 Water Table Fluctuations Regulate Hydrogen Peroxide Production and Distribution in Unconfined Aquifers Na Zhang[†], Xiaochuang Bu[†], Yiming Li[‡], Yanting Zhang[†], Songhu Yuan^{*,†} Zhang Wen[‡], Man Tong[†], Li Lin[§] [†] State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, NO. 68 Jincheng Street, East Lake High-Tech Development Zone, Wuhan, 430078, P. R. China [‡] School of Environmental Studies, China University of Geosciences, NO. 68 Jincheng Street, East Lake High-Tech Development Zone, Wuhan, 430078, P. R. China [§] Department of Water Environment Research, Changjiang River Scientific Research Institute, Wuhan, 430010, China <i>*Corresponding author.</i> Tel: +86-27-67848629, Fax: +86-27-67883456, Email yuansonghu622@cug.edu.cn (S.H. Yuan) 	1	Supplementary Information for
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89 **Text S1: Sampling and analysis.**

(a) Groundwater sampling. Groundwater was sampled at 6 locations with different 90 distance to the river and at different depths at each location in the field site (Figures 91 S1, S2). At each location, 10 (for ST1) or 6 (for the other locations) polyvinyl chloride 92 93 (PVC) pipes (an inner diameter: 14 mm) were drilled into different depths. The 94 bottom 5 cm of pipes were perforated and wrapped with gauze for groundwater flow. Local sands were backfilled into the wells around the pipes. The pipes at ST1 location 95 were installed on March 28, 2017, and at the other locations were installed at least 2 96 days before each sampling event. Before sampling, about 2 L of water, 2.8 folds of the 97 pipe volume, was pumped out slowly at 0.1 L/min. Measurements proved that 98 99 groundwater chemistry stabilized. Then, groundwater was pumped at 50 mL/min to a 20-mL glass syringe sheltered by a silver paper, and H₂O₂ concentration was 100 101 measured within 5 min in the site.

102 (b) H_2O_2 measurement in the field. H_2O_2 concentration was measured in site by chemiluminescing reaction with acridinium ester (AE, 10-methyl-9-103 the acridinium carboxylate trifluoromethanesulfonate, (p-formylphenyl) Cayman 104 Chemical, USA).^{1,2} AE reagent of 2 µM was prepared daily by adding a refrigerated 105 AE stock solution (565 µM) to 1.0 mM phosphate buffer (pH 3.0). Carbonate buffer 106 (100 mM, pH 11.3) was prepared weekly. To eliminate the background H₂O₂, 107 deionized water containing 1.0 mg/L catalase (Sigma-Aldrich) was used to prepare 108 109 the solutions at least 24 h ahead. The remaining catalase could react with the H₂O₂ in the sample, but the loss of H_2O_2 was negligible because the half-life of H_2O_2 in the 110 presence of 1.0 mg/L catalase (45 min) was much longer than the time of flow 111 injection analysis (<30 s). Groundwater was mixed with 0.5 or 1 mM 112 1,10-phenanthroline (phen) to screen the interfere of reduced metals, i.e., Fe(II), 113 before it was pumped to a flow cell and mixed with the deoxygenated AE regent and 114 115 0.1 M carbonate (pH 11.3). Interferences of reduced metals in groundwater and of 116 Fe(phen)₃ due to photon absorption could be screened by using groundwater matrix as the background for calibration curves (Text S2). The emitted luminescence at 470 nm 117 was detected by flow injection analysis using a chemiluminesce instrument (IFFM-E, 118 Xi'an Ruimai Analytical Instrument Co., Ltd., Xi'an, China). The H₂O₂ 119 concentrations were determined by applying a calibration factor to the blank values. 120 The calibration factor was determined by the standard addition of H_2O_2 into each 121 groundwater sample. Groundwater samples with addition of 8 mg/L catalase (H₂O₂ 122 decay half-life is 5.6 min under this condition) and after reaction for 12 min were 123 utilized as the blanks. It is notable that all the samples, blanks, and data points for the 124 calibration curves were measured one by one using the groundwater that was 125 immediately pumped out from the wells. The detection limit of H₂O₂ in the 126 groundwater was 5.0 nM. 127

(c) Groundwater chemistry analysis. The groundwater passed through a gastight
chamber with different probes for measuring dissolved oxygen (DO),
oxidation-reduction potential (Eh), pH and electrical conductivity (EC). Groundwater
DO was measured in site by a DO meter (JPB-607A, LeiCi, China), and Eh, pH and
EC values were measured using a portable meter (HQ40D Field Case, HACH, USA).

133 Ferrous ion was measured in site after coloration with 1,10-phenanthroline by a portable spectrophotometer (HACH, 1900, USA). Two portions of groundwater were 134 collected in 50-mL centrifuge tubes for later analysis in lab. One was acidified with 135 concentrated HCl for dissolved organic carbon (DOC) measurement, and the other 136 one was frozen at -20 °C for anions measurement. Cations were determined by 137 inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer SCIEX 138 ICP-Mass Spectrometer ELAN DRC II). Anions were measured by an ionic 139 140 chromatography equipped with a suppressed conductivity detector (Metrohm 761 compact IC), a Metrosep A Supp 4 analytical column (250×4.0 mm) and a Metrosep 141 A Supp 4/5 guard column. DOC was measured on a TOC analyzer (TOC-L CPH/CPN, 142 Shimadzu, Japan). 143

