Supporting Information for:

Trace Element Removal in Distributed Drinking Water Treatment Systems by Cathodic H$_2$O$_2$ Production and UV Photolysis

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1. INTRODUCTION

1.1 Electronic absorption and irradiance spectra

![UV-visible absorbance spectra](image)

**Figure S1.** UV-visible absorbance spectra of Suwannee River natural organic matter (pH 9; 0.5 mgC L$^{-1}$; left y-axis). Spectral photon flux of solar sunlight and from a low-pressure UV lamp per nm increment quantified using a spectroradiometer (right y-axis).

2. MATERIALS AND METHODS

2.1 HO$^\cdot$ yield from UV photolysis of NO$_3^-$ counter-ions

HO$^\cdot$ is formed through the photolysis of H$_2$O$_2$, NO$_3^-$, and NOM. The formation rate of HO$^\cdot$ from the photolysis of H$_2$O$_2$ can be expressed as:

$$R_{\text{form, HO}^\cdot, H_2O_2} = 2k'_{H_2O_2}$$
\[
k'_{\text{H}_2\text{O}_2} = S_{254} \frac{l_{254}^\circ \varepsilon_{254} \Phi_{254}[1 - 10^{-\alpha z}]}{\alpha z} [\text{H}_2\text{O}_2]
\]

where \(l_{254}^\circ\) is the incident photon fluence rate (Ei m\(^{-2}\) s\(^{-1}\)) at 254 nm, \(\varepsilon_{254}\) is the decadic molar extinction coefficient of the organic compound at 254 nm (M\(^{-1}\) cm\(^{-1}\)), \(\Phi_{254}\) is the quantum yield at 254 nm (mol Ei\(^{-1}\)), \(\alpha\) is the solution absorbance (cm\(^{-1}\)), and \(z\) is the light path length (cm). \(S_{254}\) is the screening factor of the water due to light absorption from NOM and other constituents that absorb light at 254 nm:

\[
S_{254} \approx \frac{[1 - 10^{-\alpha z}]}{(2.3)(1.2)\alpha z}
\]

\(R_{\text{form,H0,NO}_3}\) and \(R_{\text{form,H0,DOM}}\) are the formation rates (M s\(^{-1}\)) of HO\(^*\) from \(\text{NO}_3^-\), and NOM, which may be calculated using:

\[
R_{\text{form,H0,NO}_3} = S_{254} \frac{l_{254}^\circ \varepsilon_{\text{NO}_3}^{254} \Phi_{\text{NO}_3}^{254} [1 - 10^{-\alpha z}]}{\alpha z} [\text{NO}_3^-]
\]

\[
R_{\text{form,H0,NOM}} = \frac{l_{254}^\circ \Phi_{\text{NOM,254}} [1 - 10^{-\alpha z}]}{\alpha}
\]

Compound specific parameters are listed below (Table S1). Trace metals and divalent cations from 1% nitric acid stocks (0.159 M) were diluted 670 times into the 4 L influent vessel.

**Table S1.** Concentrations, molar absorptivities, and quantum yields of solution constituents.

| Species | \(\text{H}_2\text{O}_2\) \((^2)\) | \(\text{NO}_3^-\) \((^3)\) | NOM\(^1\) |
|---------|-------------------------------|-----------------|---------|
| \(\varepsilon_{254}\) (M\(^{-1}\) cm\(^{-1}\)) | 18.6 | 4 | - |
| \(\Phi_{254}\) | 1 | 1.6 \times 10^{-2} | 3.7 \times 10^{-5} |
| Conc (M) | \(-0.5 \times 10^3\) | 240 \times 10^6 | 0.5\(^a\) |

\(^a\)NOM concentration is given in mgC L\(^{-1}\).

Given \(z = 0.043\) m, where \(l_{254}^\circ = 106.9\) \(\mu\)Ei m\(^{-2}\) s\(^{-1}\), and \(\alpha = 3.93\) m\(^{-1}\), we obtain:

\[
R_{\text{form,H0*,H}_2\text{O}_2} = 6.18 \times 10^{-4}\text{ M s}^{-1}
\]
\[ R_{\text{form}, \text{HO}^* \text{NO}_3^-} = 1.03 \times 10^{-6} \text{ M s}^{-1} \]

HO\(^*\) formed from the photolysis of NO\(_3^-\) amounts to 0.17\% of the HO\(^*\) formed from the photolysis of H\(_2\)O\(_2\) and is therefore considered to have a negligible effect on the transformation processes.

### 2.2 Gas diffusion cathode fabrication

The gas diffusion cathode was created by modifying carbon fiber paper (AvCarb P75T, 10 × 10cm\(^2\), Fuel Cell Store, College Station, TX) with a conductive, hydrophobic support layer and a carbon catalyst\(^4\). The air-facing side of the cathode was prepared by coating a mixture of 60 wt\% PTFE and 30 wt\% graphite powder (200 mesh, Alfa Aesar, Ward Hill, MA) onto one side of the carbon base layer. The cathode was then air-dried at room temperature, followed by sintering at 350\(^\circ\)C for 40 minutes. The liquid-facing side was prepared by applying a mixture of 3 mL propanol with 150 mg carbon black (Cabot Black Pearls 2000, Cabot, Boston, MA) and 50 mg PTFE onto the other side of the carbon base layer. The cathode was again air-dried at room temperature, followed by sintering at 350\(^\circ\)C for 40 minutes.

