

Quantifying Hydrated Electron Transformation Kinetics in UV-Advanced Reduction Processes Using the $R_{e-,UV}$ Method

Benjamin D. Fennell, Adam Odorisio, and Garrett McKay*



Cite This: *Environ. Sci. Technol.* 2022, 56, 10329–10338



Read Online

ACCESS |



Metrics & More



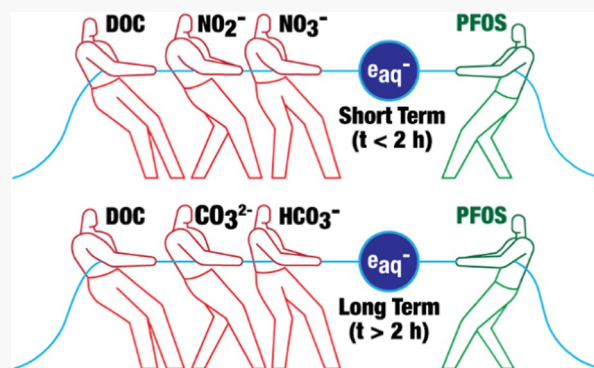
Article Recommendations



Supporting Information

ABSTRACT: Ultraviolet advanced reduction processes (UV-ARP) have garnered significant attention recently for the degradation of several hard to treat contaminants, including recalcitrant per- and polyfluoroalkyl substances (PFAS). The rate of contaminant degradation in UV-ARP is directly related to the available hydrated electron concentration ($[e_{aq}^-]$). However, reports of $[e_{aq}^-]$ and other parameters typically used to characterize photochemical systems are not widely reported in the UV-ARP literature. Deploying monochloroacetate as a probe compound, we developed a method ($R_{e-,UV}$) to quantify the time-based hydrated electron concentration ($[e_{aq}^-]_t$) available for contaminant degradation relative to inputted UV fluence. Measured $[e_{aq}^-]_t$ was then used to understand the impact of e_{aq}^- rate of formation and scavenging capacity on the degradation of two contaminants—nitrate and perfluorooctane sulfonate (PFOS)—in four source waters with varying background water quality. The results show that the long-term treatability of PFOS by UV-ARP is not significantly impacted by the initial e_{aq}^- scavenging conditions but rather is influenced by the presence of e_{aq}^- scavengers like dissolved organic carbon and bicarbonate. Lastly, using $[e_{aq}^-]_t$, degradation of nitrate and PFOS was modeled in the source waters. We demonstrate that the $R_{e-,UV}$ method provides an effective tool to assess UV-ARP treatment performance in a variety of source waters.

KEYWORDS: hydrated electron, PFAS, PFOS, nitrate, UV-ARP, monochloroacetate, scavenging capacity



1. INTRODUCTION

The rate of contaminant degradation in ultraviolet advanced reduction processes (UV-ARP) is directly related to the available concentration of hydrated electron (e_{aq}^-). Acting as a powerful reductant (E° of -2.9 V),¹ e_{aq}^- is produced through the illumination of a chemical sensitizer (e.g., sulfite) and has been explored for the treatment of a wide range of contaminants, such as oxyanions,^{2–6} high-valence transition metals and metalloids,^{7,8} and halogenated organic compounds,^{9–12} including per- and polyfluoroalkyl substances (PFAS).^{13–26} Furthermore, extensive laboratory studies within the past decade^{13–22} and a recent pilot-scale study²³ suggest that e_{aq}^- -based UV-ARP are a promising technology for degrading PFAS, which are resistant to direct photolysis and ultraviolet advanced oxidation processes (UV-AOP).^{13,14,27} Despite the growing success of e_{aq}^- -based UV-ARP treatment, a method to determine the available e_{aq}^- concentration for contaminant degradation has yet to be developed.

Quantifying the time-based hydrated electron concentration ($[e_{aq}^-]_t$) is important in UV-ARP treatment due to the varied treatment times required for contaminant degradation and the potential for e_{aq}^- formation and scavenging conditions to change over these time scales. For instance, nitrate, which has high reactivity with e_{aq}^- , completely degrades on the time scale

of minutes in UV-ARP systems,^{2,28,29} whereas degradation half-lives of hours are typical for more recalcitrant contaminants like PFAS.^{15,22} It is likely that the $[e_{aq}^-]_t$ experienced by nitrate and PFAS at early treatment times is not the same as at later treatment times. This contrasts with UV-AOP in which hydroxyl radical ($\cdot OH$)-mediated contaminant transformation kinetics occur on much shorter time scales,³⁰ such that the $[\cdot OH]$ in these systems is assumed to be at a steady state. The $[e_{aq}^-]_t$ available for contaminant degradation is impacted by e_{aq}^- scavengers present in water. Past studies have demonstrated the inhibitory impacts e_{aq}^- scavengers such as dissolved oxygen,^{6,31} nitrate,¹⁰ dissolved organic matter (DOM),^{8,11} and bicarbonate¹¹ have on contaminant degradation. While these studies highlight the importance of individual e_{aq}^- scavengers, the combined, long-term impact of e_{aq}^- scavengers most often present in natural waters has not been considered.

Received: March 22, 2022

Revised: June 17, 2022

Accepted: June 20, 2022

Published: July 6, 2022



Table 1. Water Quality Parameters for the Four Source Waters Used in This Study

	Simsboro Aquifer ^a	Lake Bryan ^a	LWC RBF ^a	Ohio River ^a
DOC (mgC L ⁻¹)	1.1	9.8	1.7	3.9
NO ₃ ⁻ (mg L ⁻¹ or μ M)	BDL	BDL	0.46 or 7.4	4.57 or 73.8
alkalinity (mg L ⁻¹ as CaCO ₃)	580	679	161	92
fluoride (mg L ⁻¹)	0.30	0.54	0.0	0.0
pH	8.6	9.4	7.9	7.9
SUVA ₂₅₄ (L mgC ⁻¹ m ⁻¹)	1.0	2.4	1.9	3.5
A _{254 nm} (cm ⁻¹)	0.011	0.238	0.033	0.137
specific conductance (μ S cm ⁻¹)	1,084	1,414	393	302
R _{eq} ^c (M s ⁻¹) ^b	3.6×10^{-7}	2.9×10^{-7}	3.6×10^{-7}	3.1×10^{-7}

^aNO₂⁻ concentration below detection limit (BDL). ^bComputed with eq 3.6 under the following experimental conditions: 10 W low-pressure Hg lamp, pH₀ = 9.4–9.7, 20 °C, [MCAA]₀ = 20 μ M, [SO₃²⁻]₀ = 10.0 mM, [PFOS]₀ = 20.0 μ M (Simsboro Aquifer [PFOS]₀ = 16.3 μ M).

The purpose of this paper is to develop a method for characterizing the key properties of e_{aq}⁻-mediated transformation kinetics in UV-ARP, namely, [e_{aq}⁻]_t and k'_{S,t} (e_{aq}⁻ scavenging capacity). To this end, we deployed a probe compound selective for e_{aq}⁻ in the UV/sulfite system, monochloroacetate (MCAA), and developed the R_{e-UV} method (defined as the e_{aq}⁻ exposure per UV fluence) in analogy to R_{OH,UV} previously used for the UV/H₂O₂ system.³² We then use the R_{e-UV} method to model the degradation rates of two contaminants—nitrate (NO₃⁻) and perfluorooctane sulfonate (PFOS)—in four source waters with varying water quality. The results demonstrate that a water's initial e_{aq}⁻ scavenging capacity does not necessarily determine the ultimate treatability of PFOS. Rather, the extent of PFOS degradation is determined by the total e_{aq}⁻ exposure as measured by the R_{e-UV} method.

2. MATERIALS AND METHODS

2.1. Chemicals. A list of chemicals and standards is available in Table S1 in the Supporting Information (SI). Details on solution preparation can be found in SI Text S1. Ultrapure water (≥ 18.2 M Ω cm) for solution preparation and photochemistry experiments was obtained from a Barnstead purification system (ThermoFisher).

2.2. Source Waters. Four source waters with different background matrix compositions were selected for analysis (Table 1). The samples included groundwater from the Simsboro Aquifer (Brazos County, TX), Lake Bryan surface water (Brazos County, TX), Ohio River surface water (Louisville, KY), and Louisville Water Company (Louisville, KY) post riverbank filtration (LWC RBF). The LWC RBF source water is the Ohio River filtered naturally by the riverbank. Source water samples were filtered through muffled (500 °C, 4 h) and prerinsed 1.6 μ m Whatman glass microfiber filters (GF/A) and stored at 4 °C until use.³³ Water quality parameters including dissolved organic carbon (DOC), nitrate, nitrite, fluoride, alkalinity, pH, specific conductance, and absorbance at 254 nm (A₂₅₄) were measured for each source water (see SI Text S2).

2.3. Photochemical Irradiation Experiments. Irradiation experiments were performed in duplicate immersion well reactors (Ace Glass) containing 570 mL of total solution. The reactors included an exterior glass body and an interior quartz immersion sleeve. A low-pressure Hg, nonozone forming lamp emitting at 254 nm (10 W LSE Lighting GPH212TSL/4P or 11 W Philips TUV T5 4P-SE) was placed into each quartz sleeve and powered on for at least 15 min before each experiment. UV irradiance was measured monthly using

uridine actinometry³⁴ with a range of 9.58×10^{-9} – 1.15×10^{-8} Es cm⁻² s⁻¹ observed over the study period. The average path length for each reactor was determined as 2.23 ± 0.02 cm using the H₂O₂ method.^{35,36} SI Text S4–S5 further explain UV irradiance and path length measurements. Kinetic parameters will be reported below as the reactor average with error bars corresponding to the minimum and maximum for each reactor.

