1	Supporting information for
2	Thallium(I) Oxidation by Permanganate and Chlorine: Kinetics and
3	Manganese Dioxide Catalysis
4	
5	Yijie Zou ^a , Haijun Cheng ^{b,#} , Hainan Wang ^a , Ruixing Huang ^a , Yanghui Xu ^a , Jin Jiang ^c ,
6	Qiang He ^a , Caihong Liu ^a , Juchao Liu ^a , Jiaming Xiong ^a , Jinni Yao ^a , Xiaoliu
7	Huangfu ^{a,*} , Jun Ma ^b
8	
9	^a Key Laboratory of Eco-environments in Three Gorges Reservoir Region, Ministry of
10	Education, College of Environment and Ecology, Chongqing University, Chongqing
11	400044, China
12	^b State Key Laboratory of Urban Water Resource and Environment, School of
13	Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin
14	150090, China
15	^c Institute of Environmental and Ecological Engineering, Guangdong University of
16	Technology, Guangzhou 510006, China
17	
18	
19	
20	
21	25 Pages, 2 Text Sections, 8 Tables, 18 Figures

22 **Contents**

- 23 Text S1. ABTS spectrophotometric method
- 24 **Text S2.** Preparation and Characterization of nMnO₂
- 25 **Table S1**. Equilibrium constants for thallium-related reaction
- **Table S2.** XPS spectra analysis results of Mn $2p_{3/2}$ and Tl $4f_{7/2}$ on the oxidation of
- 27 Tl(I) by KMnO₄ at different time. $[Tl(I)]_0 = 2.0 \text{ mM}$, $[KMnO_4]_0 = 1.0 \text{ mM}$, with 10.0
- 28 mM tetraborate buffer, pH = 9, 25°C.
- **Table S3.** XPS spectra analysis results of Mn $2p_{3/2}$ and Tl $4f_{7/2}$ on the oxidation of
- 30 Tl(I) by KMnO₄ with MnO₂ at different time. $[Tl(I)]_0 = 2.0 \text{ mM}$, $[KMnO_4]_0 = 1.0$
- 31 mM, with 5.0 μ M nMnO₂ and 10.0 mM acetate buffer, pH = 5, 25°C..
- 32 **Table S4.** Apparent second-order rate constant of Tl(I) oxidation by KMnO₄ under
- 33 alkaline conditions
- 34 **Table S5.** The simulation of the autocatalytic model constants of Tl(I) oxidation by
- 35 KMnO₄ under acidic conditions
- **Table S6.** Order of HOCl in Tl(I) oxidation by HOCl
- 37 **Table S7.** Appearent pseudo-first-order reaction rate constants of Tl(I) oxidation by 10
- 38 mM chlorine
- **Table S8.** XPS spectra analysis results of Tl $4f_{7/2}$ on the oxidation of Tl(I) by HOCl
- 40 with MnO₂ at different time. $[Tl(I)]_0 = 2.0 \text{ mM}$, $[HOCI]_0 = 20.0 \text{ mM}$, with 5.0 μ M
- 41 $nMnO_2$ and 10.0 mM acetate buffer, pH = 8.5, 25°C.
- 42 **Figure S1.** Absorbance of ABTS⁺ in Tl(III)-ABTS reaction. The reaction system was
- 43 5.0 ml in total, including 1.0 ml of pH 4.6 acetate buffer and 0.5 ml of 2.0 mM ABTS.
- 44 $[Tl(III)]_0 = 1.0-20.0 \ \mu M, 25^{\circ}C.$
- 45 **Figure S2.** Performance of DMSO as the terminator in the oxidation of Tl(I) by
- 46 HOCl. (a) 2.5 mM HOCl concentration determined by ABTS in 50.0 mM DMSO
- 47 solutions; (b) absorbance of ABTS.⁺ in 50.0 mM DMSO solutions; (c) 10.0 μ M
- 48 Tl(III) concentration determined by ABTS in 50.0 mM DMSO solutions, buffered
- 49 with 10.0 mM tetraborate, pH = 8.5, 25°C.

