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Comparison of the Effects of Sonolysis and γ -Radiolysis on Dissolved Organic Matter

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The effects of 640 kHz sonolysis and ^{60}Co γ -radiolysis on dissolved organic matter (DOM) were compared through UV/vis absorption spectrometric, dissolved organic carbon concentration ([DOC]), and potentiometric titration analyses. A reverse-phase chromatographic technique was used to compare changes in the DOM hydrophobicity distribution, and a size exclusion chromatographic technique with inline UV-A absorbance, fluorescence, and [DOC] detectors was used to compare changes in the DOM molecular weight distribution. Whereas upon radiolysis major decreases in absorbance and [DOC] were induced and near-total DOC removal was achieved, upon sonolysis there were major decreases in UV/vis absorbance but only minor decreases in [DOC], and a substantial quantity of hydrophilic nonchromophoric material remained in solution. In radiolysis, hydrophilic and hydrophobic DOM solution components were exposed to equal hydroxyl radical ($\cdot\text{OH}$) concentrations. However, in sonolysis, hydrophobic DOM components were exposed to more elevated $\cdot\text{OH}$ concentrations than the hydrophilic components and consequently had enhanced rates of degradation. Sonolysis may be of interest in the design of advanced oxidation processes in which the selective elimination of hydrophobic solution components, such as hydrophobic organic contaminants and hydrophobic DOM domains into which they partition, is desired.

Introduction

Dissolved organic matter (DOM), which is ubiquitous in aquatic earth-surface environments, is a major carbon reservoir (1), provides nutrition for aquatic microorganisms (2), can affect the behavior of toxic metals (3) and hydrophobic organic compounds (4), and can control the penetration of solar ultraviolet radiation into surface waters (5). In drinking-water treatment, DOM is of concern as a precursor to toxic disinfection byproducts (6). The properties of a given DOM sample depend on its physicochemical characteristics such as its elemental composition, functional group content (7), and molecular weight (8) and hydrophobicity (9) distributions. Most if not all of these parameters can substantially

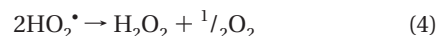
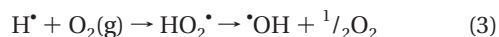
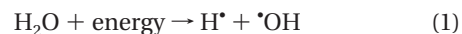
change when DOM is transformed in natural and engineered aquatic systems.

An important channel through which the composition and properties of DOM can be transformed in aquatic systems is reaction with hydroxyl radicals ($\cdot\text{OH}$) (5, 10–12). $\cdot\text{OH}$ is generated in the photic zones of surface waters through the photolysis of solutes such as nitrate (13, 14) and Fe–hydroxy complexes (15, 16) and through reaction between photo-produced Fe(II) ions and H_2O_2 molecules (17). Local $\cdot\text{OH}$ production rates depend on the concentration of $\cdot\text{OH}$ -producing species (18, 19) and the depth-dependent radiation flux (20). $\cdot\text{OH}$ reacts with nearly diffusion-controlled rates with many organic solutes (21), and DOM may be the largest sink for $\cdot\text{OH}$ in natural waters (22). $\cdot\text{OH}$ is also the primary transient in advanced oxidation processes (AOPs), which have been developed to decontaminate waters containing various toxic compounds (23, 24). In existing AOPs, however, the efficiencies of the degradation of target species are, due to the unselective nature of $\cdot\text{OH}$, greatly decreased in the presence of DOM (25, 26). One approach in the development of more efficient AOPs may be to employ degradation processes in which target contaminants are brought spatially closer to the sites of $\cdot\text{OH}$ production (27).

In this study, we compare the effects of 640 kHz sonolysis and ^{60}Co radiolysis on a surface-water reverse osmosis (RO) DOM isolate by measuring changes in the dissolved organic carbon concentration ([DOC]), UV/vis light absorbance, and DOM acidity. We also used a reverse-phase high performance liquid chromatography (RP-HPLC) technique to monitor changes in the DOM polarity ($\log K_{\text{ow}}$) distributions and a high performance size exclusion chromatographic (HPSEC) technique with inline UV-A, fluorescence, and [DOC] detectors to monitor changes in the DOM molecular weight distributions and optical properties as a function of molecular weight. The goal of this study was to add to the understanding of the effects of these oxidation methods on the physicochemical properties of DOM. These results may assist workers, who either investigate natural or engineered DOM– $\cdot\text{OH}$ reactions or seek to achieve desired DOM transformations, select the oxidation method best suited to their goals.