Sulfite was selected as the e_{aq}⁻ source for these experiments because of its extensive use in prior UV-ARP studies.^{5,10,21} UV/sulfite experiments were conducted under anaerobic conditions at 2 pH units above the pK_a of HSO₃⁻ (pK_a = 7.2) to minimize the e_{aq}⁻ scavenging impacts of HSO₃⁻.^{1,37,38} The initial pH of the groundwater and surface water experiments was adjusted to 9.4–9.7 using a 1.0 M sodium hydroxide solution. All ultrapure water experiments utilized a 1.0 mM borate buffer (pH 9.9) with the exception of one control experiment that used a 10.0 mM NaHCO₃⁻ buffer (pH 9.8). Nitrogen gas was bubbled for 45 min prior to initiating an experiment and continuously thereafter to remove O₂. The temperature of the reactors was maintained at 20 °C by a recirculating chiller while a magnetic stir bar maintained a 400-rpm stirring speed. After warming the lamp for at least 15 min, the lamp was briefly turned off while concentrated stock solutions of PFOS, MCAA, or sodium sulfite were spiked into the reactors and allowed to mix for at least 30 s. Lamps were then turned back on and aliquots of solution (1–3 mL) were collected at specific time intervals using a stainless-steel needle and syringe. PFOS samples were stored in 15 mL polypropylene Falcon tubes at 4 °C before analysis. Anion samples were collected in 10 mL polystyrene vials and analyzed within 48 h.

Numerous UV/sulfite experiments were conducted to assess e_{aq}⁻-mediated transformation kinetics. Generally, experiments presented in Sections 3.1 and 3.2 focus on initial transformation kinetics deploying 20 μ M MCAA under varying sulfite concentrations. Sections 3.3 and 3.4 investigate temporal variations in e_{aq}⁻-mediated transformation kinetics by spiking 20 μ M MCAA at various time points throughout a 24 h experiment (20 μ M PFOS and 10 mM sulfite were spiked at time zero only). Experimental results presented in Sections 3.1–3.4 utilize all four source waters and ultrapure water. A 20 μ M MCAA probe compound concentration was selected to minimize its contribution to the total e_{aq}⁻ scavenging capacity while also permitting quantification of kinetic degradation within analytical detection limits.

2.4. Analytical Methods. Nitrate, nitrite, fluoride, and MCAA concentrations were measured on a Dionex Integriion ion chromatography system (ThermoFisher). Sulfite concen-

trations were determined spectrophotometrically using 5,5'-dithiobis(2-nitrobenzoic acid) (DTNB).³⁹ PFOS was isolated using solid-phase extraction (SPE) and quantified on a triple quadrupole mass spectrometer (Altis, Thermo Scientific, Waltham, MA) coupled to a binary pump HPLC (Vanquish, Thermo Scientific) in the Texas A&M University Integrated Metabolomics Analysis Core lab. Detailed analytical methods for anion and PFOS analysis are provided in SI Text S7 and SI Text S8.

Electron pulse radiolysis was used to measure the bimolecular reaction rate constant of e_{aq}^- with Suwannee River fulvic acid (SRFA, 2S101F), a surrogate for DOM in our source waters. Briefly, a linear accelerator system at the University of Notre Dame Radiation Laboratory was used to produce e_{aq}^- from the radiolysis of water.⁴⁰ Transient e_{aq}^- decays at 720 nm were measured at a range of [SRFA] (between 0 and 200 mg/L) at pH 9.0 (10 mM phosphate). Rate constants were normalized to carbon concentration using the carbon mass % of SRFA (52.34%). Additional details for bimolecular rate constant measurements are provided in SI Text S9.

3. RESULTS AND DISCUSSION

3.1. Probe Compound Selection and Deployment. We chose MCAA to probe the $[e_{aq}^-]$ formed in the UV/sulfite system based on its use in previous UV-ARP.^{10–12,41} Control experiments were performed to verify that MCAA reacts selectively with e_{aq}^- in the UV/sulfite system (SI Figure S3). Briefly, the results indicate that MCAA undergoes no direct photolysis at 254 nm, no dark reduction with SO_3^{2-} over the experimental time scale, and that its transformation is mediated by e_{aq}^- and not other reactive species produced in the UV/sulfite system (e.g., $SO_3^{\bullet-}$). Additional benefits of MCAA as a probe compound include its low vapor pressure, high water solubility, and occurrence as the chloroacetate anion over a broad pH range ($pK_a = 2.87$).⁴² We selected a 20 μM $[MCAA]_0$ to minimize its contribution to the total e_{aq}^- scavenging capacity.

The $[e_{aq}^-]$ can be measured using the rate law for the loss of MCAA in the UV/sulfite system (eq 3.1)

$$\frac{d[MCAA]}{dt} = -(k'_d + k_{MCAA,e_{aq}^-}[e_{aq}^-])[MCAA] \quad (3.1)$$

where k'_d is the rate constant for MCAA loss by direct photolysis (s^{-1}), k_{MCAA,e_{aq}^-} is the bimolecular rate constant for the transformation of MCAA ($1.0 \times 10^9 M^{-1} s^{-1}$),¹ $[MCAA]$ is the concentration of MCAA (M) remaining, and $[e_{aq}^-]$ is the concentration of hydrated electron (M). To use this model in natural waters, k_{MCAA,e_{aq}^-} must be corrected for ionic strength using the Brønsted-Bjerrum equation. SI Text S10 and SI Table S3 provide additional details on ionic strength calculations for the four source waters. Since MCAA experiences no direct photolysis at 254 nm, eq 3.1 can be simplified and integrated to form eq 3.2.

$$\ln\left(\frac{[MCAA]_t}{[MCAA]_0}\right) = -k_{MCAA,e_{aq}^-} \int_0^t [e_{aq}^-]_t dt \quad (3.2)$$

The time interval from 0 to t represents the MCAA decay kinetics from the time that MCAA was spiked into the solution to the last quantifiable concentration at time t . $\int_0^t [e_{aq}^-]_t dt$ represents the e_{aq}^- exposure over this time interval and is a

function of water quality parameters, accounting for both the rate of e_{aq}^- formation and the e_{aq}^- scavenging capacity. Dividing both sides of eq 3.2 by the UV fluence, H (i.e., the average fluence rate, E_0 ($mJ cm^{-2} s^{-1}$) multiplied by the exposure time, t (s)), normalizes the e_{aq}^- exposure to the inputted UV fluence and yields $R_{e-,UV}$ in units of $M s cm^2 mJ^{-1}$ (eq 3.3).

$$R_{e-,UV} = \frac{-\ln\left(\frac{[MCAA]_t}{[MCAA]_0}\right)}{E_0 \times t \times k_{MCAA,e_{aq}^-}} = \frac{\int_0^t [e_{aq}^-]_t dt}{H} \quad (3.3)$$

The method for calculating E_0 is provided in SI Text S6. $R_{e-,UV}$ was determined experimentally by plotting $\ln\left(\frac{[MCAA]_t}{[MCAA]_0}\right)$ against t to obtain the first-order rate constant k' (min^{-1}), which was then divided by E_0 and k_{MCAA,e_{aq}^-} (eq 3.4),

$$R_{e-,UV} = \frac{-k'}{E_0 \times k_{MCAA,e_{aq}^-}} = \frac{-k'_D}{k_{MCAA,e_{aq}^-}} = \frac{\int_{t_1}^{t_2} [e_{aq}^-]_t dt}{H} \quad (3.4)$$

where k'_D is a fluence-based rate constant with units ($cm^2 mJ^{-1}$). An example calculation is provided in SI Text S11.

$R_{e-,UV}$ can be used to calculate the e_{aq}^- formation and scavenging conditions. If we assume that the $[e_{aq}^-]$ does not change appreciably over the interval in which $[MCAA]$ loss is monitored, we can then multiply $R_{e-,UV}$ by E_0 and obtain the concentration of e_{aq}^- at time t , $[e_{aq}^-]_t$. This $[e_{aq}^-]_t$ is equivalent to the e_{aq}^- formation rate, $R_{e_{aq}^-}^{eq}$ ($M s^{-1}$), divided by the total e_{aq}^- scavenging capacity (e_{aq}^- scavenging capacity of the water matrix, $k'_{S,t}$, plus e_{aq}^- scavenging capacity of MCAA, $k'_{MCAA,t}$ (s^{-1})) at time t and is shown in eq 3.5.

$$[e_{aq}^-]_t = \frac{R_{e_{aq}^-}^{eq}}{k'_{S,t} + k'_{MCAA,t}} \quad (3.5)$$

Furthermore, under the monochromatic UV/sulfite conditions employed in this study, eq 3.5 can be expanded to yield eq 3.6

$$[e_{aq}^-]_t = \left(\frac{\Phi_{e_{aq}^-} \frac{I_0}{l} (1 - 10^{-(\epsilon_{SO_3^{2-}}[SO_3^{2-}]_t + \alpha_t)l})}{k'_{S,t} + k'_{MCAA,t}} \right) \left(\frac{\epsilon_{SO_3^{2-}}[SO_3^{2-}]_t}{\epsilon_{SO_3^{2-}}[SO_3^{2-}]_t + \alpha_t} \right) \quad (3.6)$$

where $\Phi_{e_{aq}^-}$ is the e_{aq}^- quantum yield of sulfite (0.116 Mol Es^{-1}),¹⁰ I_0 is the photon irradiance ($mmol photons cm^{-2} s^{-1}$), $\epsilon_{SO_3^{2-}}$ is the molar absorption coefficient at 254 nm ($18.14 M^{-1} cm^{-1}$),¹⁰ $[SO_3^{2-}]_t$ is the sensitizer's concentration (M) at time t , α_t is the absorption coefficient of the background water matrix (cm^{-1}) at time t , $[e_{aq}^-]_t$ is the concentration of e_{aq}^- measured by MCAA in eq 3.4 at time t , and l is the path length (2.23 cm).⁴³

Deploying MCAA as a selective e_{aq}^- probe compound allows key variables such as $[e_{aq}^-]_t$, $R_{e_{aq}^-}^{eq}$, and $k'_{S,t}$ to be measured in the UV/sulfite system. Reporting $R_{e-,UV}$ further allows the e_{aq}^- exposure to be normalized to the inputted UV fluence, affording an equivalent comparison between different UV-ARP treatment systems and different water types.