Separation of anode and cathode chambers via a cation exchange membrane creates a basic catholyte, favoring H\(_2\)O\(_2\) production, while minimizing wasteful oxidation of H\(_2\)O\(_2\) at the anode. More significantly, recirculation of the H\(_2\)O\(_2\)-containing catholyte to the anode following photolysis provides a means of quenching reactive chlorine and minimizes halogenated byproduct accumulation.
2.3 Absorbance spectra of reactive intermediate quenchers

A series of quencher experiments were conducted to determine the contributions of photochemically produced reactive intermediates to Fe-NOM phototransformation. Due to significant light absorption of many compounds at 254 nm, which would screen incident UV light and influence photolysis, UV-visible absorption spectra were recorded for different concentrations of the sodium azide (\(^1\text{O}_2\) quencher) as well as sorbic acid, 2,4,6-trimethylphenol, and isoprene (\(^3\)NOM quenchers). Results indicate that 50 µM sodium azide and 500 µM isoprene could be employed due to the small overlap between their light absorption spectra and that of Suwannee River NOM, therefore minimizing light screening to an acceptable level (6.2% and 0.9%, respectively).
2.4 NOM characterization by mass spectroscopy

Double bond equivalents (DBE) were calculated as: \( \{C - 0.5(H) + 1\} \).\(^5\) NOM average apparent molecular weight (MW\(_{NOM,Avg}\)), H/C ratio (H/C\(_{Avg}\)), O/C ratio (O/C\(_{Avg}\)), and DBE (DBE\(_{Avg}\))
were calculated as the weighted average of the peak intensity of a given chemical formula with either the molecular weight, H/C ratio, or O/C ratio, respectively:

$$MW_{NOM, Avg} = \frac{\sum MW_i \times P_i}{\sum P_i}$$

$$H/C_{Avg} = \frac{\sum H/C_i \times P_i}{\sum P_i}$$

$$O/C_{Avg} = \frac{\sum O/C_i \times P_i}{\sum P_i}$$

$$DBE_{Avg} = \frac{\sum DBE_i \times P_i}{\sum P_i}$$

where $MW_i$, $H/C_i$, $O/C_i$, and $DBE_i$ are the molecular weight, H/C ratio, O/C ratio, and DBE of a distinct chemical formula, $i$, and $P_i$ is the peak intensity. An example calculation to determine weighted standard deviations is provided below:

$$MW_{NOM, STD} = \sqrt{\frac{\sum P_i \times (MW_i - MW_{NOM, Avg})^2}{\left(\frac{N - 1}{N}\right) \sum P_i}}$$

where $N$ is the number of observations.

2.5 Absorbance measurements and spectral slope calculations

Absorption spectra, $A(\lambda)$, of the different electrolytes were recorded. To isolate the absorbance of the electrolyte solely due to NOM, the absorbance spectra was deconvoluted by subtracting the absorbance spectra of the background electrolytes (i.e., $Ca^{2+}$ and $Mg^{2+}$, $H_2O_2$ at each treatment location, $NO_3^-$, and the $HCO_3^-$ and halides comprising the synthetic groundwater).
Spectral slope coefficients of the NOM absorption spectra, $S$ (nm$^{-1}$), were obtained by nonlinear least-squares fitting of NOM absorption data from $\lambda = 275$ to 295 and 240 to 500 nm using a single exponential decay function in MATLAB$^7,8$

$$a(\lambda) = a(\lambda_{ref}) \exp(-S(\lambda - \lambda_{ref}))$$

where $\lambda_{ref} = 350$ nm for the 275 to 295 nm range and $\lambda_{ref} = 500$ nm for the 240 to 500 nm range.
2.6 Linear sweep voltammetry to assess trace metal reduction on cathode

To assess the possibility of sorption and reduction of trace metals on the electrode as a removal mechanism, linear sweep voltammetry was performed in a 0.1 M NaClO₄ electrolyte containing 0.1 M borate buffer (pH 8). Voltammograms were performed in the presence and absence of elevated concentrations of trace metals (50 mg L⁻¹) with both the gas-diffusion (open air) cathode and stainless steel cathode at a scan rate of 10 mV s⁻¹ from 0 to -3 V vs. SHE.

![Figure S4](image.jpg)

**Figure S4.** Linear sweep voltammogram of a stainless steel cathode and open air cathode in the absence (solid lines) and presence (dashed lines) of 50 mg L⁻¹ Cu²⁺, Pb²⁺, and As in a 0.1 M NaClO₄ electrolyte containing 0.1 M borate buffer (pH 8).