(d) Sediment collection and storage. Sediment cores of 4-m depth were drilled at 144 JB4 and ST1 locations by a handheld soil sampling drill (SD-1, Australia) on October 145 25, 2017. Immediately after drilled to the ground, the sediments were wrapped tightly 146 by a foil. The wrapped sediments were sealed in a plastic bag under vacuum. They 147 were then transported to the lab and refrigerated at 4 °C in the dark. Wet sediments 148 149 were used for the measurements of 6 M HCl-extractable Fe(II) and of H₂O₂ production upon oxygenation in lab experiments. In order to avoid the artifact due to 150 possible air oxidation, we carefully abandoned the surface layers of wet sediments and 151 used the core for the measurements and experiments. For XRF and XRD analysis, the 152 sediments were dried in a vacuum freezer dryer (Lab-1A-50E, Biocool, China) and 153 passed through a 200-mesh screen. The main elemental compositions were 154 determined by X-ray fluorescence spectrometer (Epsilon 3 XLE, Panalytical, 155 Holland). The sediments were characterized by X-ray diffractometer (XRD) on a 156 D8–FOCUS X–ray diffractometer with Cu K radiation (Bruker AXS., Germany) at 40 157 kV and 40 mA, at a scanning step size of 0.01 and step time of 0.05s. A small degree 158 159 of sediment oxidation is inevitable during these processes, but the results do not 160 influence the mechanistic discussion.

161

162 Text S2: Strategies for screening the interferes in H₂O₂ measurement

163 H_2O_2 measurement by acridinium ester (AE) method has been used previously in 164 several field studies.³⁻⁵ However, this method could be potentially interfered by the 165 reduced transition metals in groundwater matrix and by Fe(phen)₃ using 166 phenanthroline as stabilizing agent due to photon absorption. Thus, special strategies 167 were employed to screen the interferes, as described below.

(a) Strategies for screening the interfere of reduced transition metals in 168 groundwater matrix. We employed two strategies to screen the interfere of reduced 169 transition metals in groundwater matrix when we did the field measurement. First, we 170 171 added phenanthroline to stabilize the reduced transition metals. Phenanthroline 172 stabilizes reduced transition metals more strongly than diethylenetriaminepentaacetic acid (DTPA) that has been used previously.³ For example, the complex constant for 173 phenanthroline and Fe(II), the most important reduced transition metals in 174 groundwater, is about 3 orders of magnitude higher than that for DTPA and Fe(II) 175 $(10^{21.4} \text{ versus } 10^{18})$.⁶ We evaluated the influence of different Fe(II) concentrations on 176

177 H₂O₂ measurement in deionized water. Using 0.5 mM phenanthroline as background, presence of less than 20 µM Fe(II), the most common concentration levels measured 178 in our samples, did not significantly influence the measurements (Figure S23a, p < p179 0.01), and presence of 80 μ M Fe(II) slightly influenced the measurements. In all the 180 tested Fe(II) concentrations ($\leq 260 \ \mu$ M), good linear correlation (R² > 0.95) appeared 181 182 for all the calibration curves (Figure S23, Table S6), which proved the applicability of measurements when the same background solution was used for making the 183 calibration curves. As a result, phenanthroline was added at the same time when 184 groundwater samples were pumped out from the polyvinyl chloride (PVC) pipes to 185 screen the interference of reduced transition metals, particularly Fe(II). After 186 measurement of Fe(II) concentration in the field, H₂O₂ was measured with added 187 phenanthroline concentrations at 0.5 and 1 mM for Fe(II) concentrations lower and 188 higher than 80 µM Fe(II), respectively. 189

190 Then, we specially made calibration curves for each groundwater sample using the sampled groundwater matrix, instead of deionized water, as the background solution. 191 Note that phenanthroline was added before the contact with AE agent. Phenanthroline 192 193 concentration (0.5 or 1 mM) was set according to the groundwater Fe(II) 194 concentration that had been determined before H₂O₂ measurement. Two representative calibration curves for two groundwater samples with different Fe(II) concentrations 195 (8.65 and 1.01 μ M) are shown in Figure S24. As can be seen, good correlation (R² > 196 0.98, p < 0.01) was obtained regardless of different intercepts and slopes. During field 197 measurement, the intensity sensitivity of our chemiluminesce instrument was about 20 198 199 unit (the readable limit is 1 unit), which was translated to 0.51 and 0.76 nM H₂O₂ using the two calibration curves. This concentration variation is acceptable for the 200 concentration levels (i.e., several tens of nM) in our field measurements. Therefore, 201 the AE method is applicable to H_2O_2 measurement in the field when the specific 202 203 groundwater matrix was used as the background solution for making the calibration 204 curves.

(b) Strategies for screening the interfere of $Fe(phen)_3$ using phenanthroline as 205 stabilizing agent due to photon absorption. To evaluate the photon absorption by 206 Fe(phen)₃, we first scanned the UV-vis spectra of different concentrations of Fe(II) 207 and Fe(III) complexed by phenanthroline. The pH was adjusted to 11, the same as that 208 in AE measurements. Results show that Fe(phen)₃ complex, particularly Fe(II)(phen)₃ 209 210 complex, did absorb photon at 470 nm, and the absorption increased with the increase in Fe concentration (Figure S25). This could be the reason that the intercept of H_2O_2 211 calibration curve decreased with the increase in coexisting Fe(II) concentrations 212 (Table S6). Fortunately, the absorption did not influence the applicability of 213 calibration curve of H₂O₂ measurement because this background absorption could be 214 215 screened when the same groundwater matrix was used as the background solution for making the calibration curves. Another beneficial fact is that most of our groundwater 216 samples contained less than 20 µM Fe(II), which does not strongly absorb photons 217 (Figure S25). 218

