Supplementary Information

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Hydrogen peroxide quenching by bisulfite and chlorine in drinking water

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Text S1. Calculating the pH change due to the addition of hypochlorite to pure water

Hypochlorite is a weak base, so its addition into water will raise water pH. The resulting pH was calculated using the ICE (Initial, change, and equilibrium) table at initial pH of 6.5–8.5 and hypochlorite concentrations of 4.2, 10, and 20 mg/L as Cl_2, corresponding to a molar ratio of 1:1 to hydrogen peroxide concentrations of 2, 5, and 10 mg/L. The details of the calculations are shown below.

The ionization reaction of hypochlorite (OCl^-):

$$OCl^- + H_2O \rightleftharpoons HOCl + OH^- \tag{1}$$

At the initial condition, the molar concentration of OCl^- was C_0, HOCl molar concentration was zero, and OH^- concentration was $10^{-(pKw-pH0)}$ M (pK_w was 14.78 and 14.16 at 4 and 20°C and pH0 was the initial water pH). Assume x M OCl^- will react to reach equilibrium, then the concentration changes are $-x$, x, and x M for OCl^-, HOCl, and OH^-. At equilibrium, the concentrations of each species would be their initial concentrations plus the concentration change, i.e., C_0-x, x, and $10^{-(pKw-pH0)} + x$ M. These mentioned initial, change, and equilibrium values are shown in Table 1.

Table ST1. Initial, change, and equilibrium concentrations for hypochlorite ionization reaction

	OCl^-	HOCl	OH
Initial	C_0	0	$10^{-(pKw-pH0)}$
Change	$-x$	x	x
Equilibrium	C_0-x	x	$10^{-(pKw-pH0)} + x$

At equilibrium, the concentrations of OCl^-, HOCl, and OH^- should follow the equilibrium equation:

$$\frac{[HOCl][OH^-]}{[OCl^-]} = K_b \tag{2}$$

Substitute the OCl^-, HOCl, and OH^- concentrations by the expressions for their concentrations at equilibrium in Table ST1:

$$\frac{x(10^{-(pK_w-pH0)}+x)}{C_0-x} = K_b \tag{3}$$

Expand this equation and arrange it in a quadratic form:

$$x^2 + \left(10^{-(pK_w-pH0)} + K_b\right)x - K_b C_0 = 0 \tag{4}$$

The value of x can be found by:

$$x = \frac{-\left(10^{-(pK_w-pH0)}+K_b\right)+\sqrt{\left(10^{-(pK_w-pH0)}+K_b\right)^2+4K_bC_0}}{2} \tag{5}$$

The resulting pH can be found by:

$$pH = pK_w + \log(10^{-(pK_w-pH0)} + x) \tag{6}$$

The value of K_b at 4°C and 20°C was 9.42×10^{-8} and 2.64×10^{-7} M, which was calculated from the p*K*a of HOCl (7.754 and 7.582 at 5 C and 20 C) (Morris, 1966) and pK_w 14.78 and 14.16 at 4°C and 20°C (Bandura and Lvov, 2006). The results are shown in Figure S12-S13.

Text S2. Calculating the pH change due to the addition of hypochlorite to water with bicarbonate buffer

Bicarbonate can accept/release H^+, thus providing buffer capacity to the water matrix and influencing the water pH when hypochlorite is added. The amount of bicarbonate can be measured by water alkalinity. As bicarbonate is the dominant species among alkalinity components (i.e., bicarbonate, carbonate, and hydroxide) at water pH 6.5–8.5, it was assumed to be the only alkalinity component. The concentration of bicarbonate can be calculated from the alkalinity value:

$$[HCO_3^-] = \frac{alk(mg/L\ as\ CaCO_3)}{1000\times 100} \times 2 \tag{7}$$

where $[HCO_3^-]$ is the molar concentration of bicarbonate, alk is the water alkalinity with the unit of mg/L as $CaCO_3$. Before hypochlorite is added, the carbonic acid ionization reaction is:

$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \tag{8}$$

The concentrations of H_2CO_3, HCO_3^-, and H^+ at equilibrium follow:

$$\frac{[HCO_3^-][H^+]}{[H_2CO_3]} = K_{a1} \tag{9}$$

The value of $[H^+]$ was calculated from the initial pH_0 (i.e., $[H^+] = 10^{-pH0}$ M), $[HCO_3^-]$ was obtained by alkalinity, Ka_1 was calculated from pKa_1= 6.52 and 6.38 at 4°C and 20°C (Harned and Davis, 1943). Therefore, the $[H_2CO_3]$ can be obtained. In order to show these values as the initial concentrations before hypochlorite was added, they are denoted by $[HCO_3^-]_0$, $[H_2CO_3]_0$, and $[H^+]_0$. The amount of total inorganic carbon is $C_{T,\ inorganic-C}=[HCO_3^-]_0+[H_2CO_3]_0$.

When hypochlorite (OCl^-) is added, it introduces another reaction:

$$HOCl \rightleftharpoons OCl^- + H^+ \tag{10}$$

When the reaction reaches equilibrium, the concentrations of HOCl, OCl^-, and H^+ should follow:

$$\frac{[OCl^-][H^+]}{[HOCl]} = K_{a2} \tag{11}$$

Ka_2 was calculated from pKa_2= 7.75 and 7.58 at 5°C and 20°C (Morris, 1966). As the amount of total chlorine added is known ($C_{T,chlorine}$), [HOCl] and $[OCl^-]$ can be found at a given pH with Equation 11 and:

$$[HOCl] + [OCl^-] = C_{T,chlorine} \tag{12}$$

The expressions for HOCl and OCl^- are:

$$[HOCl] = \frac{C_{T,chlorine}}{1+\frac{K_{a2}}{[H^+]}} \tag{13}$$

$$[OCl^-] = \frac{C_{T,chlorine}}{1+\frac{[H^+]}{K_{a2}}} \tag{14}$$

Similarly, the expressions for carbonic acid and bicarbonate are:

$$[H_2CO_3] = \frac{C_{T,inorganic-C}}{1+\frac{K_{a1}}{[H^+]}} \tag{15}$$

$$[HCO_3^-] = \frac{C_{T,inorganic-C}}{1+\frac{[H^+]}{K_{a1}}} \tag{16}$$

When the new equilibrium is reached after hypochlorite is added, the proton (H^+) obtained by OCl^- (i.e., the concentration of HOCl) should equal to the proton lost by H_2CO_3, which can be expressed as:

$$[HOCl] = [H_2CO_3]_0 - [H_2CO_3] \tag{17}$$

The H^+ from water ionization is very small and thus ignored. An error in Equation 17 at a pH value can be calculated as:

$$Error = |[HOCl] - ([H_2CO_3]_0 - [H_2CO_3])| \tag{18}$$

The final pH of the solution was found by trial and error. For a given chlorine dose, alkalinity, and initial pH value, a final pH value was assumed to calculate the $[H_2CO_3]_0$, $[H_2CO_3]$, and [HOCl] by Equation 7-15. By these calculated values, the error (Equation 18) can be calculated. Then, by trying different final pH values, the error was gradually minimized by a genetic algorithm through iterations. When the error was less than 10^{-20} M or after 100 times iteration, the pH assumed was regarded as the true final pH when both HOCl-OCl^- and H_2CO_3-HCO_3^- equilibria were reached simultaneously. Alkalinity values of 20–300 mg/L as $CaCO_3$ and chlorine concentrations of 4.2, 10, and 20 mg/L as Cl_2 were used in the calculations for the final pH at equilibrium when the initial pH was 6.5–8.5. The final pH at both 20°C and 4°C were calculated. The results are shown in Figure S12-S13.