2.7 Photochemical Fe(II) formation using ferrozine

Fe(II) formation from Fe(III)-NOM complexes via ligand-to-metal charge transfer reactions was assessed using the ferrozine (FZ₃) assay.⁹,¹⁰ Under the experimental conditions employed ([FZ₃] = 0.1 mM, pH = 6.5), any Fe(II) formed in the bulk electrolyte will preferentially complex with FZ₃ to form an Fe(II) - FZ₃ complex before being aerobically oxidized. Using a simplified
branching ratio with rate constants described elsewhere, we can compare the rate of complex formation to the rate of oxidation by O₂:

\[
\frac{k_{\text{Fe(II), FZ}[\text{FZ}]} }{k_{\text{Fe(II), O}_2[\text{O}_2]} } = \frac{(3.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1})(10^{-4}\text{M})}{2.2 \times 10^{-4} \text{ s}^{-1}} = 14091
\]

Due to the absorbance of ferrozine at 254 nm (\(\varepsilon_{\text{FZ, } \lambda=254\text{nm}} = 12,900 \text{ M}^{-1} \text{ cm}^{-1}\)), roughly 93% of the UV light was absorbed by ferrozine and unable to react with NOM in solution. Therefore, rates of Fe(II) formation were corrected for light screening to accurately reflect production that would occur during treatment.

**Figure S5.** Absorption spectra of synthetic ground water (SGW) in the presence and absence of 100 µM ferrozine at pH 6.5 as well as the light transmission through the solution at different wavelengths.
2.8 Aerobic oxidation of ferrous iron

The oxidation rate for ferrous iron (Fe[II]) to ferric iron (Fe[III]) by O$_2$ can be described by:

$$\frac{-d[\text{Fe}(\text{II})]}{dt} = 6 \times 10^{-5} [\text{Fe}^{2+}] + 1.7 [\text{FeOH}^+] + 4.3 \times 10^5 [\text{Fe(OH)}_2^0]$$

At pH 8, [Cl$^-$] = 5 × 10$^{-4}$ M, and Fe(II)$_{\text{TOT}}$ = 10 µM, the concentrations of Fe$^{2+}$, FeOH$^+$, and Fe(OH)$^0$ are:

| Species       | log β | [L-]$^n$ | °B[L-]$^n$ | α | Concentration (M) | Oxygenation Rate (M min$^{-1}$) |
|---------------|-------|----------|------------|---|-------------------|-------------------------------|
| Fe$^{2+}$     | -     | -        | 1.00E+00   | 0.97 | 9.66E-06 | 5.79E-10 |
| FeOH$^+$      | 4.5   | 1.00E-06 | 3.16E-02   | 0.03 | 3.05E-07 | 5.19E-07 |
| Fe(OH)$_2^0$  | 7.43  | 1.00E-12 | 2.69E-05   | 0.00 | 2.60E-10 | 1.12E-04 |
| Fe(OH)$_3^-$  | 11    | 1.00E-18 | 1.00E-07   | 0.00 | 9.66E-13 | -               |
| FeCl$^+$      | 0.9   | 5.00E-04 | 3.97E-03   | 0.00 | 3.84E-08 | -               |
| FeCl$_2^0$    | 0.04  | 2.50E-07 | 2.74E-07   | 0.00 | 2.65E-12 | -               |
| SUM:          | 1.04  | 1.00     | 1.00E-05   |     | 1.12E-04 |                 |

For Fe(II)$_{\text{TOT}}$ = 10 µM, the half-life for oxidation from Fe(II) to Fe(III) is 3.7 s at pH 8. At pH 6.5, this corresponds to a half-life for oxidation from Fe(II) to Fe(III) of 52.2 min.
3. RESULTS AND DISCUSSION

3.1 Concentration of filterable iron in the absence of NOM

![Graph showing concentration of filterable iron](image1)

Figure S6. Predicted and measured concentrations of filterable dissolved iron during treatment of synthetic groundwater in the absence of natural organic matter.

3.2 H₂O₂ removal in dark experiments

![Bar chart showing H₂O₂ removal](image2)

Figure S7. H₂O₂ production and effluent concentration leaving the system during treatment of authentic groundwater from Colusa County, CA.
Figure S8. Concentration of dissolved Fe during treatment of authentic groundwater irradiated with UV light in the absence of H$_2$O$_2$ (i.e., UV only; experiments conducted with a stainless steel cathode) as well as in the absence of current (i.e., no pH increase). Solid lines correspond to dissolved Fe concentration (left y-axis); Dashed lines correspond to pH (right y-axis).

3.3 Gravitational settling of iron colloids

Figure S9. Total iron (dissolved and colloidal) concentration after treatment followed by overnight gravitational settling of authentic groundwater.
3.4 Photochemical transformation of Fe(III)-NOM complexes

**Figure S10.** Measured concentrations of filterable dissolved iron during treatment of both synthetic and authentic groundwaters.