3.2. Hydrated Electron Formation Rates, Scavenging Capacities, and $R_{e-,UV}$ at Initial Conditions. The

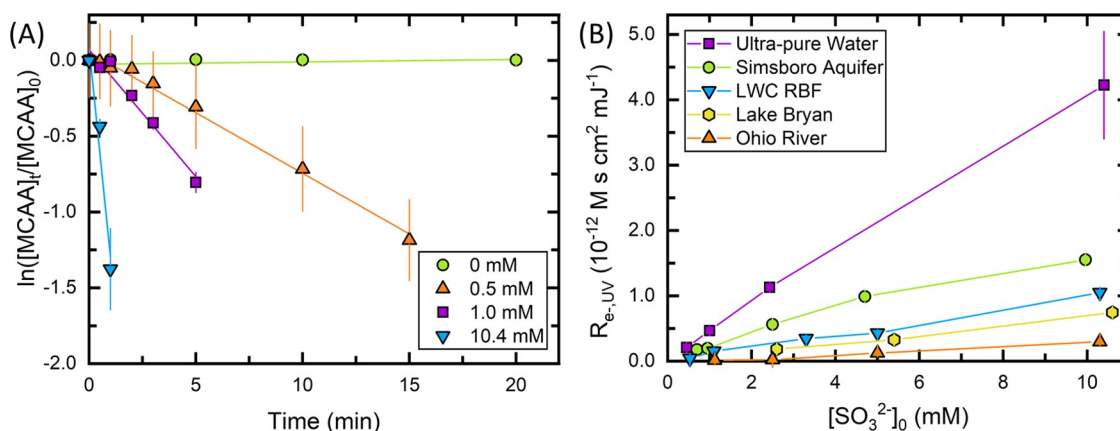


Figure 1. R_{e-UV} at initial conditions. (A) Measured MCAA degradation (symbols) as a function of time with variable $[SO_3^{2-}]_0$ in ultrapure water. Lines represent a linear fit to the data. (B) R_{e-UV} with variable $[SO_3^{2-}]_0$ for all waters. All experiments in panels (A) and (B) include the following conditions: 10 W low-pressure Hg lamp, $pH_0 = 9.1\text{--}9.7$, 20°C , $[MCAA]_0 = 20 \mu\text{M}$, and $[\text{borate}] = 1.0 \text{ mM}$ (ultrapure water only). Markers represent the mean of duplicate measurements and error bars represent the range between the duplicates.

concentration of reactive species is a key variable influencing the rate of target contaminant degradation in advanced oxidation and reduction technologies.^{10,44} It is generally recognized that the background water quality exerts a significant influence on the availability of reactive species for contaminant degradation in advanced oxidation and reduction processes.^{45,46} For example, the scavenging capacity of $\bullet\text{OH}$ in UV-AOP systems is impacted by DOM, carbonate/bicarbonate, and nitrite.⁴⁵ However, in UV-ARP systems, there is a lack of quantitative understanding of the effect of background water quality parameters on e_{aq}^- availability.⁴⁶ Thus, we used MCAA transformation to measure $R_{f,t}^{e_{aq}^-}$, $k'_{S,t}$, and R_{e-UV} for four water samples with varying background water quality.

To evaluate these factors under initial conditions, we examined the transformation kinetics of MCAA in the UV/sulfite system for $[SO_3^{2-}]_0$ ranging from 0.5 to 10.4 mM (Figure 1). Figure 1A displays the kinetic data for ultrapure water at different $[SO_3^{2-}]_0$, which were fit with a first-order model to obtain the slope k' and calculate R_{e-UV} (Figure 1B). For ultrapure water, if we invoke the steady-state assumption, in which we reasonably expect that $R_{f,t}^{e_{aq}^-}$ and $k'_{S,t}$ will not change appreciably over a 30 min period (SI Table S5), then the calculated reactor average $[e_{aq}^-]_{ss}$ values range from $2.5 \times 10^{-12} \text{ M}$ ($[SO_3^{2-}]_0 = 1.0 \text{ mM}$) to $1.6 \times 10^{-11} \text{ M}$ ($[SO_3^{2-}]_0 = 10.4 \text{ mM}$).

Similar kinetic experiments were performed for all source waters and the resulting R_{e-UV} values (within the first 30 min of irradiation) are plotted in Figure 1B. Significant variation in R_{e-UV} values occurred amongst the different source waters. For example, R_{e-UV} at 10 mM sulfite for the Simsboro Aquifer sample ($1.6 \times 10^{-12} \text{ M s cm}^2 \text{ mJ}^{-1}$) was more than 5-folds higher than for the Ohio River ($3.0 \times 10^{-13} \text{ M s cm}^2 \text{ mJ}^{-1}$). R_{e-UV} increased with increasing $[SO_3^{2-}]_0$ for all samples. Ohio River had the largest relative change in R_{e-UV} between 2.5 and 10 mM (13.7-fold), whereas Simsboro Aquifer had the lowest (2.8-fold). These results indicate that R_{e-UV} measured via MCAA can detect changes in e_{aq}^- formation and scavenging conditions in the UV/sulfite system.

We calculated $R_{f,0}^{e_{aq}^-}$ and $k'_{S,0}$ based on the measured R_{e-UV} and eq 3.6 for each source water under 10 mM $[SO_3^{2-}]_0$ conditions. Table 1 lists the water quality parameters associated with the formation and scavenging of e_{aq}^- for

each source water. Lake Bryan and the Ohio River (surface waters) both have a higher DOC concentration than LWC RBF and Simsboro Aquifer (groundwaters) and, consequently, at least an order of magnitude greater $A_{254 \text{ nm}}$. The Ohio River had the highest level of nitrate while Lake Bryan had the highest alkalinity. According to eq 3.6, the variability of $R_{f,0}^{e_{aq}^-}$ is attributable to the background absorbance of the source water (α_t in eq 3.6 is $A_{254 \text{ nm}}$ in Table 1) as the other terms remain equivalent between samples. However, the computed $R_{f,0}^{e_{aq}^-}$ values shown in Table 1 vary by less than 20% between the source waters, indicating that $R_{f,0}^{e_{aq}^-}$ has a minor influence on R_{e-UV} at a $[SO_3^{2-}]_0$ of 10 mM.

The minor variations in $R_{f,0}^{e_{aq}^-}$ between the source waters suggest that differences in R_{e-UV} are attributable to the e_{aq}^- scavenging capacity; thus, we assessed the $k'_{S,0}$ for each source water using two approaches. First, $k'_{S,0}$ was calculated using eq 3.6, which is based on the measured values of R_{e-UV} and $R_{f,0}^{e_{aq}^-}$. Second, $k'_{S,0}$ was calculated using eq 3.7

$$k'_{S,t} = \sum_i k_{S,e_{aq}^-} [S_i]_t \quad (3.7)$$

where k_{S,e_{aq}^-} is the e_{aq}^- bimolecular rate constant and $[S_i]_t$ is the scavenger concentration at time t . Note that $k'_{S,t}$ is the e_{aq}^- scavenging capacity of the water matrix and does not include the e_{aq}^- scavenging capacity of MCAA ($k_{MCAA,t}$). All bimolecular rate constants were taken from literature values,³⁸ with the exception of k_{DOC,e_{aq}^-} , and adjusted for aqueous ionic strength impacts using the Brønsted-Bjerrum equation.¹ k_{DOC,e_{aq}^-} was measured for SRFA using pulse radiolysis as described in Section 2.4 and is reported as $1.97 \times 10^4 \text{ L mgC}^{-1} \text{ s}^{-1}$. We did not apply ionic strength corrections to k_{DOC,e_{aq}^-} , which may underestimate the calculated contribution of DOC to e_{aq}^- scavenging.

Figure 2 shows the measured (eq 3.6) and estimated (eq 3.7) $k'_{S,0}$ for all of the source waters. Regardless of the method employed, $k'_{S,0}$ followed the order Ohio River $\gg$ Lake Bryan $>$ LWC RBF $>$ Simsboro Aquifer. For Ohio River and LWC RBF, the largest fraction of the calculated e_{aq}^- scavenging was due to nitrate, whereas for Lake Bryan, DOC was the most important e_{aq}^- scavenger. Simsboro Aquifer had the lowest

measured $k'_{S,0}$ ($4.2 \times 10^4 \text{ s}^{-1}$) amongst the source waters, equating to only 5% of the measured $k'_{S,0}$ for the Ohio River ($7.9 \times 10^5 \text{ s}^{-1}$). e_{aq}^- quenching by SO_3^{2-} is presented using the reported upper limit of the bimolecular rate constant ($\leq 1.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$),³⁸ which gives the impression that SO_3^{2-} is a significant scavenger for Simsboro Aquifer. The variability in $k'_{S,0}$ directly impacts the $[e_{aq}^-]$ available for contaminant degradation, implying that the Ohio River will have the lowest $[e_{aq}^-]$ and that Simsboro Aquifer will have the highest $[e_{aq}^-]$. This is exactly the trend observed for $R_{e-,UV}$ (Figure 1B). Thus, significant differences in initial e_{aq}^- scavenging capacities between the four source waters (Figure 2) are the main contributors to the variation in initial $R_{e-,UV}$ (Figure 1B).