Text S3. Calculating the pH change due to the addition of chlorine of Cl_2 gas source to pure water

When molecular chlorine (Cl_2) is used as a chlorine source, it would introduce extra H^+ into the solution due to the H^+ formation from Cl_2 dissolution reaction:

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \tag{19}$$

Therefore, when chlorine of Cl_2 gas source is added into water, an equimolar of H^+ would also be added, lowering the water pH. The ionization of HOCl will also happen:

$$HOCl \rightleftharpoons OCl^- + H^+ \tag{20}$$

The final pH after the addition of chlorine of Cl_2 source was calculated by ICE (Initial, change, and equilibrium) table. The initial concentration of HOCl, OCl^-, and H^+ was C_0, 0, and C_0+10^{-pH0}, where pH_0 is the initial water pH and C_0 was the added chlorine concentration which also equals to the added H^+ concentration. Assume *x* M of HOCl was ionized for the reaction to reach equilibrium, by the reaction stoichiometry, the concentration changes of HOCl, OCl^-, and H^+ were -x, x, and x. At equilibrium, the concentrations of HOCl, OCl^-, and H^+ were C_0–x, x, and C_0+10^{-pH}. These concentrations of initial, change, and at equilibrium are shown in the table below:

Table ST2. Initial, change, and equilibrium concentrations for hypochlorous acid ionization reaction

	HOCl	OCl^-	H^+
Initial	C_0	0	C_0+10^{-pH0}
Change	$-x$	x	x
Equilibrium	C_0-x	x	$C_0+10^{-pH0}+x$

At equilibrium, the concentrations of HOCl, OCl^-, and H^+ should follow:

$$\frac{[OCl^-][H^+]}{[HOCl]} = K_{a2} \tag{21}$$

Substitute the OCl^-, H^+, and HOCl concentrations by the expressions for their concentrations at equilibrium in Table ST2:

$$\frac{x(C_0+10^{-pH0}+x)}{C_0-x} = K_{a2} \tag{22}$$

Expand this equation and arrange it in a quadratic form:

$$x^2 + (C_0 + 10^{-pH0} + K_{a2})x - K_{a2}C_0 = 0 \tag{23}$$

The value of x can be found by:

$$x = \frac{-(C_0+10^{-pH0}+K_{a2})+\sqrt{(C_0+10^{-pH0}+K_{a2})^2+4K_{a2}C_0}}{2} \tag{24}$$

The resulting pH can be found by:

$$pH = -\log(C_0 + 10^{-pH0} + x) \tag{25}$$

The value of Ka_2 was calculated from pKa_2= 7.75 and 7.58 at 5°C and 20°C (Morris, 1966). The pH values were calculated for chlorine dose of 4.2, 10, and 20 mg/L as Cl_2 for initial pH of 6.5–8.5. The results are shown in Figure S12-S13.

Text S4. Calculating the pH change due to the addition of Cl_2 gas to water with bicarbonate buffer

First, ignore the extra H^+ from the addition of chlorine from the Cl_2 gas source. Calculate the initial concentrations of H_2CO_3 and HCO_3^- at pH 6.5–8.5 with the initial pH and alkalinity value by Equation 7-9. Similarly, by equation 12-14, the HOCl and OCl^- concentrations were also calculated at initial pH range of 6.5–8.5. These concentrations were denoted by $[H_2CO_3]_0$, $[HCO3^-]_0$, $[HOCl]_0$, and $[OCl^-]_0$. The amount of chlorine added and inorganic carbon are $C_{T,\ chlorine}$ and $C_{T,\ inorganic\text{-}C}$=$[H_2CO_3]_0$, $[HCO3^-]_0$.

Now, consider the impact of the extra H^+ from the added chlorine. When H^+ is added, OCl^- and HCO_3^- would partly convert to HOCl and H_2CO_3. Therefore, the amount of HOCl and H_2CO_3 formed after the addition of H^+ should equal the H^+ added (which equals to $C_{T,\ chlorine}$, as the added H^+ is equimolar to chlorine). This relationship can be expressed as:

$$added\ [H^+] = ([H_2CO_3] - [H_2CO_3]_0) + ([HOCl] - [HOCl]_0) \tag{26}$$

The H^+ from water ionization was small and thus ignored. An error in equation 26 can be formulated as:

$$Error = \left|([H_2CO_3] - [H_2CO_3]_0) + ([HOCl] - [HOCl]_0) - \mathrm{C_{T,chlorine}}\right| \tag{27}$$

The final pH of the solution was found by trial and error. For a given chlorine dose, alkalinity, and initial pH value, $[H_2CO_3]_0$ and $[HOCl]_0$ can be obtained by Equation 7-15, then assume a final pH value to calculate the $[H^+]$, $[H_2CO_3]$ and [HOCl] by Equation 7-15. By these calculated values, the error (Equation 27) can be calculated. Then, by assuming different final pH values, the error was gradually minimized by a genetic algorithm through iterations. When the error was less than 10^{-20} M or the iteration is 100 times, the assumed final pH was regarded as the true final pH when HOCl-OCl and H_2CO_3-HCO_3^- equilibria were reached simultaneously. Alkalinity values of 20-300 mg/L as $CaCO_3$ and chlorine concentrations of 4.2, 10, and 20 mg/L as Cl_2 were used in the calculations for the final pH at equilibrium when the initial pH was 6.5–8.5. The final pH at 4 and 20°C were both calculated. The results are shown in Figure S12-S13.

Table S1. Water quality of the collected natural water sample.

pH	TOC (mg/L as C)	Alkalinity (mg/L as $CaCO_3$)	Chloride (mg/L)	Hardness (mg/L as $CaCO_3$)
8.1–8.5	1.6–2.0	90–100	20–30	110–120

Table S2. The experimental conditions

	Milli-Q with buffer												Natural water			
	4°C						20°C						4°C		20°C	
H_2O_2 dose (mg/L)	5			10			5			10			5	10	5	10
pH	**5**	**7**	**9**	**5**	**7**	**9**	**5**	**7**	**9**	**5**	**7**	**9**	**Ambient pH: 8.3**			
thiosulfate	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
bisulfite	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
chlorine (NaOCl)	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
chlorine (Cl_2 gas)													✓	✓	✓	✓
sulfite													✓	✓	✓	✓
bisulfite (SO_2)													✓	✓	✓	✓

Table S3. Fitted second-order rate constants (k_{obs}) for thiosulfate, bisulfite, chlorine reaction with H_2O_2 in buffered Milli-Q water at different water temperature, H_2O_2 dose, and pH. The coefficient of determination (R^2) is also shown to reflect the quality of regression.

Water temperature (°C)	H_2O_2 (mg/L)	pH	Thiosulfate (k_{obs}, $M^{-1} \cdot s^{-1}$)	R^2	Bisulfite (k_{obs}, $M^{-1} \cdot s^{-1}$)	R^2	Chlorine (k_{obs}, $M^{-1} \cdot s^{-1}$)	R^2
20	10	5	0.058	*0.98*	487	*1.00*	20	*0.94*
		7	0.082	*0.97*	13.5	*0.96*	779	*1.00*
		9	0.076	*0.93*	0.31	*0.95*	4225	*1.00*
	5	5	0.088	*0.96*	562	*1.00*	13	*0.96*
		7	0.088	*0.97*	6.5	*0.81*	827	*0.99*
		9	0.042	*0.67*	0.27	*0.97*	4411	*0.98*
4	10	5	0.015	*0.70*	518	*1.00*	2.7	*0.97*
		7	0.013	*0.98*	8.3	*0.83*	339	*1.00*
		9	0.015	*0.95*	0.14	*0.98*	1420	*1.00*
	5	5	0.015	*0.84*	377	*1.00*	2.3	*0.96*
		7	0.014	*0.66*	3.5	*0.79*	357	*1.00*
		9	0.012	*0.78*	0.11	*0.90*	1636	*1.00*

Table S4. Fitted second-order rate constants (k_{obs}) for bisulfite made of bisulfite ($NaHSO_3$), sulfite (Na_2SO_3), and SO_2, and chlorine (NaOCl) made of hypochlorite and Cl_2 gas reaction with H_2O_2 in natural water sample (pH 8.3) at different water temperature and H_2O_2 dose. The coefficient of determination (R^2) is also shown to reflect the quality of regression.

Water temperature (°C)	20				4			
H_2O_2 (mg/L)	10		5		10		5	
	k_{obs}, $M^{-1}\cdot s^{-1}$	R^2	k_{obs}, $M^{-1}\cdot s^{-1}$	R^2	k_{obs}, $M^{-1}\cdot s^{-1}$	R^2	k_{obs}, $M^{-1}\cdot s^{-1}$	R^2
Bisulfite ($NaHSO_3$)	2.96	*0.98*	1.19	*0.99*	1.89	*0.96*	0.77	*0.91*
Sulfite (Na_2SO_3)	0.28	*0.99*	0.42	*0.99*	0.11	*1.00*	0.16	*0.97*
Bisulfite (SO_2)	16	*0.90*	3	*0.95*	8.1	*0.54*	1.1	*0.78*
chlorine (NaOCl)	2342	*1.00*	2161	*0.99*	820	*1.00*	808	*0.96*
chlorine (Cl_2)	328	*0.99*	575	*0.98*	67	*0.89*	117	*0.96*

Table S5. Reactions and parameters used in the model to predict the time needed to quench 95% H2O2 by chlorine