**Figure S11.** Speciation of dissolved Fe in simulated electrolytes exposed to the combined EC/UV treatment system in the presence and absence of Ca$^{2+}$ and Mg$^{2+}$, NOM, and reactive intermediate quenchers: N$_3$ (50 µM), isoprene (500 µM), and tertiary butanol (1 mM). Air cathode corresponds to experiments performed with the gas diffusion electrode capable of producing H$_2$O$_2$. S.S cathode refers to experiments performed with a stainless steel cathode.
**Figure S12.** Distribution of unique masses lost (red) and gained (blue) during the photolysis of groundwater from Colusa County, CA (~0.5 mgC L\(^{-1}\) NOM).

**Figure S13:** Spectral slope values (nm\(^{-1}\)) of authentic groundwater from Colusa County, CA following different treatment regimes (~0.5 mgC L\(^{-1}\) NOM). The spectral slopes, S, were fitted over the wavelength intervals from 275 to 295 nm and from 240 to 500 nm.
Figure S14. Effects of chemical treatment on the absorption spectra of authentic groundwater from Colusa County, CA (~0.5 mgC L\(^{-1}\) NOM).

3.5 Fe removal and optical properties during respike experiments

Figure S15. Concentration of dissolved (filterable) Fe in synthetic groundwater containing Ca\(^{2+}\) and Mg\(^{2+}\) exposed to the combined EC/UV treatment system. After the first pass, effluent iron oxides were filtered through a 0.22 µm filter, respiked with 10 µM Fe(II), and subjected to the treatment system for a second time.
Figure S16. Absorption spectra of synthetic groundwater containing Fe\(^{2+}\), Ca\(^{2+}\), and Mg\(^{2+}\) exposed to the combined EC/UV treatment system. Two passes of synthetic groundwater solution through the treatment system were performed. After the first pass, effluent iron oxides were filtered through a 0.22 µm filter and respiked with 10 µM Fe(II).

3.6 Reduction of steady-state concentrations of reactive intermediates in the presence of quenchers.

HO\(^{•}\) may be formed from the photolysis of H\(_2\)O\(_2\), chromophoric dissolved organic matter, or NO\(_3^{-}\). HO\(^{•}\) is primarily scavenged by DOM, H\(_2\)O\(_2\), HCO\(_3^{-}\), and CO\(_3^{2-}\). Therefore, \([\text{HO}^{•}]_{\text{SS}}\) can be calculated by:

\[
[\text{HO}^{•}]_{\text{SS}} = \frac{R_{\text{form,HO}^{•},H_2O_2} + R_{\text{form,HO}^{•},\text{CDOM}} + R_{\text{form,HO}^{•},\text{NO}_3^{-}}}{k_{\text{HO}^{•},\text{DOM}}[\text{DOM}] + k_{\text{HO}^{•},H_2O_2}[H_2O_2] + k_{\text{HO}^{•},\text{HCO}_3^{-}}[\text{HCO}_3^{-}] + k_{\text{HO}^{•},\text{CO}_3^{2-}}[\text{CO}_3^{2-}]}\]

where \(R_{\text{form,HO}^{•},H_2O_2}\), \(R_{\text{form,HO}^{•},\text{CDOM}}\), and \(R_{\text{form,HO}^{•},\text{NO}_3^{-}}\) are the formation rates (M s\(^{-1}\)) of HO\(^{•}\) and \(k_{\text{HO}^{•},\text{DOM}}\), \(k_{\text{HO}^{•},H_2O_2}\), \(k_{\text{HO}^{•},\text{HCO}_3^{-}}\), and \(k_{\text{HO}^{•},\text{CO}_3^{2-}}\) are the second-order reaction rate constants between HO\(^{•}\) and water constituents. Assuming the formation rate is unaffected by the presence of the radical quencher (in this case tertiary butanol), then the percent reduction in the steady-
state concentration of HO\(^+\) can be expressed as the ratio of the denominator in the presence and absence of tertiary butanol (i.e., \(k_{\text{HO,tertBuOH}(\text{tBuOH})}\)): 

\[
\text{Reduction in } [\text{HO}^+]_{\text{ss}} = \frac{k_{\text{HO^*}_{\text{DOM}}}[\text{DOM}] + k_{\text{HO^*}_{\text{H}_2\text{O}_2}}[\text{H}_2\text{O}_2] + k_{\text{HO^*}_{\text{HCO}_3^-}}[\text{HCO}_3^-] + k_{\text{HO^*}_{\text{CO}_3^-}}[\text{CO}_3^-] + k_{\text{HO^*}_{\text{tBuOH}}}(\text{tBuOH})}{k_{\text{HO^*}_{\text{DOM}}}[\text{DOM}] + k_{\text{HO^*}_{\text{H}_2\text{O}_2}}[\text{H}_2\text{O}_2] + k_{\text{HO^*}_{\text{HCO}_3^-}}[\text{HCO}_3^-] + k_{\text{HO^*}_{\text{CO}_3^-}}[\text{CO}_3^-] + k_{\text{HO^*}_{\text{tBuOH}}}(\text{tBuOH})}
\]

At pH 9.3, the alpha values for carbonate speciation are: \(\alpha_1 = 0.914\), \(\alpha_2 = 0.085\). Considering 5 mM [HCO\(_3^-\)]\(_{\text{TOTAL}}\), 0.5 mM H\(_2\)O\(_2\), and 1 mgC L\(^{-1}\) DOM, and using the rate constants provided in below in Table S4, one gets a reduction in HO\(^+\) of \(71.8\%\) with the addition of 1 mM tertiary butanol.

