-base systems contributing to A_T. For this, we numerically estimated both RF and $\frac{dpH}{dY}$ (where Y can refer to either TotX or A_T) for the contemporary ocean (Table E.1 in the Supplementary Information). A centred-finite-difference approach was used in which small (1 and 0.1%) in- and decrements were applied to the variable of interest (A_T or TotX), after which both resulting pH values (in the case of $\frac{dpH}{dY}$) or CO_2 values (in the case of RF) were taken and used to calculate the corresponding sensitivity. TotF and $TotSO_4$ were discarded from this analysis, as with this numerical

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estimation it is not possible to distinguish between the actual change in pH resulting from a change in concentration ($\frac{dpH}{dTotF}$ and $\frac{dpH}{dTotSO_4}$), and the effects related to pH scale conversion (see part C of the Supplementary Information). In addition, we also analytically calculated the factors β_D, Φ_D and Φ_H of Frankignoulle (1994), which are equivalent to RF, $\frac{\partial pH}{\partial DIC}$ and $\frac{\partial pH}{\partial A_T}$, respectively. The results of both calculations were compared with the analytically-calculated sensitivities using the generalised expressions of this work.

This comparison (Table 5) shows that Frankignoulle's factors β_D, Φ_D and Φ_H, without all acid-base systems included, deviate most from the analytically-derived factors and the numerical estimates with smallest disturbance (0.1%), which may be assumed to be more accurate than the estimate using a higher disturbance. This shows that our method is indeed capable of analytically calculating sensitivities more accurately than previously. It is thus possible to analytically calculate RF and other sensitivities at high accuracy even in nutrient-rich waters. Table 5 also shows that when under these initial conditions the variable of interest is changed by 1%, in most cases $\frac{dpH}{dY}$ equals $\frac{\partial pH}{\partial Y}$. Exceptions here are A_T and DIC, the two variables with highest concentrations, where a smaller disturbance (0.1%) is required to arrive at a result identical up to 5 significant digits. Note that it is not the focus of this paper to determine which disturbance is preferentially used for each factor; this may be system-specific and has been previously discussed for the Revelle factor (Orr and Epitalon, 2015). We rather encourage the use of analytically-calculated sensitivities using this novel approach.

4 Conclusions and implications

Inspired by Frankignoulle (1994), we derived generic expressions describing the change in pH_F or an acid-base species due to changes in A_T or the total concentration of that particular acid-base system. These sensitivities are valid for any combination of acid-base systems and any total concentration, or any of the species contributing to the total concentration, as independent state variable, assuming that all other factors remain constant. They are therefore ideal when attributing which factors drive a change in pH or X. Most sensitivities in a warmer, more acidified ocean increase, thus decreasing the ocean's capacity to buffer

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changes in pH. This decrease is mostly driven by the increase in pCO_2 and slightly tempered by the increase in T.

Previous studies have shown that seawater buffering capacity will decrease in a warmer, high-CO_2 ocean (e.g. Hofmann et al., 2010a; Egleston et al., 2010; Hagens et al., 2014). Our work supports this finding, but additionally is the first to give a comprehensive overview of all sensitivities and shows which of these factors are most affected by global change. The lower capacity of the global ocean to buffer changes in TA and most total concentrations of acid-base species by the end of the 21st century has important implications. For example, we may expect more pronounced diurnal (Schulz and Riebesell, 2013) and seasonal pH variabilities resulting from photosynthesis and subsequent organic matter remineralisation. This effect may be amplified if productivity were to increase in the future ocean (Low-Décarie et al., 2014), though whether this will happen is subject of debate (Joint et al., 2011; Eichner et al., 2014).

Both Frankignoulle (1994) and Egleston et al. (2010) discussed some useful applications of the buffer factors derived in their papers. Among these are estimating the ratio of organic matter production to calcification in, e.g., coral reefs, aiding experimental designs, testing model parameter sensitivities, as well as error propagation (Dickson and Riley, 1978). The sensitivities derived in this paper can be applied to the same questions and are particularly useful in waters where the contribution of acid-base systems other than the carbonate and borate systems to A_T is high. Examples of these are pore waters, upwelling regions, the deep ocean, high-nutrient-low-chlorophyll regions, and anoxic bottom waters in stratified seas or rivers (Gaines Jr and Pilson, 1972; Ben-Yaakov, 1973; Dugdale et al., 1977; Ulfsbo et al., 2011).