#	Reaction	Rate constant (k)		Reference
		4°C	20°C	
1[a]	$H_2O_2 + HOCl \rightarrow O_2 + H_2O + HCl$	$0.266 \times k_{theory,obs,20C}$	$\frac{k_b}{(1+\frac{K_1}{[H^+]})(1+\frac{[H^+]}{K_2})}$ $k_b = 4.4 \times 10^7\ M^{-1}s^{-1}$, $K_1 = 2.9 \times 10^{-8}\ M$, and $K_2 = 2.2 \times 10^{-12}\ M$	Held et al., 1978
2	$HOCl \rightarrow OCl^- + H^+$	$890\ s^{-1}$	$1.4 \times 10^3\ s^{-1}$	Kwon et al., 2020; Morris, 1966
3	$OCl^- + H^+ \rightarrow HOCl$	$5.0 \times 10^{10}\ M^{-1}s^{-1}$	$5.0 \times 10^{10}\ M^{-1}s^{-1}$	Kwon et al., 2020; Morris, 1966
4	$H_2O_2 \rightarrow HO_2^- + H^+$	$0.13\ s^{-1}$	$0.13\ s^{-1}$	Evans and Uri, 1949; Yang et al., 2014
5	$HO_2^- + H^+ \rightarrow H_2O_2$	$1.6 \times 10^{11}\ M^{-1}s^{-1}$	$7.3 \times 10^{10}\ M^{-1}s^{-1}$	Evans and Uri, 1949; Yang et al., 2014
6	$H_2CO_3 \rightarrow HCO_3^- + H^+$	$3.0 \times 10^3\ s^{-1}$	$5.0 \times 10^3\ s^{-1}$	Harned and Davis, 1943; Kwon et al., 2020
7	$HCO_3^- + H^+ \rightarrow H_2CO_3$	$1.0 \times 10^{10}\ M^{-1}s^{-1}$	$1.0 \times 10^{10}\ M^{-1}s^{-1}$	Harned and Davis, 1943; Kwon et al., 2020
8	$HO_2^- + HOCl \rightarrow O_2 + Cl^- + H_2O$	$1.2 \times 10^7\ M^{-1}s^{-1}$	$4.4 \times 10^7\ M^{-1}s^{-1}$	Held et al., 1978

[a] Observational reaction. H_2O_2 and HOCl represent total H_2O_2 and total chlorine

Reaction #2–8 were used to determine solution pH.

The formation of singlet oxygen from chlorine- H_2O_2 reaction is minor (< 10%) thus not included in the model.

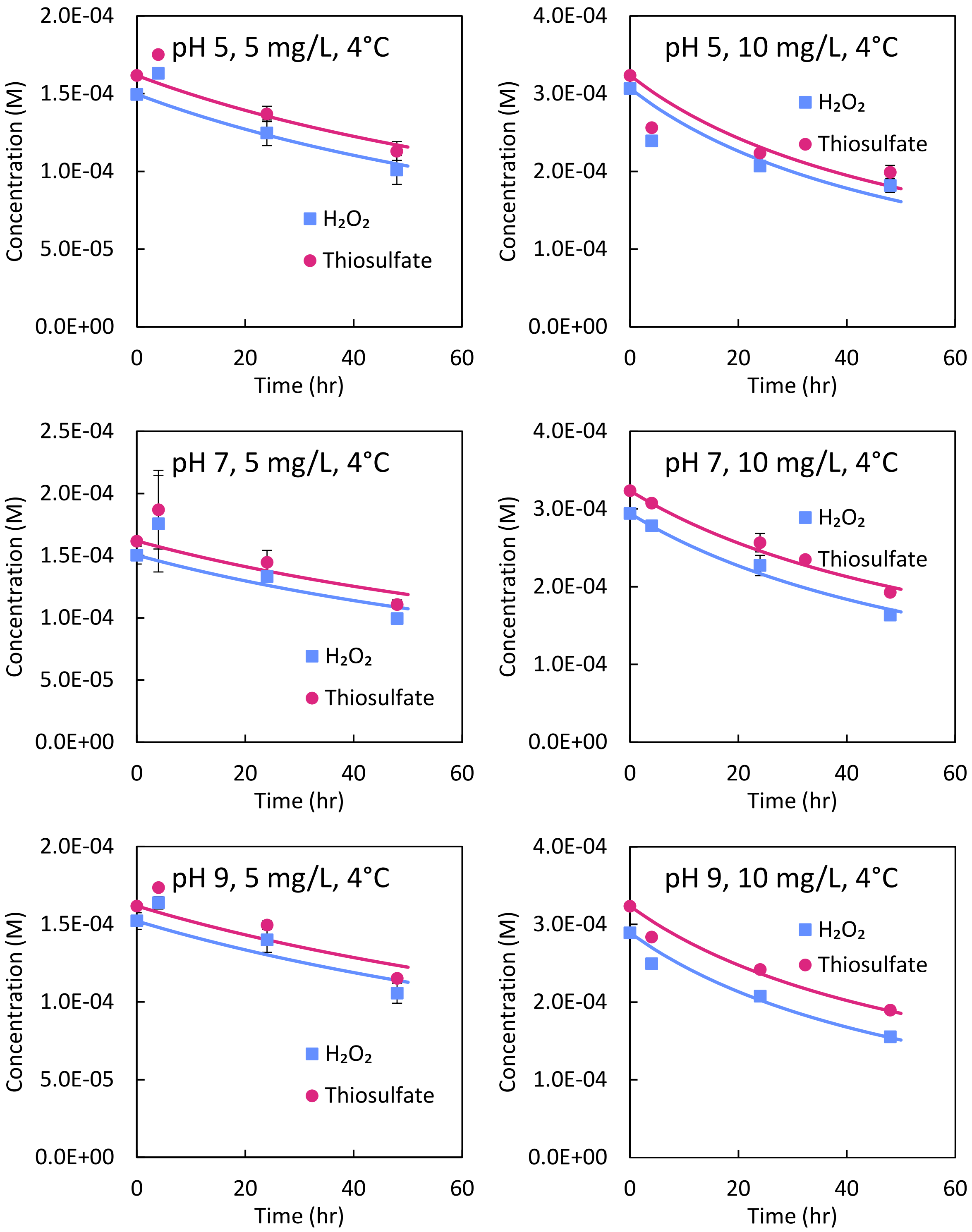

Figure S1. Concentrations of H_2O_2 and thiosulfate in the reaction in buffered Milli-Q water at 4°C. Error bars for experimental results represent standard deviation.

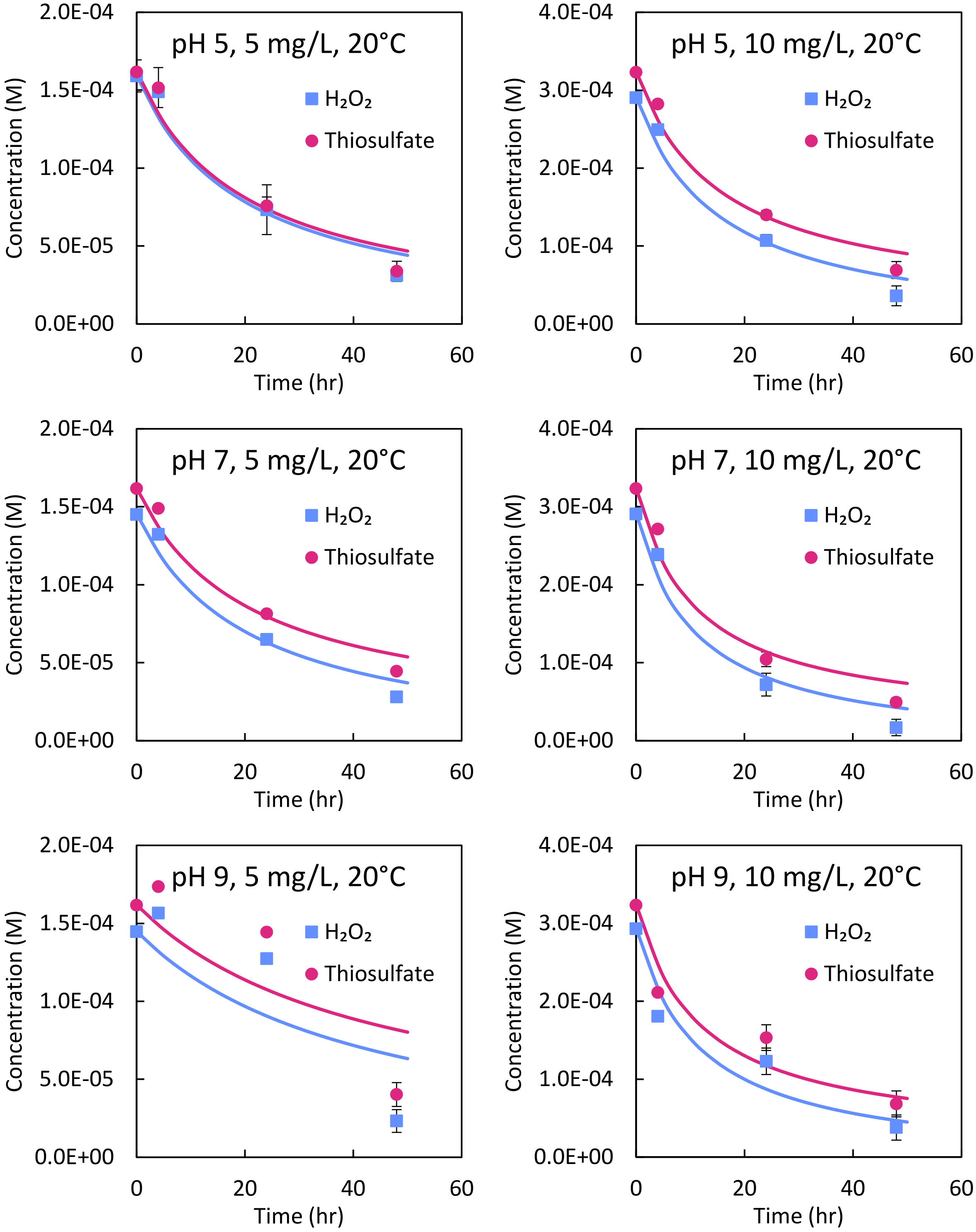

Figure S2. Concentrations of H_2O_2 and thiosulfate in the reaction in buffered Milli-Q water at 20°C. Error bars for experimental results represent standard deviation.