**Table S3.** Rate constants for hydroxyl radical and water constituents.

| Rate Constant | Value     | Citation               |
|---------------|-----------|------------------------|
| \(k_{\text{HO^*}_{\text{DOM}}(\text{mg-C}^{-1}\text{ L}^{-1})}\) | \(1.7 \times 10^4\) | Jasper et al. 2013 \(^1\) |
| \(k_{\text{HO^*}_{\text{H}_2\text{O}_2}(\text{M}^{-1}\text{ s}^{-1})}\) | \(2.7 \times 10^7\) | Buxton et al. 1988 \(^13\) |
| \(k_{\text{HO^*}_{\text{HCO}_3^-}(\text{M}^{-1}\text{ s}^{-1})}\) | \(8.5 \times 10^6\) | Buxton et al. 1988 \(^13\) |
| \(k_{\text{HO^*}_{\text{CO}_3^-}(\text{M}^{-1}\text{ s}^{-1})}\) | \(3.9 \times 10^8\) | Buxton et al. 1988 \(^13\) |
| \(k_{\text{HO^*}_{\text{tBuOH}}(\text{M}^{-1}\text{ s}^{-1})}\) | \(6 \times 10^8\) | Buxton et al. 1988 \(^13\) |

A similar approach can be applied for \(^3\)NOM. In surface waters, the primary loss mechanism is through reaction with dissolved oxygen ([O\(_2\)] \(\approx 250\) µM for oxygenated waters), which has a rate constant of \(2 \times 10^9\) M\(^{-1}\) s\(^{-1}\).\(^14\) Although the exact bimolecular rate constant between \(^3\)NOM and isoprene is unknown, previous researchers have observed that conjugated dienes quench high energy sensitizers (i.e., \(^3\)NOM) at rates close to diffusion controlled limits using laser flash photolysis.\(^15,16\) Therefore, assuming a reaction rate constant of \(1 \times 10^9\) M\(^{-1}\) s\(^{-1}\) and 500 µM
isoprene, one gets a reduction in steady-state $^3$NOM of $50\%$ with the addition of the $^3$NOM quencher.

For $^1$O$_2$, the percent reduction in steady-state values is a combination of reduction in the formation rate due to light screening by 50 µM NaN$_3$ ($\sim$7%, See Figure S2) and the increase in scavenging rate by the $^1$O$_2$ quencher. In the absence of NaN$_3$, $^1$O$_2$ is primarily quenched by water and has a decay rate constant of $2.5 \times 10^5$ s$^{-1}$. As the second order reaction rate constant between $^1$O$_2$ and NaN$_3$ is $5 \times 10^8$ M$^{-1}$ s$^{-1}$, the decrease in steady-state $^1$O$_2$ due to quenching is $\sim$10%. Therefore, the total decrease in steady-state $^1$O$_2$ can be estimated to be close to $\sim$17%.

Note, that the quenching rate obtained with NaN$_3$ needs to be interpreted with caution, due to the formation of azide radicals. However, as $^1$O$_2$ are formed through reactions of O$_2$ with $^3$NOM, the previous example using isoprene which quenches 50% of the $^3$NOM should also lower the steady state $^1$O$_2$ by 50%. Collectively, the observed results (i.e., Figure S10) and calculations rule out the importance of reactive radical species to the removal of Fe from the system.

**Table S4.** Total and dissolved iron measured during respike experiments.

|                     | Total Fe (µM) | Dissolved Fe (µM) |
|---------------------|---------------|-------------------|
|                     | Influent      | Influent | Post H$_2$O$_2$ | Post UV | Effluent   |
| FCM + NOM Pass 1    |               |          |                |         |            |
| Average             | 10.898        | 8.461    | 8.208          | 0.495   | 0.441      |
| Standard            | 0.213         | 0.529    | 1.250          | 0.007   | 0.120      |
| FCM + NOM Pass 2    |               |          |                |         |            |
| Average             | 11.762        | 0.242    | 0.216          | 0.176   | 0.184      |
| Standard            | 0.181         | 0.028    | 0.103          | 0.008   | 0.044      |
| No NOM              |               |          |                |         |            |
| Average             | 11.578        | 0.249    | 0.192          | 0.141   | 0.148      |
| Standard            | 0.297         | 0.007    | 0.027          | 0.005   | 0.021      |

*For Pass 2, effluent of Pass 1 was filtered through a 0.22 µm filter, respiked with ~10 µM Fe, and exposed to the treatment system for a second time. No NOM corresponds to a single pass of synthetic groundwater containing Fe, Ca$^{2+}$, and Mg$^{2+}$ (FCM) without NOM through the treatment system.*
3.7 Light screening and branching ratio for hydroxyl radical

The absorbance of 510 µM H$_2$O$_2$ at pH 9 at 254 nm is approximately 0.0114 while the absorbance of NOM in the authentic water at 254 nm, when corrected for background constituents (See Figure S3), is approximately 0.061. Therefore, the fraction of UV light at 254 nm going to the photolysis of H$_2$O$_2$ is $18\%$. In other words, NOM screens $\sim$82% of the incident light at 254 nm.

