Supporting Information for

Determination of Hydroxyl Radical Production from Sulfide Oxidation Relevant to Sulfidic Pore-Waters

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Figure S1. The Prairie Pothole Region (PPR) is outlined in red (map adapted from USGS). The inset shows the Cottonwood Lakes Study Area near Jamestown, ND. The sampled wetlands (T9, P7, P1, and P8) are marked. Figure reproduced from Karpuzcu et al. *Environ. Sci. Process Impacts*, 2016, 18, 237-245, published by The Royal Society of Chemistry.



Figure S2: Hydroxyl radical (·OH) production data in reactors with initial $[H_2S]_T = 1 \text{ mM}$ measured and with TPA (90 μ M). To initiate the reaction, dissolved O₂ (closed symbols) or H₂O₂ (open symbols) at 52 μ M was introduced with the 150 μ L TPA spike. Over the course of the reaction, additional oxygen diffuses in through the pierced HPLC vial septum. Error bars represent the standard error from replicate experiments.



Figure S3: NMR spectra of 1 mM $[H_2S]_T$ solution and methane 1 minute (pink line) and 3 hours (grey) after the addition of oxygenated deuterium oxide to initiate reaction. Spectra of 1 mM $[H_2S]_T$ solution (black), methane dissolved in water (red, contaminated with sulfide solution), and 100 μ M methanol in water (blue) were also conducted to identify peaks in the reaction spectra.

Table S1: Total sulfide concentrations and hydroxyl radical production rates related to Figures 4 and 5.

Nominal [H2S]T (µM)	Arithmetic Mean [H2S]T (µM)	Standard Error of mean [H2S]T (µM)	Arithmetic Mean of Initial •OH Production Rate (nM/hr)	Average of Standard Error for Rate (nM/hr)
10	10.9	1.1	1.13	0.19
20	20.3	0.75	2.97	0.51
50	51.2	2.0	5.36	0.51
75	77.0	1.3	7.78	0.40
100	95.8	1.5	7.85	0.50



Figure S4: Control experiment demonstrating the lack of reaction between TPA and $[H_2S]_T$. Initial conditions were 1 mM TPA and 0.1 mM $[H_2S]_T$ at pH 9, and the stock solutions mixed to create the reaction solution were deoxygenated. A series of replicate HPLC vials were prepared, and no oxygen was introduced to the vials. No reaction of TPA (closed circles, left axis) or production of hTPA (open squares, right axis), which would indicate production of (·OH), was observed.

MATLAB Code for Model in Figure 6:

```
%Create vectors for each compound in environmental ranges
 s=linspace(0.00005,0.002,20);
 doc=linspace(10,100,20);
 me=linspace(0.0001,0.0015,20);
 %Put each compound vector into a 3D matrix (grid)
[DOC, ME, S] = meshgrid(doc, me, s);
%Rate Parameters for Model
 KQme=1.2e8; % (M*s)^−1
 KQdoc=1.9e4;
                %[mqC/L*s)^-1
                  %(M*s)^−1
 KQs=9e9;
Kprime=1.04e-4; \% \frac{mol \cdot OH/L}{hr * mol H_2S/L}
                            (pseudo first order; assume 52
uM oxygen concentration)
%Equation for [•OH]ss (eq. 7): Rate formation/rate
quenching
%Factor of 3600 converts Kprime to a time-scale of seconds
OH= ((Kprime*(1/3600)).*S)./(KQs.*S+KQme.*ME+KQdoc.*DOC);
%Where the 3D prism is sliced to show graph data
xslice=[10];
yslice= [0.00012, 0.0008, 0.0015];
zslice=[0.00005,0.001,0.002];
%Graph (slice) with interpolation of color for [·OH]ss
h= slice(DOC,ME,S,OH,xslice,yslice,zslice);
set(h, 'EdgeColor', 'none', 'FaceColor', 'interp');
xlabel('DOC [mg/L]');
ylabel('CH4 [M]');
zlabel('HS- [M]');
hcb = colorbar;
title(hcb, '[OH]');
```