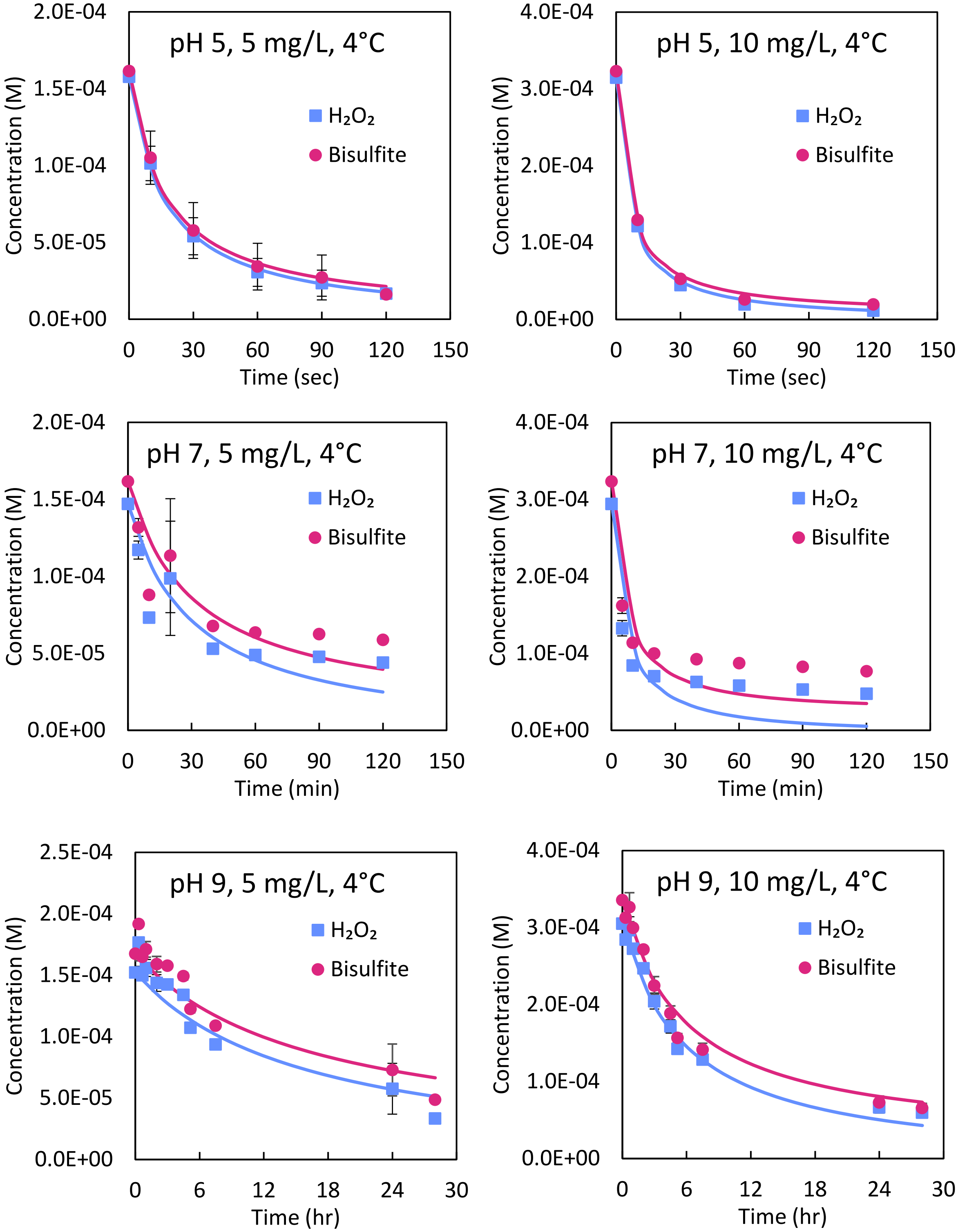

Figure S3. Concentrations of H_2O_2 and bisulfite in the reaction in buffered Milli-Q water at 4°C. Error bars for experimental results represent standard deviation.

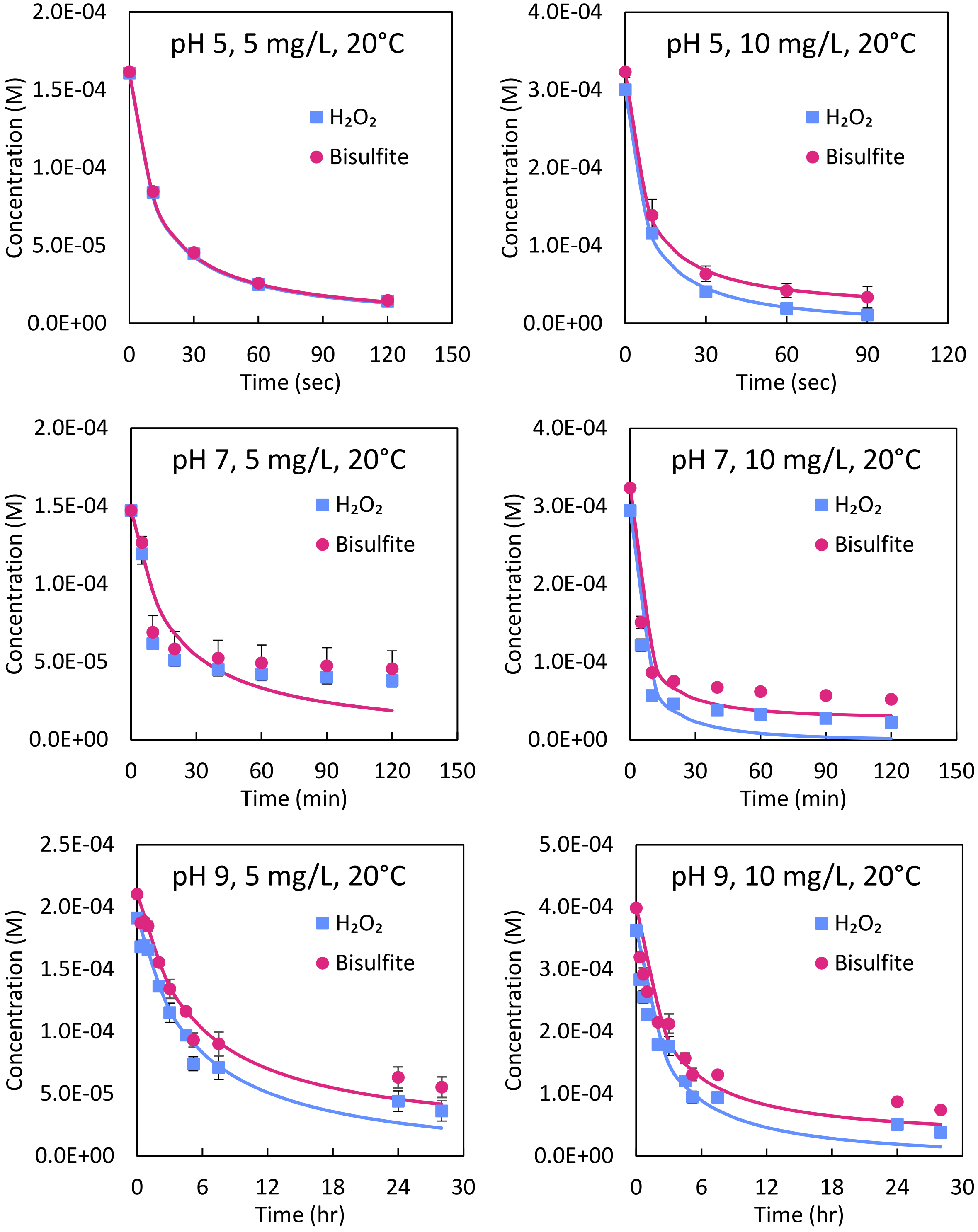

Figure S4. Concentrations of H_2O_2 and bisulfite in the reaction in buffered Milli-Q water at 20°C. Error bars for experimental results represent standard deviation.

