Original Research

An Estimate of Possible Impacts of Superoxide Chemistry on Seawater pH: A Mapping Exercise

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Abstract

Superoxide, produced photochemically as well as microbially, is an important reactant present in seawater and a major source of hydrogen peroxide. Superoxide decay may occur through catalyzed or uncatalyzed dismutation forming H_2O_2 and O_2, through oxidation to O_2, or through reduction into H_2O_2. Under definite circumstances, the redox processes that are different from dismutation could produce or consume H^+, thereby altering the pH of seawater. In order to alter the pH, these processes have to involve, together with $O_2^{\bullet-}$, redox couples that exchange e^- and H^+ in a ratio other than 1:1. This potential pH modification is dependent on several factors, including the extent of H^+ imbalance, the rate of formation/transformation of superoxide (which reaches a steady-state concentration in seawater), and the alkalinity of seawater (which varies globally from 2.10 to 2.45 mmol L^{-1} and buffers the pH variations). In the present study, an estimate of the possible pH changes associated with photochemically-produced superoxide in the global ocean has been provided. Among the important approximations that were required to perform the calculations, one

was that it was not possible to include the microbially generated $O_2^{\bullet-}$, as a geographic distribution of microbial processes is not available. Unfortunately, the microbial production of $O_2^{\bullet-}$ is comparable to or at certain times even higher than its photochemical production. Despite the above-stated and certain other limitations, it may be inferred that the tropical and equatorial oceans, because of the high $O_2^{\bullet-}$ photoproduction rates, would be having the highest potential of undergoing pH variations (up to 0.005 pH units in ten years). Along the tropical/equatorial latitude belt, at comparable sunlight irradiance, such variations are expected to be the largest (0.005 pH units) in the Indian Ocean due to a relatively low alkalinity, in the range of 2.2–2.3 mmol L^{-1}. The lowest variations (0.003–0.004 pH units) are expected in the Atlantic Ocean, because of a relatively high alkalinity in the range of 2.3–2.4 mmol L^{-1}. The main requirement for the $O_2^{\bullet-}$ chemistry to impact the pH of seawater significantly is that the H^+-imbalance reactions should be maintained for a sufficiently long period of time. The pH effect is most probably to be operational in the river-impacted coastal areas (potential candidates are the areas affected by the following rivers: Ganges, Mekong, Irrawaddy, Zambezi, Amazon River, Orinoco, Mississippi, and Rio Grande), which are characterized by a continuous flow of redox-active organic compounds into the seawater.

Keywords
Seawater photochemistry; superoxide; coastal areas; seawater pH; redox reactions

1. Introduction

Superoxide ($O_2^{\bullet-}$) is an unstable reactive oxygen species that is formed in the seawater through a combination of photochemical and biological reactions, with an overall $O_2^{\bullet-}$ formation rate in the range of $2 \cdot 10^{-12}$ to $2 \cdot 10^{-10}$ mol L^{-1} s^{-1} [1, 2]. The chemistry of superoxide is important because $O_2^{\bullet-}$ is involved in the redox cycling of metals (especially Fe, Cu, and Mn) and exerts a strong impact on the availability of metals as nutrients [3-5]. The chemistry of $O_2^{\bullet-}$ is also the main source of H_2O_2 in seawater, a compound that is involved in several processes including the Fenton and photo-Fenton reactions [6].

As a transient species, superoxide immediately reaches a steady-state concentration in the surface waters because of the balance between its formation and degradation. Interestingly, $O_2^{\bullet-}$ and its conjugated acid $HO_2^{\bullet}$ participate in both oxidation and reduction processes that involve the exchange of H^+ and electrons [7]:

$$O_2^{\bullet-} + 2\,H^+ + e^- \rightarrow H_2O_2 \qquad\qquad (1)$$

$$O_2^{\bullet-} \rightarrow O_2 + e^- \qquad\qquad (2)$$

These redox processes may also be combined into a dismutation reaction. In the majority of the photochemical (and possibly biological) processes, the radical species is initially produced in the form of $HO_2^{\bullet}$ (or equivalently as $O_2^{\bullet-} + H^+$) [8, 9]. Therefore, if dismutation occurs, the H^+ budget reaches zero:

$$2\ HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \qquad\qquad (3)$$

Certain redox couples, which exchange H^+ and e^- in a ratio other than 1:1 (including certain easily oxidized organic compounds that react with two $O_2^{\bullet-}$ radicals in sequence), may be able to produce a net release or consumption of H^+ upon interaction with $O_2^{\bullet-}$. Examples of such reactions include the couple MnO_2/Mn^{2+} and ascorbic acid (mainly occurring as HA^-). In the latter case, $O_2^{\bullet-}$ behaves as an oxidant toward both the reduced molecule and the partially oxidized radical [7]. In reactions (4)–(6), superoxide is assumed to participate as $HO_2^{\bullet}$, instead of as $O_2^{\bullet-}$ which would prevail under seawater conditions, because the $HO_2^{\bullet}$ that is originally produced photochemically or microbially [8, 9] would rapidly undergo deprotonation to $O_2^{\bullet-} + H^+$. On the other hand, reprotonation of $O_2^{\bullet-}$ in a redox process would just consume the initially released H^+.