Background

In sonolysis, ultrasonic pressure waves induce *acoustic cavitation*, a phenomenon in which transient gas bubbles grow in size and accumulate energy during cycles of compression and expansion. Local “hot spots” having gas-phase temperatures as high as 5200 K (28) arise when cavitation bubbles decay through collapse, and an important chemical consequence of the focus and release of energy at bubble collapse sites is the formation of $\cdot\text{OH}$ and $\cdot\text{H}$ radicals via the homolysis of water. The formation of oxidizing species in the sonolysis of $\text{O}_2(\text{g})$ -saturated aqueous solutions (as used here) is described in reactions 1–4



The cavitation bubble yield and exact conditions associated with bubble implosion depend on several variables including the frequency and power of the sound waves and

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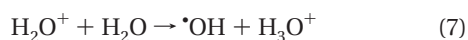
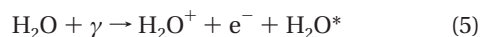
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the identities and concentrations of the solutes and dissolved gases present in solution (29–31).

The process(es) by which a solute degrades in sonolysis depends on solute chemical properties including volatility (32) and hydrophobicity (33). The spatial distribution of $\cdot\text{OH}$ radicals around collapsed cavitation bubbles is heterogeneous, with $\cdot\text{OH}$ concentrations that are as high as 0.1 M at the point of bubble collapse (34) but that decrease rapidly with distance from the collapse site. Hydrophobic solutes that accumulate in bubble/solution interfacial regions encounter greater $\cdot\text{OH}$ concentrations and consequently have enhanced rates of chemical degradation relative to hydrophilic solutes. Mechanical shear forces resulting from high solvent flow fields around collapsing cavitation bubbles also contribute to degradation for synthetic polymers (35) and microorganisms such as microcystin (36).

In the radiolysis of water, high energy photons passing through solution yield ionized water molecules, photoejected electrons, and highly excited water molecules. $\cdot\text{OH}$ is produced in rapid chemical processes that follow the initial ionization events. The radiolytic generation of $\cdot\text{OH}$ in nitrous oxide ($\text{N}_2\text{O}(\text{g})$)-saturated aqueous solutions (as used here) is described by eqs 5–8 (37, 38)



Solutes may also undergo direct photoionization; however, at low solute concentrations such as used here, such processes are insignificant. In radiolysis, the maximum transient $\cdot\text{OH}$ concentrations also occur at specific locations, i.e., the “spurs” at which primary photoelectrons induce secondary ionizations along their “tracks” through solution (37). In radiolysis, however, there are no reported mechanisms by which the approach of a solute to the sites of the highest concentrations of transients is controlled by its chemical nature. Hence, in radiolysis, unlike in sonolysis, all solutes apparently encounter similar $\cdot\text{OH}$ concentrations regardless of differences in structure.

Materials and Methods

Materials. A DOM reverse osmosis (RO) isolate was used here because RO concentrates a wide range of hydrophobic and hydrophilic DOM components (39). The RO isolate, which has been described elsewhere (40), was collected from DOM-rich surface water at Nelson’s Creek, a first-order stream in the Ottawa National Forest, MI, using methods described previously (41, 42). As is common practice in DOM research (7), a freeze-dried DOM isolate was used here because it enables DOM to be stored for extended periods with reproducible properties and allows facile control over concentration. For reactions, 1 L DOM solutions with [DOC] \approx 15–25 mg C/L were prepared by dissolving freeze-dried isolate in Milli-Q UV-treated water and filtering (0.22 μm). Disodium terephthalate (Alfa Aesar, 99+%) and hexachloroiridate(IV) pentahydrate (Aldrich, 99.9%) were used as supplied.