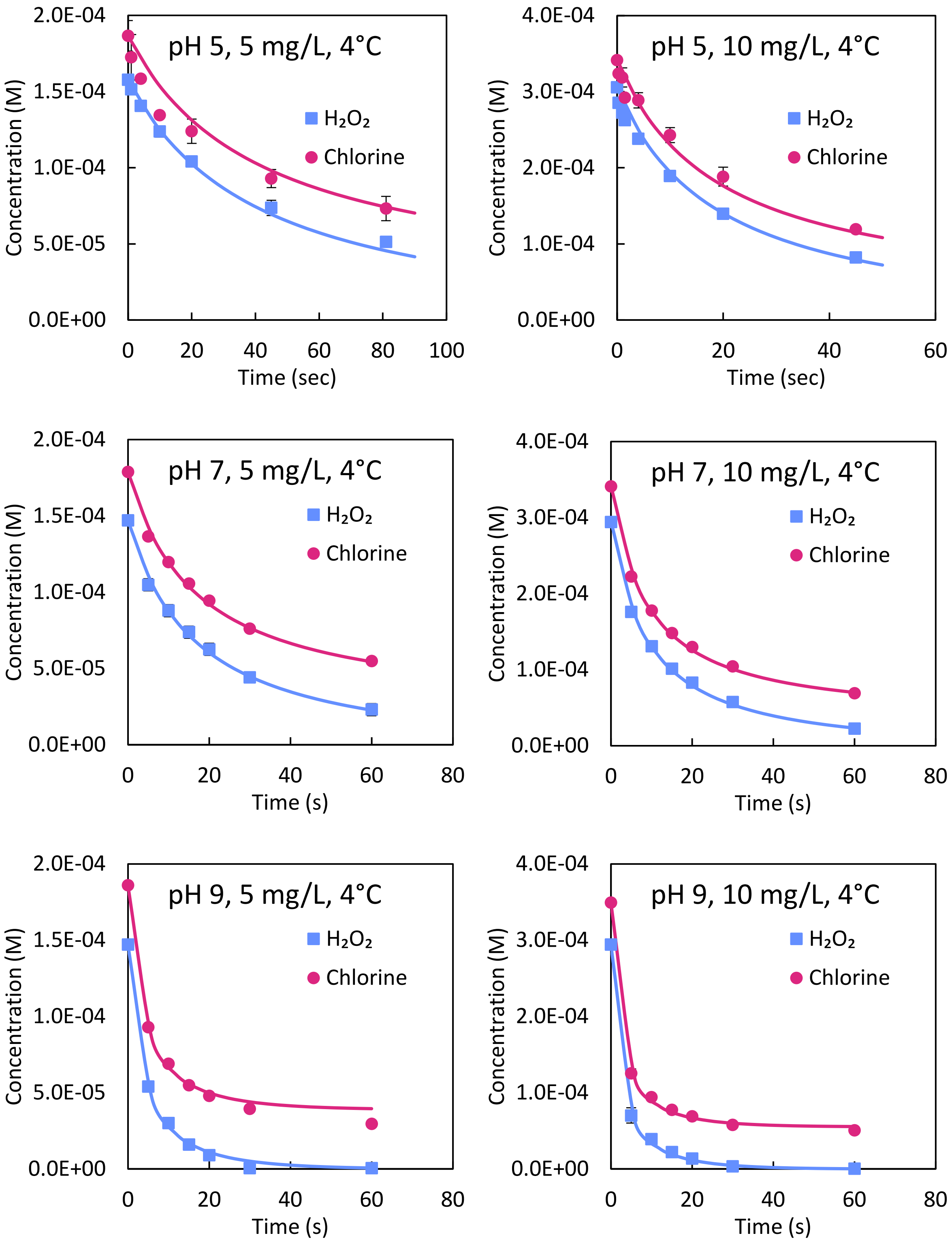

Figure S5. Concentrations of H_2O_2 and chlorine in the reaction in buffered Milli-Q water at 4°C. Error bars for experimental results represent standard deviation.

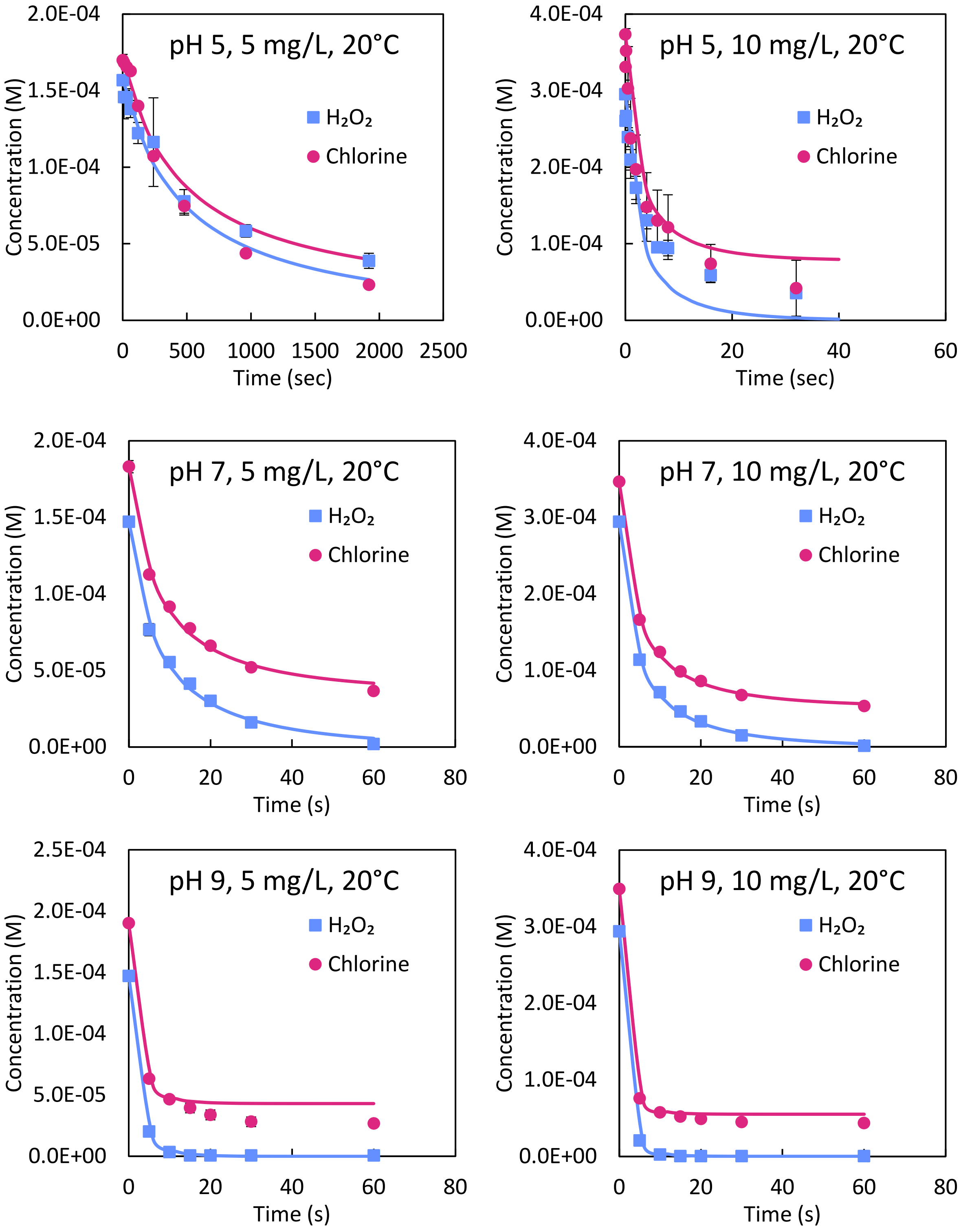

Figure S6. Concentrations of H_2O_2 and chlorine in the reaction in buffered Milli-Q water at 20°C. Error bars for experimental results represent standard deviation.

