

Quantifying the Possible Short- and Long-term Impacts of Superoxide Redox Chemistry on Seawater pH

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Abstract: We show here that the redox chemistry of superoxide (dismutation, oxidation and reduction), involving exchange of H⁺ upon reaction with some metals and organic compounds, is potentially able to alter the pH of seawater at time scales of several months to some years. The relevant pH effect could be locally significant in river-impacted coastal areas, where lower alkalinity compared to the open ocean combines with inputs of terrestrial matter that might produce imbalances in superoxide redox chemistry. The related effect may act as a local confounding factor in the assessment of seawater acidification.

Keywords: Acidification; CO₂; organic matter; biological processes; global warming; superoxide redox chemistry.

Superoxide (O₂^{-•}) is produced in seawater by a variety of abiotic (mostly photochemical) and biological processes and it is rapidly transformed, by metal-catalyzed dismutation into H₂O₂ and O₂, by oxidation to O₂ and by reduction to H₂O₂ [1, 2]. The transformation processes involve exchange of H⁺, to a different extent depending on the relevant reaction as shown in Figure 1.

To ensure that no previous H⁺ exchange occurred during superoxide formation, one can assume that O₂^{-•} is initially formed as HO₂[•] (see Figure 1). In this way, all pH-affecting reactions would take place after superoxide formation. According to Figure 1, superoxide dismutation into H₂O₂ and O₂ causes the net H⁺ budget to close to zero. However, O₂^{-•} oxidation to O₂ induces a net release of a H⁺ ion per processed O₂^{-•}, while reduction to H₂O₂ entails a corresponding H⁺ consumption. In the latter two cases, the overall H⁺ budget also depends on the other redox couple involved. Couples exchanging H⁺ and electrons in a different ratio than 1:1 would introduce an imbalance in the H⁺ budget when reacting with superoxide, with the potential to locally modify the pH of seawater. Examples of such couples are Fe^{II}-Fe^{III}, Mn^{II}-Mn^{IV} and, among organic compounds, quinones/hydroquinones with electron withdrawing substituents (Φ in reaction (3) is a C₆ ring) [1,2]:

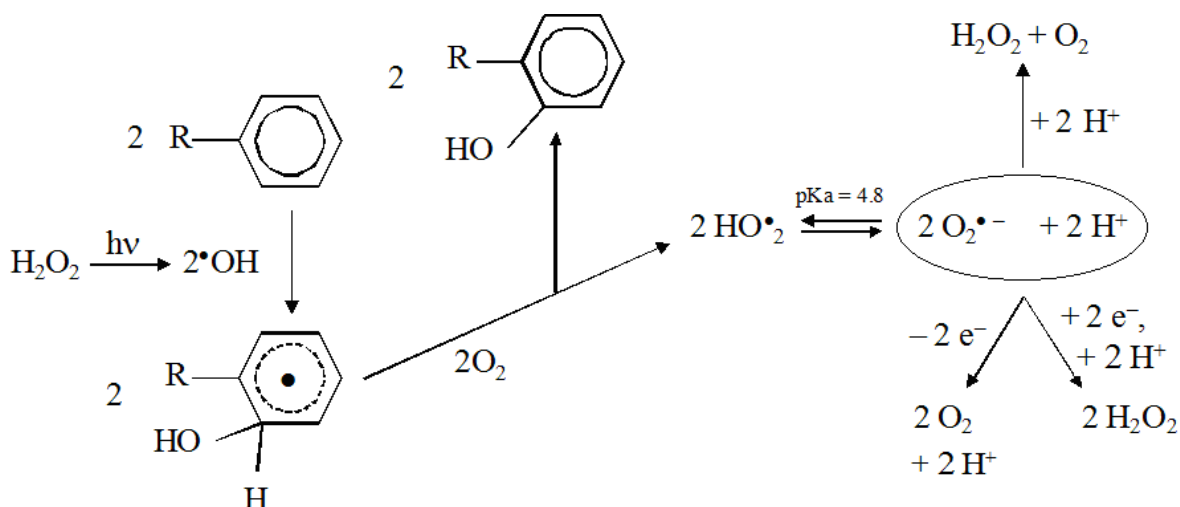
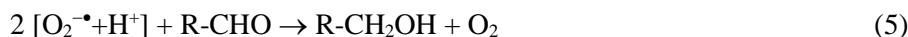
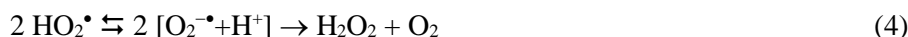


Figure 1. Processes involved in superoxide chemistry. A possible pathway leading to the production of the hydroperoxyl radical (HO_2^\bullet) is also reported. Note that the HO_2^\bullet formation reaction does not involve any exchange of H^+ .