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Table 1a: Expressions for A_X for the major acid-base systems present in marine waters in terms of the reference species (X_{ref}), $[H^+]$ and dissociation constants. The reference species, or the zero level of protons, is that species of an acid-base system that does not contribute to A_T, i.e., the stoichiometric contribution to A_T (n) equals 0. These expressions are applicable when the total concentration of the acid-base system TotX, or any of its species X, is the state variable. Expressions are taken from Park (1969) and Stumm and Morgan (1996).

Acid-base system (TotX)	**Reference species (X_{ref})**	**Contribution to A_X (A_X)**	**A_X (TotX or X is state variable)**
Ammonium ($TotNH_4$)	NH_4^+	$[NH_3]$	$\left(\frac{K_{NH_4}}{[H^+]}\right)[NH_4^+]$
Borate (TotB)	$B(OH)_3$	$[B(OH)_4^-]$	$\left(\frac{K_B}{[H^+]}\right)[B(OH)_3]$
Carbonate (DIC)	H_2CO_3	$[HCO_3^-] + 2\,[CO_3^{2-}]$	$\left(\frac{K_{C_1}}{[H^+]}+\frac{2K_{C_1}K_{C_2}}{[H^+]^2}\right)[CO_2^*]$
Phosphate ($TotPO_4$)	$H_2PO_4^-$	$[HPO_4^{2-}] + 2[PO_4^{3-}] - [H_3PO_4]$	$\left(\frac{K_{P_2}}{[H^+]}+\frac{2K_{P_2}K_{P_3}}{[H^+]^2}-\frac{[H^+]}{K_{P_1}}\right)[H_2PO_4^-]$
Nitrate ($TotNO_3$)	NO_3^-	$-\,[HNO_3]$	$\left(\frac{-[H^+]}{K_{NO_3}}\right)[NO_3^-]$
Nitrite ($TotNO_2$)	NO_2^-	$-\,[HNO_2]$	$\left(\frac{-[H^+]}{K_{NO_2}}\right)[NO_2^-]$
Sulphide (TotS)	H_2S	$[HS^-] + 2[S^{2-}]$	$\left(\frac{K_{HS_1}}{[H^+]}+\frac{2K_{HS_1}K_{HS_2}}{[H^+]^2}\right)[H_2S]$
Silicate (TotSi)	$Si(OH)_4$	$[SiO(OH)_3^-] + 2[SiO_2(OH)_2^{2-}]$	$\left(\frac{K_{Si_1}}{[H^+]}+\frac{2K_{Si_1}K_{Si_2}}{[H^+]^2}\right)[Si(OH)_4]$
Fluoride (TotF)	F^-	$-\,[HF]$	$\left(\frac{-[H^+]}{K_F}\right)[F^-]$

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Sulphate ($TotSO_4$)	SO_4^{2-}	- $[HSO_4^-]$ - $2[H_2SO_4]$	$\left(\frac{-[H^+]}{K_{SO_2}} - \frac{2[H^+]^2}{K_{SO_1}K_{SO_2}}\right)[SO_4^{2-}]$
Water (auto-dissociation)	H_2O	$[OH^-]$ - $[H^+]$	-

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Table 1b: Expressions for A_X for the major acid-base systems present in marine waters in terms of the total concentration (TotX), $[H^+]$ and dissociation constants. These expressions are applicable when the total concentration of the acid-base system (TotX) is reaction invariant. The final expression for A_T (Eq. (6)) for the specific situation is arrived at by summing the appropriate term (a or b) for each acid-base system involved.