- 50 Figure S3. XPS spectra of Mn $2p_{3/2}$ on the Tl(I) oxidation by KMnO₄ at (a) 45 min and
- 51 (b) 90 min and (c) 180 min. $[Tl(I)]_0 = 2.0 \text{ mM}$, $[KMnO_4]_0 = 1.0 \text{ mM}$, with 10.0 mM
- 52 tetraborate buffer, pH = 9, 25°C.
- 53 Figure S4. XPS spectra of Mn $2p_{3/2}$ on the Tl(I) oxidation by KMnO₄ at (a) 45 min and
- 54 (b) 120 min and (c) 240 min. $[Tl(I)]_0 = 2.0 \text{ mM}$, $[KMnO_4]_0 = 1.0 \text{ mM}$, with 5.0 μ M
- 55 $nMnO_2$ and 10.0 mM acetate buffer, pH = 5, 25°C.
- 56 Figure S5. Kinetics of the Tl(I) oxidation by KMnO₄ under alkaline conditions. A = (
- 57 $[KMnO_4]_0([Tl(I)]_0 \frac{3x}{2}))/([Tl(I)]_0([KMnO_4]_0 x)))$, where x represents the consuming
- 58 oxidant concentrations. $[KMnO_4]_0 = 18.0 \ \mu M$, $[Tl(I)]_0 = 30.0 \ \mu M$, buffered with 10.0
- 59 mM tetraborate, pH = 8-10, $25^{\circ}C$.
- 60 **Figure S6.** Relation between pH and the apparent second-order rate constants of Tl(I)
- 61 by KMnO₄ under alkaline conditions. (a) Effect of pH on the apparent second-order
- 62 rate constants of the Tl(I) oxidation by KMnO₄; (b) simulation of kinetics model
- 63 containing thallium species in the Tl(I) oxidation by KMnO₄. [KMnO₄]₀ = 18.0 μ M,
- 64 $[Tl(I)]_0 = 30.0 \ \mu\text{M}$, buffered with 10.0 mM tetraborate, pH = 8-10, 25°C.
- 65 **Figure S7.** Relation between standard reduction potential and the second-order rate
- 66 constants of SO_4^{-}/SO_4^{2-} , $SCN^{-}/(SCN)_2$, $S_2O_3^{2-}/S_4O_6^{2-}$, $HONH_3Cl/N_2O$, N_2H_4/N_2H_2 ,
- AsO_2^{-}/AsO_4^{3-} , SO_3^{2-}/SO_4^{2-} , and Tl^+/Tl^{3+} at pH 9. The value calculated in this study
- 68 was chosen as the second-order rate constants of Tl(I), others were chosen according
- 69 to previous study and handbook of chemistry and physics.
- Figure S8. Effect of Mn^{2+} on the Tl(I) oxidation by $KMnO_4$ at (a) pH 5 and (b) pH 6.
- 71 $[KMnO_4]_0 = 18.0 \ \mu M$, $[Tl(I)]_0 = 30.0 \ \mu M$, buffered with 10.0 mM acetate, pH = 5-6,
- 72 25°C.
- Figure S9. Effect of Tl(III) on Tl(I)-KMnO₄ reaction. $[KMnO_4]_0 = 18.0 \ \mu M$, $[Tl(I)]_0 = 18.0 \ \mu M$
- 74 30.0 μ M, pH was adjusted by HNO₃, pH = 4, 25°C.
- 75 **Figure S10.** Simulation of autocatalytic model in Tl(I) oxidation by KMnO₄ (a) at pH
- 76 4 and (b) at pH 5 and (c) at pH 6. $[KMnO_4]_0 = 18.0 \ \mu M$, $[Tl(I)]_0 = 30.0 \ \mu M$, buffered
- 77 with 10.0 mM acetate, pH = 4-6, 25°C.