The fraction of HO$^\cdot$ going to NOM can be expressed as:

$$\text{fraction} = \frac{k_{\text{HO}^\cdot,\text{NOM}}[\text{NOM}]}{k_{\text{HO}^\cdot,\text{NOM}}[\text{NOM}] + k_{\text{HO}^\cdot,\text{HCO}_3^-}[\text{HCO}_3^-] + k_{\text{HO}^\cdot,\text{CO}_3^{2-}}[\text{CO}_3^{2-}] + k_{\text{HO}^\cdot,\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2]}$$

Where $k_{\text{HO}^\cdot,\text{NOM}} = 1.7 \times 10^4$ mg-C$^{-1}$ L$^{-1}$ s$^{-1}$, $k_{\text{HO}^\cdot,\text{HCO}_3^-} = 8.5 \times 10^6$ M$^{-1}$ s$^{-1}$, $k_{\text{HO}^\cdot,\text{CO}_3^{2-}} = 3.9 \times 10^8$ M$^{-1}$ s$^{-1}$, and $k_{\text{HO}^\cdot,\text{H}_2\text{O}_2} = 2.7 \times 10^7$ M$^{-1}$ s$^{-1}$. In groundwater at pH 9.1 in the presence of 510 µM H$_2$O$_2$, $\sim$5 mM DIC, and 0.5 mg-C L$^{-1}$ NOM, approximately 11.7% of HO$^\cdot$ reacts with NOM.
3.8 Metal removal during treatment of synthetic groundwater

Figure S17. Concentration of dissolved (A) $\text{Ca}^{2+}$ and (B) $\text{Mg}^{2+}$ during treatment of synthetic groundwater in the presence and absence of UV light and natural organic matter.
Figure S18. Concentration of dissolved (filterable) Fe in synthetic groundwater in the presence and absence of Ca$^{2+}$ and Mg$^{2+}$ exposed to treatment. Experiments were performed both with and without UV irradiation. Green dotted line corresponds to the average total iron (i.e., dissolved and colloidal).

3.9 Changes in chemical composition of NOM during treatment of authentic and synthetic groundwater

Table S5. FT-ICR MS characterization of authentic GW from Colusa County, CA exposed to UV irradiation.

| Individual Formulas | Molecular Weight (Da) | H/C Ratio | O/C Ratio |
|---------------------|-----------------------|-----------|-----------|
|                     | Average | Stdev  | Average  | Stdev  | Average  | Stdev  |
| **Total**          |         |        |          |         |          |        |
| Non-Irradiated     | 1011    | 81.5683| 1.1707   | 0.1526  | 0.5193   | 0.1257 |
| Irradiated         | 1207    | 70.7139| 1.1133   | 0.2333  | 0.4880   | 0.1210 |
| **Individual Formulas** | **Average** | **Stdev** | **Average** | **Stdev** | **Average** | **Stdev** |
| **Common**         |         |        |          |         |          |        |
| Non-Irradiated     | 763     | 72.1991| 1.1720   | 0.2079  | 0.5179   | 0.1220 |
| Irradiated         | 763     | 70.7703| 1.1771   | 0.2103  | 0.5235   | 0.1129 |
| **Unique**         |         |        |          |         |          |        |
| Non-Irradiated     | 248     | 71.6408| 1.1509   | 0.2270  | 0.5393   | 0.1397 |
| Irradiated         | 444     | 104.2617| 1.2420  | 0.3050  | 0.4761   | 0.1529 |

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Table S6. FT-ICR MS characterization of Suwanee River NOM exposed to UV irradiation.

| Individual Formulas | Molecular Weight (Da) | H/C Ratio | O/C Ratio |
|---------------------|-----------------------|-----------|-----------|
|                     | Average    | Stdev     | Average   | Stdev     | Average   | Stdev     |
| Total               |            |           |           |
| Non-Irradiated      | 745        | 406.0590  | 81.1301   | 1.0813    | 0.1961    | 0.5814    | 0.1270    |
| Irradiated          | 816        | 362.3657  | 81.9685   | 1.1403    | 0.2351    | 0.5567    | 0.1411    |
| Individual Formulas | Average    | Stdev     | Average   | Stdev     | Average   | Stdev     |
| Common              |            |           |           |
| Non-Irradiated      | 522        | 391.5662  | 72.8168   | 1.0892    | 0.1901    | 0.5824    | 0.1196    |
| Irradiated          | 522        | 373.1958  | 75.2253   | 1.1204    | 0.2008    | 0.5693    | 0.1176    |
| Individual Formulas | Average    | Stdev     | Average   | Stdev     | Average   | Stdev     |
| Unique              |            |           |           |
| Non-Irradiated      | 223        | 494.2823  | 73.1977   | 1.0332    | 0.2193    | 0.5750    | 0.1361    |
| Irradiated          | 294        | 319.7363  | 93.1300   | 1.2469    | 0.3132    | 0.5068    | 0.3063    |