219

220 Text S3: Description of kinetic modeling.

221 Reaction network in Table S2 were used for the kinetic modeling. In Table S2, reactions in Parts I and II were used for dissolved Fe(II) oxidation in the absence of 222 HA, and in Part III were used oxidation in the presence of HA. Both complexation 223 and redox reactions between Fe and HA were included. The reactions are detailed as 224 225 follows. In the absence of HA, reactions 1-3 describe H_2O_2 production following the 226 Haber–Weiss mechanism;⁷ reaction 4 represents the regeneration of Fe(II) from Fe(III) reduction by superoxide; reactions 5-8 describe the formation of ferric precipitates 227 and an Fe(II) species adsorbed on the precipitates;⁸⁻¹⁰ reactions 9–12 were set for the 228 reactions for the adsorbed Fe(II) species in analogy to reactions 1-4 for dissolved 229 Fe(II);^{11,12} and reactions 3 and 11 represent the competition of Fe(II) species with 230 horseradish peroxidase and fluorescent agent for H_2O_2 . In the presence of HA, the 231 reactions between HA and Fe were divided into two part: redox and complexation 232 reactions. For the sake of simplicity, the redox part for HA was expressed by MH₂O 233 234 and MSQ species,⁵ and the complexation part for HA was denoted by L ligand. As a result, reactions 13–15 describe the redox interaction between HA and Fe;⁵ reactions 235 16–18 denote the direct reactions between MH₂Q and O₂^{,5} reactions 20–29 represent 236 the complexation reactions between L and Fe as well as the subsequent redox 237 reactions with O_2 and MH_2Q .^{5,13,14} The dissociation reaction was not included because 238 its influence was negligible compared with the formation under tested conditions. 239 Reaction 30 means the trapping of H₂O₂ by horseradish peroxidase and fluorescent 240 agent which follows pseudo-first-order kinetic at low H₂O₂ concentrations. Reaction 241 rate constants were mostly referred to literature,^{5,7-14} with several of them fitted from 242 the experimental data. The rate constants for reactions 13, 14 and 15 (free Fe(III) 243 species) were set as the same as those for reactions 27, 28 and 29 (organic-complexed 244 Fe(III) species), respectively, according to literature survey.¹⁴⁻²⁰ It is notable that the 245 rate constants for reactions 1, 9 and 22 were slightly modified from the reported 246 247 values.

248

249 Text S4: Description of reactive transport modeling

(*a)* General consideration. The influence of water table fluctuations on H_2O_2 distribution was modeled numerically by COMSOL Multiphysics. Distributions of dissolved oxygen (DO), dissolved Fe(II) in groundwater and reduced species in solid were also modeled. The groundwater flow was described by a general variant of Richard equation (eq. S1),^{21,22} and the reactive solute transport was simulated by the advection–dispersion equation (eq. S2).

$$\rho\left(\frac{C_m}{\rho g} + S_e S\right) \frac{\partial p}{\partial t} + \nabla \cdot \rho\left(-kk_r \left(\frac{\nabla p}{\rho g} + \nabla z\right)\right) = Q_m$$

$$\frac{\partial}{\partial t}(\theta C_i) = -\nabla \cdot \rho(uC_i) + \nabla \cdot (D\nabla C_i) + R_i$$
(S1)
(S2)

256

257

258 Where ρ [1000 kg/m³] is water density, p [pa] is pressure, C_m [0.3] is specific water 259 capacity, g [9.8m/s²] is gravity constant, S_e[-] is effective saturation, S [1/pa] is 260 storage coefficient, k [1 m/d] is saturated hydraulic conductivity, k_r[-] is relative

permeability, z [m] is altitude, Q_m [kg/m³·s] is the fluid source or sink. C_i [mol/m³] is 261 the concentration for species i, θ [-] is water content, u [m/s] is Darcy velocity, D 262 $[m^2/s]$ is hydraulic dispersion coefficient, and R_i $[mol/(m^3 \cdot s)]$ is the reaction rate 263 constant for species i. Reaction terms (R_i) were incorporated to represent the 264 generation and decomposition of the reactive species. River water carries DO into the 265 adjacent aquifer. DO is consumed by aerobic microbe and reduced species. Reaction 266 of DO with reduced species generates H_2O_2 . Reduces species also consume H_2O_2 . The 267 reduced species mainly include the dissolved Fe(II) in groundwater and the solid 268 species in aquifer matrix (i.e., Fe(II)-bearing minerals and sediment organic matter 269 (SOM)) according to our measurements. 270

(b) Modeling domain, initial and boundary conditions. To reduce the 271 calculation cost, the modeling domain was constrained to a two-dimension flow 272 section (Figure S26). The modeling aquifer has 30-m width and 4-m height in the left 273 274 and 8-m height in the right. The slopes are 3.8° from 0 to 15 m, 11.3° from 15 m to 25 m, and 18.26° from 25 m to 28 m. The aquifer dimensions were referred to the 275 conditions of our field site, but the flow section was smaller for reducing calculation 276 277 cost. The initial level of river water was set at 5 m. No flow boundary was set for the 278 aquifer bottom and the river centre line. The water head for land boundary in the right was set constant and equal to the normal river water level (5 m). The head in the 279 aquifer top underneath river water was equal to the river water level, and the aquifer 280 top exposed to air was set as no flow boundary. Precipitation and evaporation was not 281 considered. Water level fluctuations were assumed to be sinusoidal curve, with a 282 period of 365 days and an amplitude of 1 m. Water level fluctuations in the river 283 developed a pressure for the groundwater flow in the adjacent aquifer.²³ This pressure 284 was the time derivative of river water level function, which was denoted by Q_m in eq. 285 $1.^{22}$ This method has been proven to be applicable for describing groundwater flow 286 induced by river water fluctuations.^{21,22,24,25} 287

288 (c) Reactions for solute transport. The source of DO in groundwater was attributed to the inflow of river water. The sink of DO was due to the consumption by 289 aerobic microbe and reduced species. Meanwhile, DO consumption generated H₂O₂. 290 291 The initial concentrations of DO and H_2O_2 in groundwater were set at 0. Because of 292 the decrease in reduction potential with aquifer depth, the initial microbe number was set at $1 \times 10^{7/g}$ at the height of 6–8 m, and decreased linearly to $1 \times 10^{4/g}$ at the 293 height of 4 m. No aerobic microbe existed at the height below 4 m. On the contrary, 294 no reduced species existed at the height above 6 m, the reduced species increased 295 linearly from 0.83 mM to 3.59 mM with the decrease in height from 6 to 4 m, and the 296 reduced species was maintained at 3.59 mM below 4 m. The concentrations of DO 297 and Fe(II) in river water were set constant. All the values were referred to our field 298 299 measurements.