Acid-base system (TotX)	**Contribution to A_T (A_X)**	**A_X (TotX is reaction invariant)**
Ammonium ($TotNH_4$)	$[NH_3]$	$\frac{K_{NH_4}}{[H^+]+K_{NH_4}} TotNH_4$
Borate (TotB)	$[B(OH)_4^-]$	$\frac{K_B}{[H^+]+K_B} TotB$
Carbonate (DIC)	$[HCO_3^-] + 2\,[CO_3^{2-}]$	$\frac{K_{C_1}[H^+]+2K_{C_1}K_{C_2}}{[H^+]^2+K_{C_1}[H^+]+K_{C_1}K_{C_2}} DIC$
Phosphate ($TotPO_4$)	$[HPO_4^{2-}] + 2[PO_4^{3-}] - [H_3PO_4]$	$\frac{K_{P_1}K_{P_2}[H^+]+2K_{P_1}K_{P_2}K_{P_3}-[H^+]^3}{[H^+]^3+K_{P_1}[H^+]^2+K_{P_1}K_{P_2}[H^+]+2K_{P_1}K_{P_2}K_{P_3}} TotPO_4$
Nitrate ($TotNO_3$)	$- [HNO_3]$	$\frac{-[H^+]}{[H^+]+K_{NO_3}} TotNO_3$
Nitrite ($TotNO_2$)	$- [HNO_2]$	$\frac{-[H^+]}{[H^+]+K_{NO_2}} TotNO_2$
Sulphide (TotS)	$[HS^-] + 2[S^{2-}]$	$\frac{K_{HS_1}[H^+]+2K_{HS_1}K_{HS_2}}{[H^+]^2+K_{HS_1}[H^+]+K_{HS_1}K_{HS_2}} TotS$
Silicate (TotSi)	$[SiO(OH)_3^-] + 2[SiO_2(OH)_2^{2-}]$	$\frac{K_{Si_1}[H^+]+2K_{Si_1}K_{Si_2}}{[H^+]^2+K_{Si_1}[H^+]+K_{Si_1}K_{Si_2}} TotSi$
Fluoride (TotF)	$- [HF]$	$\frac{-[H^+]}{[H^+]+K_F} TotF$
Sulphate ($TotSO_4$)	$- [HSO_4^-] - 2[H_2SO_4]$	$\frac{-K_{SO_1}[H^+]-2[H^+]^2}{[H^+]^2+K_{SO_1}[H^+]+K_{SO_1}K_{SO_2}} TotSO_4$

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Water (auto-dissociation)	$[OH^-]$ - $[H^+]$	$\frac{K_W}{[H^+]} - [H^+]$

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Table 2a: Expressions for $\left(\frac{\partial A_X}{\partial [H^+]}\right)_X$ for the major acid-base systems present in marine waters. These are used when the total concentration of the acid-base system (TotX), or any of its species, is the state variable. The factor *n* corresponds to the stoichiometric factor in the contribution of X to A_T, which is by default 0 for the reference species. The reference species (X_{ref}) is that species of an acid-base system that does not contribute to A_T.

Acid-base system (TotX)	**Reference species**	$\left(\frac{\partial A_X}{\partial [H^+]}\right)_X$
Ammonium ($TotNH_4$)	NH_4^+	$\frac{-1}{[H^+]}\left(-nA_{NH_4}+([NH_3])\right)$
Borate (TotB)	$B(OH)_3$	$\frac{-1}{[H^+]}\left(-nA_B+\left([B(OH)_4^-]\right)\right)$
Carbonate (DIC)	H_2CO_3	$\frac{-1}{[H^+]}\left(-nA_C+\left([HCO_3^-]+4[CO_3^{2-}]\right)\right)$
Phosphate ($TotPO_4$)	$H_2PO_4^-$	$\frac{-1}{[H^+]}\left(-nA_P+\left([H_3PO_4]+[HPO_4^{2-}]+4[PO_4^{3-}]\right)\right)$
Nitrate ($TotNO_3$)	NO_3^-	$\frac{-1}{[H^+]}\left(-nA_{NO_3}+([HNO_3])\right)$
Nitrite ($TotNO_2$)	NO_2^-	$\frac{-1}{[H^+]}\left(-nA_{NO_2}+([HNO_2])\right)$
Sulphide (TotS)	H_2S	$\frac{-1}{[H^+]}\left(-nA_{HS}+\left([HS^-]+4[S^{2-}]\right)\right)$
Silicate (TotSi)	$Si(OH)_4$	$\frac{-1}{[H^+]}\left(-nA_{Si}+\left([SiO(OH)_3^-]+4[SiO_2(OH)_2^{2-}]\right)\right)$
Fluoride (TotF)	F^-	$\frac{-1}{[H^+]}\left(-nA_F+([HF])\right)$
Sulphate ($TotSO_4$)	SO_4^{2-}	$\frac{-1}{[H^+]}\left(-nA_{SO}+\left(4[H_2SO_4]+[HSO_4^-]\right)\right)$