- 78 Figure S11. Effect of ionic strength on the oxidation of Tl(I) by KMnO₄ under alkaline
- 79 conditions. $[KMnO_4]_0 = 18.0 \ \mu M$, $[Tl(I)]_0 = 30.0 \ \mu M$, buffered with 10.0 mM
- 80 tetraborate, pH = 8.5, $25^{\circ}C$.
- Figure S12. Effect of Na⁺ on nMnO₂ particle size. $[Na^+]_0 = 0.50.0$ mM, pH was
- 82 adjusted by HNO₃, pH = 4, 25° C.
- 83 Figure S13. HOCl concentration impact on the oxidation of Tl(I) by HOCl (a) at pH 7
- 84 and (b) at pH 8 and (c) at pH 9. $[Tl(I)]_0 = 30.0 \ \mu\text{M}$, $[HOCl]_0 = 5.0-12.5 \ \text{mM}$, buffered
- 85 with 10.0 mM tetraborate, pH = 7-9, 25°C.
- 86 Figure S14. Tl(I) oxidation by HOCl. (a) Relation between apparent first-order rate
- 87 constants and chlorine species proportion under different pH; (b) Impact of pH on the
- apparent rate constants. $[HOC1]_0 = 10.0 \text{ mM}, [T1(I)]_0 = 30.0 \mu \text{M}$, buffered with 10.0
- 89 mM acetate or 10.0 mM tetraborate, pH = 5-9, $25^{\circ}C$.
- **Figure S15.** Effect of ionic strength on Tl(I) oxidation by HOCl. [HOCl]₀ = 10.0 mM,
- 91 $[Tl(I)]_0 = 30.0 \ \mu\text{M}$, buffered with 10.0 mM tetraborate, pH = 7, 25°C.
- 92 Figure S16. XPS spectra of Tl $4f_{7/2}$ on Tl(I)-HOCl reaction at (a) 45 min and (b) 90
- 93 min and (c) 180 min. $[Tl(I)]_0 = 2.0 \text{ mM}$, $[HOCI]_0 = 20.0 \text{ mM}$, with 5.0 μ M nMnO₂ and
- 94 10.0 mM tetraborate buffer, pH = 8.5, 25°C.
- 95 Figure S17. Polynomial curves fitting of additional MnO₂ concentration and apparent
- 96 second-order rate constants. $[HOC1]_0 = 10.0 \text{ mM}$, $[T1(I)]_0 = 30.0 \mu M$, buffered with
- 97 10.0 mM sodium tetraborate, $pH = 8.5, 25^{\circ}C$.
- 98 Figure S18. Influence of pyrophosphate on the Tl(I) oxidation by HOCl with
- additional MnO₂. (a) $[HOCI]_0 = 10.0$ mM, buffered with 10.0 mM tetraborate, pH =
- 100 8.5; (b) $[HOCI]_0 = 0.3 \text{ mM}$, pH was adjusted by HNO_3 , pH = 4. $[Tl(I)]_0 = 30 \mu M$,
- 101 $[nMnO_2]_0 = 3.0 \ \mu M, 25^{\circ}C.$
- 102
- 103
- 104
- 105

106 Text S1. ABTS spectrophotometric method

107	1. The spectrophotometric determination of $KMnO_4$ by ABTS
108	1mL of the buffer reagent (pH = 4.6, 10 mM acetate buffer) and 0.5 mL of ABTS
109	reagent (0.2 mM) were added to a 10.0 mL colorimetric tube. Then, a sample containing
110	diluted KMnO ₄ solution was added and the tube was filled to 5.0 ml by ultrapure water.
111	After developing 15 s, the absorbance can be determined directly at 415 nm ($\epsilon = 31600$
112	cm ⁻¹ M ⁻¹) (dilution multiple in the measured cuvette: n).
113	$c_{KMnO_4}(mM) = A/\epsilon \times 1000 \times n$
114	2. Differential ABTS method
115	• Take a 10.0 ml colorimetric tube, adding 1 ml of 0.27 M pH 4.6 acetate buffer, 0.5
116	ml of 2.0 mM ABTS, 2.5 ml ultrapure water.
117	• At the predetermined points in time, add samples (1000.0 μ l each).
118	• Develop 15 s, and then measure the absorbance spectrophotometrically by $ABTS^{+}$
119	at 415 nm.
120	The reaction of Mn(VII) with ABTS has a stoichiometry of 1 : 5 in excess of ABTS
121	(2 mM), and the concentration of permanganate in sample can be calculated as follows:
122	$c_{KMnO_4}(\mu M) = A/\epsilon \times 10^6$
123	Where A is the absorbance of ABTS \cdot^+ at 415 nm, ϵ is the molar extinction
124	coefficient of ABTS·+ at $\lambda = 415$ nm (31600 cm ⁻¹ M ⁻¹).
125	3. Direct ABTS method
126	• Take a 10.0 ml colorimetric tube, adding 1 ml of pH 4.6 acetate buffer, 200.0 µl of