The consumption of DO by aerobic microbe was due to the presence of organic matters. As organic matters were excess relative to DO, the consumption can be described simply by eq. S3:

$$R_1 = k_1 \cdot C_{aerobe}$$

(S3)

Where R_1 is the rate of DO consumption by aerobic microbe, and k_1 is the rate constant, and C_{aerobe} is the number of aerobic microbes. During the consumption, DO may partially transform to H₂O₂, which is given by eq. S4:

 $R_2 = k_2 \cdot C_{areobe}$

(S4)

Where R_2 is the rate of DO consumption by aerobic microbes for H_2O_2 generation, and k_2 is the rate constant. DO could be also consumed directly by the reduced species, which also generated H_2O_2 . Meanwhile, the generated H_2O_2 could be decomposed by the reduced species. The reduced species mainly included the dissolved Fe(II) in groundwater and the solid species in aquifer matrix (i.e., Fe(II) –bearing minerals and sediment organic matter (SOM)) according to our measurements. Reactions are described as follows.

 $R_3 = k_3 \cdot C_{do} \cdot C_{Fe(II)} \tag{S5}$

 $R_4 = k_4 \cdot C_{H_2O_2} \cdot C_{Fe(II)} \tag{S6}$

318

$$R_6 = k_6 \cdot C_{H_2O_2} \cdot C_{RS}$$

 $R_5 = k_5 \cdot C_{do} \cdot C_{RS}$

 $R_{Fe(II)} = -R_3 - R_4$

Where R_3 and R_5 are the rates of DO reactions with dissolved Fe(II) and reduced species in solid for H_2O_2 generation, respectively; k_3 and k_5 are the corresponding rate constants for R3 and R5, respectively; R_4 and R_6 are the rates of H_2O_2 reactions with dissolved Fe(II) and reduced species in solid, respectively; k_4 and k_6 are the corresponding rate constants for R4 and R6, respectively; and $C_{Fe(II)}$ and C_{RS} are the concentrations of dissolved Fe(II) in groundwater and total reduced species in aquifer matrix. Combinations of generation and decomposition terms give:

(S7)

(S8)

(S10)

(S11)

326

$$R_{do} = -R_1 - R_3 - R_5 \tag{S9}$$

327

 $R_{RS} = -R_5 - R_6$

328 329

 $R_{H_2O_2} = R_2 + R_3 - R_4 + R_5 - R_6 \tag{S12}$

(d) Model calculations. The parameters for model settings are listed in Table S7. 330 Most of parameters were obtained from experimental measurements, and some 331 parameters were referred to literature. The aquifer is homogenous and isotropic. The 332 aquifer matrix is fine sand with hydraulic conductivity of 1 m/day. The ratio of 333 horizontal to vertical hydraulic conductivity was set at 10. The domain was 334 discretized to finite element meshes by triangle meshes, and denser meshes were set 335 336 on the top 0.1 m to alleviate the hydraulic gradient between river water and 337 groundwater. The unit size is 0.001 m on the top and 0.1 m in other locations. A total of 41836 meshes were created. The time step was created by the algorithm in 338 339 COMSOL, and the maximum simulation time step is 1 day. The simulation lasts for 365 days. 340

342 Text S5: Role of organic matter in Fe speciation

The association of dissolved Fe(II) with reduced HA was quantified in our 343 previous study.²⁸ In brief, mixed solutions of Fe(II) and HA at different molar ratios 344 (C/Fe: 0~23.3) were equilibrated at pH 7 under anoxic conditions, and then were 345 fractionated by different pore sizes of ultrafiltration membranes. Fe(II) in the size less 346 than 1 nm was considered purely dissolved form, in the size between 1 and 200 nm 347 was considered colloidal form due to complexation with HA, and in the size larger 348 than 200 nm was considered precipitates.²⁸ Note that measurement results validated 349 the predominance of colloidal form for HA whether in the absence or presence of 350 Fe(II).²⁸ The fraction of colloidal Fe(II)–HA complex was found to increase linearly 351 from 0 to 71.8% with the increase in C:Fe molar ratio from 0 to 9.3 ($R^2 = 0.978$, Slope 352 = 7.345, Figure S15), but slowly with the further increase in C:Fe molar ratio to 23 353 (Figure S15). To get insight into the influence of HA on Fe(II) speciation, we further 354 modeled the interactions between them. Due to the particle nature of HA in colloidal 355 form,²⁸ HA–Fe interaction could be explored by the surface complexation model by 356 assuming Fe(II) complexation with HA surface functional groups. Using the 357 parameters listed in Table S8, the fractions of Fe(II) complexed with HA at different 358 C:Fe molar ratios were modeled in Visual MINTEQ with Stockholm Humic Model 359 (SHM).^{29,30} As shown in Figure S15, modeled results matched well with experimental 360 results. Therefore, it is reasonable to use these complexed fractions to further evaluate 361 their influence on H₂O₂ production. 362



Figure S1. Study area adjacent to the Yangtze River. The figure was edited from a map from NASA's Earth Observing System Data and Information System (https://search.earthdata.nasa.gov). NASA promotes the full and open sharing of all data with research and applications communities, private industry, academia, and the general public (https://earthdata.nasa.gov/collaborate/open-data-services-andsoftware).

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Figure S2. (A) Location and (B) lithology of the study area adjacent to the Yangtze

- 376 River. The map in panel A was drawn by hand in Microsoft PowerPoint.
- 377



Figure S3. Historical water level fluctuations in the Yangtze River. The water level
(relative to Wusong elevation) was recorded in the Hankou Hydrological Station (30
km away from the field site).