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Water (H_2O)	-	-

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Table 2b: Expressions for $\left(\frac{\partial A_X}{\partial[H^+]}\right)_{TotX}$ for the major acid-base systems present in marine waters. These are valid when the total concentration of the acid-base system (TotX) is reaction invariant. The final expression for $\left(\frac{\partial A_T}{\partial[H^+]}\right)_X$ for the specific situation (Eq. (15)) is arrived at by summing the appropriate term (a or b) for each acid-base system involved.

Acid-base system (TotX)	$\left(\frac{\partial A_X}{\partial[H^+]}\right)_{TotX}$
Ammonium ($TotNH_4$)	$\frac{-1}{[H^+]}\left([NH_3]\frac{[NH_4^+]}{TotNH_4}\right)$
Borate (TotB)	$\frac{-1}{[H^+]}\left([B(OH)_4^-]\frac{[B(OH)_3]}{TotB}\right)$
Carbonate (DIC)	$\frac{-1}{[H^+]}\left([HCO_3^-]\left(\frac{[H_2CO_3]-[CO_3^{2-}]}{DIC}\right)+2[CO_3^{2-}]\left(\frac{2[H_2CO_3]+[HCO_3^-]}{DIC}\right)\right)$
Phosphate ($TotPO_4$)	$\frac{-1}{[H^+]}\left(-[H_3PO_4]\left(\frac{-[H_2PO_4^-]-2[HPO_4^{2-}]-3[PO_4^{3-}]}{TotPO_4}\right)+[HPO_4^{2-}]\left(\frac{2[H_3PO_4]+[H_2PO_4^-]-[PO_4^{3-}]}{TotPO_4}\right)+2[PO_4^{3-}]\left(\frac{3[H_3PO_4]+2[H_2PO_4^-]+[HPO_4^{2-}]}{TotPO_4}\right)\right)$
Nitrate ($TotNO_3$)	$\frac{-1}{[H^+]}\left(-[HNO_3]\frac{[NO_3^-]}{TotNO_3}\right)$
Nitrite ($TotNO_2$)	$\frac{-1}{[H^+]}\left(-[HNO_2]\frac{[NO_2^-]}{TotNO_2}\right)$
Sulphide (TotS)	$\frac{-1}{[H^+]}\left([HS^-]\left(\frac{[H_2S]-[S^{2-}]}{TotS}\right)+2[S^{2-}]\left(\frac{2[H_2S]+[HS^-]}{TotS}\right)\right)$

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Silicate (TotSi)	$\frac{-1}{[H^+]}\left(\begin{array}{l}[SiO(OH)_3^-]\left(\frac{[Si(OH)_4]-[SiO_2(OH)_2^{2-}]}{TotSi}\right)\\ +2[SiO_2(OH)_2^{2-}]\left(\frac{2[Si(OH)_4]+[SiO(OH)_3^-]}{TotSi}\right)\end{array}\right)$
Fluoride (TotF)	$\frac{-1}{[H^+]}\left(-[HF]\frac{[F^-]}{TotF}\right)$
Sulphate ($TotSO_4$)	$\frac{-1}{[H^+]}\left(\begin{array}{l}-2[H_2SO_4]\left(\frac{-[HSO_4^-]-2[SO_4^{2-}]}{TotSO_4}\right)\\ -[HSO_4^-]\left(\frac{[H_2SO_4]-[SO_4^{2-}]}{TotSO_4}\right)\end{array}\right)$
Water (auto-dissociation)	$\frac{-1}{[H^+]}\left([OH^-]+[H^+]\right)$