Oxidation Reactions. The sonolysis and radiolysis facilities used are property of the U. S. Department of Energy (DOE) Notre Dame Radiation Laboratory (NDRL). The system with which 640 kHz sonolysis reactions were performed was described previously (43). During reactions, the transducer and sample chamber were held at a temperature of 303 K. Sonicated solutions were saturated with $\text{O}_2(\text{g})$ by sparging

for \sim 30 min. prior to and continuously throughout experiments. $\text{O}_2(\text{g})$ converts $\cdot\text{H}$ (a reducing species) to hydroperoxyl ($\text{HO}_2\cdot$). Radiolysis was conducted in a J. L. Shepherd 109–68 ^{60}Co γ source that was described previously (38). In typical experiments, \sim 20 mL portions of a stock DOM solution were placed in sealed 24 mL glass vials and sparged with $\text{N}_2\text{O}(\text{g})$ for at least 10 min prior to being placed in the radiation source. $\text{N}_2\text{O}(\text{g})$ scavenges reducing photoelectrons, converting them quantitatively into $\cdot\text{OH}$ radicals (21).

DOM Analyses. [DOC] measurements were made with a Shimadzu TOC-5000A, and absorbance measurements were made with a standard Cary 300 spectrophotometer. Whereas the 280 nm absorbance directly correlates with DOM aromaticity (44), the 200 nm absorbance is likely somewhat less sensitive to aromaticity and a more general indicator of total DOM. The comparison of absorbances at long and short wavelengths (here 400 and 280 nm), often in the form of a ratio such as A_{400}/A_{280} , is common in DOM research. Changes in such ratios relate to changes in DOM spectral slope (45, 46). For titrations, DOM samples having [DOC] \approx 200 mg C/L were prepared in \sim 30 mL of 0.1 N NaCl, adjusted to pH \approx 2.5 with 1.0 M HCl, sparged with N_2 for 15 min, and then titrated under an N_2 atmosphere at 298 K with 0.1001 M NaOH to a pH 9.0 endpoint. To prepare titration samples, DOM was reacted until its absorbance at 280 nm was decreased to 60% of its initial value, then collected by rotary evaporation and freeze-drying. The control unreacted titration sample was subjected to the same isolation procedure as the reacted samples. To limit the interference of organically complexed Fe(III), which was high in the RO isolate used (40), the reacted and unreacted DOM titration samples were treated using Chelex-100 resin (Biorad). Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis indicated that this procedure decreased the Fe content of the DOM by \sim 80%. The HPSEC method using optical detectors is described elsewhere (44, 47). In HPSEC analyses with online DOC analysis (GE Analytical) 250 μL sample injections were made onto a TSK G3000 PWxl column (Tosoh Biosciences) with an aqueous mobile phase with 0.1 M Na_2SO_4 and 40 mM pH 6.8 phosphate buffer. Calibration used poly(ethylene glycol) standards (48) (Aldrich). Measurements of hydrophobicity ($\log K_{\text{ow}}$) distributions were performed by an RP-HPLC technique described elsewhere (9).

Estimation of Relative Rates of $\cdot\text{OH}$ Scavenging by DOM in Sonolysis and Radiolysis. The initial rates of DOM \rightarrow $\cdot\text{OH}$ scavenging in the reactions were estimated by placing solutions of the $\cdot\text{OH}$ -specific terephthalate ion (49) in the reactions chambers and comparing, via fluorescence, the rate of formation of 2-hydroxyterephthalate. Full detail of the method of the application of the terephthalate dosimeter in the sonolysis and radiolysis reactors is given in the Supporting Information. Briefly, the initial rate of $\cdot\text{OH}$ scavenging in the radiolysis reaction was determined to be greater than that in the sonolysis reaction by a factor of 2.6 ± 0.4 .

Due to major differences in the mechanisms of $\cdot\text{OH}$ production in sonolysis and radiolysis, attempts to quantitatively compare the rates at which DOM undergoes property changes in these techniques as a function of either the rate of energy deposition or $\cdot\text{OH}$ production in solution are likely subject to serious errors. There are, however, ways in which the effects of alternate reactions on DOM can be meaningfully compared. For example, techniques can be evaluated and compared on the basis of the “within technique” relative rates of change in individual DOM parameters. Such relations have been used elsewhere (50) and presumably are independent of exact $\cdot\text{OH}$ formation or scavenging rates.

