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Hydroxyl radical (•OH) scavenging reaction rate constants of standard natural organic matter (NOM) isolates ($k_{•OH,NOM}$) were measured with a rapid background scavenging method.
This work provides insight into the fate of organic pollutants in natural and engineered waters. Although hydroxyl radicals play a principal role in the degradation of organic pollutants, their reactivity is largely dependent on the concentration and availability of hydroxyl radical scavenging compounds. We introduce a new, rapid method for assessing background scavenging levels and apply the technique to determine $k_{\text{OH}}$ for several natural organic matter (NOM) isolates. Because NOM is often the predominant background hydroxyl radical scavenger in waters, a method that allows the rapid analysis of $k_{\text{OH,NOM}}$ will lead to a better understanding of the fate of organic contaminants in aqueous systems.
Photometric hydroxyl radical scavenging analysis of standard natural organic matter isolates

J. E. Donham, E. J. Rosenfeldt, and K. R. Wigginton

Hydroxyl radical (•OH) scavenging reaction rate constants of standard natural organic matter (NOM) isolates \( (k_{\text{OH,NOM}}) \) were measured with a rapid background scavenging method, to expand the dataset of published \( k_{\text{OH,NOM}} \) values. The proposed method relies on •OH generation with a simple UV/H\(_2\)O\(_2\) AOP-based system. The associated decay of a •OH probe compound is monitored with a field-deployable spectrophotometer and \( k_{\text{OH,NOM}} \) is determined through competition kinetics. The resulting \( k_{\text{OH,NOM}} \) values for the six NOM standard isolates ranged from \( 1.02 \pm 0.10 \) \( \times 10^{-5} \) M\(^{-1}\)s\(^{-1}\) for Suwannee River Fulvic Acid I Standard to \( 2.03 \pm 0.12 \) \( \times 10^{-5} \) M\(^{-1}\)s\(^{-1}\) for Pony Lake Fulvic Acid Reference NOM, which is within the range reported with more elaborate and time-consuming \( k_{\text{OH,NOM}} \) methods. A slight correlation between nitrogen content and scavenging rate constant was evident while no significant correlation was evident between \( k_{\text{OH,NOM}} \) and atomic composition, carbon structure, weight-average molecular weight, UV absorbance (SUVA\(_{254}\)), or fluorescence index (FI) was observed. Overall, the results demonstrate that \( k_{\text{OH,NOM}} \) can be rapidly assessed in NOM isolate samples. The results suggest that this type of rapid field-deployable spectrophotometric method may minimize the need for expensive and time-consuming background scavenging methods, and for models that predict \( k_{\text{OH,NOM}} \) based on other NOM characteristics.

1 Introduction

Hydroxyl radical (•OH) transient species play a principal role in aqueous photochemistry.\(^1\) They can form naturally in sunlit waters by direct photolysis of nitrate\(^2\) and NOM, through photo-Fenton reactions,\(^5\) and other routes.\(^5\) Once formed, •OH react rapidly with organic and inorganic solutes, with rate constants that can approach diffusion-controlled limits.\(^7\) Environmental engineers are increasingly harnessing the high reactivity of •OH with advanced oxidation processes (AOPs) to treat water contaminants.\(^8,9,10\) AOP treatment technologies often employ ozone decomposition, ozone coupled with H\(_2\)O\(_2\) (O\(_3\)/H\(_2\)O\(_2\)), or ultraviolet light photolysis of hydrogen peroxide to produce •OH (UV/H\(_2\)O\(_2\)).