$$Mn^{2+} + 2\ HO_2^{\bullet} + 2\ H_2O \rightarrow 2\ H_2O_2 + MnO_2\ (s) + 2\ H^+ \qquad (4)$$

$$HA^- + HO_2^{\bullet} \rightarrow A^{\bullet-} + H_2O_2 \qquad\qquad (5)$$

$$A^{\bullet-} + HO_2^{\bullet} + H^+ \rightarrow A + H_2O_2 \qquad\qquad (6)$$

The reaction rate constants of these processes are in the range of 10^6 to $10^8\ M^{-1}\ s^{-1}$ [7], and the potential environmental significance of these and other similar reactions is yet to be determined. However, reactions such as those in (4)–(6) might affect the seawater pH in the river-impacted coastal areas, which are characterized by a continuous input of redox-active terrestrial material into the seawater. It is important that the input is continuous because the $O_2^{\bullet-}$ reactions might affect the seawater pH significantly only in time scales of a few months or longer [8, 9]. Finally, it should be considered that $O_2^{\bullet-}$ is able to react both as an oxidant and a reductant [7]. The combination of an oxidation and a reduction process would ultimately result in catalyzed dismutation, often without a net H^+ exchange. Interestingly, reactions (4)–(6) involve superoxide as an oxidant only.
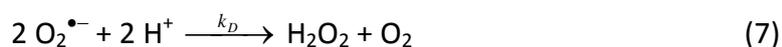
2. Theoretical Background and Methods

The formation of superoxide in seawater is dependent on a combination of biological and photochemical processes, which remain to be completely understood so far. The biological processes result in the extracellular production of $O_2^{\bullet-}$ for reasons that are not yet completely known, although could involve cell growth and signaling as well as cellular warfare [10]. Photochemical reactions involve chromophoric dissolved organic matter (CDOM) in electron or H-atom transfer processes between donors and acceptors (one of which requires light-excitation), producing relatively long-lived reduced transient species that are able to convert O_2 into $HO_2^{\bullet}$ [11]. Previous studies have provided indications that the biological processes may hold importance, at the least, comparable to the photochemical ones [2, 9], although currently, sufficient data are unavailable to decipher the possible role of extracellular $O_2^{\bullet-}$ production in the different locations of the global ocean. In regard to photochemical processes, which constitute just a part of the complete scenario, certain estimates have been obtained on a global scale [6], suggesting a possible geographic distribution. These estimates are based on satellite data of water temperature and water-leaving radiance (combined with the incident radiance data), as well as on the laboratory experiments on H_2O_2 and $O_2^{\bullet-}$ photoproduction in seawater samples irradiated at

different wavelengths. On the basis of these data, Powers and Miller estimated the absorption of sunlight by seawater in the global ocean, and obtained representative apparent quantum yields (AQY) of H_2O_2 photoproduction as a function of irradiation wavelengths. Using these data, the authors approximately estimated the rate of H_2O_2 photogeneration upon seawater irradiation [6]. A major approximation in that study was that, while the data related to sunlight absorption could be obtained with certain limitations on a geographical basis that spans the global ocean, the data related to H_2O_2 AQY were dependent on the samples that were actually irradiated and were, therefore, limited in range. A comparison between the AQY results reported by Powers and Miller and those available in the literature suggests that the former may be a conservative (lower-limit) estimate of H_2O_2 photogeneration upon seawater irradiation [6].

The photochemical generation of H_2O_2 is largely a consequence of $O_2^{\bullet-}$ photoproduction and decay [12, 13]. The unstable transient species $O_2^{\bullet-}$ achieves a steady-state concentration in the irradiated seawater, at which the rates of generation and decay are equal and the decay process is in relationship with H_2O_2 generation. In the case of uncatalyzed $O_2^{\bullet-}$ dismutation (reaction 3), the formation rate of H_2O_2 is one-half of the $O_2^{\bullet-}$ decay rate. However, if $O_2^{\bullet-}$ behaves as an oxidant (reaction 1), it results in the generation of one H_2O_2 per transformed $O_2^{\bullet-}$. In contrast, if $O_2^{\bullet-}$ behaves as a reductant (reaction 2), no H_2O_2 is formed [7]. In the case of catalyzed dismutation, in which $O_2^{\bullet-}$ oxidation and $O_2^{\bullet-}$ reduction are combined through reaction with additional inorganic or organic compounds, again a ratio of 1:2 between the H_2O_2 formation and $O_2^{\bullet-}$ decay rates is obtained.