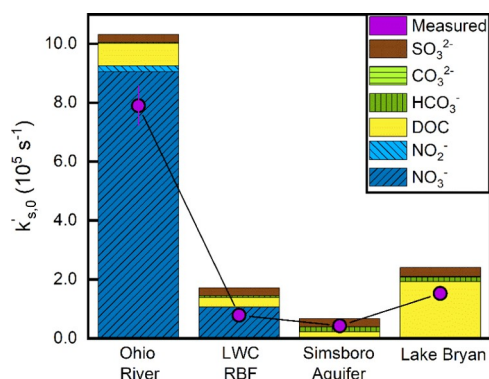


Figure 2. Measured (eq 3.6) and estimated (eq 3.7) $k'_{S,0}$ for each source water. Adjusted bimolecular rate constants accounting for ionic strength were used to calculate $k'_{S,0}$. Nonadjusted bimolecular rate constants ($\text{M}^{-1} \text{ s}^{-1}$) used are as follows: $k_{\text{SO}_3^{2-}, e_{aq}^-} = 1.3 \times 10^6$, $k_{\text{MCAA}, e_{aq}^-} = 1.0 \times 10^9$, $k_{\text{CO}_3^{2-}, e_{aq}^-} = 3.9 \times 10^5$, $k_{\text{HCO}_3^-, e_{aq}^-} = 1.0 \times 10^6$, $k_{\text{DOC}, e_{aq}^-} = 1.97 \times 10^4 \text{ L mgC}^{-1} \text{ s}^{-1}$, $k_{\text{NO}_2^-, e_{aq}^-} = 3.5 \times 10^9$, and $k_{\text{NO}_3^-, e_{aq}^-} = 9.7 \times 10^9$.³⁸ Formation of NO_2^- was observed in the Ohio River and LWC RBF source waters due to direct photolysis of NO_3^- (see SI Text S12). Experimental conditions include 10 W low-pressure Hg lamp, $\text{pH}_0 = 9.4\text{--}9.7$, 20°C , $[\text{MCAA}]_0 = 20 \text{ }\mu\text{M}$, $[\text{SO}_3^{2-}]_0 = 10.0 \text{ mM}$, and $[\text{PFOS}]_0 = 20.0 \text{ }\mu\text{M}$ (Simsboro Aquifer $[\text{PFOS}]_0 = 16.3 \text{ }\mu\text{M}$). All chemicals were spiked into the waters at time 0. Markers represent the mean of duplicate measurements and error bars represent the range between the duplicates.

It is also clear from Figure 2 that the measured $k'_{S,0}$ values ($R_{e-,UV}$ method, eq 3.6) are lower than those estimated via eq 3.7. We attribute these differences to two possible explanations. First, the measured $k'_{S,0}$ values rely on the assumption that $k'_{S,0}$ remains constant over the time that MCAA kinetic transformation experiments are performed ($\sim 10 \text{ min}$). However, as an example, the nitrate concentration in the Ohio River decreases from 65 to 2 μM after 10 min of irradiation using 10 mM $[\text{SO}_3^{2-}]_0$ (see SI Figure S4), indicating that the e_{aq}^- scavenging capacity changes markedly over this time scale. The measured value for the Ohio River thus represents an average scavenging capacity over the 10 min period. In comparison, the calculated value is based on the measured initial concentration of e_{aq}^- scavengers. A second possibility is that the overestimation in $k'_{S,0}$ comes from the fact that e_{aq}^- bimolecular rate constants for SO_3^{2-} , CO_3^{2-} , and HCO_3^- are reported only as an upper limit.^{47,48} If the bimolecular rate constants are slower than the upper limit, the $k'_{S,0}$ calculated via eq 3.6 will be lower. These upper limits will have the largest relative impact for the Simsboro Aquifer since this sample has the lowest overall $k'_{S,0}$.

Overall, both approaches to characterizing $k'_{S,0}$ (eqs 3.6 and 3.7) appear to have limitations. Use of eq 3.7 is limited by the availability of accurate bimolecular rate constants and known e_{aq}^- scavenger concentrations. For the measurement approach with MCAA, the chosen concentration of probe compound (20 μM) does not scavenge enough e_{aq}^- to be transformed substantially over the time scale at which scavenging conditions remain constant. It is possible to increase the concentration of the probe compound to achieve more MCAA degradation and thus more accurately measure the scavenging capacity. However, doing so will impact the system's $[e_{aq}^-]_0$, which we desired to measure concomitantly to $k'_{S,0}$. In summary, the MCAA transformation kinetics measured after the time zero spike provide an average e_{aq}^- scavenging capacity due to rapid changes in background e_{aq}^- scavenger concentrations.

3.3. PFOS Degradation is Influenced by Source Water Composition. UV-ARP have received significant attention recently for the degradation of PFAS;^{15,22,25,46,49,50} however, the impact of water quality on PFAS degradation rates in UV-

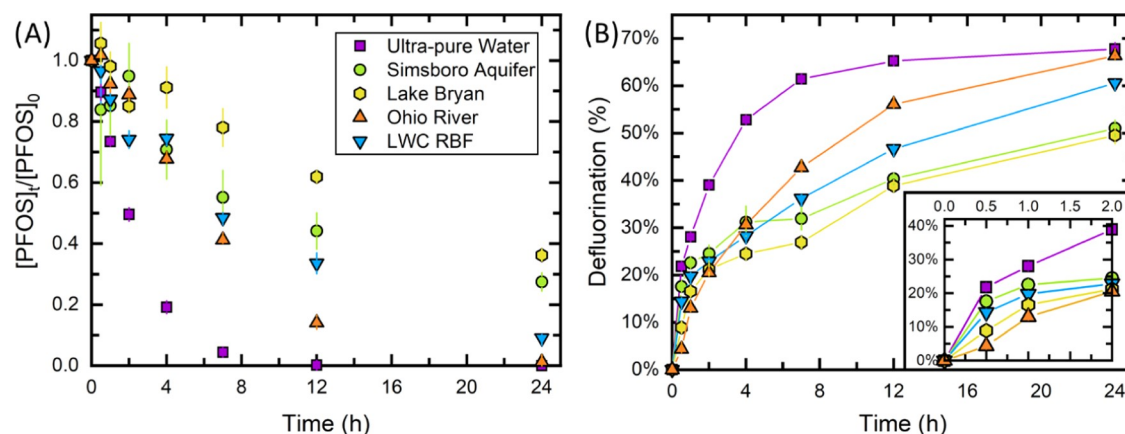


Figure 3. PFOS transformation in the UV/sulfite system in ultrapure water and four source waters. (A) PFOS degradation and (B) defluorination as a function of time. Legend in panel (A) applies to panel (B). All experiments include the following conditions: 10 W low-pressure Hg lamp, $\text{pH}_0 = 9.4\text{--}9.7$, 20°C , $[\text{MCAA}]_0$ spikes = 20 μM , $[\text{SO}_3^{2-}]_0 = 10.0 \text{ mM}$, $[\text{PFOS}]_0 = 20.0 \text{ }\mu\text{M}$ (Simsboro Aquifer $[\text{PFOS}]_0 = 16.3 \text{ }\mu\text{M}$), and $[\text{borate}] = 1.0 \text{ mM}$ (ultrapure water only). All chemicals were spiked into the waters at time 0. Markers represent the mean of duplicate measurements and error bars represent the range between the duplicates.