S5

- 127 1M DMSO, 1.2 ml ultrapure water.
- At the predetermined points in time, add samples (1000.0 μl each), shaking up with
 50 s static duration.
- Add 0.5 ml of 2.0 mM ABTS and 100.0 μl of 1.0 mM KI, develop several minutes,
- 131 and then measure the absorbance spectrophotometrically by $ABTS^{+}$ at 415 nm.
- 132 The reaction of Tl(III) with ABTS has a stoichiometry of 1 : 2 in excess of ABTS
- 133 (2 mM), and the concentration of permanganate in sample can be calculated as follows:

134
$$c_{Tl(III)}(\mu M) = A/\epsilon \times 10^6 \times 5/2$$

- 135 Where A is the absorbance of $ABTS^{+}$ at 415 nm, ε is the molar extinction
- 136 coefficient of ABTS + at $\lambda = 415$ nm (31600 cm⁻¹M⁻¹).
- 137

138

139 Text S2. Preparation and Characterization of nMnO₂

140 **Preparation.** KMnO₄ solution purging with N₂ was rapidly stirred with a magnetic 141 stirrer, then the stoichiometric amount of Na₂S₂O₃ solution was added dropwise 142 according to Eq 1. Formed brown MnO₂ colloids were continuously stirred over 12 h 143 and stored in the dark at 4°C.

144
$$3S_2O_3^{2^-} + 8MnO_4^- + 4OH^- \rightarrow 5MnO_2 + 2H_2O$$
 (1)

145 **Characterization**. After reducing MnO_2 by hydroxylamine hydrochloride, the 146 concentration of Mn content was determined by ICP-MS (NexION300Q, PerkinElmer 147 Corp.). The average oxidation state of MnO_2 was obtained as by the iodimetric method¹⁻ 148 ² as Eq 2:

149
$$OS_{avg} = 2 + \frac{2A}{\epsilon L[Mn]_T}$$
(2)

where A is the absorbance of the solution in excess of I⁻ at 351 nm, ε is the molar absorptivity of tri-iodide ion (I³⁻) at 351 nm, L is the optical path length of the cuvettes (1 cm), [Mn]_T is the total manganese concentration.

153

Table S1. Equilibrium constants for thallium-related reaction

Reaction	log <i>K</i> (25°C)	Reference
$Tl^+ + H_2O = TlOH(aq) + H^+$	-13.207	3
$2Tl^{+} + H_2O = Tl_2O(s) + 2H^{+}$	-27.091	3
$Tl^+ + SO_4^2 = TlSO_4$	1.37	3
$2Tl^{+} + SO_4^{2^-} = Tl_2SO_4(s)$	3.787	3
$Tl^{3+} + H_2O = TlOH^{2+} + H^+$	-2.7	4
$Tl^{3+} + 2H_2O = Tl(OH)_2^+ + 2H^+$	-9.1	4
$Tl^{3+} + 3H_2O = Tl(OH)_3(aq) + 3H^+$	-16.5	4
$Tl^{3+} + 4H_2O = Tl(OH)_4^{-} + 4H^{+}$	-25.3	4

Table S2. XPS spectra analysis results of Mn $2p_{3/2}$ and Tl $4f_{7/2}$ on the oxidation of

157	Tl(I) by KMnO ₄ at different time	$[Tl(I)]_0 = 2.0 \text{ mM}$	$, [KMnO_4]_0 = 1.0 \text{ mN}$	1, with 10.0

mM tetraborate buffer, $pH = 9, 25^{\circ}C.^{a}$

Time (min)	Mn(II) (%)	Mn(III) (%)	Mn(IV) (%)	Tl(I) (%)	Tl(III) (%)
45	3.6	63.0	33.4	81.4	18.6
90	6.6	65.1	28.2	75.4	24.6
180	7.8	62.6	29.6	73.6	26.4

^a correspongding figure as Figure S3.