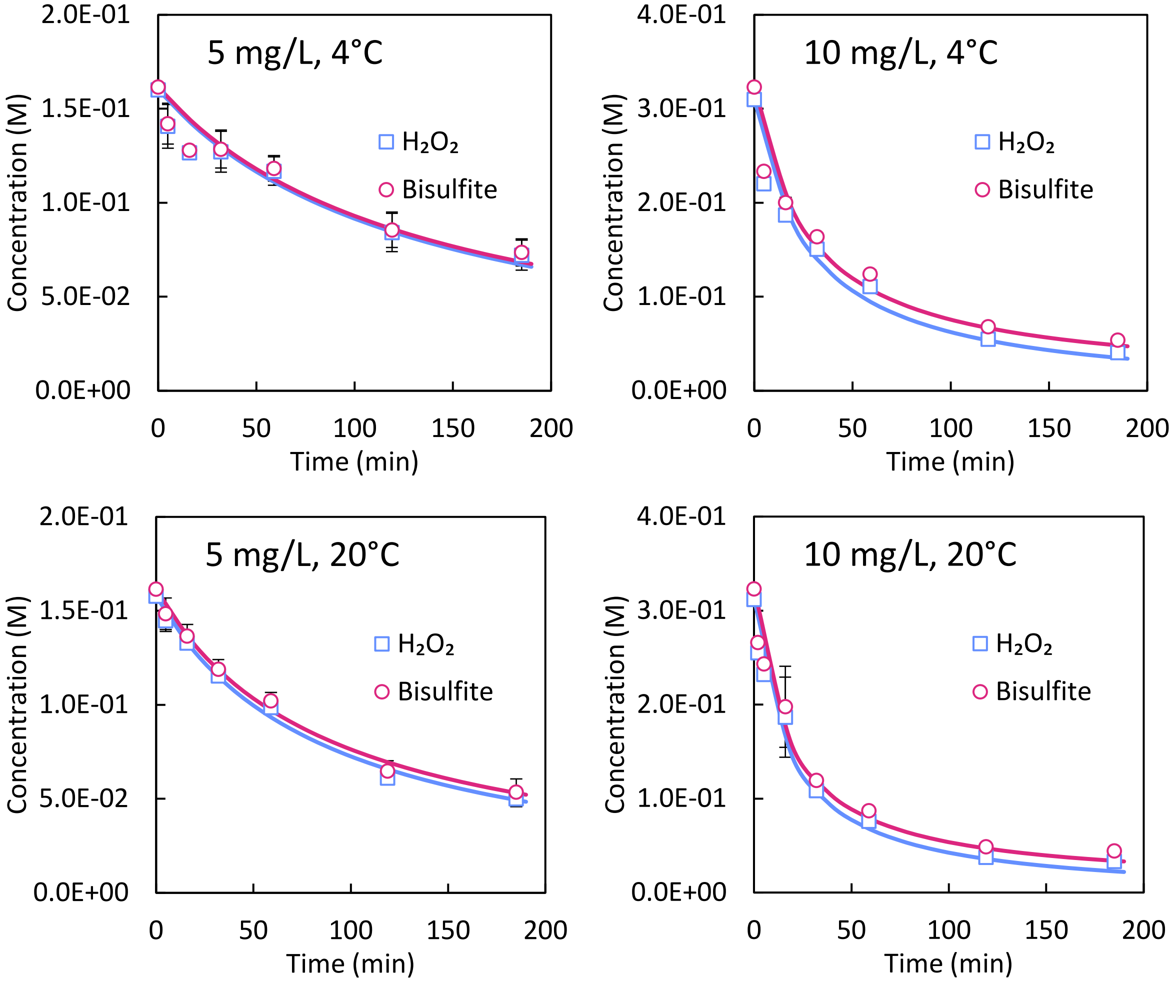

Figure S7. Concentrations of H_2O_2 and bisulfite in the reaction in natural water sample at 4 and 20°C. Error bars for experimental results represent standard deviation.

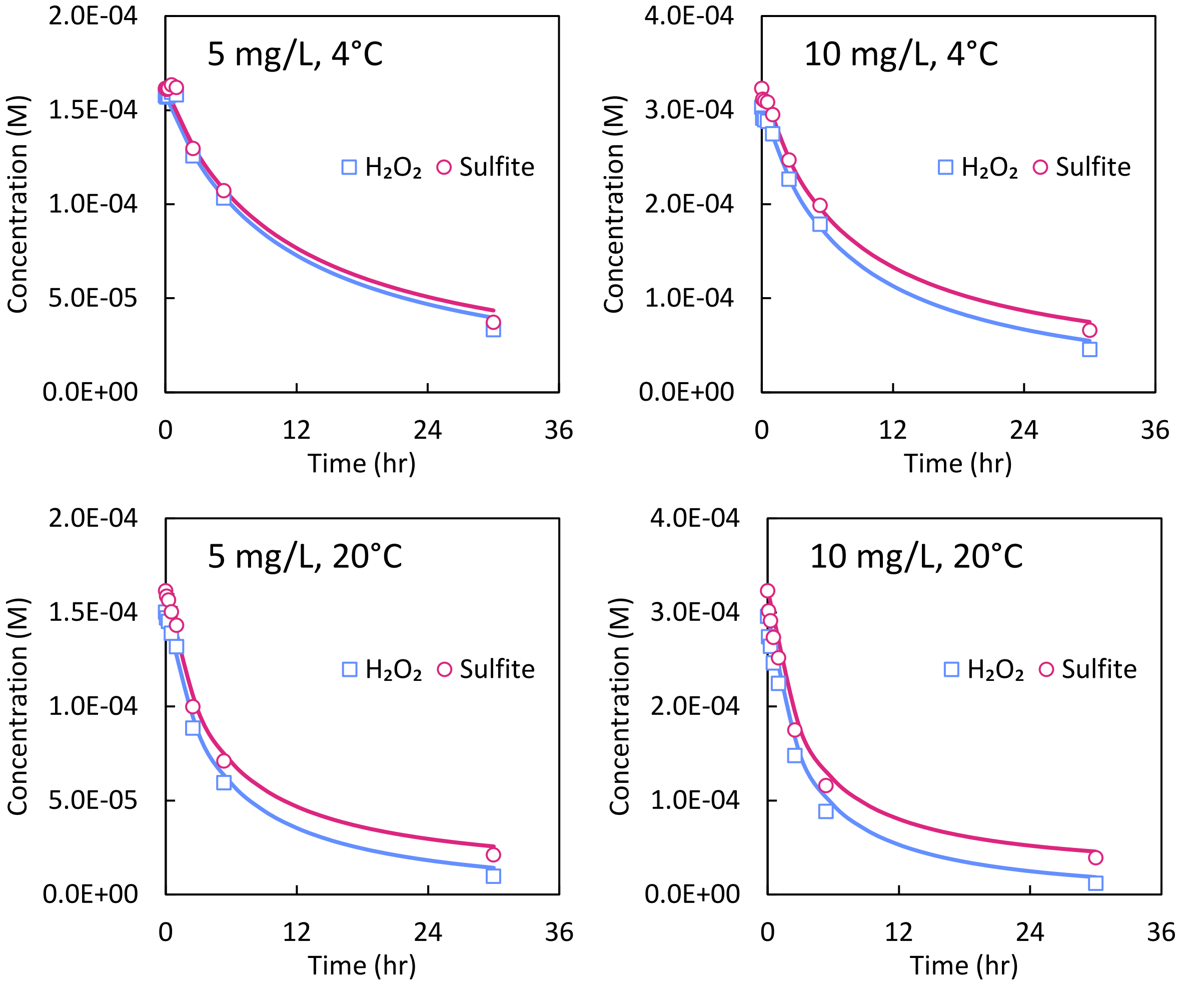

Figure S8. Concentrations of H_2O_2 and sulfite in the reaction in natural water sample at 4 and 20°C. Error bars for experimental results represent standard deviation.