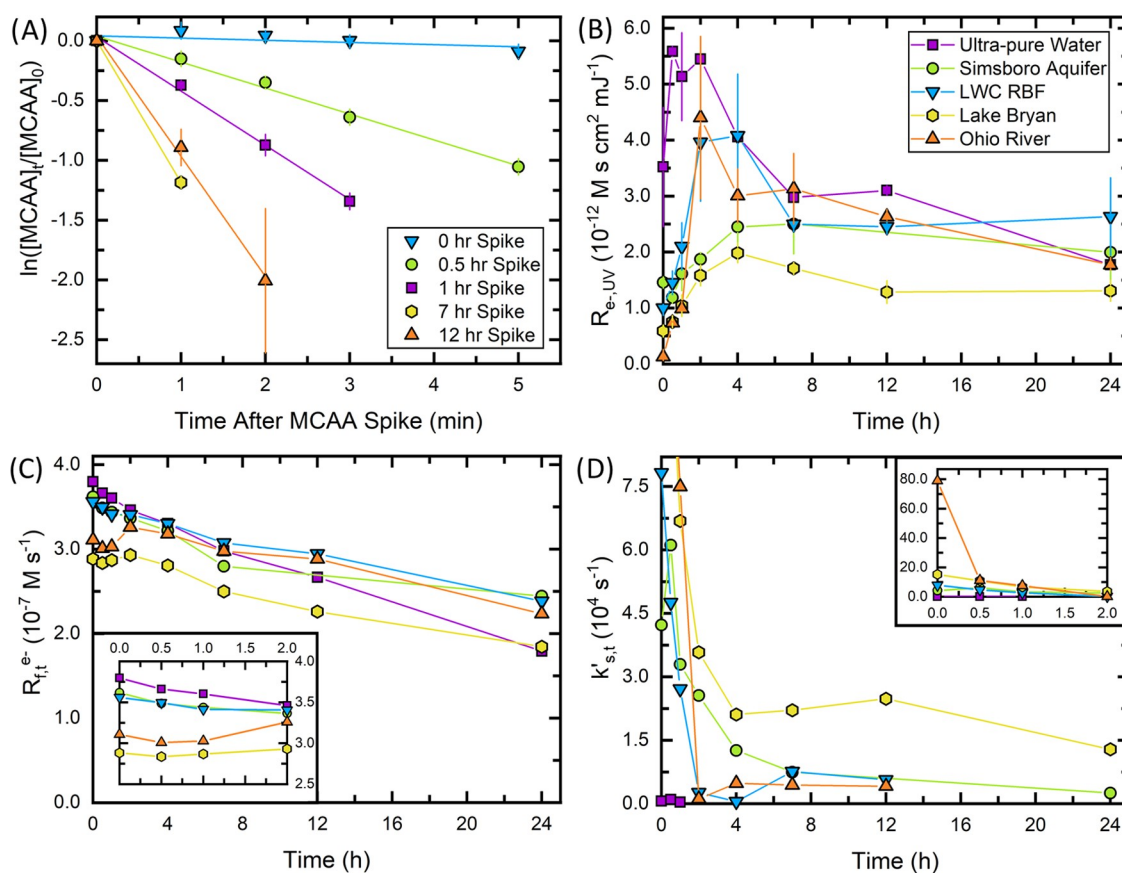


Figure 4. Temporal variation in e_{aq}^- availability during a 24 h UV/sulfite experiment. (A) Measured MCAA degradation (symbols) as a function of time in Ohio River ($20 \mu\text{M}$ $[\text{MCAA}]_0$ spiked into reactor prior to each time point). The best linear fit (line) is also shown. (B) R_{e-UV} , (C) $R_{ft}^{e_{aq}^-}$, and (D) k'_{st} (eq 3.6) as function of time for all waters ($20 \mu\text{M}$ $[\text{MCAA}]_0$ spiked into reactor prior to each time point). Legend in panel (B) applies to panels (C) and (D). Reported k'_{st} values in panel (D) are within the e_{aq}^- scavenging capacity measurement limit established by the probe compound. All experiments include the following conditions: 10 W low-pressure Hg lamp, $\text{pH}_0 = 9.4\text{--}9.7$, 20°C , $[\text{MCAA}]_0$ spikes = $20 \mu\text{M}$, $[\text{SO}_3^{2-}]_0 = 10.0 \text{ mM}$, $[\text{PFOS}]_0 = 20.0 \mu\text{M}$, and $[\text{borate}] = 1.0 \text{ mM}$ (ultrapure water only). All chemicals were spiked into the waters at time 0. Markers represent the mean of duplicate measurements and error bars represent the range between the duplicates.

ARP is not well-constrained. Using PFOS as a model contaminant, we evaluated whether R_{e-UV} and $k'_{s,0}$ measured by the MCAA probe could predict the degradation and defluorination rate of PFOS in different source waters. We expected that PFOS degradation kinetics in each source water would correlate to the R_{e-UV} and e_{aq}^- scavenging capacity under initial conditions (Figures 1 and 2). For example, the Ohio River sample (with the lowest R_{e-UV} and highest $k'_{s,0}$) was expected to have the slowest PFOS degradation rate, while Simsboro Aquifer (highest R_{e-UV} and lowest $k'_{s,0}$) would have the fastest.

However, Figure 3 reveals that rates of PFOS degradation and defluorination did not hold to this anticipated pattern throughout a 24 h experiment. PFOS transformation kinetics (Figure 3A) and defluorination percentage (Figure 3B) vary considerably between each source water. PFOS spiked into both the Ohio River and ultrapure water were degraded below the quantification limit ($0.04 \mu\text{M}$) at 24 h, with nearly identical defluorination percentage ($\sim 67\%$), yet $k'_{s,0}$ was the highest for the Ohio River and lowest for ultrapure water (Figure 2). Considering other samples, PFOS transformation at 24 h increased with the following order: ultrapure water $\approx$ Ohio River < LWC RBF < Simsboro Aquifer < Lake Bryan. Conversely, within the first 2 h (see the inset in Figure 3B), the defluorination percentages are consistent with predictions

based on $k'_{s,0}$. These results indicate that the $[e_{aq}^-]$ available for PFOS degradation varies throughout the 24 h experiment. At shorter treatment times ($<2 \text{ h}$), PFOS transformation is limited by the background e_{aq}^- scavenging, consistent with predictions from the initial MCAA probe experiments. However, our results show that a source water's initial e_{aq}^- scavenging conditions have little influence on the extent of PFOS degradation or defluorination achievable by 24 h.

3.4. Temporal Variation in Hydrated Electron Formation Rates, Scavenging Capacities, and R_{e-UV} . To characterize $[e_{aq}^-]_t$ during a PFOS degradation experiment, we measured R_{e-UV} using the MCAA probe at several time points during 24 h UV/sulfite experiments ($20 \mu\text{M}$ PFOS was also present). Based on the measured R_{e-UV} , absorbance, $[\text{SO}_3^{2-}]$, path length, and irradiance, we were able to calculate $R_{ft}^{e_{aq}^-}$ and k'_{st} at each MCAA spike (SI Table S6). Results from these experiments indicate that R_{e-UV} changes throughout 24 h for all of the samples studied but to different extents depending on the background water chemistry (Figure 4). The kinetic data for MCAA transformation in Ohio River after each MCAA spike provide a representative example (Figure 4A). After the 0 h MCAA spike, little to no change in $[\text{MCAA}]$ is seen over the first 5 min. Conversely, a progressive increase in the slope k' is observed at the 0.5, 1, and 7 h MCAA spikes. The resulting

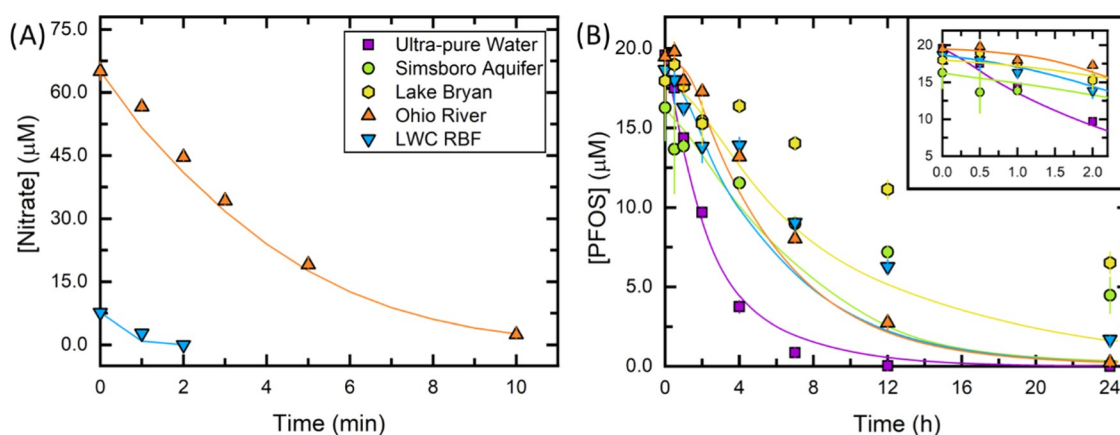


Figure 5. Modeling contaminant transformation rates in the UV/sulfite system using $R_{e-,UV}$. (A) Measured nitrate (symbols) and modeled nitrate degradation (lines) based on measured $[e_{aq}^-]_t$ and eq 3.2. (B) Measured PFOS degradation (symbols) and modeled PFOS degradation (lines) based on measured $[e_{aq}^-]_t$ and eq 3.2. Experimental conditions include: 10 W low-pressure Hg lamp, $pH_0 = 9.4–9.7$, $20\text{ }^\circ\text{C}$, $[PFOS]_0 = 20.0\text{ }\mu\text{M}$ (Simsboro Aquifer $[PFOS]_0 = 16.3\text{ }\mu\text{M}$), $[MCAA]_0$ spikes = $20\text{ }\mu\text{M}$, $[SO_3^{2-}]_0 = 10.0\text{ mM}$, and $[borate] = 1.0\text{ mM}$ (ultrapure water only). All chemicals were spiked into the waters at time 0. $k_{NO_3^-,e_{aq}^-} = 9.7 \times 10^9\text{ M}^{-1}\text{ s}^{-1}$ and k_{PFOS,e_{aq}^-} fitted = $5.7 \times 10^6\text{ M}^{-1}\text{ s}^{-1}$. Markers represent the mean of duplicate measurements and error bars represent the range between the duplicates.

$R_{e-,UV}$ calculated from these data changes with time as well (Figure 4B).

Several trends in the temporal nature of $R_{e-,UV}$ are observed amongst the source waters (Figure 4B). $R_{e-,UV}$ is the lowest for each source water at the initial MCAA spike, increases to a maximum value between 2 to 4 h, followed by a more tempered decrease or a leveling off up to 24 h. The increase in $R_{e-,UV}$ values range from 2.1-fold (Simsboro Aquifer) to 34.0-fold (Ohio River). Ultrapure water had the highest $R_{e-,UV}$ value ($5.6 \times 10^{-12}\text{ M s cm}^2\text{ mJ}^{-1}$), which is 2.8-fold higher than the maximum for Lake Bryan ($2.0 \times 10^{-12}\text{ M s cm}^2\text{ mJ}^{-1}$).