Due to its nonselective reactivity, the role that •OH plays in the destruction of organic contaminants in water is largely dictated by the presence and concentrations of background “scavenging” compounds that exhibit a demand for •OH. High scavenging levels negatively impact treatment, since these compounds reduce the •OH available to react with the targeted organic contaminants. Organic matter is arguably the most important scavenger\(^11,12,13,14\) as it often dominates the •OH demand, even in waters with relatively low DOC (~ 2.5 mg/L total organic carbon (TOC)). Carbonate (CO\(_3^{2-}\)), bicarbonate (HCO\(_3^-\)), and halide species can contribute to hydroxyl scavenging, though typically to a lesser extent in drinking water treatment.\(^15,16\)

To model and predict the availability of •OH to degrade target analytes in engineered and natural systems, the effective scavenging rate as determined by the concentration and reaction rate of each species involved must be well defined. Common relevant species include HCO\(_3^-\) and CO\(_3^{2-}\), NOM, as well as the contaminant of interest. Reactions between •OH and organic contaminants have been widely studied and corresponding rate constants are in the range of \( 10^{-7}-10^{-10} \) M\(^{-1}\)s\(^{-1}\).\(^17,18\) Rate constants for •OH with HCO\(_3^-\) and CO\(_3^{2-}\) are reported as \( 8.5 \times 10^6 \) and \( 3.9 \times 10^6 \) M\(^{-1}\)s\(^{-1}\), respectively.\(^19,20\) NOM scavenging rates are harder to typify and vary significantly amongst sources. The reported second-order •OH-NOM reaction rate constants \( (k_{\text{OH,NOM}}) \) span up to an order of magnitude \( (10^3-10^5 \) M\(^{-1}\)s\(^{-1}\)\); Table 1),\(^3,21,22,23,24,25\) although an average DOM rate constant...
of $2.1 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$ has been used for predictive purposes. Ultimately, this variability makes it difficult to accurately predict steady state •OH concentrations in water samples, particularly those dominated by NOM scavenging.

Table 1: $k_{\text{OH,NOM}}$ values from previous work, with probe / •OH source used for measurement. (a) $^{13}$C-labeled formate / γ-radiolysis competition kinetics; (b) Direct growth of transient byproducts measured at 272 nm / pulse radiolysis; (c) Direct growth of transient byproducts measured at 272 nm / pulse radiolysis; (d) Direct growth of transient byproducts measured at 272 nm / pulse radiolysis; (e) Direct growth of transient byproducts measured at 272 nm / pulse radiolysis; (f) Direct growth of transient byproducts measured at 272 nm / pulse radiolysis.

Several methods have been applied to measure $k_{\text{OH,NOM}}$. In one method, the oxidation of SCN$^-$ to •SCN$^-_2$ in the presence of known competitors is measured photometrically at 475 nm. $^{13,24,25}$ Another method tracks the formation of NOM oxidation byproducts photometrically at 272 or 400 nm. $^{24}$ Due to the instability of •SCN$^-_2$ and NOM oxidation byproducts, these methods require specialized equipment that allows concurrent absorbance analysis with very high •OH production rates—this is typically achieved via pulse radiolysis of water. Other methods involve monitoring the decay of a tracer compound via high performance liquid chromatography (parachlorobenzoic acid (pCBA)), gas chromatography (butyl chloride) or scintillation counting ($^{14}$C-labeled formate). In these methods, •OH is formed with UV/H$_2$O$_2$, UV photolysis of nitrate, or with γ-radiolysis. Measurements made using different methods conducted by the same research group have produced similar $k_{\text{OH,NOM}}$ for the same isolates. Unfortunately, there are few examples of the same isolate $k_{\text{OH,NOM}}$ reported by different laboratories (Table 1). Consequently, the reproducibility of $k_{\text{OH,NOM}}$ values is largely unknown.

The $k_{\text{OH,NOM}}$ methods discussed above can be time consuming and costly, particularly when pulse radiolysis is used for •OH production. As a result, researchers have attempted to relate or even predict $k_{\text{OH,NOM}}$ based on NOM characteristics. Weight-average molecular weight ($M_w$), elemental content (C, H, N, O), and ratios of aliphatic to aromatic carbon have each been proposed as predictors of $k_{\text{OH,NOM}}$, though none have been independently correlated with $k_{\text{OH,NOM}}$. $^{13,24}$ An analysis of six wastewater effluent organic matter (EfOM) samples, however, did successfully correlate $k_{\text{OH,NOM}}$ with EfOM characteristics using multivariate regressions. $^{26,27}$ Specifically, the former multivariate analysis included $M_w$, specific UV absorbance at 254 nm (SUVA$_{254}$), dispersity, the ratio of the fluorescence emission intensities at 450 nm to 500 nm after excitation at 370 nm (fluorescence index; FI), hydrophobicity, and anionic characteristics, and the latter included chemical oxygen demand, TOC, anionic character, and FI. While the models were not used to predict $k_{\text{OH,EfOM}}$ for samples outside the calibration set, the results do suggest that NOM characteristics can predict $k_{\text{OH,EfOM}}$ in at least some instances.