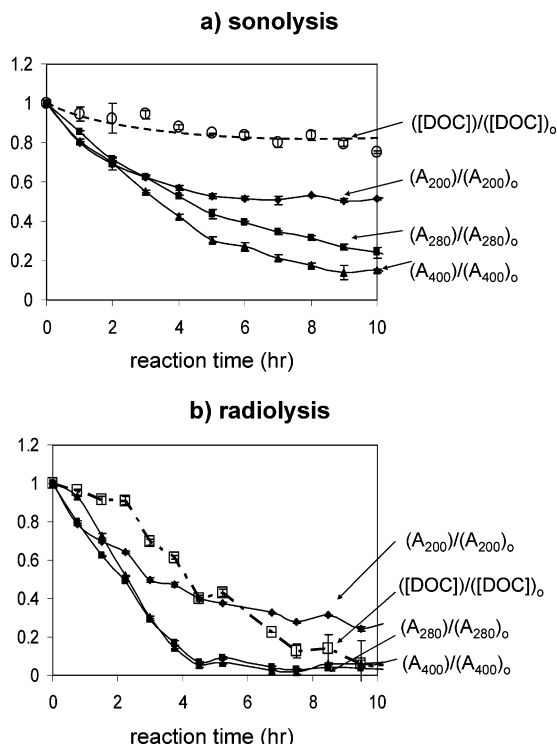


FIGURE 1. [DOC] and UV/vis absorbance data (at 200, 280, and 400 nm), relative to initial values, for DOM reacted by sonolysis (panel a) or radiolysis (panel b). Error bars represent 1 standard deviation from triplicate samples.

Results and Discussion

Relative Changes in [DOC] and UV/Vis Absorptivity. Although an alternative saturation gas such as Ar could have provided an optimized rate of $\cdot\text{OH}$ production in sonolysis (30), O_2 was used here because our interest was to study changes induced in DOM under oxidizing sonochemical conditions. Figure 1 presents [DOC] and absorbance data (at 200, 280, and 400 nm), relative to initial values, for DOM solutions reacted by sonolysis (panel a) or ^{60}Co radiolysis (panel b). Whereas upon radiolysis major decreases in both absorbance and [DOC] were induced and near-total DOC removal was achieved, upon sonolysis major decreases in UV/vis absorbance but only minor decreases in [DOC] occurred. These results are consistent with previous studies (22, 50). The reactions also differed in the relative rates of absorbance decrease at 280 and 400 nm. Whereas upon sonolysis the absorbance at 400 nm decreased at a significantly greater rate than did the absorbance at 280 nm, upon radiolysis the absorbances at these two wavelengths decreased at the same rate.

Observed differences in the “within reaction” relative rates of bleaching and mineralization likely resulted from differences in the ways in which $\cdot\text{OH}$ was produced and spatially distributed in the two reactors. In sonolysis, due to interfacial effects (33), hydrophobic DOM moieties such as chromophores were likely degraded more rapidly than the hydrophilic DOM bulk. In radiolysis, all DOM solution components were exposed to equal $\cdot\text{OH}$ concentrations, leading to less divergent bleaching and mineralization rates.

The observation that upon sonolysis the DOM 400 nm absorbance decreased more rapidly than the 280 nm absorbance was also seen in a greater increase of the “spectral slope” upon sonolysis relative to radiolysis, as calculated by standard methods (45, 46) (data not shown). Previously, the photodegradation of DOM was observed to increase the spectral slope (51). The present results may suggest that long-