Table S3. XPS spectra analysis results of Mn $2p_{3/2}$ and Tl $4f_{7/2}$ on the oxidation of

Tl(I) by KMnO₄ with MnO₂ at different time. $[Tl(I)]_0 = 2.0$ mM, $[KMnO_4]_0 = 1.0$

mM, with 5.0 μ M nMnO₂ and 10.0 mM acetate buffer, pH = 5, 25°C.^a

Time (min)	Mn(II) (%)	Mn(III) (%)	Mn(IV) (%)	Tl(I) (%)	Tl(III) (%)
45	31.0	50	19.0	74.1	25.9
120	27.3	50.6	22.0	56.4	43.5
240	22.4	44.7	32.9	52.4	47.6

^a correspongding figure as Figure S4.

Table S4. Apparent second-order rate constant of Tl(I) oxidation by KMnO₄ under

	alkaline conditions	
pH	$k_{\rm app, \ permanganate} \ ({ m M}^{-1}{ m s}^{-1})^{ m a}$	Half-life period (min) ^b
8.0	3.78±0.12	379.6±12.4
8.5	8.30±0.15	173.0±3.1
9.0	21.00±0.30	68.4±1.0
9.5	48.67±1.01	29.5±0.6
10.0	152.17±1.69	9.4±0.1

^a Refer to the apparent second-order rate constant of Tl(I) oxidation by KMnO₄ in Eq 3

170	^b Presume the initial	oxidant	concentration i	is 1.	0 mg/L	(Mn co	ontent).
-----	----------------------------------	---------	-----------------	-------	---------	--------	----------

171

172 **Table S5.** The simulation of the autocatalytic model constants of Tl(I) oxidation by

173

pН	$k_0 (M^{-1}s^{-1})$	$k_1 (M^{-1}s^{-1})$	R ²
4.0	1.49	5.20	0.9887
5.0	1.90	14.40	0.9962
6.0	0.13	17.08	0.9915

^a The autocatalytic model is shown as Eq 11.

175

176

 Table S6. Order of HOCl in Tl(I) oxidation by HOCl

			5
	pH	Order of [HOC1]	R ²
	7.0	2.451	0.998
	8.0	1.926	0.999
	9.0	1.283	0.998
177			
178			
179			
180			
181			
182	Table S7. Appearent pse	eudo-first-order reaction rate consta	ints of Tl(I) oxidation by