To advance $k_{\text{OH,NOM}}$ methods and also expand and verify the dataset of published $k_{\text{OH,NOM}}$ values, we employed a simple and rapid method to measure $k_{\text{OH,NOM}}$ in NOM isolates. $k_{\text{OH,NOM}}$ (M$^{-1}$s$^{-1}$) was measured in six NOM isolates from the International Humic Substances Society (IHSS) using a field-deployable rapid scavenging analysis method (R-SAM). The correlation between the measured $k_{\text{OH,NOM}}$ values and nitrogen, hydrogen, carbon and oxygen elemental composition, aliphatic/aromatic carbon content, $M_w$, specific UV absorbance (SUVA$_{254}$), and fluorescence index (FI) was evaluated to replicate previous analyses of potential relationships between NOM properties and $k_{\text{OH,NOM}}$. Our results suggest that rapid measurement techniques can provide accurate $k_{\text{OH,NOM}}$ values, and may therefore minimize the need for complex and expensive $k_{\text{OH,NOM}}$ measurement methods as well as predictive models that rely on multiple NOM characteristics.

2 Experimental

2.1 Materials

Unless otherwise noted, chemicals were reagent grade and used as received from Fisher Scientific (Waltham, MA). Six NOM isolates, Pony Lake Fulvic Acid Reference (PLFA-R, IHSS #1R109F); Eliot Soil Humic Acid Standard (ESH-S-IHSS #1S102H); Pahokee Peat Fulvic Acid II Standard (PPFA-II-S, IHSS #2S103F); Pahokee Peat Humic Acid Standard (PPHA-S, IHSS #1S103H); Suwannee River Fulvic Acid I Standard (SRFA-I-S, IHSS #1S101F); and Suwannee River Humic Acid II Standard (SRHA-II-S, IHSS #2S101H) were obtained from the International Humic Substances Society (IHSS; Denver, CO).

NOM stock solutions were prepared by dissolving 30-60 mg of the isolates in 0.5 L ultrapure water (>18 MΩ cm$^{-1}$) to create final stock concentrations of approximately 5,000 µM$_C$; isolates were used directly from sealed containers as received, or if previously opened, stored in a desiccator, and re-dried in a
furnace at 90 °C for 4 hours prior to weighing. All isolates were used within six months of purchase. The pH was adjusted to above 8.0 with NaOH to deprotonate the humic and fulvic acid isolates. The stock solutions were stirred vigorously for one hour and then left to sit at room temperature for 24 hours to ensure complete dissolution. Stocks were stored at 4 °C and used within four weeks of preparation.

Isolate stock concentrations were determined with a TOC-5000 (Shimadzu Corp., Tokyo, Japan) analyser with a minimum detection level of 0.2 mgC/L. The TOC-5000 was calibrated daily with potassium hydrogen phthalate. Fluorescence and specific absorbance measurements were made on a Horiba Scientific Aqualog Fluorometer (Horiba Ltd., Edison, NJ, USA). Fluorescence excitation-emission matrices (EEMs) were corrected for inner filter effects and Raleigh scatter using MATLAB R2012b (8.0.0.783). Select isolate \( M_w \) values were obtained from the literature, and elemental compositions were available from IHSS. Correlations between \( k_{\text{OH,NOM}} \) and NOM characteristics were performed using Excel (Microsoft Corporation, Redmond, WA).