In the literature, contrasting evidence concerning the stoichiometric ratio between H_2O_2 and $O_2^{\bullet-}$, as derived from the respective formation (or decay) rates, is available. In open ocean water, a ratio of 0.5 has been obtained, which would be consistent with the catalyzed or uncatalyzed dismutation [6]. However, the ratio of 0.6–0.75 obtained in the case of coastal seawater suggests a prevalence of reaction (1) over reaction (2) [14]. Interestingly, a stoichiometric ratio other than 0.5 suggests the occurrence of net oxidation or reduction reactions, which may allow proton-imbalance processes with definite redox couples. Moreover, as outlined in the Introduction section, one may infer from the known $O_2^{\bullet-}$ reactions that a proton imbalance may be more probable to occur if $O_2^{\bullet-}$ is reduced to H_2O_2. This circumstance also produces a stoichiometric $H_2O_2:O_2^{\bullet-}$ ratio larger than 0.5, as reported for coastal seawater. Therefore, coastal areas appear to be the most promising zones for investigating the effect of $O_2^{\bullet-}$ chemistry on the pH of seawater.

The decay of superoxide can be expressed as the combination of a second-order process (uncatalyzed dismutation) and a pseudo-first order one (oxidation or reduction), as follows [6]:

$$2\ O_2^{\bullet-} + 2\ H^+ \xrightarrow{\ k_D\ } H_2O_2 + O_2 \qquad\qquad (7)$$

$$O_2^{\bullet-} \xrightarrow{\ k_{Pseudo}\ } Products \qquad\qquad (8)$$

Unfortunately, no simple relationship exists between the reactions (7,8) and the observed $H_2O_2:O_2^{\bullet-}$ stoichiometric ratio. Reaction (8), which proceeds through $O_2^{\bullet-}$ oxidation or reduction in the presence of organic and inorganic compounds, may partially result in catalyzed $O_2^{\bullet-}$ dismutation. However, considering that the proton imbalance could be caused by certain pseudo-first-order reactions, it is interesting to develop an insight into the relative importance of the two

families of processes. Assuming $R_{O_2^{\bullet-}}$ to be the formation rate of the superoxide that reaches a steady-state concentration in natural waters [15-18], at the steady state it is implied that the formation rate equals the decay rate. At a given pH value, if only reaction (7) is operational, one obtains the following relationship:

$$[O_2^{\bullet-}]_7 = \sqrt{\frac{R_{O_2^{\bullet-}}}{2k_D}} \tag{9}$$

If both reactions (7) and (8) are operational, one obtains:

$$[O_2^{\bullet-}]_{7+8} = \frac{-k_{Pseudo} + \sqrt{k_{Pseudo}^2 + 8k_D R_{O_2^{\bullet}}}}{4k_D} = \frac{-k_{Pseudo}}{4k_D} + \sqrt{\left(\frac{k_{Pseudo}}{4k_D}\right)^2 + \left([O_2^{\bullet-}]_7\right)^2} \tag{10}$$

By assuming $\gamma = k_{Pseudo}(k_D)^{-1}$, equation (10) converts into the following expression:

$$[O_2^{\bullet-}]_{7+8} == \sqrt{\left(\frac{\gamma}{4}\right)^2 + \left([O_2^{\bullet-}]_7\right)^2} - \frac{\gamma}{4} \tag{11}$$

Considering all the uncertainties mentioned earlier regarding the relationship between H_2O_2 generation and $O_2^{\bullet-}$ decay, Powers and Miller tentatively derived the global-ocean maps for both $[O_2^{\bullet-}]_7$ and $[O_2^{\bullet-}]_{7+8}$ [6]. In the present study, these maps were divided into sectors by means of a 20×20 grid, and to each grid element corresponding to seawater, a couple of $([O_2^{\bullet-}]_7, [O_2^{\bullet-}]_{7+8})$ values were attributed, which were then used to derive γ from equation (11) using the Maple V software [19]. The relative importance of the pseudo-first order $O_2^{\bullet-}$ decay with respect to non-catalyzed dismutation may be expressed as the ratio of the rate of reaction (8) to the rate of reaction (7), as presented below:

$$\beta = \frac{k_{Pseudo}}{k_D[O_2^{\bullet-}]_{7+8}} = \frac{\gamma}{[O_2^{\bullet-}]_{7+8}} \tag{12}$$

Briefly, $\beta > 1$ implies that pseudo-first order decay prevails over non-catalyzed dismutation, while the reverse is true when $\beta < 1$. In the relevant map of β, the regions where the values of β are in the same range were identified, highlighting these regions with a color code, in order to obtain an insight into the (approximate) trend of the ratio between reaction (8) and reaction (7) on a global scale. A smoothing procedure based on a finer analysis of the source maps at particular locations, with respect to the initial grid elements, was performed in order to derive the final version of the map.