	10 mM chlorine	
рН	$k_{\text{app, chlorine}} \times 10^{-3} \text{ (min}^{-1}\text{)}$	R ²
5.0	59.3±2.78	0.970
7.0	53.8±1.06	0.998
7.5	35.9±0.07	0.999
8.0	12.9±0.02	0.999
8.5	$7.4{\pm}0.08$	0.999
9.0	$6.4{\pm}0.08$	0.999
Table S8. XPS spectra	a analysis results of Tl $4f_{7/2}$ on the oxid	dation of Tl(I) by HOC
with MnO ₂ at differen	nt time. $[Tl(I)]_0 = 2.0 \text{ mM}, [HOC1]_0 =$	20.0 mM, with 5.0 µM
with MnO ₂ at different nMnO ₂	nt time. $[Tl(I)]_0 = 2.0 \text{ mM}, [HOCl]_0 =$ 2 and 10.0 mM acetate buffer, pH = 8.3	20.0 mM, with 5.0 μM 5, 25°C. ^a
with MnO ₂ at differen nMnO ₂ Time (min)	t time. $[Tl(I)]_0 = 2.0 \text{ mM}, [HOCI]_0 =$ and 10.0 mM acetate buffer, pH = 8.3 Tl(I) (%)	20.0 mM, with 5.0 μM 5, 25°C. ^a Tl(III) (%)
with MnO ₂ at different nMnO ₂ <u>Time (min)</u> 45	t time. $[Tl(I)]_0 = 2.0 \text{ mM}, [HOCI]_0 =$ and 10.0 mM acetate buffer, pH = 8.3 Tl(I) (%) 26.5	20.0 mM, with 5.0 μM 5, 25°C. ^a Tl(III) (%) 73.5
with MnO ₂ at different nMnO ₂ Time (min) 45 90	nt time. $[Tl(I)]_0 = 2.0 \text{ mM}, [HOCI]_0 =$ 2 and 10.0 mM acetate buffer, pH = 8.3 $\frac{Tl(I) (\%)}{26.5}$ 21.9	20.0 mM, with 5.0 μM 5, 25°C. ^a Tl(III) (%) 73.5 78.1
with MnO ₂ at different nMnO ₂ Time (min) 45 90 180	nt time. $[Tl(I)]_0 = 2.0 \text{ mM}, [HOCl]_0 =$ and 10.0 mM acetate buffer, pH = 8.3 Tl(I) (%) 26.5 21.9 20.7	20.0 mM, with 5.0 μM 5, 25°C. ^a Tl(III) (%) 73.5 78.1 78.7
with MnO ₂ at different $nMnO_2$ Time (min) 45 90 180 ^a correspongding figure	nt time. $[Tl(I)]_0 = 2.0 \text{ mM}, [HOCI]_0 =$ and 10.0 mM acetate buffer, pH = 8.3 Tl(I) (%) 26.5 21.9 20.7 as Figure S15.	20.0 mM, with 5.0 μM 5, 25°C. ^a Tl(III) (%) 73.5 78.1 78.7
with MnO ₂ at different nMnO ₂ Time (min) 45 90 180 ^a correspongding figure	and 10.0 mM acetate buffer, pH = 8.3 Tl(I) (%) 26.5 21.9 20.7 as Figure S15.	20.0 mM, with 5.0 μM 5, 25°C. ^a Tl(III) (%) 73.5 78.1 78.7
with MnO ₂ at different nMnO ₂ Time (min) 45 90 180 ^a correspongding figure	and 10.0 mM acetate buffer, pH = 8.3 Tl(I) (%) 26.5 21.9 20.7 as Figure S15.	20.0 mM, with 5.0 μM 5, 25°C. ^a Tl(III) (%) 73.5 78.1 78.7
with MnO ₂ at different nMnO ₂ Time (min) 45 90 180 ^a correspongding figure	and 10.0 mM acetate buffer, pH = 8.3 T1(I) (%) 26.5 21.9 20.7 as Figure S15.	20.0 mM, with 5.0 μM 5, 25°C. ^a Tl(III) (%) 73.5 78.1 78.7
with MnO ₂ at different nMnO ₂ Time (min) 45 90 180 ^a correspongding figure	and time. $[Tl(I)]_0 = 2.0 \text{ mM}, [HOCI]_0 =$ and 10.0 mM acetate buffer, pH = 8.3 Tl(I) (%) 26.5 21.9 20.7 as Figure S15.	20.0 mM, with 5.0 μM 5, 25°C. ^a Tl(III) (%) 73.5 78.1 78.7
with MnO ₂ at different nMnO ₂ Time (min) 45 90 180 ^a correspongding figure	and time. $[Tl(I)]_0 = 2.0 \text{ mM}, [HOCI]_0 =$ and 10.0 mM acetate buffer, pH = 8.3 Tl(I) (%) 26.5 21.9 20.7 as Figure S15.	20.0 mM, with 5.0 μM 5, 25°C. ^a Tl(III) (%) 73.5 78.1 78.7
with MnO ₂ at different nMnO ₂ Time (min) 45 90 180 ^a correspongding figure	nt time. $[Tl(I)]_0 = 2.0 \text{ mM}, [HOCI]_0 =$ and 10.0 mM acetate buffer, pH = 8.3 Tl(I) (%) 26.5 21.9 20.7 as Figure S15.	20.0 mM, with 5.0 μM 5, 25°C. ^a Tl(III) (%) 73.5 78.1 78.7





Figure S2. Performance of DMSO as the terminator in the oxidation of Tl(I) by HOCl. (a) 2.5 mM HOCl concentration determined by ABTS in 50.0 mM DMSO solutions; (b) absorbance of ABTS⁺ in 50.0 mM DMSO solutions; (c) 10.0 μ M Tl(III) concentration determined by ABTS in 50.0 mM DMSO solutions, buffered with 10.0 mM tetraborate, pH = 8.5, 25°C.