382



Figure S4. (A) Removal of H_2O_2 in DI water by 0.01 mg/L catalase; (B) influence of remaining catalase on the stability of 100 nM H_2O_2 within 3 h.



Figure S5. Fluorescent microscopy images of bacteria cells stained by live-dead kit 387 (green = live, red = dead) in sediment (a) before and (b) after microwave irradiation 388 treatment. A suspension of 1 g of sediment (ST1 location at 3.4 m depth) in 10-mL 389 deionized water was shocked at 220 rpm for 4 h in the dark. Afterwards, 1-mL 390 391 supernatant was mixed with the fluorescent nucleic acid stains (PI and SYTO9). The number of live (green color) and dead (red color) bacteria was measured on a 392 fluorescent microscope (DM 5000B, 10×HC PLAN ocular, 100× PL APO objective; 393 Leica Microsystems, Wetzlar GmbH, Germany). 394



Figure S6. Depth profiles of (A) H₂O₂, (B) DO and (C) Fe²⁺ concentrations in JB1
location at the stage of low water table. Meaning of "L4" is described in Figure 1B in
the main manuscript.



402 Figure S7. Depth profiles of (A–C) H₂O₂ and (D–F) DO concentrations in JB
403 locations at the stage of rising water tables. Meanings of "L1, L3 and R2" are
404 described in Figure 1B in the main manuscript.
405



406 407 **Figure S8.** Depth profiles of (A) H_2O_2 and (B) DO concentrations in JB locations at 408 the stage of high water tables. Meaning of "L2" is described in Figure 1B in the main 409 manuscript.



412 **Figure S9.** Depth profiles of (A) H_2O_2 , (B) DO and (C) Fe^{2+} concentrations in JB1

- 413 location at the stage of falling water tables. Meanings of "F1 and F2" are described in
- 414 Figure 1B in the main manuscript.
- **41**5



Figure S10. Depth profiles of DO concentrations in ST1 wells. Water table was 2.3 m
below the ground surface on June 17 and June 22, 2017. The dates of sample
detection on site were noted in the legend.

422



- 424 **Figure S11.** Depth profiles of Fe^{2+} concentrations in JB locations at the stage of rising
- 425 water tables. Meaning of "R2" is described in Figure 1B in the main manuscript.



Figure S12. XRD patterns of sediments from JB4 location at 1.6 m depth (green line),
and from ST1 location at 1.4 m depth (red line) and at 3.4 m depth (blue line). The
groundwater level is 0.8 m and 1.2 m (below the ground surface) for ST1 and JB4
locations, respectively, during sampling. Abbreviations are expressed as follows: A,
albite; B, biotite; C, chlorite; I, illite; Q, quartz; S, smectite.



Figure S13. Variation of Fe(II) content with sediment depth at (A) ST1 and (B) JB4
location. The Fe(II) was extracted using 6 M HCl for 24 h.



437 **Figure S14.** Representative time profile of H_2O_2 production upon oxygenation of (A) 438 sediments and (B) synthetic groundwater at different site and depths. The groundwater 439 level is 0.8 m for ST1 well and 1.2 m for JB4 well (below the ground). All the 440 oxidation experiments were performed under the air condition.

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- 442



Figure S15. Validation of surface complex model for Fe(II) complexation with HA by
experimental data. Experimental data were extracted from our previous study,²³ in
which Fe(II)–HA complex occurring in colloidal size (1~200 nm) was separated by
ultrafiltration membrane and measured. Fe(II) complexation with HA was modeled by
Visual MINTEQ using Stockholm Humic Model (SHM) with parameters given in
Table S8.



452 **Figure S16.** Relative importance of reactions no. 1-29 in Table S2 for H₂O₂ 453 production at (a, c) 1 and (b, d) 20 min during oxygenation of Fe(II) in the absence (a, 454 b) and (c, d) presence of HA. The modeling settings are the same as those in Figure 4 455 in the main manuscript. X-axis, modeled reactions in Table S2 without inclusion of 456 reactions 3, 11, 19 and 24 for H₂O₂ decomposition; Y-axis, normalized sensitivity

457 coefficients (NSCs). The reactions with large positive NSCs represent major sources,

- 458 whereas those with large negative NSCs denote major sinks.³¹
- 459



463 **Figure S17.** Modeled variations of (a) total Fe(II), (b) Fe(II) complexed with HA, and 464 (c) cumulative H_2O_2 concentrations during Fe(II)–HA oxygenation with fixed Fe(II)

but different HA concentrations. The reaction network for modeling were listed in Table S2, with the removal of the decomposition reactions of H_2O_2 by reduced species. Reduced HA was used as DOC proxy for modeling. Fe(II) and DO concentrations were set constant at 5 and 250 μ M, respectively. Reaction pH was set at 7.0.



471 Figure S18. Modeled variations of (a) total Fe(II), (b) Fe(II) complexed with HA, and

472 (c) cumulative H_2O_2 concentrations during Fe(II)–HA oxygenation with fixed HA but 473 different Fe(II) concentrations. The reaction network for modeling were listed in 474 Table S2, with the removal of the decomposition reactions of H_2O_2 by reduced species. 475 Reduced HA was used as DOC proxy for modeling. DOC and DO concentrations 476 were set constant at 100 and 250 μ M, respectively. Reaction pH was set at 7.0. 477



479 Figure S19. H₂O₂ generation from simulated groundwater under different redox
480 conditions. The simulated groundwater was prepared by soaking the sediments from
481 (A) ST1 location at 1.4 m depth and (B) JB4 location at 1.6 m depth.

- 482
- 483



485 **Figure S20.** Modeled variations of (a) total Fe(II), (b) Fe(II) complexed with HA, and 486 (c) cumulative H_2O_2 concentrations during Fe(II)–HA oxygenation at different initial 487 DO concentrations. The reaction network for modeling were listed in Table S2, with 488 the removal of the decomposition reactions of H_2O_2 by reduced species. Reduced HA 489 was used as DOC proxy for modeling. Fe(II) and HA concentrations were set constant 490 at 5 and 100 μ M, respectively. Reaction pH was set at 7.0.