The trends in $R_{e-,UV}$ were explored further by analyzing the temporal nature of $R_{f,t}^{e_{aq}^-}$ (Figure 4C) and $k'_{S,t}$ (Figure 4D using eq 3.6). Note that $k'_{S,t}$ could not be quantified in some cases because of the large influence of $k'_{MCAA,p}$ meaning that the measured scavenging capacity was completely attributable to MCAA. This was the case for ultrapure water at most treatment times and for Ohio River and LWC RBF past 12 h. See SI Text 13 for additional discussion.

Fluctuations in $R_{e-,UV}$ are mainly attributed to changes in $k'_{S,t}$ during the first 2 h for the Ohio River and LWC RBF, whereas variation in $R_{f,t}^{e_{aq}^-}$ impacts $R_{e-,UV}$ at longer irradiation times. For example, a 99% decrease in $k'_{S,t}$ is observed for Ohio River in the first 2 h, while $R_{f,t}^{e_{aq}^-}$ changes by only 4%. Extending this evaluation from 4 to 12 h results in a 9% decrease in $k'_{S,t}$ and a 30% decrease in $R_{f,t}^{e_{aq}^-}$ for the Ohio River. This trend implies that a majority of the initial e_{aq}^- scavengers (e.g., nitrate and DOC) and scavenging byproducts (e.g., nitrite) have been consumed in these source waters after ~ 2 h of UV/sulfite treatment. A different trend was observed for the Simsboro Aquifer and Lake Bryan source waters with high alkalinity. Changes in $R_{e-,UV}$ at longer treatment times for these source waters were also significantly influenced by the change in $k'_{S,t}$. For example, $k'_{S,t}$ decreased by 80% and 39% from 4 to 24 h for the Simsboro Aquifer and Lake Bryan waters, respectively. This implies that after ~ 2 h, other e_{aq}^- scavengers such as bicarbonate and carbonate become dominant, therein accounting for the long-term inhibitory effects of alkalinity on $R_{e-,UV}$. Lake Bryan also has the lowest $R_{f,t}^{e_{aq}^-}$ for the first 12 h and

largest baseline $k'_{S,t}$ which we attribute to its high DOC concentration compared to other source waters. SI Text S14 further confirms the long-term inhibitory effects of alkalinity by showing the results of a control experiment with a 10.0 mM NaHCO_3 buffer. Additional discussion about the time-based role of specific e_{aq}^- scavengers is provided in SI Text S15.

The variation in $R_{e-,UV}$ over the 24 h UV/sulfite treatment helps to explain the PFOS degradation and defluorination rates previously discussed in Section 3.3. One major takeaway is that e_{aq}^- scavengers with larger bimolecular rate constants such as nitrate ($9.7 \times 10^9\text{ M}^{-1}\text{ s}^{-1}$),¹ nitrite ($3.5 \times 10^9\text{ M}^{-1}\text{ s}^{-1}$),¹ and DOC ($1.97 \times 10^4\text{ L mgC}^{-1}\text{ s}^{-1}$ or $2.37 \times 10^8\text{ L MC}^{-1}\text{ s}^{-1}$) impact PFOS degradation at shorter time scales, while e_{aq}^- scavengers with smaller bimolecular rate constants such as bicarbonate ($\leq 1.0 \times 10^6\text{ M}^{-1}\text{ s}^{-1}$)¹ and carbonate ($\leq 3.9 \times 10^5\text{ M}^{-1}\text{ s}^{-1}$)⁵¹ impact treatment at longer time scales. PFOS degradation is limited during the first 2 h of treatment in all source waters, whereas 50% of the PFOS is degraded in ultrapure water over the same time scale. On the other hand, PFOS degradation is most inhibited at longer treatment times in Lake Bryan and Simsboro Aquifer, which have a high concentration of e_{aq}^- scavengers with slower bimolecular rate constants. SI Figure S5 further supports this finding by demonstrating the inhibitory impact of 10.0 mM HCO_3^- on PFOS degradation relative to ultrapure water. DOC plays a dualistic role in PFOS degradation by screening light from the e_{aq}^- sensitizer sulfite and scavenging e_{aq}^- .

The $R_{e-,UV}$ method provides a way to quantify the $[e_{aq}^-]_t$, $R_{f,t}^{e_{aq}^-}$, and $k'_{S,t}$ available for contaminant degradation in any source water. Furthermore, the results demonstrate that a water's initial $k'_{S,t}$ does not determine the ultimate treatability of PFOS. Rather, the extent of PFOS degradation is determined by the total e_{aq}^- exposure as measured by the $R_{e-,UV}$ method.

3.5. Contaminant Degradation Modeling. Measuring temporal $R_{e-,UV}$ values provides a means for modeling the concentration of contaminant in UV-ARP as a function of time, background water matrix, and treatment conditions. Equation 3.2 was used to model the degradation of nitrate and PFOS in the UV/sulfite system (Figure 5). Using a $k_{NO_3^-,e_{aq}^-} =$

$9.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$,¹ which was adjusted for ionic strength, and $[\text{e}_{\text{aq}}^-]_t$ calculated from $R_{\text{e-UV}}$, the model accurately predicted the degradation of nitrate in both the Ohio River and LWC RBF (Figure 5A). SI Text S16 provides sample calculations for nitrate degradation modeling using this approach. Modeling PFOS degradation was also attempted using eq 3.2 and $[\text{e}_{\text{aq}}^-]_t$ calculated from $R_{\text{e-UV}}$ for each source water. Unfortunately, literature-reported PFOS- e_{aq}^- bimolecular rate constants vary significantly (e.g., a pulse radiolysis study measured $k_{\text{PFOS,e}_{\text{aq}}^-}$ as $7.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$,⁵² whereas Maza et al. recently measured a value of $2.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).⁵³ Both PFOS- e_{aq}^- bimolecular rate constants were tried to see which generated a better fit, and both vastly overpredicted PFOS degradation, even for ultrapure water (SI Figure S9 shows complete degradation of PFOS within minutes using a value of $2.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). A PFOS- e_{aq}^- bimolecular rate constant was fitted for the ultrapure water system by using the method of least squares between the measured and modeled PFOS degradation values. The $k_{\text{PFOS,e}_{\text{aq}}^-}$ fitted value ($5.7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) was used to model PFOS degradation in the remaining source waters (Figure 5B).

Even with the $k_{\text{PFOS,e}_{\text{aq}}^-}$ fitted value, the model overpredicted PFOS degradation for the four source waters, with the most significant deviation occurring at longer irradiation times in Lake Bryan and Simsboro Aquifer. The model was more successful at predicting PFOS degradation from 0–1 h for all source waters using the $k_{\text{PFOS,e}_{\text{aq}}^-}$ fitted value (see inset in Figure 5B). The source of discrepancies between the model and measured values at long irradiation times could not be determined with certainty, although uncertainty in reported PFOS- e_{aq}^- bimolecular rate constants is one possibility. SI Text S17 provides additional discussion on the variability in PFOS degradation modeling results.

While MCAA can measure $R_{\text{e-UV}}$, there are some inherent limitations to modeling contaminant degradation using eq 3.2. We observed more accurate results at shorter time periods (1 h or less). Modeling PFOS degradation at longer time periods (2 h or more) tended to overpredict PFOS degradation. We anticipate that short-term modeling will be sufficient for a majority of contaminants treated with UV-ARP, since they degrade within 1 h.³⁸ Long-term modeling of PFOS and other PFAS destruction in UV-ARP remains a challenge. In addition, while $[\text{e}_{\text{aq}}^-]_t$ is an important factor influencing the degradation rate of PFAS, treatability is also determined by the e_{aq}^- bimolecular rate constant. Some PFAS tend to be more recalcitrant to e_{aq}^- reduction, like perfluorobutanesulfonic acid or fluorotelomers;^{21,22,26} however, e_{aq}^- bimolecular rate constants for these PFAS are unknown. Future modeling efforts in UV-ARP may be enhanced with a resolution of PFAS- e_{aq}^- bimolecular rate constant discrepancies.

4. ENVIRONMENTAL SIGNIFICANCE

In this study, we used MCAA as an e_{aq}^- probe compound to demonstrate that the e_{aq}^- exposure ($R_{\text{e-UV}}$) varies significantly in a set of diverse source waters. Notably, the factors that determine e_{aq}^- availability are shown to vary considerably over 24 h, which is a typical treatment time in UV-ARP. The $R_{\text{e-UV}}$ method allows for the characterization of $[\text{e}_{\text{aq}}^-]_t$ and other key parameters (e.g., $R_{\text{e}_{\text{aq}}^-}$ and $k'_{\text{e},t}$) that can be used to compare and optimize UV-ARP for any source water. Treatment of contaminants with fast bimolecular rate constants will be most

impacted by other e_{aq}^- scavengers with fast bimolecular rate constants. On the other hand, more recalcitrant contaminants requiring longer treatment times such as PFOS will be inhibited by e_{aq}^- scavengers with slower bimolecular rate constants (e.g., bicarbonate).

Our results suggest that high alkalinity may inadvertently increase the treatment time or amount of sensitizer chemical required for complete PFOS degradation when applying UV-ARP treatment to groundwaters. Furthermore, DOC was shown to both increase the e_{aq}^- scavenging capacity by having a moderately fast e_{aq}^- bimolecular rate constant ($\sim 10^8 \text{ M}^{-1} \text{ s}^{-1}$) and decrease $R_{\text{e}_{\text{aq}}^-}$ by shielding sulfite from incoming photons. The role of DOC in e_{aq}^- scavenging deserves further attention. For example, we observed that Lake Bryan (with an initial [DOC] of almost $10 \text{ mg}_\text{C} \text{ L}^{-1}$) exhibited a higher e_{aq}^- scavenging capacity than other source waters after $\sim 12 \text{ h}$ of treatment. This is particularly relevant for UV-ARP treatment of concentrated PFAS sources such as ion exchange regenerate and reverse osmosis concentrate. Effective UV-ARP treatment in waters with high DOC may require pretreatment to lessen the impacts of this e_{aq}^- scavenger.