Figure S3. XPS spectra of Mn $2p_{3/2}$ on the Tl(I) oxidation by KMnO₄ at (a) 45 min



223 mM tetraborate buffer, pH = 9, 25°C.



Figure S4. XPS spectra of Mn $2p_{3/2}$ on the Tl(I) oxidation by KMnO₄ at (a) 45 min

228 and (b) 120 min and (c) 240 min. $[Tl(I)]_0 = 2.0 \text{ mM}$, $[KMnO_4]_0 = 1.0 \text{ mM}$, with 5.0





Figure S5. Kinetics of the Tl(I) oxidation by KMnO₄ under alkaline conditions. A = ([KMnO₄]₀([Tl(I)]₀ - $\frac{3x}{2}$)/([Tl(I)]₀([KMnO₄]₀ - x)), where x represents the consuming oxidant concentrations. [KMnO₄]₀ = 18.0 µM, [Tl(I)]₀ = 30.0 µM, buffered with 10.0 mM tetraborate, pH = 8-10, 25°C.



Figure S6. Relation between pH and the apparent second-order rate constants of Tl(I) by KMnO₄ under alkaline conditions. (a) Effect of pH on the apparent second-order rate constants of the Tl(I) oxidation by KMnO₄; (b) simulation of kinetics model containing thallium species in the Tl(I) oxidation by KMnO₄. [KMnO₄]₀ = 18.0 μ M, [Tl(I)]₀ = 30.0 μ M, buffered with 10.0 mM tetraborate, pH = 8-10, 25°C.



Figure S7. Relation between standard reduction potential and the second-order rate constants of $SO_4^{-.}/SO_4^{2-}$, $SCN^{-}/(SCN)_2$, $S_2O_3^{2-}/S_4O_6^{2-}$, $HONH_3Cl/N_2O$, N_2H_4/N_2H_2 , AsO_2^{-}/AsO_4^{3-} , SO_3^{2-}/SO_4^{2-} , and Tl^+/Tl^{3+} at pH 9. The value calculated in this study was chosen as the second-order rate constants of Tl(I), others were chosen according to previous study and handbook of chemistry and physics⁵⁻⁷.



Figure S8. Effect of Mn^{2+} on the Tl(I) oxidation by $KMnO_4$ at (a) pH 5 and (b) pH 6.

 $[KMnO_4]_0 = 18.0 \ \mu M$, $[Tl(I)]_0 = 30.0 \ \mu M$, buffered with 10.0 mM acetate, pH = 5-6,



Figure S9. Effect of Tl(III) on Tl(I)-KMnO₄ reaction. [KMnO₄]₀ = 18.0 μ M, [Tl(I)]₀

= 30.0 μ M, pH was adjusted by HNO₃, pH = 4, 25°C.



Figure S10. Simulation of autocatalytic model in Tl(I) oxidation by KMnO₄ (a) at pH 4 and (b) at pH 5 and (c) at pH 6. [KMnO₄]₀ = 18.0 μ M, [Tl(I)]₀ = 30.0 μ M, buffered with 10.0 mM acetate, pH = 4-6, 25°C.



Figure S11. Effect of ionic strength on the oxidation of Tl(I) by KMnO₄ under

alkaline conditions. [KMnO₄]₀ = 18.0 μ M, [Tl(I)]₀ = 30.0 μ M, buffered with 10.0 mM

800 0mM Na⁺ 10mM Na⁺ 8 20mM Na⁺ Particle Size (nm) 007 007 007 007 600 50mM Na⁺ \$\$^{\$} $\overline{\nabla} \overline{\aleph} \nabla$ ĒĒ 上 0 60 80 0 20 40 Time (min)

tetraborate, pH = 8.5, $25^{\circ}C$.