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Table 3: Expressions for some sensitivities of interest when studying global change. TotX refers to the total concentration of the acid-base system of interest, X to the species of interest of that acid-base system (which equals the reference species for A_T (X_{ref}) in the case a change in TotX is specified), *n* to the stoichiometric factor in the contribution of X to A_T (which equals 0 in the case a change in TotX or X_{ref} is specified) and A_X to the contribution of all species of TotX to A_T.

Table 3a

Sensitivity	**Expression**
$\left(\frac{\partial A_T}{\partial [H^+]}\right)_X$	$\beta_H - \left(\frac{\partial A_X}{\partial [H^+]}\right)_{TotX} + \left(\frac{\partial A_X}{\partial [H^+]}\right)_X$
$\left(\frac{\partial TotX}{\partial [H^+]}\right)_X$	$\frac{nTotX - A_X}{[H^+]}$
$\left(\frac{\partial A_T}{\partial [X]}\right)_{H^+}$	$\frac{A_X}{[X]}$
$\left(\frac{\partial TotX}{\partial [X]}\right)_{H^+}$	$\frac{TotX}{[X]}$
$\left(\frac{\partial A_T}{\partial pH}\right)_X$	$-\ln(10)[H^+]\left(\beta_H - \left(\frac{\partial A_X}{\partial [H^+]}\right)_{TotX} + \left(\frac{\partial A_X}{\partial [H^+]}\right)_X\right)$
$\left(\frac{\partial TotX}{\partial pH}\right)_X$	$-\ln(10)\left(nTotX - A_X\right)$

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Table 3b	
Sensitivity	**Expression**
$\frac{\partial[H^+]}{\partial A_T}$	$\frac{TotX[H^+]}{A_X^2+\left([H^+]\left(\frac{\partial A_T}{\partial[H^+]}\right)_X-nA_X\right)TotX}$
$\frac{\partial[H^+]}{\partial TotX}$	$\frac{-A_X[H^+]}{A_X^2+\left([H^+]\left(\frac{\partial A_T}{\partial[H^+]}\right)_X-nA_X\right)TotX}$
$\frac{\partial X}{\partial A_T}$	$\frac{-[X](-A_X+nTotX)}{A_X^2+\left([H^+]\left(\frac{\partial A_T}{\partial[H^+]}\right)_X-nA_X\right)TotX}$
$\frac{\partial X}{\partial TotX}$	$\frac{[X][H^+]\left(\frac{\partial A_T}{\partial[H^+]}\right)_X}{A_X^2+\left([H^+]\left(\frac{\partial A_T}{\partial[H^+]}\right)_X-nA_X\right)TotX}$
$\frac{\partial pH}{\partial A_T}$	$\frac{-TotX}{\ln(10)\left(A_X^2+\left([H^+]\left(\frac{\partial A_T}{\partial[H^+]}\right)_X-nA_X\right)TotX\right)}$
$\frac{\partial pH}{\partial TotX}$	$\frac{A_X}{\ln(10)\left(A_X^2+\left([H^+]\left(\frac{\partial A_T}{\partial[H^+]}\right)_X-nA_X\right)TotX\right)}$

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Table 4: Global mean values for all derived sensitivities at present and in 2100, using various scenarios. Contemporary average surface seawater conditions were obtained from Table E.1 (Supplementary Information). Using the dissociation constants as outlined in Sect 3.1, this corresponds to pH_F = 8.21 and pCO_2 = 324 ppmv. Changes in temperature (Bopp et al., 2013) and $pCO_{2,atm}$ (Meinshausen et al., 2011) until 2100 (pCO_2 = 891 ppmv, T = 21.0°C) were considered both separately and combined.