491

493 Figure S21. Modeled water flow and distributions of DO, dissolved Fe(II) and
494 reduced species in solid at different stage of water table fluctuations. Modeling
495 settings are given in Text S4.

496



497

498 **Figure S22.** Effect of speed of river water level rise on cumulative H_2O_2 in the 499 modeled domain. Note that cumulative H_2O_2 means the integration of H_2O_2 500 concentration at different locations with the modeling area. Modeling settings are 501 given in Text S4.



Figure S23. Effect of Fe(II) concentrations on the calibration curves of H_2O_2 504 505 measurement in deionized water. The pH of the samples was 6.6-7.4 and the measurement procedure was the same as described for the field in Text S1. As results 506 in (a) and (b) were measured at different time using two AE agents that were 507 purchased at different time, the intensity appeared to be different to some extent. It is 508 notable that the sample intensity may vary according to the adjustment of instrumental 509 parameters, which is not like the case for UV. For different groundwater background, 510 we adjusted the instrumental parameters (i.e., photo multiplier tube (PMT) voltage) to 511 optimize the intensity for calibration curves. 512 513



Figure S24. Two representative calibration curves of H₂O₂ measurement using 515 groundwater matrix as the background solution. Fe(II) concentrations in the 516 groundwater samples from ST1 1.6 and 3.4 m were 8.65 and 1.01 µM, respectively. It 517 is notable that the sample intensity may vary according to the adjustment of 518 instrumental parameters besides the difference of calibration background, which is not 519 the same as for UV measurements. For different groundwater background, we 520 adjusted the instrumental parameters (i.e., photo multiplier tube (PMT) voltage) to 521 optimize the intensity for calibration curves. 522



Figure S25. UV-vis spectra of different concentrations of Fe(II) and Fe(III) complexed by phenanthroline. The pH of the Fe(phen)₃ solution was adjusted to 11, the same as that in AE measurement. The concentration of phenanthroline was 0.5 and 1 mM for Fe concentrations lower and higher than 80 µM Fe, respectively.



Name	Cl ⁻ (mg/L)	NO ₃ ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	NPOC (mg/L)	IC (mg/L)	Fe ²⁺ (mg/L)
ST1-0.2 m	0.59	ND	0.64	1.73	8.25	ND
ST1-0.6 m	0.32	ND	1.40	1.13	12.44	ND
ST1-1.4 m	0.61	ND	0.92	1.23	10.41	ND
ST1-2.0 m	0.56	ND	Ν	1.99	6.59	ND
ST1-3.4 m	0.62	ND	1.73	1.23	9.01	ND
JB6-0.6 m	0.71	ND	1.94	2.48	11.32	ND
JB6–1.6 m	0.64	ND	3.03	1.90	11.86	ND
JB6–2.8 m	0.59	ND	1.84	2.35	13.23	ND
JB6–3.4 m	0.78	ND	2.00	2.42	10.65	ND

536 **Table S1.** Main components of simulated groundwater

Table S2. Reaction network for modeling Fe(II) oxidation and H_2O_2 accumulation

	No.	Reactions	Rate Constant	Source
	1	$Fe(II) + O_2 \rightarrow Fe(III) + \bullet O_2^-$	$0.3 \text{ M}^{-1}\text{s}^{-1}$	Ref. 7
I	2	$Fe(II) + \bullet O_2^- \rightarrow Fe(III) + H_2O_2$	$1.00 \times 10^7 \text{ M}^{-1} \text{s}^{-1}$	Ref. 7
	3	$Fe(II) + H_2O_2 \rightarrow Fe(III) + \bullet OH + OH^-$	$4.79 \times 10^3 \text{ M}^{-1} \text{s}^{-1}$	Ref. 7
	4	$Fe(III) + \bullet O_2^- \rightarrow Fe(II) + O_2$	$1.50 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$	Ref. 7
	5 ^a	$Fe(III) + Fe(III) \rightarrow LEP + LEP$	$3.40 \times 10^{6} \text{ M}^{-1} \text{s}^{-1}$	Ref. 8
	6	$Fe(III) + LEP \rightarrow LEP + LEP$	$3.40 \times 10^{6} \text{ M}^{-1} \text{s}^{-1}$	Ref. 8
	7	$Fe(II) + LEP \rightarrow FeII-LEP$	$1.00 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$	Ref. 9
П	8	$FeII-LEP \rightarrow Fe(II) + LEP$	$2.30 \times 10^3 \text{ s}^{-1}$	Ref. 9
	9 ^b	$FeII-LEP + O_2 \rightarrow LEP + LEP_i + \bullet O_2^-$	$7.0 \text{ M}^{-1}\text{s}^{-1}$	Ref. 10
	10	$FeII-LEP + \bullet O_2^- \rightarrow LEP + LEP_i + H_2O_2$	$1.00 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	Ref. 7
	11	$FeII\text{-}LEP + H_2O_2 \rightarrow LEP + LEP_i + \bullet OH + OH^-$	$4.79 \times 10^3 \text{ M}^{-1} \text{s}^{-1}$	Ref. 7
	12	$\text{LEP} + \bullet \text{O}_2^- \rightarrow \text{Fe(II)} + \text{LEP} + \text{O}_2$	6.50×10 ⁻² M ⁻¹ s ⁻¹	Ref. 11
	13 ^c	$MH_2Q + Fe(III) \rightarrow Fe(II) + MSQ^{-1}$	$2.4 \times 10^3 \text{ M}^{-1} \text{s}^{-1}$	Ref. 5
	14 ^d	$MSQ^{-} + Fe(III) \rightarrow Fe(II) + MBQ$	$1.2 \times 10^7 \text{ M}^{-1} \text{s}^{-1}$	Ref. 5
	15	$MSQ^{-} + Fe(II) \rightarrow MH_2Q + Fe(III)$	$1.0 \times 10^5 \text{ M}^{-1} \text{s}^{-1}$	Ref. 5
	16	$MSQ^- + O_2 \rightarrow MBQ + \bullet O_2^-$	$1.5 \times 10^{6} \text{ M}^{-1} \text{s}^{-1}$	Ref. 5
	17	$MH_2Q + \bullet O_2^- \longrightarrow MSQ^- + H_2O_2$	$7.0 \times 10^5 \text{ M}^{-1} \text{s}^{-1}$	Ref. 5
	18	$MBQ + \bullet O_2^- \to MSQ^- + O_2$	$3.3 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$	Ref. 5
III	19	$MH_2Q + H_2O_2 \longrightarrow MBQ + 2OH^-$	$4.79 \times 10^3 \text{ M}^{-1} \text{s}^{-1}$	Fitted
	20 ^e	$L + Fe(II) \rightarrow Fe(II)-L$	$2.45 \times 10^4 \text{ M}^{-1} \text{s}^{-1}$	Ref. 13
	21	$Fe(II)$ - $L \rightarrow L + Fe(II)$	7.87×10 ⁻⁴ s ⁻¹	Ref. 13
	22	$Fe(II)$ -L + O ₂ \rightarrow $Fe(III)$ -L + \bullet O ₂ ⁻	$2.0 \times 10^1 \text{ M}^{-1} \text{s}^{-1}$	Ref. 14