Figure S12. Effect of Na⁺ on nMnO₂ particle size. $[Na^+]_0 = 0-50.0$ mM, pH was

adjusted by HNO₃, pH = 4, 25°C.



Figure S13. HOCl concentration impact on the oxidation of Tl(I) by HOCl (a) at pH 7 and (b) at pH 8 and (c) at pH 9. $[Tl(I)]_0 = 30.0 \ \mu\text{M}$, $[HOCl]_0 = 5.0-12.5 \ \text{mM}$, buffered with 10.0 mM tetraborate, pH = 7-9, 25°C.



Figure S14. Tl(I) oxidation by HOCl. (a) Relation between apparent first-order rate constants and chlorine species proportion under different pH; (b) Impact of pH on the apparent rate constants. $[HOCl]_0 = 10.0 \text{ mM}, [Tl(I)]_0 = 30.0 \text{ }\mu\text{M}$, buffered with 10.0

mM acetate or 10.0 mM tetraborate, pH = 5-9, $25^{\circ}C$.



Figure S15. Effect of ionic strength on Tl(I) oxidation by HOCl. [HOCl]₀ = 10.0 mM,

 $[Tl(I)]_0 = 30.0 \mu$ M, buffered with 10.0 mM tetraborate, pH = 7, 25°C. S22



Figure S16. XPS spectra of Tl $4f_{7/2}$ on Tl(I)-HOCl reaction at (a) 45 min and (b) 90 min and (c) 180 min. [Tl(I)]₀ = 2.0 mM, [HOCl]₀ = 20.0 mM, with 5.0 μ M nMnO₂

and 10.0 mM tetraborate buffer, pH = 8.5, 25°C.



Figure S17. Polynomial curves fitting of additional MnO_2 concentration and apparent second-order rate constants. $[HOCl]_0 = 10.0 \text{ mM}$, $[Tl(I)]_0 = 30.0 \text{ }\mu\text{M}$, buffered with

10.0 mM sodium tetraborate, $pH = 8.5, 25^{\circ}C$.



Figure S18. Influence of pyrophosphate on the Tl(I) oxidation by HOCl with additional MnO₂. (a) [HOCl]₀ = 10.0 mM, buffered with 10.0 mM tetraborate, pH = 8.5; (b) [HOCl]₀ = 0.3 mM, pH was adjusted by HNO₃, pH = 4. [Tl(I)]₀ = 30 μ M,

$$[nMnO_2]_0 = 3.0 \ \mu M, 25^{\circ}C.$$

Reference

1. Perez-Benito, J. F.; Arias, C.; Amat, E., A kinetic study of the reduction of colloidal manganese dioxide by oxalic acid. *Journal of Colloid and Interface Science* **1996**, *177* (2), 288-297.

2. Huangfu, X.; Jiang, J.; Ma, J.; Liu, Y.; Yang, J., Aggregation Kinetics of Manganese Dioxide Colloids in Aqueous Solution: Influence of Humic Substances and Biomacromolecules. *Environmental Science & Technology* **2013**, *47* (18), 10285-10292.

3. Laforte, L.; Tessier, A.; Gobeil, C.; Carignan, R., Thallium diagenesis in lacustrine sediments. *Geochimica et Cosmochimica Acta* **2005**, *69* (22), 5295-5306.

4. Nriagu, J. O., Thallium in the Environment. Wiley: 1998.

5. Liang, C.; Su, H.-W., Identification of Sulfate and Hydroxyl Radicals in Thermally Activated Persulfate. *Industrial & Engineering Chemistry Research* **2009**, *48* (11), 5558-5562.

6. Haynes, W. M., CRC handbook of chemistry and physics. CRC press: 2014.

7. Sharma, V. K.; Dutta, P. K.; Ray, A. K., Review of kinetics of chemical and photocatalytical oxidation of Arsenic(III) as influenced by pH. *Journal of Environmental Science and Health, Part A* **2007**, *42* (7), 997-1004.