### 2.2 R-SAM scavenging measurements

Scavenging values of NOM \( (k_{\text{OH,NOM}}) \) were determined by competition kinetics using high-absorbance dyes as probe compounds. Methylene blue (MB) and fluorescein were both evaluated as probe dyes. Prior to NOM measurements, the R-SAM competition kinetics method was validated with isopropyl alcohol. The resulting \( k_{\text{OH,IPA}} \) values were consistently within 26% of reported values.

For NOM measurements, 1 L samples of 270-300 \( \mu \)M \( \text{DOC} \) NOM were spiked with fluorescein or MB probe molecules to 5 and 1 \( \mu \)M, respectively, and 0.59 mM (20 mg/L) H\(_2\)O\(_2\). Aliquots of the mixture (40 mL) were spiked with tertiary butyl alcohol (t-BuOH) with final concentrations ranging from 0-1,000 \( \mu \)M (0-74.12 mg/L). Each aliquot was then exposed to a low-pressure ultraviolet lamp (Phillips Inc. #TUV PL-S 13W/2P) in a standard florescent light fixture with constant stirring. UV\(_{254}\) irradiance was determined by potassium iodide actinometry. The measured intensity was 0.54 mW/cm\(^2\) at 254 nm. The produced \( \cdot \text{OH} \) reacts with the NOM, t-BuOH, probe molecules, and is also scavenged by remaining H\(_2\)O\(_2\).

In each experiment, the spectrophotometer was zeroed with the NOM sample solution prior to the addition of the probe compound. The decay of the probe molecules was measured with an AvaSpec-2048 fiber optic spectrophotometer system, including an AvaLight-HAL tungsten halogen light source and AvaSoft software (Avantes Inc., Broomfield, CO). The decay of the probe molecules was monitored via their absorbance peaks at 460 nm and 664 nm for fluorescein and MB, respectively. The data for each t-BuOH concentration were converted to an apparent first-order degradation rate constant of the probe dye \( (k_{\text{app}}) \) based on

\[
-k_{\text{app}} = \frac{\ln\left(\frac{a_{\text{abs}}(P)}{a_{\text{abs}}(P)_0}\right)}{t} = k_{\text{app}}
\]

where \( t \) is the time of UV exposure in seconds, \( a_{\text{abs}}(P) \), and \( a_{\text{abs}}(P)_0 \) are the absorbance-based concentration of the probe dye at time \( t \) and time \( 0 \), respectively. Values of \( k_{\text{app}} \) were measured in samples with various concentrations of t-BuOH. The steady-state \( \cdot \text{OH} \) concentration could then be determined with a nonlinear fit of Eq. 2

\[
k_{\text{app}} = \frac{k_{\text{app}} \times \alpha_{\text{OH}}}{k_{\text{OH,NOM}}[\text{NOM}] + k_{\text{OH,IPA}}[t-BuOH] + k_{\text{OH,MB}}[t-BuOH] + k_{\text{OH,H}_2\text{O}_2}[H_2O_2]} \tag{2}
\]

where \( \alpha_{\text{OH}} \) is the production rate of \( \cdot \text{OH} \), \( P \) represents the probe dye, \( k_{\text{OH,X}} \) is the reaction rate constant of \( \cdot \text{OH} \) with a species \( X \), and \([\text{NOM}]\) is the concentration of NOM in the test water (the derivation of Eq. 2 is provided in the Supporting Information). The fitted data generates values for \( \alpha_{\text{OH}} \) and the NOM scavenging rate \( (k_{\text{OH,NOM}}[\text{NOM}]) \). The second-order rate constants \( k_{\text{OH,NOM}} \) were obtained by dividing \( k_{\text{OH,NOM}}[\text{NOM}] \) by sample NOM concentrations (M\(_0\)). Curves were fit and errors were determined using GraphPad Prism 6 software (GraphPad Software, Inc., La Jolla, CA). Standard error was propagated from independent TOC measurements and curve fitting errors. Reported values are inverse standard error weighted averages of two independent replicates (Table SI-1).