In the presence of $\text{O}_2^\bullet/\text{O}_2$ or $\text{O}_2^\bullet/\text{H}_2\text{O}_2$ as additional redox couples, the above equilibria tend to favor the oxidation of Fe^{2+} and Mn^{2+} as well as the reduction of quinones [1], and in all such cases the process would cause water acidification. The formation of dissolved Fe(III), and of Mn^{III} in the first monoelectronic step of reaction (2) could induce metal-catalyzed dismutation of O_2^\bullet [3] with no effect on pH, but reaction between O_2^\bullet and Mn^{2+} is also known to produce Mn^{IV} oxides [2]. Interestingly, the reaction with organic compounds (which would often induce different processes than dismutation) could be the main O_2^\bullet sink under several seawater conditions [3].

The O_2^\bullet production rate in seawater ($R_{\text{O}_2^\bullet}$) amounts to $6 \cdot 10^{-5}$ - $6 \cdot 10^{-3}$ M year^{-1} [4,5], which would be equal to the O_2^\bullet transformation rate and to the associated rate of H^+ exchange (Figure 1). The latter does not necessarily have an impact on pH: dismutation and reaction with compounds exchanging H^+ and e^- in 1:1 ratio would have no pH effect (see for instance reactions (4,5)).



A pH modification occurs when O_2^\bullet takes part to a process involving net H^+ exchange, as for instance half-reactions (1-3) coupled with the following O_2^\bullet half-reactions: $[\text{O}_2^\bullet + \text{H}^+] \rightarrow \text{O}_2 + \text{H}^+ + \text{e}^-$ or $[\text{O}_2^\bullet + \text{H}^+] + \text{H}^+ + \text{e}^- \rightarrow \text{H}_2\text{O}_2$.

Because the O_2^\bullet reactions might or might not involve H^+ exchange, the net rate of H^+ variation

due to these processes would be a fraction of the $O_2^{\bullet-}$ generation rate ($R_{H^+} = \alpha R_{O_2^{\bullet-}}$, where $\alpha \leq 1$). The net H^+ variation would then modify seawater alkalinity by $\Delta Alk = \alpha R_{O_2^{\bullet-}} t$, where t is the time in years if $R_{O_2^{\bullet-}}$ is expressed in $[M \text{ year}^{-1}]$. The fraction of superoxide reacting in oxidation or reduction processes (excluding dismutation) is expected to be significant (it may be the majority of $O_2^{\bullet-}$ transformation, although not always with a pH effect) [3], thus the potential pH impact of this process appears to be worth investigating.

A simplified model for seawater pH can take into account the partitioning equilibrium of CO_2 between the atmosphere and the aqueous phase, the acid-base chemistry of the carbonate species as well as a fixed seawater alkalinity. If, as allowed by the pH of seawater, one assumes $[CO_3^{2-}] \ll [HCO_3^-]$, a manageable second-order equation is obtained that allows the equilibrium $[H^+]$ to be expressed as follows:

$$[H^+] = \frac{-Alk + \sqrt{Alk^2 + 4(Ka_1 K_H pCO_2 + K_W)}}{2} \quad (6)$$

where Alk is seawater's alkalinity (initially taken as 1.5 mM as per river-impacted coastal conditions, vide *infra* for the rationale of this choice), Ka_1 is the equilibrium constant of $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$, K_W the autoprotolysis constant of water, K_H the Henry's law constant of CO_2 and pCO_2 its partial pressure [6].

Figure 2 reports the link between $[H^+]$ and pCO_2 as foreseen by model calculations. According to the model, an increase in pCO_2 from 370 to 390 ppmv (that is, the same increase observed over the last 20 years in the Earth's troposphere [7]) would cause a decrease of ~ 0.015 pH units in seawater, which corresponds to about $1.1 \cdot 10^{-3}$ pH units year^{-1} .