Sensitivity	**Unit**	**Present**	**2100 CO_2**	**2100 T**	**2100 T+CO_2**
$\frac{\partial pH}{\partial A_T}$	$(\text{mol kg}^{-1})^{-1}$	1601.50	2622.39	1513.21	2474.51
$\frac{\partial pH}{\partial TotNH_4}$	$(\text{mol kg}^{-1})^{-1}$	-65.01	-45.38	-75.46	-53.43
$\frac{\partial pH}{\partial TotB}$	$(\text{mol kg}^{-1})^{-1}$	-349.00	-272.51	-348.33	-276.36
$\frac{\partial pH}{\partial DIC}$	$(\text{mol kg}^{-1})^{-1}$	-1751.84	-2700.35	-1669.69	-2562.20
$\frac{\partial pH}{\partial TotPO_4}$	$(\text{mol kg}^{-1})^{-1}$	-1801.31	-2730.96	-1728.16	-2601.70
$\frac{\partial pH}{\partial TotNO_3}$	$(\text{mol kg}^{-1})^{-1}$	$4.21\cdot10^{-7}$	$1.66\cdot10^{-6}$	$3.92\cdot10^{-7}$	$1.53\cdot10^{-6}$
$\frac{\partial pH}{\partial TotNO_2}$	$(\text{mol kg}^{-1})^{-1}$	$6.23\cdot10^{-3}$	$2.45\cdot10^{-2}$	$5.80\cdot10^{-3}$	$2.26\cdot10^{-2}$
$\frac{\partial pH}{\partial TotS}$	$(\text{mol kg}^{-1})^{-1}$	-1553.79	-2441.35	-1472.15	-2319.77
$\frac{\partial pH}{\partial TotSi}$	$(\text{mol kg}^{-1})^{-1}$	-64.47	-44.99	-67.51	-47.65
$\frac{\partial pH}{\partial TotF}$	$(\text{mol kg}^{-1})^{-1}$	$3.72\cdot10^{-3}$	$1.46\cdot10^{-2}$	$3.64\cdot10^{-3}$	$1.42\cdot10^{-2}$
$\frac{\partial pH}{\partial TotSO_4}$	$(\text{mol kg}^{-1})^{-1}$	$7.71\cdot10^{-5}$	$3.03\cdot10^{-4}$	$7.97\cdot10^{-5}$	$3.10\cdot10^{-4}$

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$\frac{\partial pH}{\partial T}$	$(ºC)^{-1}$	$-1.37\cdot10^{-2}$	$-1.26\cdot10^{-2}$	$-1.34\cdot10^{-2}$	$-1.24\cdot10^{-2}$
$\frac{\partial pH}{\partial p}$	$(bar)^{-1}$	$-4.17\cdot10^{-4}$	$-4.31\cdot10^{-4}$	$-4.15\cdot10^{-4}$	$-4.27\cdot10^{-4}$
$\frac{\partial pH}{\partial S}$	-	$-9.91\cdot10^{-3}$	$-9.14\cdot10^{-3}$	$-1.01\cdot10^{-2}$	$-9.44\cdot10^{-3}$

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Table 5: Comparison between analytical and numerical calculation of sensitivities as defined for the contemporary average global surface ocean (see Table 4). The percentages in the headings of the numerical calculation refer to the relative in- and decrements to which the state variable was subjected.

Sensitivity (mol kg^{-1})$^{-1}$	**Analytical**	**Numerical (0.1%)**	**Numerical (1%)**	**Frankignoulle expression**
RF (dimensionless)	9.901	9.901	9.936	9.912
$\frac{\partial pH}{\partial A_T}$	1601.50	1601.52	1603.32	1603.62
$\frac{\partial pH}{\partial TotNH_4}$	-65.01	-65.01	-65.01	-
$\frac{\partial pH}{\partial TotB}$	-349.00	-349.00	-349.00	-
$\frac{\partial pH}{\partial DIC}$	-1751.84	-1751.86	-1753.10	-1754.16
$\frac{\partial pH}{\partial TotPO_4}$	-1801.31	-1801.31	-1801.31	-
$\frac{\partial pH}{\partial TotNO_3}$	$4.21 \cdot 10^{-7}$	0	0	-
$\frac{\partial pH}{\partial TotNO_2}$	$6.23 \cdot 10^{-3}$	0	0	-
$\frac{\partial pH}{\partial TotS}$	-1553.79	-1553.78	-1553.78	-
$\frac{\partial pH}{\partial TotSi}$	-64.47	-64.46	-64.46	-