Control experiments were conducted to assess potential photo bleaching of NOM isolates and \( \cdot \text{OH} \) probes with UV\(_{254}\) doses equivalent to five times the highest doses used in the experiments. Additional control experiments examined NOM absorbance at 664 or 460 nm following exposure to \( \cdot \text{OH} \) in order to confirm that the decreasing absorbance values at these wavelengths corresponded to probe dye reactions with \( \cdot \text{OH} \) and not NOM reactions.

### 3 Results and discussion

#### 3.1 Comparison of probe compounds

Probe compounds used in the R-SAM must: (1) have high molar absorptivity in the visible spectrum; (2) produce minimal reactive byproducts when oxidized by \( \cdot \text{OH} \); (3) be insensitive to pH changes in the neutral range (pH from 5 - 9); (4) have an established reaction rate with \( \cdot \text{OH} \); (5) be photostable under direct UV\(_{254}\) exposure; and (6) interact minimally with sample constituents, such as NOM.

Herein, we tested two potential probes molecules, MB and fluorescein, for R-SAM \( k_{\text{OH,NOM}} \) measurements (Table 2). Both compounds have been used previously in similar applications. Fluorescein was used to assess the ability of antioxidants to suppress \([\cdot \text{OH}]_s\) in living tissues by comparing fluorescein decay rates, which were measured with fluorometry. MB has
been previously employed to detect the presence of \( \cdot \text{OH} \) via visual colorimetric test strips.\(^{30}\)

With regards to the probe compound criteria listed above, both MB and fluorescein have high molar absorptivity coefficients, approximately \( 7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1} \) at 664 nm and \( 3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1} \) at 460 nm, respectively.\(^{31,32}\) When reacted with \( \cdot \text{OH} \), both probes exhibited second order decay behaviour over a large range (C/C\(_0 \) \( \leq 0.2 \)), suggesting limited effects from oxidation byproducts (Supporting Information Figs. SI-1 and SI-2).

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>( k_{\text{on}} ) (M(^{-1}) s(^{-1}))</th>
<th>pKa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylene Blue</td>
<td><img src="image" alt="Methylene Blue Structure" /></td>
<td>( 1.2 \times 10^{10} )</td>
<td>(&lt;1^{34})</td>
</tr>
<tr>
<td>Fluorescein</td>
<td><img src="image" alt="Fluorescein Structure" /></td>
<td>( 1.16 \pm 0.21 \times 10^{10} )</td>
<td>6.4(^{11})</td>
</tr>
</tbody>
</table>

Table 2: Methylene blue and fluorescein parameters.

Due to its low pKa, absorption characteristics of MB are not affected over a pH range of 3.4-11.2.\(^{34}\) With a pKa\(_2\) of 6.4, however, fluorescein absorption is highly pH dependent.\(^{35}\) To minimize the effects of pH on fluorescein measurements, fluorescein decay was tracked by measuring absorbance at an isosbestic (i.e., pH independent) wavelength of 460 nm and solution pH was maintained at least two units above the pKa\(_2\) to ensure a deprotonated molecule.

A reaction rate constant with \( \cdot \text{OH} \) was previously reported for MB,\(^{33}\) but was not available for fluorescein. Therefore, the second order rate constant for fluorescein was measured by competition kinetic experiments, in which the reaction of fluorescein with \( \cdot \text{OH} \) was monitored in the presence of a competitive scavenger (t-BuOH) in lab-grade water, over a range of concentrations.\(^{14}\) A non-linear fit of the data provided a \( k_{\text{OH,fluorescein}} \) value of \( 1.16 (\pm 0.21) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \).