The possible effect of the superoxide decay on the pH of seawater is dependent on several factors, which most notably include the following: (i) The formation/decay rate of the superoxide itself (note that the formation and decay rates are equal under steady-state conditions); (ii) The hypothesized imbalance in the H^+ budget; and (iii) Seawater alkalinity [8, 9, 20]. As stated earlier, the formation/decay rate $R_{O_2^{\bullet-}}$ is linked to the H_2O_2 formation rate ($R_{H_2O_2}$) in a manner that is dependent on the details of the process. In case of uncatalyzed or catalyzed dismutation,

$R_{H_2O_2} = 0.5\,R_{O_2^{\bullet-}}$, while $R_{H_2O_2} = R_{O_2^{\bullet-}}$ in $O_2^{\bullet-}$ reduction and $R_{H_2O_2} = 0$ in $O_2^{\bullet-}$ oxidation. Moreover, there is evidence that $R_{O_2^{\bullet-}}$ and $R_{H_2O_2}$ are of the same order of magnitude, with a value of $R_{H_2O_2}\,(R_{O_2^{\bullet-}})^{-1}$ ratio that is often in the range of 0.5–1 [6]. In the present study, for simplicity, it was assumed that $R_{H_2O_2} = R_{O_2^{\bullet-}}$. Although this is an approximation, it is not higher than the other approximations already applied and is even further justified in the case of coastal seawater [14]. Coastal seawater is also the environment in which an H^+ imbalance or a pH impact of the $O_2^{\bullet-}$ chemistry is most likely to be observed [8, 9]. If α is the average number of H^+ ions produced or consumed per $O_2^{\bullet-}$ undergoing decay (we expect α to be <1 as there would be certain compensation in the H^+ exchange between different processes), the net rate of H^+ release or consumption is as follows: $R_{H^+} = \alpha\,R_{O_2^{\bullet-}}$. It is difficult to predict whether the resulting H^+ modification would be acidification or basification. If Alk_o is the initial alkalinity of the seawater and t is the time period during which the process is operational, the following relationships are obtained: $Alk_t = Alk_o - \alpha\,R_{O_2^{\bullet-}}\,t$ or

$$Alk_t = Alk_o + \alpha\,R_{O_2^{\bullet-}}\,t.$$

The modification of alkalinity is the basis for the change in pH, which may be calculated by means of *CO2calcNet* application. This application performs calculations of seawater pH by considering multiple equilibria and the ionic strength effect [20]. In *CO2calcNet* we chose the following options among those available in alternative: pCO_2 = 400 µatm, CO_2 constants according to Lueker, $KHSO_4$ as described by Dickson, total boron as reported by Lee, air-sea flux according to Ho, and the seawater pH scale [20]. Using the calculated value of Alk_t at a given time as input datum, the pH trend (in absolute values, $\Delta pH_t = |pH_o - pH_t|$) as a function of time was obtained. The previously reported data for seawater alkalinity on a global scale are available in the literature [21], and the calculated values of $R_{H_2O_2}$ used in the present study for deriving $R_{O_2^{\bullet-}}$ were obtained from the literature as well [6]. In both cases, the maps in the literature were assessed by means of the 20 × 20 grid mentioned earlier, deriving ΔpH_t with t = 10 years in each seawater-relevant grid element. In the map generated in the present study, a color code was assigned to the ΔpH values according to their range, and a smoothing procedure was applied when delimiting the seawater regions having the same ΔpH values.

It is clear that a number of important approximations were required in order to perform the described calculations. The main approximations have been listed below for sake of clarity:

(i) Only the photochemical $O_2^{\bullet-}$ sources were considered, neglecting the biological ones which might have been, at the least, equally important if not more; therefore, a lower-limit estimate of the superoxide formation and occurrence was obtained; (ii) the values of $[O_2^{\bullet-}]_7$ and $[O_2^{\bullet-}]_{7+8}$ were derived from the literature [6], and relied on a number of assumptions concerning the photochemical $R_{H_2O_2}$ values and their relationship with $R_{O_2^{\bullet-}}$, as well as on further (reasonable) assumptions on the values of k_D, and most notably, k_{Pseudo}; (iii) the values of $R_{H_2O_2}$ [6] used in the present study were derived from the satellite data of water-leaving radiance and from the laboratory values of AQY of H_2O_2 photo-generation, where the latter ones were most probably underestimated (although not by the same amount for all the locations) when applied to the global ocean; (iv) by assuming $R_{H_2O_2} = R_{O_2^{\bullet-}}$, $R_{O_2^{\bullet-}}$ was probably underestimated, although the approximation was less important for the coastal seawater (potentially further interesting for the purpose of the present study) rather than for the open ocean; (v) the literature values concerning