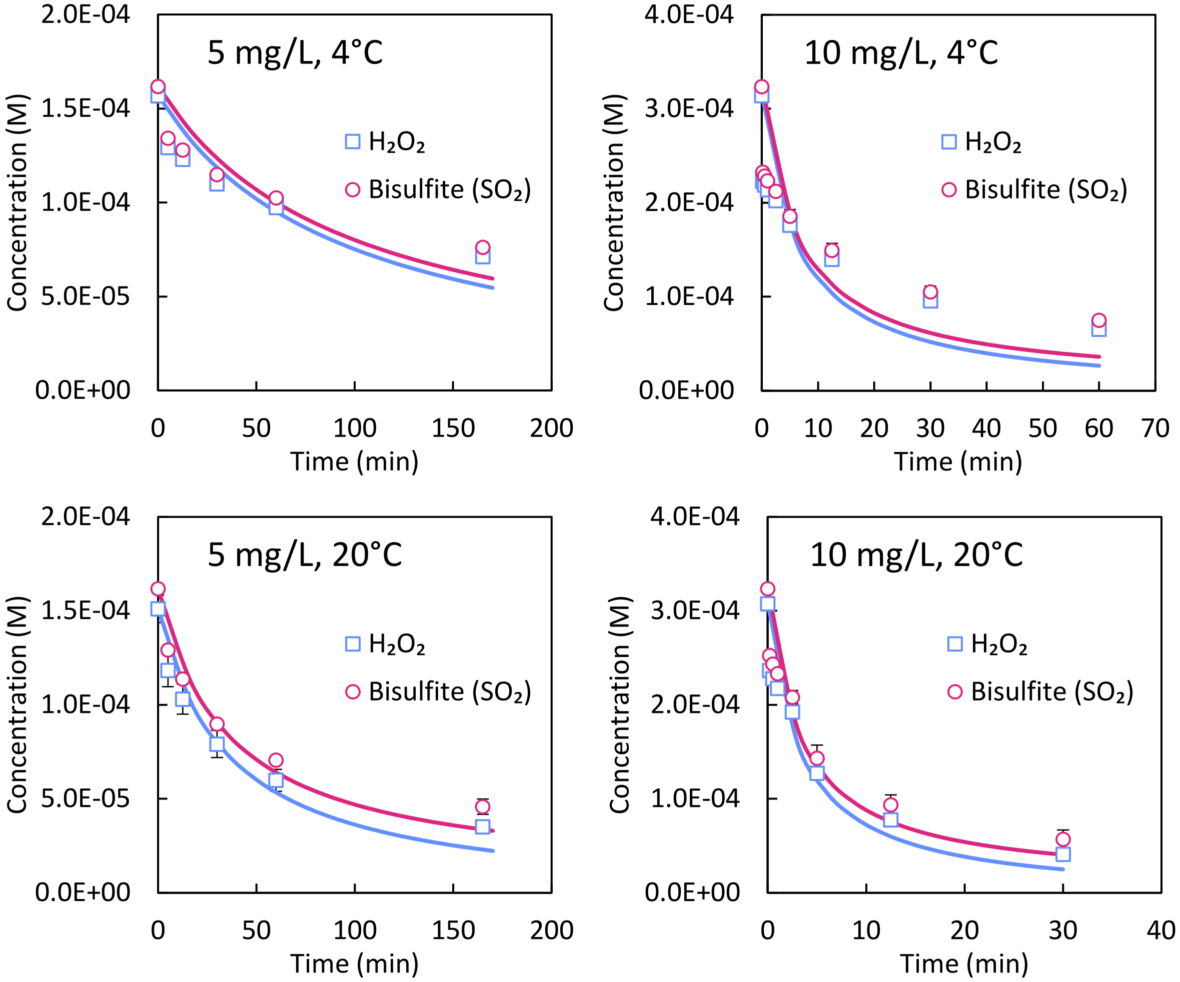

Figure S9. Concentrations of H_2O_2 and bisulfite made of SO_2 in the reaction in natural water sample at 4 and 20°C. Error bars for experimental results represent standard deviation.

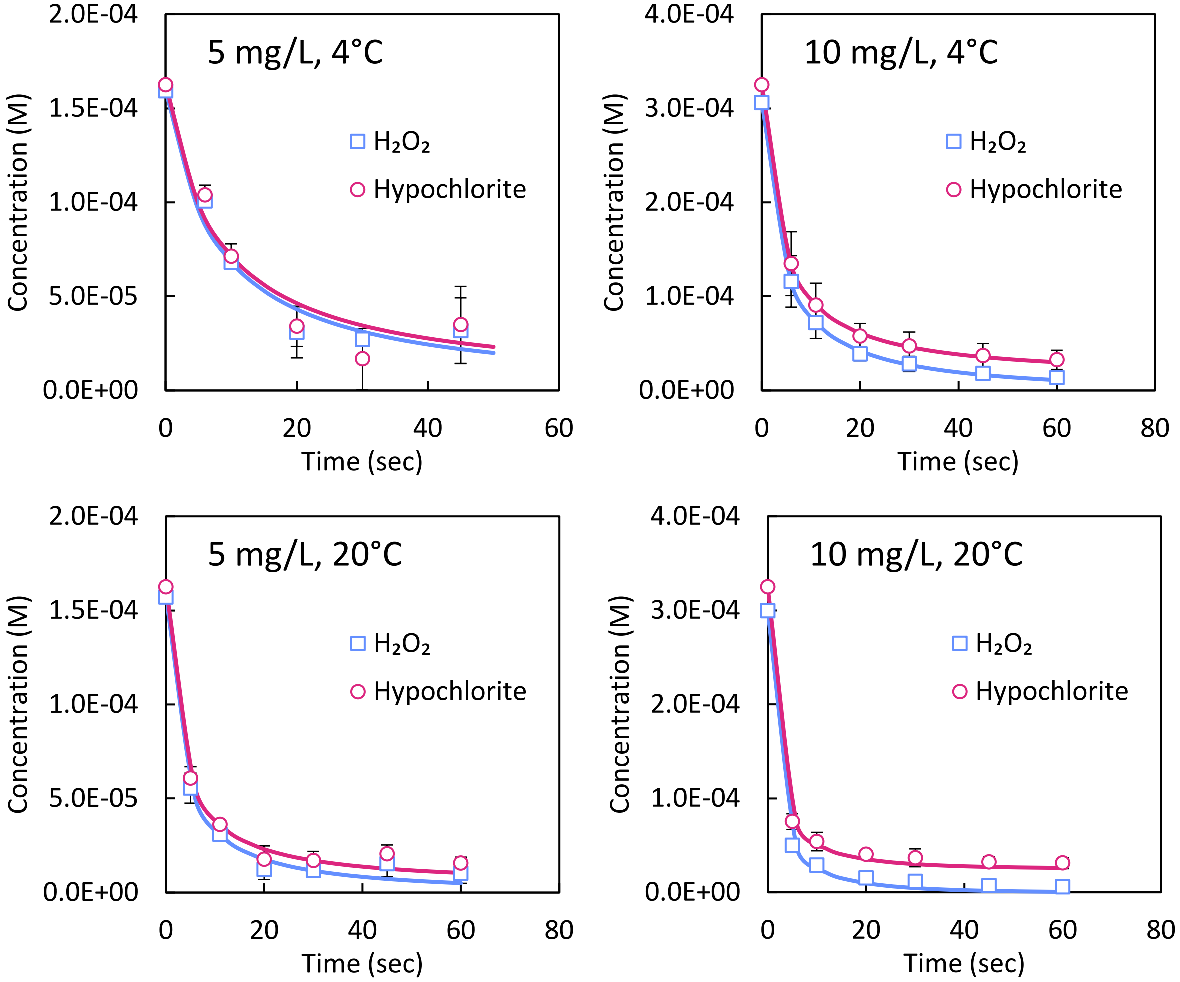

Figure S10. Concentrations of H_2O_2 and hypochlorite in the reaction in natural water sample at 4 and 20°C. Error bars for experimental results represent standard deviation.

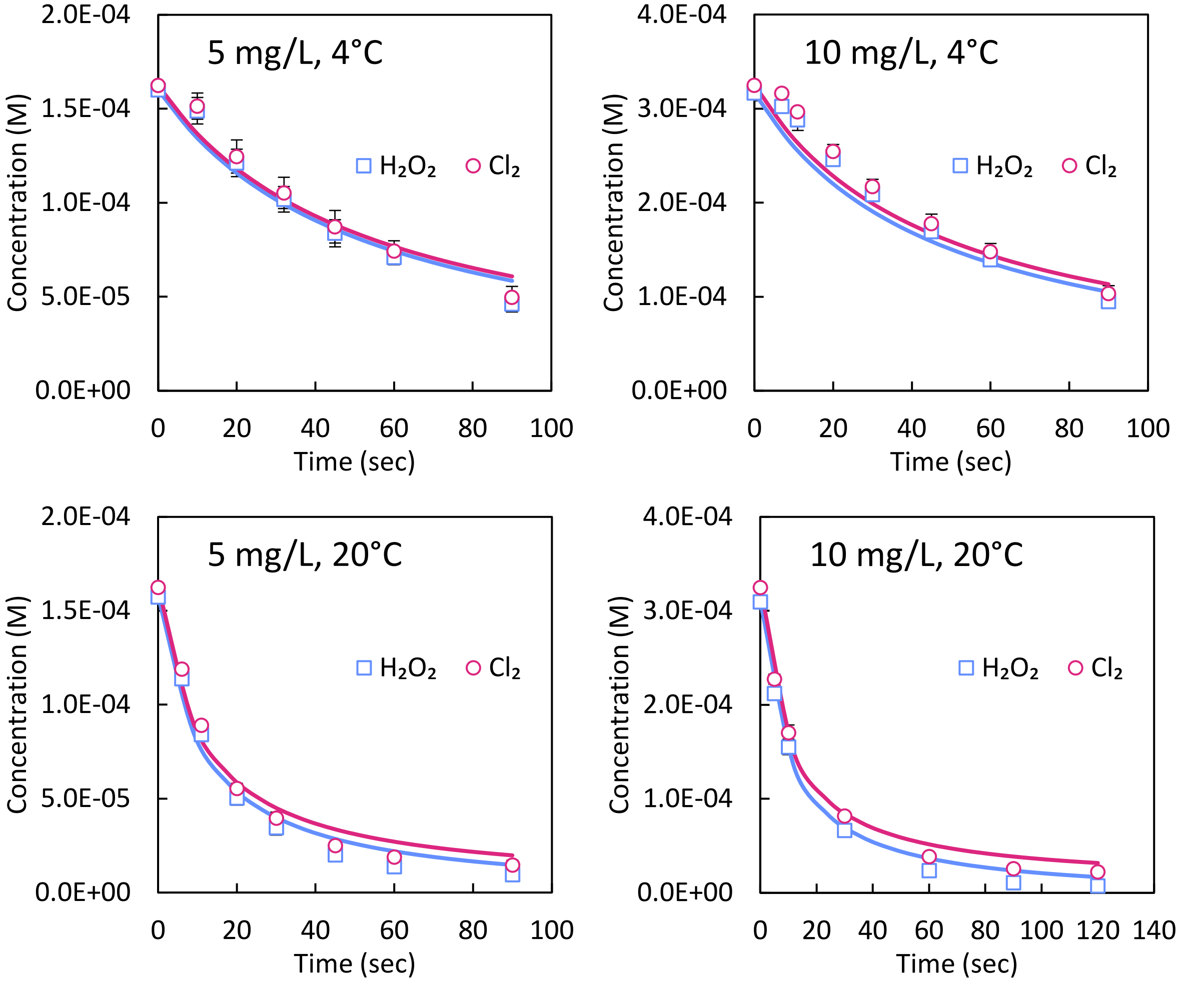

Figure S11. Concentrations of H_2O_2 and chlorine made of Cl_2 gas in the reaction in natural water sample at 4 and 20°C. Error bars for experimental results represent standard deviation