Neither probe decayed by more than 1% following exposure to 300 s of UV\(_{254}\) (Figure 1 and Supporting Information Figure SI-1); this was five times the maximum dose in the \( k_{\text{OH,NOM}} \) experiments. Both probes were therefore determined photostable with UV\(_{254}\). MB interacted significantly with NOM isolates, as the MB absorbance peak at 664 nm decreased following the addition of Elliot Soil Humic Acid (Fig. 1). This is likely due to the positive charge of MB ions and the negative charge of NOM constituents. As a result, MB was not used in experimental NOM measurements. The additive absorbance values observed in the ESHA and fluorescein absorption spectra (Fig. 1) indicates minimal interactions between the two species. Based on these observations, we recommend negatively charged probe molecules for \( \cdot \text{OH} \) scavenging measurements of concentrated NOM samples. For the remainder of this study, a fluorescein probe was used to measure \( k_{\text{OH,NOM}} \).

3.2 Rate constants for reaction of \( \cdot \text{OH} \) with NOM isolates

In total, six isolates were measured with the R-SAM technique, and the resulting \( k_{\text{OH,NOM}} \) values ranged from \( 1.02 - 2.01 \times 10^{8} \text{ M}^{-1} \text{ s}^{-1} \) (Table 2). The PLFA-R isolate resulted in the highest rate constant and SRFA S-1 resulted in the lowest rate constant (Table 2). To our knowledge, this is the first report of \( k_{\text{OH,NOM}} \) values for PPFA-S and PPHA-S isolates; ESHA-S, PLFA-R, SRFA-IS, and SRHA II-S were reported previously, but measured with different techniques (Fig. 2 and Table 3).

The range of \( k_{\text{OH,NOM}} \) values reported here is in general agreement with previous work.\(^{23,24,25}\) The \( k_{\text{OH,NOM}} \) value for ESHA-S was similar to previous reports, but the PLFA-R, SRFA-IS, and SRHA II-S values were significantly lower than values that were determined with pulse radiolysis and SCN\(^{-} \) decay measurements (Table 1; Figure 2). In particular, the SRHA II-S value measured in this work was nearly an order of magnitude lower than a value reported previously in the literature.\(^{13}\) Interestingly, the measured SRHA II-S \( k_{\text{OH,NOM}} \) value was nearly equal to three previously reported SRHA I-S \( k_{\text{OH,NOM}} \) values, each determined with different techniques (Figure; Table 1). SRHA I-S and SRHA II-S isolates were sampled from the same source on different dates—1982-1983 and 2003, respectively. In support of the SRHA II measurement made here, it seems unlikely that the humic acid characteristics from the Suwannee River source would change so drastically over twenty years to result in nearly a \( 10^{8} \) increase in \( k_{\text{OH,NOM}} \) Future work should seek to resolve discrepancies amongst \( k_{\text{OH,NOM}} \) values collected with different techniques and in different laboratories.
Table 3: \( k_{\text{OH,NOM}} \) and characteristics of studied NOM isolates.


<table>
<thead>
<tr>
<th>IHSS Catalogue Number/ acronym</th>
<th>NOM Full Name</th>
<th>Measured ( k_{\text{OH,NOM}} ) (M(_{-c})-s(^{-1}) \times 10(^{f}) ±SE)</th>
<th>%C**</th>
<th>%O**</th>
<th>%H**</th>
<th>%N**</th>
<th>%aliphatic/%aromatic</th>
<th>( M_w ) (Da)**</th>
<th>Fl</th>
<th>SUVA (_{254})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1R109F/ PLFA-R</td>
<td>Pony Lake Fulvic Acid Reference</td>
<td>2.03±0.12</td>
<td>52.50%</td>
<td>31.40%</td>
<td>5.39%</td>
<td>6.51%</td>
<td>5.08</td>
<td>2400</td>
<td>1.22</td>
<td>4.78</td>
</tr>
<tr>
<td>2S103F/ PFFA II-S</td>
<td>Pahokee Peat Fulvic Acid Standard (Sample Date 2)</td>
<td>1.53±0.13</td>
<td>51.30%</td>
<td>43.30%</td>
<td>3.53%</td>
<td>2.34%</td>
<td>---</td>
<td>---</td>
<td>0.89</td>
<td>1.63</td>
</tr>
<tr>
<td>1S102H/ ESHA-S</td>
<td>Elliot Soil Humic Acid Standard</td>
<td>1.38±0.08</td>
<td>58.10%</td>
<td>34.10%</td>
<td>3.68%</td>
<td>4.14%</td>
<td>0.32</td>
<td>3100</td>
<td>0.75</td>
<td>1.52</td>
</tr>
<tr>
<td>2S101H/ SRFA II-S</td>
<td>Suwannee River Humic Acid Standard (Sample Date 2)</td>
<td>1.37±0.10</td>
<td>52.60%</td>
<td>42.00%</td>
<td>4.28%</td>
<td>1.17%</td>
<td>94</td>
<td>4100</td>
<td>0.93</td>
<td>1.56</td>
</tr>
<tr>
<td>1S103H/ PPHA I-S</td>
<td>Pahokee Peat Humic Acid Standard (Sample Date 1)</td>
<td>1.19±0.12</td>
<td>56.40%</td>
<td>37.30%</td>
<td>3.82%</td>
<td>3.69%</td>
<td>---</td>
<td>---</td>
<td>0.86</td>
<td>1.55</td>
</tr>
<tr>
<td>1S101F/ SRFA I-S</td>
<td>Suwannee River Fulvic Acid Standard (Sample Date 1)</td>
<td>1.02±0.10</td>
<td>52.20%</td>
<td>42.20%</td>
<td>4.31%</td>
<td>0.72%</td>
<td>1.38</td>
<td>2800</td>
<td>1.09</td>
<td>2.59</td>
</tr>
</tbody>
</table>