23	$Fe(II)-L + \bullet O_2^- \rightarrow Fe(III)-L + H_2O_2$	$1.00 \times 10^7 \text{ M}^{-1} \text{s}^{-1}$	Ref. 14
24	$Fe(II)$ -L + H ₂ O ₂ \rightarrow Fe(III)-L + •OH + OH ⁻	$4.79 \times 10^3 \text{ M}^{-1} \text{s}^{-1}$	Ref. 7,14
25	$Fe(III)-L + \bullet O_2^- \to Fe(II)-L + O_2$	$1.5 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$	Ref. 14
26	$L + Fe(III) \rightarrow Fe(III)-L$	$6.0 \times 10^{6} M^{-1} s^{-1}$	Ref. 13
27	$MH_2Q + Fe(III)-L \rightarrow Fe(II)-L + MSQ^{-1}$	$2.4 \times 10^3 \text{ M}^{-1} \text{s}^{-1}$	Ref. 5
28	$MSQ^{-} + Fe(III)-L \rightarrow Fe(II)-L + MBQ$	$1.2 \times 10^7 \text{ M}^{-1} \text{s}^{-1}$	Ref. 5
29	$MSQ^{-} + Fe(II)-L \rightarrow MH_2Q + Fe(III)-L$	$1.0 \times 10^5 \text{ M}^{-1} \text{s}^{-1}$	Ref. 5
30 ^f	H_2O_2 HRP+ADHP $X + 2OH^-$	7.0×10 ⁻³ s ⁻¹	Fitted

^{*a*}LEP is lepidocrocite which represents the main composition of precipitates; ^{*b*}LEP_i is non-reactive lepidocrocite; ^cMH₂Q is hydroquinone group in HA; ^dMSQ⁻ is semiquinone groups in HA, and MBQ is quinone groups in HA; eL is the ligands of carboxyl and phenolic functional groups in HA; ^fThe symbol of "X" represents the measured cumulative H₂O₂ concentrations. DO concentration was set constant at 250 µM; MH₂Q concentration was set referring to the measured electron donating capacity (EDC), and the differences of EDC before and after reactions were assigned to 2.6 and 6.2 µM, respectively, for 250 µM HAox and 250 µM HAred; all the other initial concentrations were assigned to the experimental values.

538 539

Table S3. Water table and H_2O_2 , DO and Fe^{2+} concentrations at JB locations									
Stage of Water Table Fluctuations ^a	Well Name	Water Table (m) ^b	Sampling Depth (m) ^b	рН	H ₂ O ₂ (nM)	DO (µM)	Fe ²⁺ (µM)		
T 1	JB3	2.0	$2.0\sim 4.0$	6.91 ~ 7.18	~ 34	16~ 144	-		
LI	JB4	2.6	$3.0 \sim 4.0$	6.91 ~ 7.16	~ 42	ND	-		
	JB2	1.0	1.1 ~ 3.6	7.38~7.63	~ 27	150 ~	-		
L2	JB3	1.9	$2.0\sim4.0$	-	~ 18	9 ~ 119	-		
	JB4	2.6	$3.0 \sim 4.0$	-	ND	~ 6	-		
13	JB4	1.0	1.5 ~ 4.0	6.77 ~ 7.22	~ 53	~ 19	-		
LS	JB5	2.5	2.9 ~ 3.9	6.89 ~ 7.16	15 ~ 65	3~ 6	-		
L4	JB1	0.7	1.0 ~ 3.6	6.82 ~ 7.61	~ 29	~ 41	0.4 ~		
D)	JB3	0.7	0.7 ~ 3.5	7.57 ~ 7.84	~ 50	~ 94	1.6 ~ 9.9		
K2	JB4	1.2	1.3 ~ 2.7	7.18 ~ 7.40	~ 7	~ 6	$0.4 \sim 4.1$		
F1	JB1	0.4	0.5 ~ 2.8	7.31 ~ 7.51	ND	~ 3	0.1~33		
F2	JB1	0.8	1.0 ~ 3.6	7.11 ~ 7.52	ND	~ 113	1.0~82.0		

540 541

^a Labels in this column have the same meaning as those described in Figure 1 in the main manuscript; ^b Values in this column mean the depth below the ground surface.