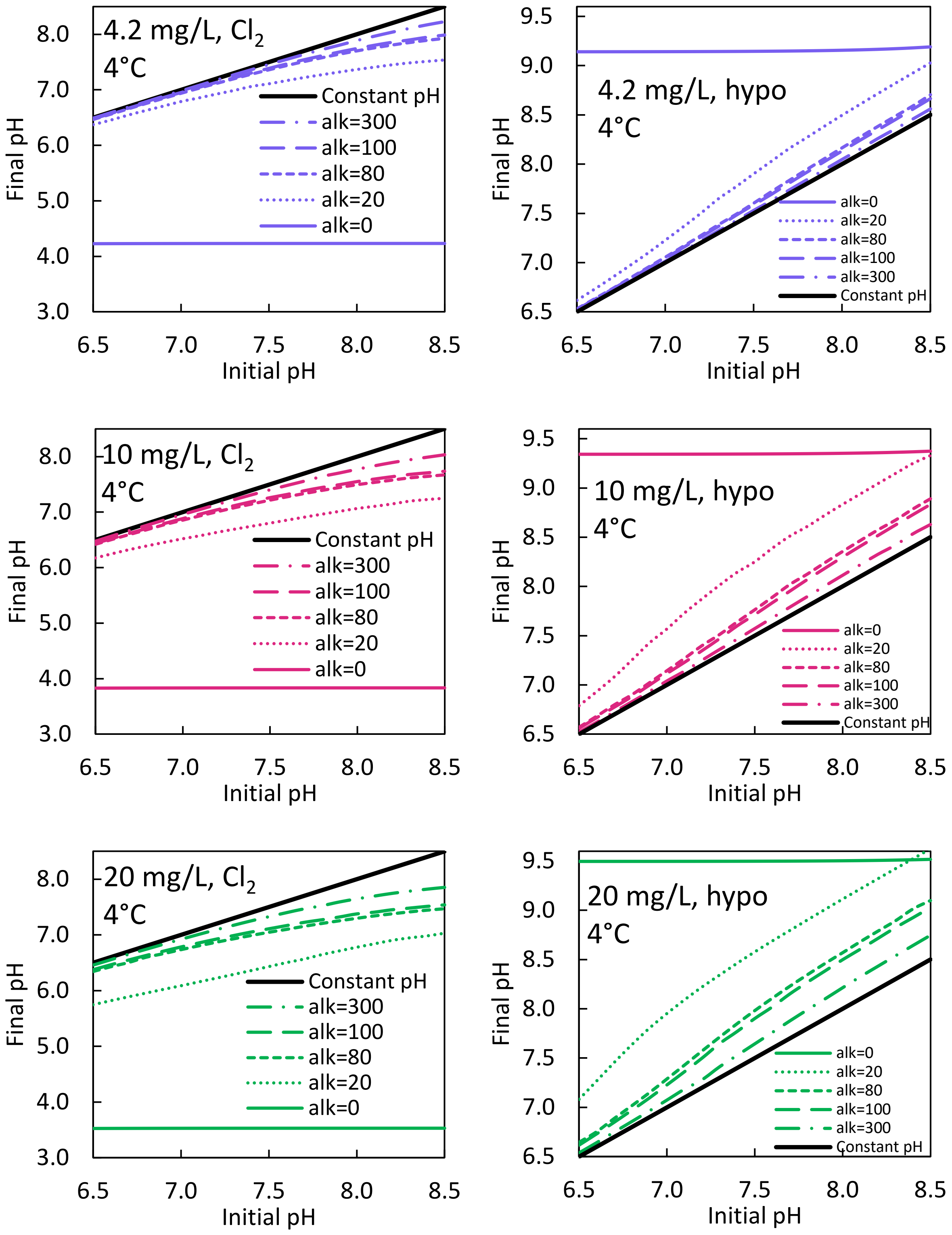

Figure S12. The calculated transient pH at 4°C right after chlorine of Cl_2 gas (left) and hypochlorite (right) source were added into water with alkalinity of 0, 20, 80, 100, and 300 mg/L as $CaCO_3$. Chlorine dose was 4.2, 10, 20 mg/L as Cl_2. Constant pH line shows no pH change (initial pH=final pH).

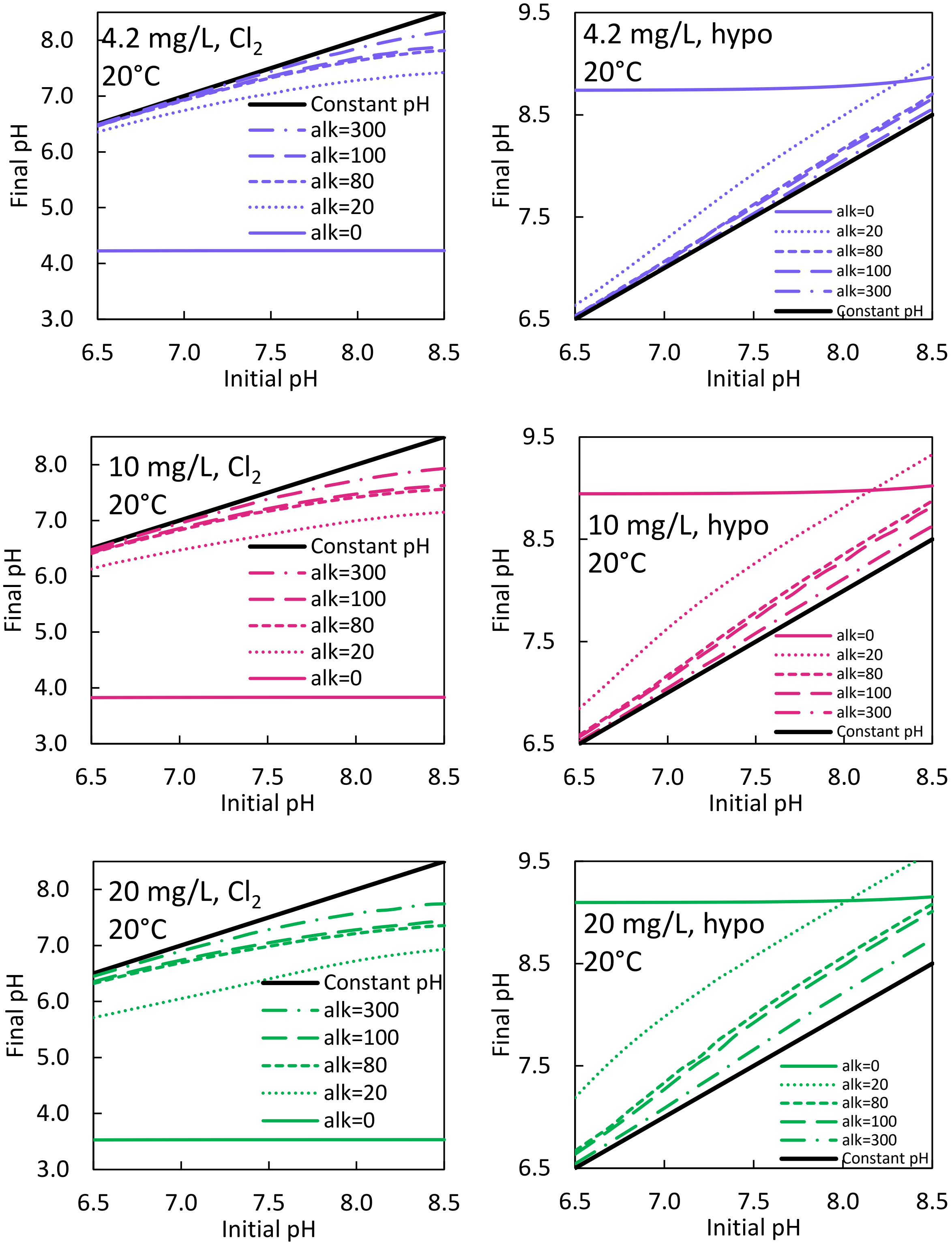

Figure S13. The calculated transient pH at 20°C right after chlorine of Cl_2 gas (left) and hypochlorite (right) source were added into water with alkalinity of 0, 20, 80, 100, and 300 mg/L as $CaCO_3$. Chlorine dose was 4.2, 10, 20 mg/L as Cl_2. Constant pH line shows no pH change (initial pH=final pH).

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