Table S7. FT-ICR MS characterization of Suwanee River NOM in the presence of 10 µM Fe exposed to UV irradiation.

| Individual Formulas | Molecular Weight (Da) | H/C Ratio | O/C Ratio |
|---------------------|-----------------------|-----------|-----------|
|                     | Average    | Stdev     | Average   | Stdev     | Average   | Stdev     |
| Total               |            |           |           |
| Non-Irradiated      | 633        | 363.2800  | 76.1362   | 1.1865    | 0.2880    | 0.5240    | 0.1598    |
| Irradiated          | 761        | 348.0328  | 79.6796   | 1.1670    | 0.2462    | 0.5477    | 0.1374    |
| Individual Formulas | Average    | Stdev     | Average   | Stdev     | Average   | Stdev     |
| Common              |            |           |           |
| Non-Irradiated      | 462        | 355.5242  | 67.3857   | 1.1929    | 0.2883    | 0.5239    | 0.1579    |
| Irradiated          | 462        | 344.3304  | 67.6283   | 1.1635    | 0.2209    | 0.5519    | 0.1257    |
| Individual Formulas | Average    | Stdev     | Average   | Stdev     | Average   | Stdev     |
| Unique              |            |           |           |
| Non-Irradiated      | 171        | 426.5756  | 96.8935   | 1.1449    | 0.2775    | 0.5244    | 0.1723    |
| Irradiated          | 158        | 444.0306  | 110.1853  | 1.1431    | 0.2700    | 0.5437    | 0.1515    |
Table S8. FT-ICR MS characterization of Suwanee River NOM in the presence of 10 µM Fe, 250 µM Ca$^{2+}$, and 250 µM Mg$^{2+}$ exposed to UV irradiation.

| Individual Formulas | Molecular Weight (Da) | H/C Ratio | O/C Ratio |
|---------------------|-----------------------|-----------|-----------|
|                     | Average | Stdev  | Average | Stdev  | Average | Stdev  |
| Total               |          |        |          |        |          |        |
| Non-Irradiated      | 731     |        | 381.5951| 87.6638| 1.1434  | 0.2164 |
| Irradiated          | 812     |        | 360.3240| 74.7247| 1.1666  | 0.2552 |
| Average Stdev       |          |        | 0.5495  | 0.1301 |
| Average Stdev       |          |        | 0.5440  | 0.1363 |
| Common              |          |        |          |        |          |        |
| Non-Irradiated      | 536     |        | 364.0336| 74.8980| 1.1486  | 0.2142 |
| Irradiated          | 536     |        | 345.3787| 74.2229| 1.1608  | 0.2405 |
| Average Stdev       |          |        | 1.1608  | 0.2405 |
| Unique              |          |        |          |        |          |        |
| Non-Irradiated      | 194     |        | 491.9768| 76.1917| 1.1136  | 0.2242 |
| Irradiated          | 214     |        | 365.1644| 108.9100| 1.1884 | 0.2960 |
| Average Stdev       |          |        | 0.5315  | 0.1509 |
| Average Stdev       |          |        | 0.4958  | 0.2060 |

Table S9. Changes in average double bond equivalents determined using the FT-ICR MS data for Suwanee River NOM in the presence and absence of 10 µM Fe, 250 µM Ca$^{2+}$, and 250 µM Mg$^{2+}$, as well as authentic groundwater, exposed to UV Irradiation.

|                     | Double Bond Equivalents |
|---------------------|-------------------------|
|                     | Non-Irradiated | Irradiated   |
| NOM                 | 9.601            | 8.407        |
| Fe                  | 8.602            | 8.184        |
| Fe, Ca, Mg          | 8.445            | 8.051        |
| Authentic GW        | 9.404            | 8.708        |
Figure S19. Changes in relative peak intensity after UV irradiation of formulas that were common to both the non-irradiated and irradiated synthetic solutions containing A) 1 mg L\(^{-1}\) Suwanee River NOM and B) 0.5 mgC L\(^{-1}\) Suwanee River NOM with either Fe (10 µM) or Fe (10 µM), Ca\(^{2+}\) (250 µM), and Mg\(^{2+}\) (250 µM).
3.10 Changes in UV absorbance during treatment of synthetic groundwater

Figure S20. Changes in absorption spectra of synthetic groundwater containing 0.5 mgC L⁻¹ Suwannee River NOM with UV irradiation time. Inset: differential absorbance relative to non-irradiated solution (i.e., t=0). Experiments were performed in batch ($V_{TOT} = 900$ mL).