Table S4. Groundwater chemistry at ST1 location 544

Sampling	pН	Eh	EC	Cl-	NO ₃ -	SO4 ²⁻	NPOC
depth (m) $^{\mathbf{a}}$		(mV)	(µs/cm)	(mg/L)	(mg/L)	(mg/L)	(mg/L)

1.20	7.75	64	810	10.8	0.25	25.7	1.74
1.60	7.16	14.7	824	9.2	0.24	21.7	1.07
2.00	7.19	-30.5	695	10.7	ND	19.1	1.31
2.40	7.12	20.9	624	10.3	0.255	26.1	0.65
2.90	7.01	14	683	8.6	ND	5.0	1.41
3.40	7.08	32.9	641	7.2	ND	6.0	1.81

^a Values in this column mean the depth below the ground surface. The groundwater
table was 1.0 meter below the ground surface. Note the analysis was performed on
September 23, 2017.

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Location	Depth (m)	SiO ₂ (%)	Al ₂ O ₃ (%)	Na ₂ O (%)	MgO (%)	K2O (%)	CaO (%)	Mn (ppm)	Fe ₂ O ₃ (%)	P (ppm)	Ti (ppm)	TOC (%)
	0.2	67.73	9.75	1.95	2.03	2.02	5.22	450.9	3.50	739.0	3669.5	1.42
	0.6	65.02	12.06	1.63	2.23	2.10	4.48	509.0	4.69	860.5	4651.0	2.44
ST1	1.4	63.02	12.64	1.55	2.37	2.21	4.79	603.5	5.23	847.3	5451.8	1.52
	2.0	69.91	10.95	2.03	2.40	2.06	5.28	652.2	4.18	791.2	4859.8	0.21
	3.4	71.34	10.19	2.11	1.93	2.19	4.68	451.6	3.36	632.9	3410.1	0.99
	0.6	61.94	12.71	1.47	2.34	2.21	4.68	612.3	5.28	820.0	4464.9	0.16
JB4	1.6	60.58	14.05	1.29	2.31	2.15	4.06	1037.6	5.81	1052.9	5173.8	-
	2.8	66.37	9.85	1.65	2.34	1.58	5.51	720.5	4.42	976.5	5677.2	1.00
	3.4	63.08	11.11	1.58	2.51	1.90	5.28	474.2	4.78	871.4	5076.7	2.32

Table S5. Sediment compositions for ST1 and JB4 locations

Table S6. Results summarized for the calibration curves of H_2O_2 in Figure S23

Figure S23a	Slope	Intercept	R-Square
Deionized water	29.0	2865	0.997
0.5 mM phen	25.6	2253	0.999
0.5 mM phen + 5 μ M Fe(II)	24.0	2278	0.995
0.5 mM phen + 20 µM Fe(II)	22.6	2144	0.997
Figure S23b	Slope	Intercept	R-Square
DI water	22.9	2669	0.998
0.5 mM phen	19.9	2281	0.999
$0.5 \text{ mM phen} + 80 \mu \text{M Fe(II)}$	15.4	1900	0.997
1 mM phen	15.6	2031	0.998
1 mM phen + 260 µM Fe(II)	10.3	1324	0.958

Parameter	Value	Unit	Source
For water flow			
Hydraulic conductivity	1	m/d	Determined
Porosity	0.3		Ref.26
Saturated water content	0.25		Ref. 22
Residual water content	0.1		Ref. 27
Longitudinal dispersivity	1	m	Ref. 22
van Genuchten (α)	10	1/m	Ref. 22
van Genuchten (n)	2		Ref. 22
Period (T)	12-720	d	
Amplitude (A)	1	m	
For reactive solute transport			
DO concentration in river water	0.25	mol/m³	
Dissolved Fe(II) concentration in groundwater	0.02	mol/m ³	Determined
Aerobic microbe number in sediment	0-1E7	1/g	Determined
Reduced species content in sediment	0-5.13	mol/m ³	Determined
Aerobic reaction rate constant(k1)	5.00E-03	1/h	Determined
Rate constant of microbial H2O2 production (k2)	1.00E-06	1/h	Ref. 4
Rate constant of H ₂ O ₂ production from Fe(II) oxygenation (k ₃)	1.24	L/(s·mol)	Ref. 5
Rate constant of H_2O_2 decomposition by Fe(II) (k ₄)	3400	$L/(s \cdot mol)$	Ref. 5
Rate constant of H ₂ O ₂ production from oxygenation of reduced species in sediments (k ₅)	0.2115	L/(s·mol)	Determined
Rate constant of H ₂ O ₂ decomposition by reduced species in sediments (k ₆)	58.23	L/(s·mol)	Determined

Table S7. Parameters for reactive transport modeling

	1 1	
Parameters	Description	Value
nA	Abundance of type A sites (mol g ⁻¹)	0.00427 ^a
n _B	Abundance of type B sites (mol g ⁻¹)	0.00213 ^a
pK _A	Intrinsic proton dissociation constant for A sites	4.1 ^b
pK_B	Intrinsic proton dissociation constant for B sites	8.8 ^b
$ riangle pK_A$	Distribution term that modifies pK _A	2.1 ^b
$\triangle pK_B$	Distribution term that modifies pK _B	3.6 ^b
Log K _{MA}	Intrinsic equilibrium constant for metal binding at type	2.19 ^b
	A sites	
Log K _{MB}	Intrinsic equilibrium constant for metal binding at type	4.46 ^b
	B sites	

561 Table S8. Parameters for surface complexation model of Fe(II) adsorption on HA

^a Type A and B sites refer to the surface carboxyl and phenolic groups on HA. The content of carboxyl groups in HA for Type A sites was determined to be 4.25 mmol/g experimentally in our previous study,¹ which was translated to 0.00427 mol/g. The abundance of Type B sites for phenolic groups was generally assigned to be one half of Type A sites. ^b These parameters were set referring to a previous study with similar modeling Fe(II) adsorption on HA.^{29,30}

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