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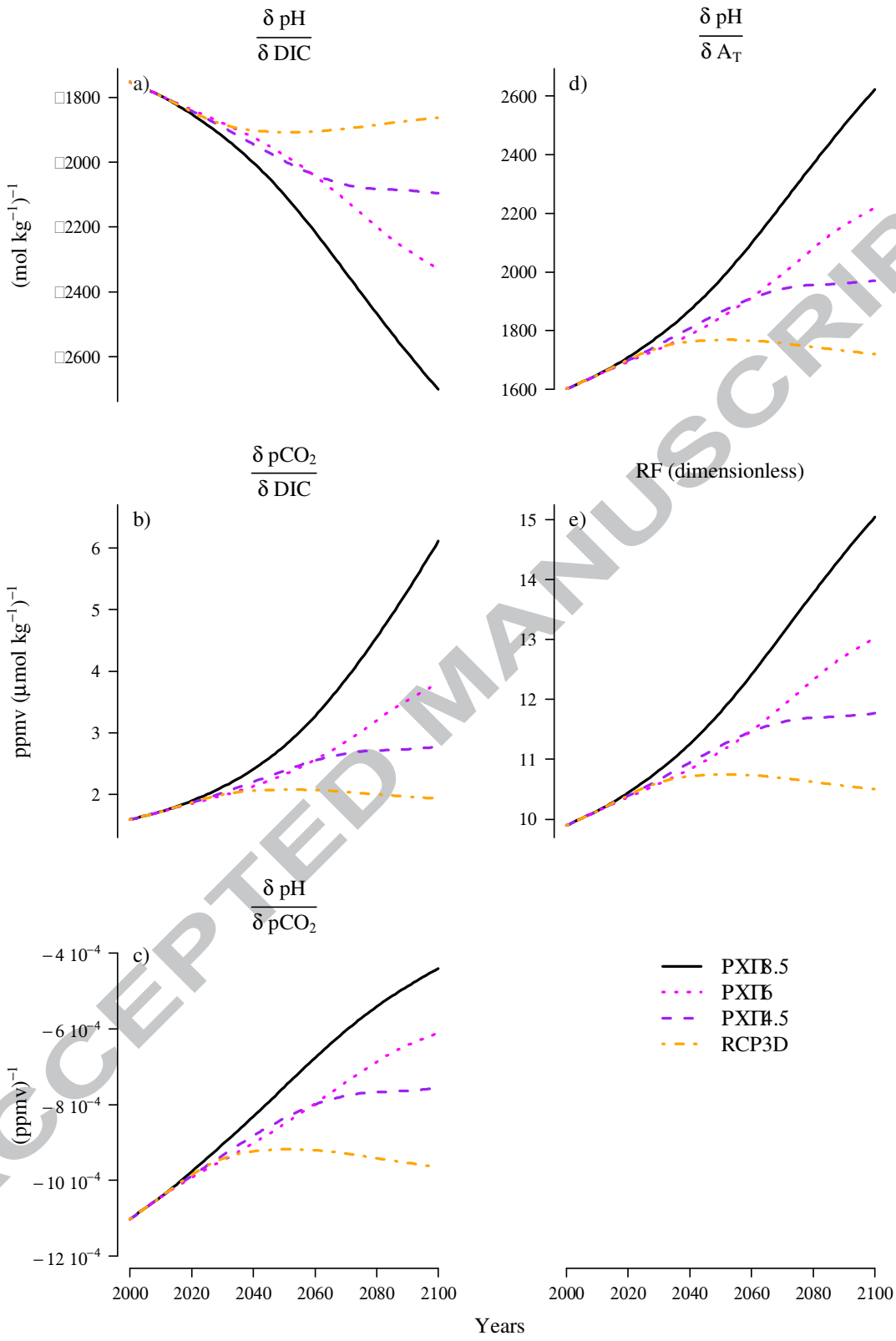