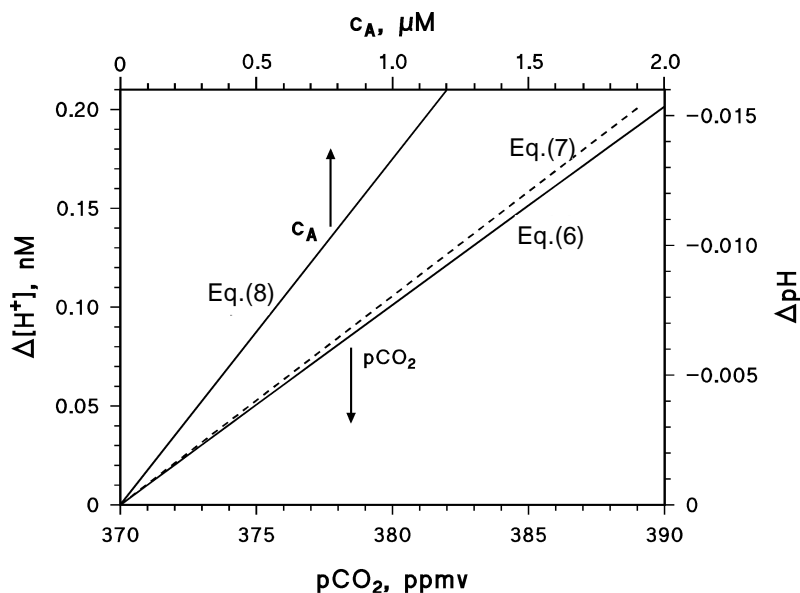


Figure 2. Variation of $[H^+]$ ($\Delta[H^+]$, left Y-axis) as a function of pCO_2 (lower X-axis, equation (6) solid and equation (7) dashed) and of the concentration of added acid (c_A , upper X-axis, equation (8)). The corresponding pH variation is also reported (ΔpH , right Y-axis).

An alternative model approach (approximated as well) for seawater pH takes into account the dissolution of carbonate minerals, here assumed to be represented by CaCO_3 . By so doing one obtains the following equation (7), where K_{PS} is the solubility product of CaCO_3 :

$$[H^+] = \sqrt[3]{\frac{(K_{a1} K_H p\text{CO}_2)^2 K_{a2}}{2 K_{PS}}} \quad (7)$$

By both equations (6) and (7) one can reproduce reasonably well the initial pH of seawater (model results range between 8.2 and 8.3). Equation (7) foresees a very similar pH decrease as equation (6), which can fix the expected pH decrease at about $1 \cdot 10^{-3}$ pH units year^{-1} (or 0.015 pH units in 20 years).

An analogous pH variation at constant $p\text{CO}_2$ could be caused by the addition of a strong acid, which is equivalent to a net addition of H^+ . In this case the second model approach (CaCO_3 dissolution) returns a third-order equation that cannot be solved as simply as equation (7). In contrast, the first model approach (fixed initial alkalinity) can be easily applied with some modifications. The initial seawater alkalinity is decreased upon addition of an acid at concentration c_A and, to obtain a straightforward and manageable solution, the concentration values of the carbonate species should be expressed as a function of Alk and $[\text{H}^+]$ rather than of $p\text{CO}_2$. This closed-system approach yields the following equation:

$$[H^+] = \frac{c_A K_{a1} + \sqrt{(c_A K_{a1})^2 + 4(\text{Alk} + K_{a1})(\text{Alk} K_{a1} K_{a2} + K_w K_{a1})}}{2(\text{Alk} + K_{a1})} \quad (8)$$

where K_{a2} is the constant of the equilibrium $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$. The link between $[\text{H}^+]$ and c_A is reported in Figure 1. To reproduce the CO_2 -associated decrease of 0.015 pH units in 20 years one needs an acid addition of $c_A = 1.1 \mu\text{M}$, which corresponds to $R_{\text{H}^+} = 5.5 \cdot 10^{-8} \text{ M year}^{-1}$. This value can be compared with the molarity of H^+ that is involved in the chemistry of superoxide.