$O_2^{\bullet-}$ and H_2O_2 were reported for 1 m water depth [6], and no mixing was assumed, which could have led to an important overestimation of the relevant quantities in the open ocean. This overestimation would be less marked for shallower coastal areas; (vi) there is presently no indication as to what values α might assume, and a model sensitivity analysis of ΔpH vs. α was performed (*vide infra*). It is noteworthy that the approximations (i) and (v) apply to the calculation of both γ and ΔpH, the approximation (ii) applies to γ alone, and the approximations (iii), (iv), and (vi) apply to ΔpH alone.

3. Results and Discussion

A map for $\beta = k_{Pseudo} (k_D [O_2^{\bullet-}])^{-1} = \gamma ([O_2^{\bullet-}])^{-1}$ for the global ocean is presented in Figure 1. The calculated values of β were considerably high ($\beta > 400$) throughout, suggesting that reaction (8) strongly prevails over reaction (7). Therefore, the pseudo-first order decay of $O_2^{\bullet-}$ could be much faster than the non-catalyzed dismutation of the radical species. The β values might be overestimated owing to an underestimation of $[O_2^{\bullet-}]$, given that the biological sources of $O_2^{\bullet-}$ were not considered in the present study and that the literature values of $R_{H_2O_2}$ have most probably been underestimated as well. However, while the biological processes might be comparable in importance to the photochemical ones, or may be even more important, they are unlikely to overcome the photochemical reactions by high orders of magnitude. For instance, the rate of extracellular $O_2^{\bullet-}$ generation [2] is just 2–3 times higher than the photochemical $R_{H_2O_2}$ [6], from which an estimate of the photochemical $R_{O_2^{\bullet-}}$ was derived in the present study. Therefore, although the actual values of β are probably lower than those presented in the figure, $\beta > 1$ should nonetheless hold true. In consideration of this result, it may be inferred that the non-catalyzed dismutation of $O_2^{\bullet-}$ is a secondary process. The pseudo-first order decay of $O_2^{\bullet-}$ may be attributed to reactions with metals and organic compounds, the relative importance of which has been observed to vary with location [22-24].

Interestingly, the calculated values of β were observed to be minimum in the equatorial oceans and maximum in those closer to the poles. The reason for this is that reaction (7) (non-catalyzed dismutation) is a bimolecular process and its rate is proportional to $[O_2^{\bullet-}]^2$, while the rate of reaction (8) (pseudo-first order decay) is proportional to $[O_2^{\bullet-}]$. Since the steady-state $[O_2^{\bullet-}]$ is maximum in the equatorial regions [6], it is expected to obtain the minimum values of β in the same locations, as β is inversely proportional to $[O_2^{\bullet-}]$ ($\beta \propto [O_2^{\bullet-}]^{-1}$ according to equation 12).

As discussed earlier, it is unfortunately not possible to correlate the β values with the stoichiometric ratio between H_2O_2 and $O_2^{\bullet-}$, because an important fraction of the pseudo-first order decay would ultimately end up in catalyzed dismutation. However, while the H^+ budget of non-catalyzed $O_2^{\bullet-}$ dismutation approaches zero, the same is not necessarily true for the pseudo-first order decay processes which are expected to prevail strongly. Therefore, the data presented in Figure 1 suggest that the concern of a possible pH effect associated with $O_2^{\bullet-}$ decay is worth investigating.
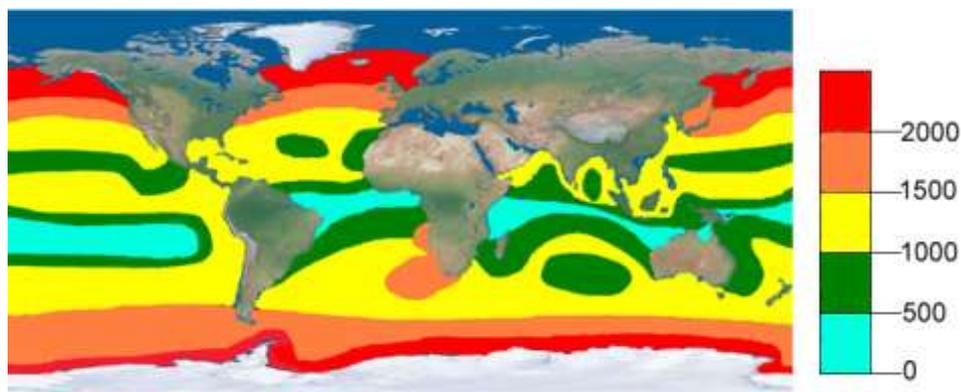
Figure 1 Map for the values of $\beta = k_{Pseudo} (k_D [O_2^{\bullet-}])^{-1} = \gamma ([O_2^{\bullet-}])^{-1}$ in the global ocean, based on the steady-state $[O_2^{\bullet-}]$ reported by Powers and Miller [6] that was used in equation 12.