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Figure 1: Changes in a) $\frac{\partial pH}{\partial DIC}$ ((mol kg^{-1})$^{-1}$), b) $\frac{\partial pCO_2}{\partial DIC}$ (ppmv (µmol kg^{-1})$^{-1}$), c) $\frac{\partial pH}{\partial pCO_2}$ (ppmv^{-1}), d) $\frac{\partial pH}{\partial A_T}$ ((mol kg^{-1})$^{-1}$) and e) the Revelle factor in the 21st century according to the four emission scenarios defined by IPCC (2013). Changes in $pCO_{2,atm}$ were taken from Meinshausen et al. (2011), while temperature was kept constant.

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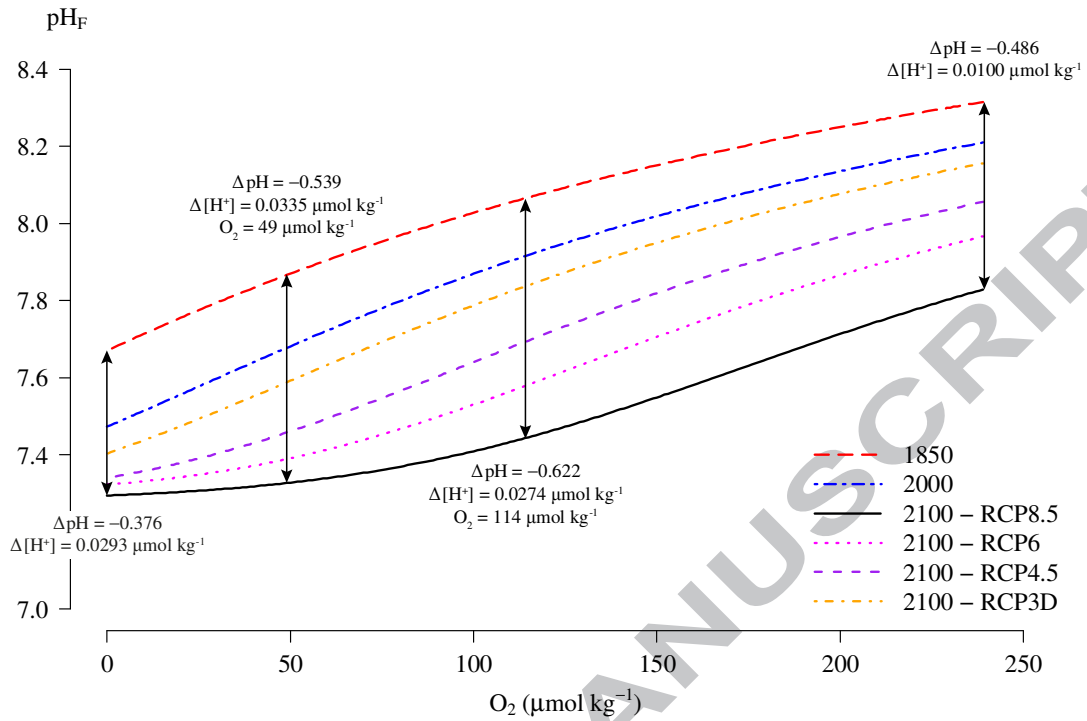

Figure 2: Changes in pH due to O_2 consumption in the pre-industrial (1850 AD), contemporary (2000 AD) and future ocean (2100 AD). For the future ocean, all four emission scenarios as defined by IPCC (2013) were modelled, with changes in $pCO_{2,atm}$ taken from Meinshausen et al. (2011). Similarly to Table 4, the effect of an increased temperature was tested for both the RCP8.5 emission scenario and the contemporary ocean.