From $R_{\text{O}_2^\bullet} = 6 \cdot 10^{-5} - 6 \cdot 10^{-3} \text{ M year}^{-1}$ [4,5], one gets $\alpha = R_{\text{H}^+} R_{\text{O}_2^\bullet}^{-1} = 10^{-5} - 10^{-3}$ as the H^+ imbalance in superoxide chemistry that would be required to reproduce the same pH change as the build-up of atmospheric CO_2 . Depending on the actual process, the superoxide-related effect of pH could cause an acidification or a basification, thereby strengthening or dampening the CO_2 -related acidification. In either case, the chemistry of superoxide may act as a confounding factor in the assessment of seawater acidification caused by atmospheric CO_2 . It should be noted that the H^+ imbalance in superoxide chemistry, which is required to have the same pH effect as the increasing atmospheric CO_2 , is very low ($\alpha = 10^{-5} - 10^{-3}$), but it should be steadily maintained over a long time period for the effect to become measurable.

To better highlight this point, Figure 3 shows the pH change that would be caused by $R_{\text{H}^+} = 5.5 \cdot 10^{-8} \text{ M year}^{-1}$, as a function of time. Three issues should be taken into account: (i) the reported time increase of ΔpH , and the facts that (ii) large imbalances in O_2^\bullet redox chemistry (leading to elevated α) are more likely to occur on the short term, and (iii) short-term (e.g. daily) pH variations tend to be larger than longer-term fluctuations [8]. The data reported in Figure 3 suggest that superoxide redox chemistry cannot possibly impact the pH changes that occur daily to monthly, which can amount to several pH decimals [8]. However, the role of superoxide could become potentially significant on time scales of

several months to some years, due to the combination (allowed by longer time scales) of higher pH impact associated with $O_2^{\bullet-}$ and of lower background variations of pH. However, the needed imbalance in $O_2^{\bullet-}$ redox chemistry should be maintained for long time periods.

The values of ΔpH in Figure 3 are larger for the coastal scenario because of the lower alkalinity. More importantly, superoxide sources and α values would be much larger in coastal areas compared to the open ocean, due to continuous riverine inputs of redox-active material and to enhanced biological and photochemical processes. Therefore, river-impacted coastal areas are the sites where the possible pH impact of superoxide chemistry should be tested. The quantification of the importance of these reactions requires: (i) an assessment of the riverine fluxes of compounds that are able to react with superoxide and alter pH; (ii) a more in-depth knowledge of the reactivity of $O_2^{\bullet-}$ with seawater organic matter (especially in terms of average kinetic constants) and with peculiar functional groups, and (iii) the determination of the redox conditions of the relevant coastal seawater systems.

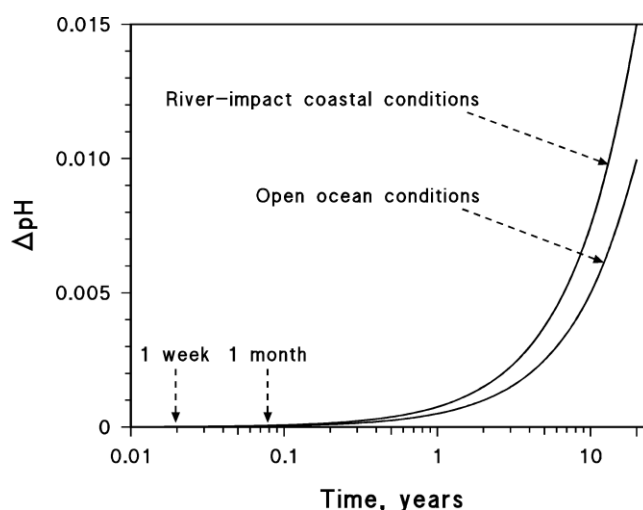


Figure 3. Variation of pH over time because of $O_2^{\bullet-}$ redox chemistry, for $R_{H^+} = 5.5 \cdot 10^{-8} \text{ M year}^{-1}$, in the scenarios of open and coastal ocean (Alk = 2.3 and 1.5 mM, respectively). The time periods corresponding to one week and one month are highlighted by arrows.

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The authors declare no conflict of interest

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