This study contributes to the development of quantitative methods to study UV-ARP systems. The results obtained using MCAA as an e_{aq}^- probe compound reveal insights into UV/sulfite treatment of PFAS. Accordingly, we expect that the $R_{\text{e-UV}}$ method will be useful for characterizing $[\text{e}_{\text{aq}}^-]_t$ availability in future UV-ARP studies.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.2c02003>.

Additional discussions, tables, and figures; see the SI table of contents for specific details (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Garrett McKay – Zachry Department of Civil & Environmental Engineering, Texas A&M University, College Station, Texas 77845, United States; orcid.org/0000-0002-6529-0892; Phone: 979.458.6540; Email: gmckay@tamu.edu

Authors

Benjamin D. Fennell – Zachry Department of Civil & Environmental Engineering, Texas A&M University, College Station, Texas 77845, United States

Adam Odorisio – Zachry Department of Civil & Environmental Engineering, Texas A&M University, College Station, Texas 77845, United States

Complete contact information is available at: <https://pubs.acs.org/10.1021/acs.est.2c02003>

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors gratefully acknowledge support from the U.S. National Science Foundation (CBET #2050934) and the Texas Hazardous Waste Research Center to G.M. B.D.F. gratefully acknowledges financial support from the Texas A&M University Graduate Merit Fellowship, Stantec & AWWA

Water Equation, and the Texas Engineering Foundation. They are thankful for the collaborative efforts of Dr. Cory Klemashevich and Smriti Shankar at the Texas A&M University Integrated Metabolomics Analysis Core and Stephen Mezyk's guidance at the Radiation Laboratory, which is supported by the Office of Basic Energy Sciences, U.S. Department of Energy. Special thanks to Louisville Water Company and the City of Bryan, TX, for their support of this project.

■ REFERENCES

- (1) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. Critical Review of Rate Constants for Reactions of Hydrated Electrons, Hydrogen Atoms and Hydroxyl Radicals ($\cdot\text{OH}/\cdot\text{O}^-$) in Aqueous Solution. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513–886.
- (2) Moussavi, G.; Shekoohiyan, S. Simultaneous Nitrate Reduction and Acetaminophen Oxidation Using the Continuous-flow Chemical-less VUV Process as an Integrated Advanced Oxidation and Reduction Process. *J. Hazard. Mater.* **2016**, *318*, 329–338.
- (3) Nawaz, S.; Shah, N. S.; Khan, J. A.; Sayed, M.; Al-Muhtaseb, A. aH.; Andersen, H. R.; Muhammad, N.; Murtaza, B.; Khan, H. M. Removal Efficiency and Economic Cost Comparison of Hydrated Electron-mediated Reductive Pathways for Treatment of Bromate. *Chem. Eng. J.* **2017**, *320*, 523–531.
- (4) Jung, B.; Nicola, R.; Batchelor, B.; Abdel-Wahab, A. Effect of Low- and Medium-pressure Hg UV Irradiation on Bromate Removal in Advanced Reduction Process. *Chemosphere* **2014**, *117*, 663–72.
- (5) Botlaguduru, V. S. V.; Batchelor, B.; Abdel-Wahab, A. Application of UV–Sulfite Advanced Reduction Process to Bromate Removal. *J. Water Process Eng.* **2015**, *5*, 76–82.
- (6) Xiao, Q.; Wang, T.; Yu, S.; Yi, P.; Li, L. Influence of UV Lamp, Sulfur(IV) Concentration, and pH on Bromate Degradation in UV/Sulfite Systems: Mechanisms and Applications. *Water Res.* **2017**, *111*, 288–296.
- (7) Xie, B.; Shan, C.; Xu, Z.; Li, X.; Zhang, X.; Chen, J.; Pan, B. One-step Removal of Cr(VI) at Alkaline pH by UV/Sulfite Process: Reduction to Cr(III) and in situ Cr(III) Precipitation. *Chem. Eng. J.* **2017**, *308*, 791–797.
- (8) Wang, X.; Liu, H.; Shan, C.; Zhang, W.; Pan, B. A Novel Combined Process for Efficient Removal of Se(VI) from Sulfate-rich Water: Sulfite/UV/Fe(III) Coagulation. *Chemosphere* **2018**, *211*, 867–874.
- (9) Liu, X.; Yoon, S.; Batchelor, B.; Abdel-Wahab, A. Photochemical Degradation of Vinyl Chloride with an Advanced Reduction Process (ARP) – Effects of Reagents and pH. *Chem. Eng. J.* **2013**, *215*–216, 868–875.
- (10) Li, X.; Ma, J.; Liu, G.; Fang, J.; Yue, S.; Guan, Y.; Chen, L.; Liu, X. Efficient Reductive Dechlorination of Monochloroacetic Acid by Sulfite/UV Process. *Environ. Sci. Technol.* **2012**, *46*, 7342–9.
- (11) Li, X.; Fang, J.; Liu, G.; Zhang, S.; Pan, B.; Ma, J. Kinetics and Efficiency of the Hydrated Electron-induced Dehalogenation by the Sulfite/UV Process. *Water Res.* **2014**, *62*, 220–8.
- (12) Yu, K.; Li, X.; Chen, L.; Fang, J.; Chen, H.; Li, Q.; Chi, N.; Ma, J. Mechanism and Efficiency of Contaminant Reduction by Hydrated Electron in the Sulfite/Iodide/UV Process. *Water Res.* **2018**, *129*, 357–364.
- (13) Qu, Y.; Zhang, C.; Li, F.; Chen, J.; Zhou, Q. Photo-reductive Defluorination of Perfluorooctanoic Acid in Water. *Water Res.* **2010**, *44*, 2939–47.
- (14) Song, Z.; Tang, H.; Wang, N.; Zhu, L. Reductive Defluorination of Perfluorooctanoic Acid by Hydrated Electrons in a Sulfite-mediated UV Photochemical System. *J. Hazard. Mater.* **2013**, *262*, 332–338.
- (15) Gu, Y.; Liu, T.; Wang, H.; Han, H.; Dong, W. Hydrated Electron Based Decomposition of Perfluorooctane Sulfonate (PFOS) in the VUV/Sulfite System. *Sci. Total Environ.* **2017**, *607*–608, 541–548.
- (16) Tian, H.; Gao, J.; Li, H.; Boyd, S. A.; Gu, C. Complete Defluorination of Perfluorinated Compounds by Hydrated Electrons Generated from 3-Indole-Acetic-Acid in Organomodified Montmorillonite. *Sci. Rep.* **2016**, *6*, No. 32949.
- (17) Tian, H.; Gu, C. Effects of Different factors on Photo-defluorination of Perfluorinated Compounds by Hydrated Electrons in Organo-montmorillonite System. *Chemosphere* **2018**, *191*, 280–287.
- (18) Chen, Z.; Mi, N.; Li, C.; Teng, Y.; Chen, Y.; Gu, C. Effects of Different Variables on Photodestruction of Perfluorooctanoic Acid in Self-assembled Micelle System. *Sci. Total Environ.* **2020**, *742*, No. 140438.
- (19) Chen, Z.; Li, C.; Gao, J.; Dong, H.; Chen, Y.; Wu, B.; Gu, C. Efficient Reductive Destruction of Perfluoroalkyl Substances under Self-Assembled Micelle Confinement. *Environ. Sci. Technol.* **2020**, *54*, 5178–5185.
- (20) Chen, Z.; Teng, Y.; Mi, N.; Jin, X.; Yang, D.; Wang, C.; Wu, B.; Ren, H.; Zeng, G.; Gu, C. Highly Efficient Hydrated Electron Utilization and Reductive Destruction of Perfluoroalkyl Substances Induced by Intermolecular Interaction. *Environ. Sci. Technol.* **2021**, *55*, 3996–4006.
- (21) Bentel, M. J.; Yu, Y.; Xu, L.; Li, Z.; Wong, B. M.; Men, Y.; Liu, J. Defluorination of Per- and Polyfluoroalkyl Substances (PFASs) with Hydrated Electrons: Structural Dependence and Implications to PFAS Remediation and Management. *Environ. Sci. Technol.* **2019**, *53*, 3718–3728.
- (22) Bentel, M. J.; Yu, Y.; Xu, L.; Kwon, H.; Li, Z.; Wong, B. M.; Men, Y.; Liu, J. Degradation of Perfluoroalkyl Ether Carboxylic Acids with Hydrated Electrons: Structure-Reactivity Relationships and Environmental Implications. *Environ. Sci. Technol.* **2020**, *54*, 2489–2499.
- (23) Liu, C. J.; McKay, G.; Jiang, D.; Tenorio, R.; Cath, J. T.; Amador, C.; Murray, C. C.; Brown, J. B.; Wright, H. B.; Schaefer, C.; Higgins, C. P.; Bellona, C.; Strathmann, T. J. Pilot-Scale Field Demonstration of a Hybrid Nanofiltration and UV-Sulfite Treatment Train for Groundwater Contaminated by Per- and Polyfluoroalkyl Substances (PFASs). *Water Res.* **2021**, *205*, No. 117677.
- (24) Liu, Z.; Bentel, M. J.; Yu, Y.; Ren, C.; Gao, J.; Pulikkal, V. F.; Sun, M.; Men, Y.; Liu, J. Near-Quantitative Defluorination of Perfluorinated and Fluorotelomer Carboxylates and Sulfonates with Integrated Oxidation and Reduction. *Environ. Sci. Technol.* **2021**, *55*, 7052–7062.
- (25) Tenorio, R.; Liu, J.; Xiao, X.; Maizel, A.; Higgins, C. P.; Schaefer, C. E.; Strathmann, T. J. Destruction of Per- and Polyfluoroalkyl Substances (PFASs) in Aqueous Film-Forming Foam (AFFF) with UV-Sulfite Photoreductive Treatment. *Environ. Sci. Technol.* **2020**, *54*, 6957–6967.
- (26) Gao, J.; Liu, Z.; Bentel, M. J.; Yu, Y.; Men, Y.; Liu, J. Defluorination of Omega-Hydroperfluorocarboxylates (omega-HPFCAs): Distinct Reactivities from Perfluoro and Fluorotelomeric Carboxylates. *Environ. Sci. Technol.* **2021**, *55*, 14146–14155.
- (27) Javed, H.; Lyu, C.; Sun, R.; Zhang, D.; Alvarez, P. J. J. Discerning the Inefficacy of Hydroxyl Radicals During Perfluorooctanoic Acid Degradation. *Chemosphere* **2020**, *247*, No. 125883.
- (28) Tan, L.; Mao, R.; Su, P.; Gu, J.; Chen, H.; Jiang, F.; Zhao, X. Efficient Photochemical Denitrification by UV/Sulfite System: Mechanism and Applications. *J. Hazard. Mater.* **2021**, *418*, No. 126448.
- (29) Vellanki, B. P.; Batchelor, B. Nitrate Reduction by the Ultraviolet-Sulfite Advanced Reduction Process. *Environ. Eng. Sci.* **2021**, *38*, 927–935.
- (30) Glaze, W. H.; Lay, Y.; Kang, J. Advanced Oxidation Processes. A Kinetic Model for the Oxidation of 1,2-Dibromo-3-chloropropane in Water by the Combination of Hydrogen Peroxide and UV Radiation. *Ind. Eng. Chem. Res.* **1995**, *34*, 2314–2323.
- (31) Xie, B.; Li, X.; Huang, X.; Xu, Z.; Zhang, W.; Pan, B. Enhanced Debromination of 4-Bromophenol by the UV/Sulfite Process: Efficiency and Mechanism. *J. Environ. Sci.* **2017**, *54*, 231–238.