The effect of the $O_2^{\bullet-}$ decay on pH may be calculated as ΔpH_t, and it is closely related to the H^+ imbalance parameter α. Unfortunately, there is little indication of the values that such a parameter might reach. However, the stoichiometric ratio between H_2O_2 and $O_2^{\bullet-}$ observed for the coastal seawater in the range of 0.6–0.75 [14] may provide a few tentative hints. First of all, both catalyzed and uncatalyzed $O_2^{\bullet-}$ dismutation processes exhibit a ratio of 0.5. A higher stoichiometric ratio suggests the prevalence of $O_2^{\bullet-}$ reduction that produces H_2O_2. The process of $O_2^{\bullet-}$ reduction might also be the one that most probably results in an H^+ imbalance, as far as the reactions with known rate constant are concerned (see Introduction). However, not all the pseudo-first order $O_2^{\bullet-}$ decay reactions proceed through reduction; otherwise the high β values presented in Figure 1 would produce an $H_2O_2:O_2^{\bullet-}$ stoichiometric ratio quite close to 1, which does not agree with most of the findings of the literature [6]. In coastal seawater, a 20%–50% excess in $O_2^{\bullet-}$ reduction with respect to oxidation (that is, a 1.2–1.5 ratio between the $O_2^{\bullet-}$ reduction and oxidation rates) might produce the observed stoichiometric ratio of 0.6–0.75. Therefore, an upper limit for α could be 0.33 when referring to a 50% excess in reduction [where 0.33 = (1.5−1.0)/1.5)].

Figure 2 presents the results of a sensitivity analysis, in which the calculated ΔpH_t has been reported as a function of time for different α values, by assuming $R_{O_2^{\bullet-}} = R_{H_2O_2}$ = 80 nM day^{-1}, as calculated for the photochemical processes occurring at low latitude [6]. The figure illustrates that ΔpH increases linearly with time as well as with α. The ΔpH values predicted at 10 years are not very far from the degree of ocean acidification occurring because of the build-up of atmospheric CO_2 [25]. In contrast, the ΔpH values observed at shorter time periods are considerably low, unless α approaches its upper limit (which appears improbable). Therefore, for the phenomenon to be significant, the proton imbalance is required to be maintained for considerably long periods of time, which requires a continuous input of compounds (metals or organic molecules) that are able to reduce $O_2^{\bullet-}$ to H_2O_2, and at the same time, modify the solution pH. This scenario is most likely to occur in the river-impacted coastal areas, owing to the continuous flow of redox-active solutes from the inland environments [26]. In the calculations that follow, $\alpha = 0.10$ has been hypothesized, and for different values of α, the predicted pH variations (ΔpH) would scale proportionally.
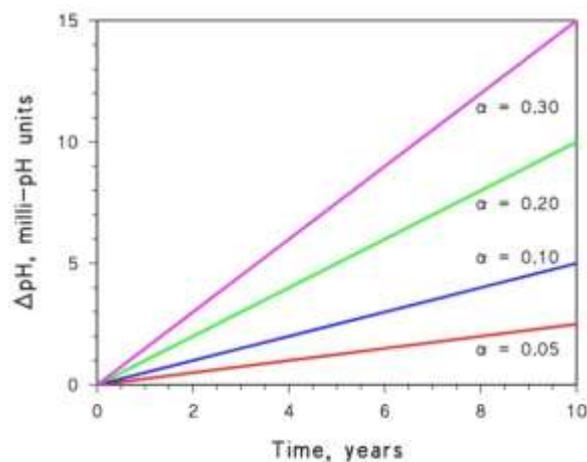
Figure 2 Trend for ΔpH (either increase or decrease) as a function of time, for the different values of proton imbalance α, for $R_{O_2^{\bullet-}}$ = 80 nM day^{-1}. The pH was calculated using *CO2calcNet*, with the following settings [20]: Alk_o = 2.3 mmol L^{-1}, pCO$_2$ = 400 µatm, CO$_2$ constants according to Lueker, KHSO$_4$ as described by Dickson, total boron as reported by Lee, air-sea flux as reported by Ho, and the seawater pH scale. Note: a pH unit is the ΔpH value separating, *e.g.* pH 7.2 from pH 8.2. A milli-unit is 1/1000 of that value, *e.g.,* the ΔpH value separating pH 7.201 from pH 7.202.