Regression Slope (w/single-tailed 95% C.I.)

\(-3.2±13.1 \times 10^{4}\) \(-4.1±6.1 \times 10^{4}\) \(3.1±4.3 \times 10^{5}\) \(1.2±1.1 \times 10^{6}\) \(-7.7±188 \times 10^{6}\) \(-2.2±11.0 \times 10^{7}\) \(9.1±19.3 \times 10^{7}\) \(1.8±2.5 \times 10^{8}\)

**Fig. 2:** Measured \( k_{\text{OH,NOM}} \) (±SE) for NOM isolates from this study and others; Fl. R-SAM: fluorescence based R-SAM, SCN: SCN fluorescence index (FI) (Table 3; Supporting Information Figure SI-3). No significant correlations between \( k_{\text{OH,NOM}} \) and most NOM characteristics were evident (Table 3). There was slight evidence of a correlation between nitrogen and scavenging rate, however, not enough to yield useful predictive capabilities. These results are in agreement with previous studies,\(^{13,24}\) and suggest that simple NOM characteristic measurements are not adequate to predict \( k_{\text{OH,NOM}} \).

Although a multivariate approach similar to that used successfully with EfOM\(^{26,27}\) may improve \( k_{\text{OH,NOM}} \) predictive capabilities, the required NOM characteristic values needed for such a model would take time, and in some cases expensive instrumentation, to collect. The R-SAM method presented here measures \( k_{\text{OH,NOM}} \) in under one hour with a field deployable unit. Consequently, we argue that in applications where the purpose is to model or predict total background scavenging, the direct measurement of effective scavenging in an unknown sample with a rapid spectrophotometric method is simpler and more straightforward than predicting \( k_{\text{OH,NOM}} \) with a multivariate predictive model based on several NOM characteristics.

### 4 Conclusions

A rapid, field-deployable, background scavenging method was optimized and successfully applied to measure \( k_{\text{OH,NOM}} \) for six NOM isolates. The resulting scavenging levels were in general agreement with previous reports of \( k_{\text{OH,NOM}} \), though some discrepancies were found for isolates measured with a method...
involving pulse radiolysis for the formation of •OH and SCN− probe transformations. No correlations existed between the physical/chemical characteristics of the NOM isolates and the measured \( k_{\text{OH,NOM}} \) values that could facilitate predicting \( k_{\text{OH,NOM}} \). Overall, the results suggest that the R-SAM is a simplified and effective approach for background scavenging measurements. Future work of our team will aim to employ the R-SAM method to track scavenging levels in surface waters and drinking water treatment plant waters over extended periods of time.

5 References