- (32) Rosenfeldt, E. J.; Linden, K. G. The $R_{OH,UV}$ Concept to Characterize and the Model UV/H_2O_2 Process in Natural Waters. *Environ. Sci. Technol.* **2007**, *41*, 2548–2553.
- (33) Karanfil, T.; Erdogan, I.; Schlautman, M. A. Selecting Filter Membranes for Measuring DOC and UV_{254} . *J. - Am. Water Works Assoc.* **2003**, *95*, 86–100.
- (34) Jin, S.; Mofidi, A. A.; Linden, K. G. Polychromatic UV Fluence Measurement Using Chemical Actinometry, Biodosimetry, and Mathematical Techniques. *J. Environ. Eng.* **2006**, *132*, 831–841.
- (35) Beltran, F. J.; Ovejero, G.; Garcia-Araya, J. F.; Rivas, J. Oxidation of Polynuclear Aromatic Hydrocarbons in Water. 2. UV Radiation and Ozonation in the Presence of UV Radiation. *Ind. Eng. Chem. Res.* **1995**, *34*, 1607–1615.
- (36) Crittenden, J. C.; Hu, S.; Hand, D. W.; Green, S. A. A Kinetic Model for H_2O_2/UV Process In a Completely Mixed Batch Reactor. *Water Res.* **1999**, *33*, 2315–2328.
- (37) Maza, W. A.; Breslin, V. M.; Plymale, N. T.; DeSario, P. A.; Epshteyn, A.; Owrutsky, J. C.; Pate, B. B. Nanosecond Transient Absorption Studies of the pH-dependent Hydrated Electron Quenching by HSO_3^- . *Photochem. Photobiol. Sci.* **2019**, *18*, 1526–1532.
- (38) Fennell, B. D.; Mezyk, S. P.; McKay, G. Critical Review of UV-Advanced Reduction Processes for the Treatment of Chemical Contaminants in Water. *ACS Environ. Au* **2022**, *2*, 178–205.
- (39) Humphrey, R. E.; Ward, M. H.; Hinze, W. Spectrophotometric Determination of Sulfite with 4,4'-Dithiodipyridine and 5,5'-Dithiobis-(2-Nitrobenzoic Acid). *Anal. Chem.* **1970**, *42*, 698–702.
- (40) Whitham, K.; Lyons, S.; Miller, R.; Nett, D.; Treas, P.; Zante, A.; Fessenden, R. W.; Thomas, M. D.; Wang, Y. In *Linear Accelerator for Radiation Chemistry Research at Notre Dame*, Proceedings Particle Accelerator Conference, 1995; pp 131–133.
- (41) Gu, J.; Ma, J.; Jiang, J.; Yang, L.; Yang, J.; Zhang, J.; Chi, H.; Song, Y.; Sun, S.; Tian, W. Q. Hydrated electron (e_{aq}^-) Generation from Phenol/UV: Efficiency, Influencing Factors, and Mechanism. *Appl. Catal., B* **2017**, *200*, 585–593.
- (42) Serjeant, E. P.; Dempsey, B. *Ionisation Constants of Organic Acids in Aqueous Solution*; Pergamon Press, Inc.: New York, New York, 1979; p 26.
- (43) Apell, J. N.; McNeill, K. Updated and Validated Solar Irradiance Reference Spectra for Estimating Environmental Photodegradation Rates. *Environ. Sci.: Process Impacts* **2019**, *21*, 427–437.
- (44) Rosenfeldt, E. J.; Linden, K. G.; Canonica, S.; von Gunten, U. Comparison of the Efficiency of $\bullet OH$ Radical Formation During Ozonation and the Advanced Oxidation Processes O_3/H_2O_2 and UV/H_2O_2 . *Water Res.* **2006**, *40*, 3695–704.
- (45) Ulliman, S. L.; Miklos, D. B.; Hübner, U.; Drewes, J. E.; Linden, K. G. Improving UV/H_2O_2 Performance Following Tertiary Treatment of Municipal Wastewater. *Environ. Sci.: Water Res. Technol.* **2018**, *4*, 1321–1330.
- (46) Ren, Z.; Bergmann, U.; Leiviska, T. Reductive Degradation of Perfluorooctanoic Acid in Complex Water Matrices by Using the UV/sulfite Process. *Water Res.* **2021**, *205*, No. 117676.
- (47) Thomas, J. K.; Gordon, S.; Hart, E. J. The Rates of Reactions of the Hydrated Electron in Aqueous Inorganic Solutions. *J. Phys. Chem. A* **1964**, *68*, 1524–1527.
- (48) Anbar, M.; Hart, E. J., On the Reactivity of Hydrated Electrons Toward Inorganic Compounds. In *Radiation Chemistry*, 1968 79–94.
- (49) Gu, Y.; Dong, W.; Luo, C.; Liu, T. Efficient Reductive Decomposition of Perfluorooctanesulfonate in a High Photon Flux UV/Sulfite System. *Environ. Sci. Technol.* **2016**, *50*, 10554–10561.
- (50) Abusallout, I.; Wang, J.; Hanigan, D. Emerging Investigator Series: Rapid Defluorination of 22 Per- and Polyfluoroalkyl Substances in Water Using Sulfite Irradiated by Medium-pressure UV. *Environ. Sci.: Water Res. Technol.* **2021**, *7*, 1552–1562.
- (51) Nash, K.; Mulac, W.; Noon, M.; Fried, S.; Sullivan, J. C. Pulse Radiolysis Studies of U(VI) Complexes in Aqueous Media. *J. Inorg. Nucl. Chem.* **1981**, *43*, 897–899.
- (52) Szajdzinska-Pietek, E.; Gebicki, J. L. Pulse Radiolytic Investigation of Perfluorinated Surfactants in Aqueous Solutions. *Res. Chem. Intermed.* **2000**, *26*, 897–912.
- (53) Maza, W. A.; Breslin, V. M.; Owrutsky, J. C.; Pate, B. B.; Epshteyn, A. Nanosecond Transient Absorption of Hydrated Electrons and Reduction of Linear Perfluoroalkyl Acids and Sulfonates. *Environ. Sci. Technol. Lett.* **2021**, *8*, 525–530.

Recommended by ACS

Critical Review of UV-Advanced Reduction Processes for the Treatment of Chemical Contaminants in Water

Benjamin D. Fennell, Garrett McKay, *et al.*

FEBRUARY 14, 2022
ACS ENVIRONMENTAL AU

READ 

Photochemical Properties of Free Chlorine and Inorganic Chloramines at 185 nm for VUV/UV/Chlorine Advanced Oxidation

Mahsa Masjoudi and Madjid Mohseni

APRIL 22, 2022
ACS ES&T WATER

READ 

Near-Ultraviolet Light-Driven Photocatalytic Chlorine Activation Process with Novel Chlorine Activation Mechanisms

Zihang Cheng, Chii Shang, *et al.*

AUGUST 27, 2021
ACS ES&T WATER

READ 

New Insights into Micropollutant Abatement in Ammonia-Containing Water by the UV/Breakpoint Chlorination Process

Ehsan Aghdam, Chii Shang, *et al.*

FEBRUARY 17, 2021
ACS ES&T WATER

READ 

Get More Suggestions >