Figure 3 presents the calculated pH variations which would be observed in the global ocean over a time scale of ten years. The pH values have been expressed in milli-units of pH (where 1 milli-unit is equal to 0.001 pH units). The pH variation could be either an increase or a decrease, and the map only reports the expected absolute variation and not its [unknown] sign. According to Figure 3, ΔpH would reach a few milli-pH units (i.e. 0.001–0.005 pH units). The largest pH variations would be observed at equatorial latitudes, where the photochemical rates of $O_2^{\bullet-}$ and H_2O_2 generation would be the highest [6]. Moreover, interesting differences exist among the global oceans. The largest pH variations would be observed in the Indian Ocean, while the lowest ones would be observed in the Atlantic Ocean, mostly because of the different values of alkalinity. In fact, alkalinity is highest in the Atlantic Ocean and lowest in the Indian Ocean among all the oceans [21]. The coasts of equatorial Africa facing the Atlantic Ocean exhibit a remarkably low pH variation because of the low rates of H_2O_2 production [6].

An important concern is that the amplitude of the pH fluctuations observed in seawater is inversely proportional to the time scale in which it has been measured [25]. In other words, diurnal pH variations due to photosynthesis may reach several tenths of pH units, and at certain times, even approach a whole pH unit; in contrast, long-term fluctuations are usually much smaller. For instance, the build-up of atmospheric CO$_2$ over the last 20 years is expected to have caused a pH decrease in the range of 0.015–0.020 pH units [9]. According to Figure 2, the possible impact of superoxide chemistry on the pH of seawater (measured as ΔpH) is expected to increase when the time scale of the phenomenon is increased, while the ΔpH amplitude of the reference processes (from photosynthesis on short term to acidification on long term) exhibits reverse behavior. Therefore, the importance of the effect of $O_2^{\bullet-}$ chemistry on pH is expected to increase if the H$^+$ imbalance is maintained over longer time scales. This event would require a continuous input of

redox-active materials, such as those transported by rivers. Moreover, the value of $R_{O_2^{\bullet-}}$ used in the calculations of the present study is relevant for a water depth of 1 m. Diffusion phenomena (not considered in the present study) would probably decrease the ΔpH values to a great extent as the water becomes deeper. All these reasons, including the shallower water columns compared to open-sea water, indicate that the river-impacted coastal areas would most likely be the locations where the superoxide affects the pH of seawater to the largest extent.
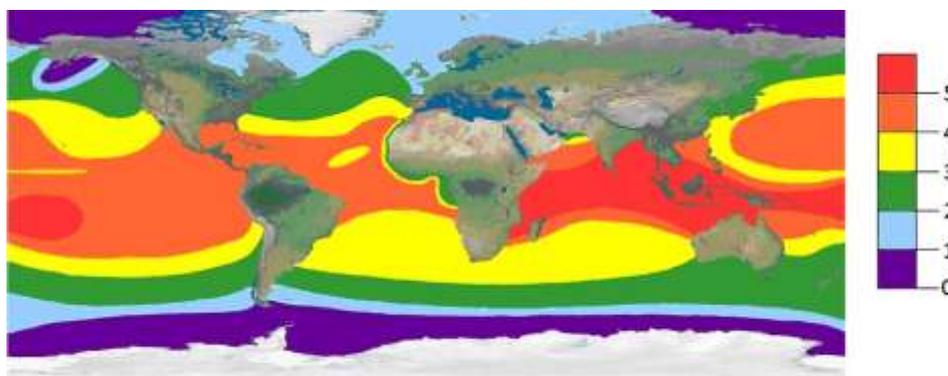
Figure 3 Map of ΔpH (milli-pH units) in the global ocean. The ΔpH calculations were performed on the basis of the assumption that $R_{O_2^{\bullet-}} = R_{H_2O_2}$, and by using the global ocean alkalinity map [21]. Alkalinity varied over time as $\Delta Alk = R_{O_2^{\bullet-}}\ \alpha\ t$, where α = 0.10 and t = 10 years. The *CO2calcNet* application was used with the following settings: pCO_2 = 400 μatm, CO_2 constants according to Lueker, $KHSO_4$ as described by Dickson, total boron as reported by Lee, air-sea flux as reported by Ho, and the seawater pH scale [20].