Figure S21. Changes in absorption spectra of synthetic groundwater containing 0.5 mgC L⁻¹ Suwannee River NOM and 10 µM Fe(II) with UV irradiation time. Inset: differential absorbance relative to non-irradiated solution (i.e., t=0). Experiments were performed in batch ($V_{TOT} = 900$ mL).
**Figure S22.** Changes in absorption spectra of synthetic groundwater containing 0.5 mgC L\(^{-1}\) Suwannee River NOM, 10 µM Fe(II), and 250 µM Ca\(^{2+}\) and Mg\(^{2+}\) with UV irradiation time. Inset: differential absorbance relative to non-irradiated solution (i.e., t=0). Experiments were performed in batch (V\(_{TOT}\) = 900 mL).

**Figure S23.** Differential absorbance at 254 nm during batch UV irradiation of synthetic groundwater containing NOM, Fe(III)-NOM, and Fe(III)-NOM-Ca\(^{2+}\)/Mg\(^{2+}\) complexes vs. UV irradiation time. Experiments were performed in batch (V\(_{TOT}\) = 900 mL). Iron was added as Fe(II). [NOM] = 0.5 mgC L\(^{-1}\); [Fe(II)] = 10 µM; [Ca\(^{2+}\)] = [Mg\(^{2+}\)] = 250 µM.
3.11 Fe(II) photoproduction

**Figure S24.** Rate of Fe(II) production during UV$_{254}$ photolysis of Fe(III)-NOM complexes as well as dark controls as determined via production of ferrous iron-ferrozine complex (Fe(II)-FZ$_3$) measured at 562 nm.$^{9,10}$ Iron was initially added as 10 µM Fe(III). All solutions were at pH 6.5.
3.12 Cyclic voltammograms of reference species

**Figure S25.** Cyclic voltammograms of 500 µM \( p \)-benzoquinone CV's were performed in anhydrous dimethyl sulfoxide (DMSO; 50 mL) containing 5 mM tetrabutylammonium hexafluorophosphate (NBu₄PF₆). Experiments were performed with a Pt wire working and counter electrode (0.25 mm diameter) and non-aqueous Ag/Ag⁺ reference electrode (BASi) at a scan rate of 10 mV s⁻¹.

**Figure S26.** Cyclic voltammogram of 500 µM ferrocene CV's were performed in anhydrous dimethyl sulfoxide (DMSO; 50 mL) containing 5 mM tetrabutylammonium hexafluorophosphate (NBu₄PF₆). Experiments were performed with a Pt wire working and counter electrode (0.25 mm diameter) and non-aqueous Ag/Ag⁺ reference electrode (BASi) at a scan rate of 10 mV s⁻¹.
3.13 Energy calculations
The total system power \( P_{\text{total}, \text{W}} \) is a combination of the UV lamp power and the electrochemical cell power, which can be expressed as a product of the current density \( I, \text{A m}^{-2} \), cell potential \( V_{\text{cell}} \), and the electrode surface area \( A, \text{m}^2 \):

\[
P_{\text{total}} = I \cdot A \cdot V_{\text{cell}} + P_{\text{lamp}}
\]

At a current density of 25 A m\(^{-2}\), cell potential of 13.6 V, flow rate of 121 L d\(^{-1}\), and lamp power of 9 W, the total power demand of the treatment system was 0.01175 kW. The energy demand per m\(^3\) can be calculated as the power demand divided by the system flow rate, which yields an energy demand per m\(^3\) of 2.21 kWh m\(^{-3}\).

3.14 Iron dosing and sludge calculations
The amount of Fe needed to reduce the arsenic concentration from 28 µg L\(^{-1}\) to below the World Health Organization Maximum Contaminant Level of 10 µg L\(^{-1}\) in authentic groundwater can be calculated using the arsenic sorption capacity of iron oxides determined in Figure 2 (i.e., 0.0123 mol\(_{\text{As}}\): mol\(_{\text{Fe}}\)). Using the ambient iron in the system (approximately 10 µM), the arsenic was reduced to 16.2 µg L\(^{-1}\). Therefore, to remove an additional 6.2 µg L\(^{-1}\) of As if would require:

\[
\left( \frac{6.2 \text{ µg As}}{\text{L}} \right) \left( \frac{1 \text{ µM As}}{74.9 \text{ µg As}} \right) \left( \frac{1 \text{ µM Fe}}{0.0123 \text{ µMAs}} \right) = 6.73 \text{ µM Fe}
\]

The total amount of iron oxide sludge produced per liter of treated water would be

\[
\left( \frac{10.5 + 6.73 \text{ µmol Fe}}{\text{L}} \right) \left( \frac{54.55 \text{ µg Fe}}{1 \text{ µmol Fe}} \right) = 1.07 \text{ mg Fe L}^{-1}
\]
4. RESULTS AND DISCUSSION

4.1.1 Cumulative density function of Fe from contaminated wells in CA

Figure S27. Cumulative density function of iron from over 7000 groundwater wells contaminated with both iron and arsenic in California from 2007-2017. Adapted from data provided by the U.S. Geological Survey (USGS). http://geotracker.waterboards.ca.gov
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