It should be underlined that the qualitative relationships (higher vs. lower) among the ΔpH values illustrated on the map in Figure 3 are more reliable than the predicted absolute values of ΔpH. This is because the latter are affected by several uncertainties, most notably by: (i) underestimations of $R_{H_2O_2}$ and $R_{O_2^{\bullet-}}$, which would be reflected as an underestimation of ΔpH; (ii) the fact that the calculations were relevant for 1 m depth which overestimates the ΔpH owing to diffusion, and (iii) uncertainties regarding the possible values of proton imbalance α. On the basis of the relative ΔpH values, Figure 3 allows a tentative prediction of the locations most likely to present the largest pH effect caused by superoxide chemistry. These locations are the river-impacted coastal areas of low-alkalinity oceans. Such areas include mostly the ones close to the deltas of Ganges, Mekong, Irrawaddy, and Zambezi rivers, followed by the Amazon River estuary, Orinoco delta, Mississippi delta, and Rio Grande estuary. A significant although, to a certain extent, lower impact of $O_2^{\bullet-}$ on pH would be expected in the Rio de la Plata estuary and the Yangtze River delta, and a further lower effect would be expected in the Yellow River and Indo deltas. Despite being located at the equatorial latitudes, the Congo and Volta estuaries, as well as the Niger delta, are characterized by peculiarly low $O_2^{\bullet-}$ formation rates, which are typical of the Atlantic coast of Africa [6]. Therefore, limited pH variations are expected in these regions. Large rivers with mouths located at elevated latitudes (*e.g.* Rhine, Saint Lawrence, Yukon, Lena, etc.) could transport significant amounts of redox-active compounds to the coastal seawater, although the low levels of

photochemical production of superoxide in high-latitude seawater would limit the pH impact of the relevant reactions. This scenario might be modified, if the microbial processes of $O_2^{\bullet-}$ generation are determined to be important at high latitudes.

4. Conclusions

In addition to catalyzed and uncatalyzed dismutation, superoxide may undergo other redox processes with the solutes present in seawater. In certain cases, these reactions might alter the pH of the seawater. In the present study, an approximate estimate of the possible impact of $O_2^{\bullet-}$ chemistry on the seawater pH at a global scale has been provided, under the following assumptions: (i) considering only the photochemical $O_2^{\bullet-}$ sources, and excluding the biological ones, as it is not currently possible to assess the latter ones on a global scale; (ii) use of steady-state $[O_2^{\bullet-}]$ values and H_2O_2 formation rates which were derived as estimates from the literature currently available, and relevant for 1 m water depth; a simple hypothesis was also developed for the ratio between the decay rate of $O_2^{\bullet-}$ and the formation rate of H_2O_2; (iii) formulation of tentative hypotheses regarding the extent of H^+ imbalance associated with the decay of $O_2^{\bullet-}$, while the actual value is currently unknown. A few of the above-stated assumptions would result in an underestimation of the pH effect, while the others could lead to overestimation.

Seawater undergoes huge short-term pH fluctuations (of up to ~1 pH unit), and relatively limited long-term drifts (of $\leq 10^{-2}$ pH units per decade), while the potential ΔpH caused by $O_2^{\bullet-}$ would increase linearly with the reaction time. Therefore, the possible effect of superoxide on the pH of seawater may be important, if the relevant H^+-imbalance processes would be sustained for relatively long periods of time. Continuous flows of redox-active compounds may typically be provided by large rivers, thereby causing the coastal zones close to their deltas and estuaries to act as the areas where $O_2^{\bullet-}$ might be modifying the seawater pH the most. The calculations in the present study demonstrate that tropical and equatorial oceans, because of higher photochemical production of superoxide, have a higher potential of undergoing pH variations (of the order of up to 0.005 pH units in ten years) compared to the oceans at higher latitudes. Moreover, owing to the difference in the seawater alkalinity (2.2–2.3 vs. 2.3–2.4 mmol L^{-1}), such pH variations would be larger in the Indian Ocean compared to the Atlantic Ocean. Clearly, these conclusions are based on assumptions that require verification. A better understanding of the microbial production of $O_2^{\bullet-}$ is required to properly assess the importance of the photochemical processes and the overall impact of the $O_2^{\bullet-}$ chemistry on seawater pH.

Author Contributions

KMGM and DV conceived the study, MM made the calculations, DV wrote the paper, KMGM, MM and CQL corrected the paper.
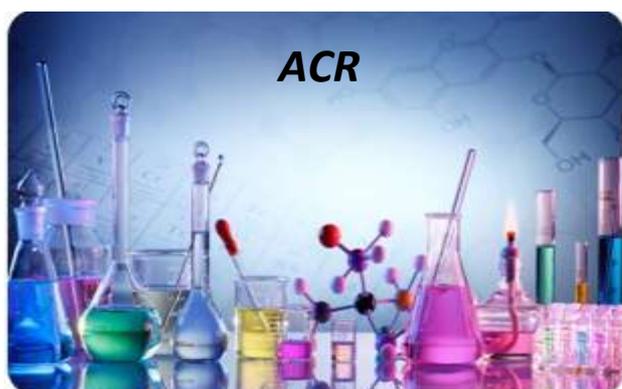
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Competing Interests

The authors have declared that no competing interests exist.

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