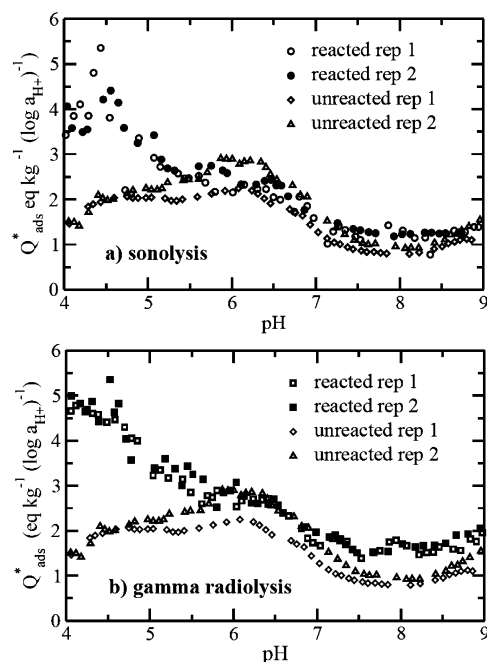


FIGURE 2. Comparison of acid/base properties of DOM samples reacted by sonolysis (panel a) or radiolysis (panel b) to unreacted DOM. Plotted are the differential buffer values, Q^*_{ads} , of the samples as a function of pH, which represents the proton buffering capacity.

wavelength-absorbing chromophores are more hydrophobic than are short-wavelength-absorbing chromophores.

In the first few hours of oxidation, the rate of [DOC] decrease was ~ 6.0 times greater in radiolysis than in sonolysis. This observation can be compared to the result of the terephthalate “DOM surrogate” $\cdot\text{OH}$ scavenging experiments, which suggested that $\cdot\text{OH}$ may have been scavenged by DOM in radiolysis at a rate that was ~ 2.6 times greater than that in sonolysis. These results hence suggest that terephthalate substantially overestimates the rate of $\cdot\text{OH}$ scavenging by DOM in sonolysis. This may possibly be because the aromatic terephthalate ions can better approach the interfacial zones around cavitation bubbles than can the bulk of hydrophilic DOM molecules.

Changes in DOM Acidity. Figure 2 compares titration results for DOM starting material to DOM that had been reacted by sonolysis (panel a) or radiolysis (panel b). Shown are buffer values, Q^*_{ads} (calculated using ProtoFit 2.0 (52)) of the samples as a function of pH, where Q^*_{ads} is the analyte proton buffering capacity calculated as $Q^*_{\text{ads}} = -dQ_{\text{ads}}/dpH$. Duplicate titrations for each sample were in good agreement, and for both reactions there was a substantial increase in Q^*_{ads} for the DOM at pH values less than 5.0. Q^*_{ads} also was increased significantly in the pH range 7.5–8.5 for both techniques, with the effect of radiolysis being more pronounced. The total organic acidity (TOA) of the DOM over the pH range 4–9 (determined by integration of Q^*_{ads}) was affected similarly by both reactions. Whereas the TOA of unreacted DOM was determined to be 8.6 ± 1.2 equiv/kg C, the TOAs of materials reacted by sonolysis or radiolysis were found to be 10.8 ± 0.4 and 13.0 ± 0.6 equiv/kg C, respectively. The observation that most new DOM acid groups formed in the reactions were highly acidic, with $pK_a < 5.0$, is consistent with a previous study of DOM ozonation (53). The similarity in the DOM acid/base property changes induced by sonolysis and radiolysis suggests that similar processes were likely responsible for the DOM degradation in the two techniques.

Changes in HPSEC Chromatograms. HPSEC chromatograms from the absorbance, fluorescence, and [DOC] detection channels for DOM samples reacted for a range of intervals

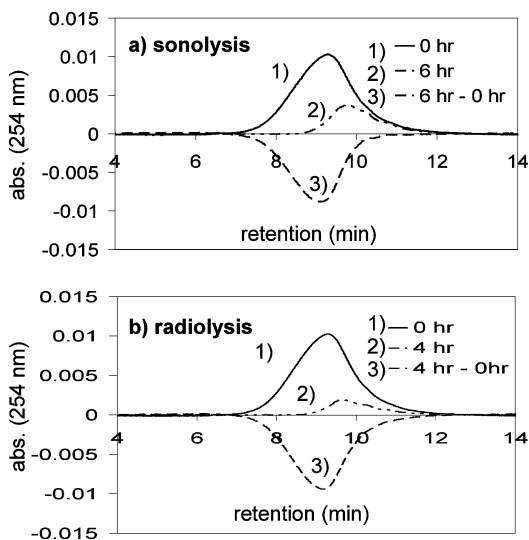


FIGURE 3. HPSEC "difference" chromatograms, from UV-A (254 nm) absorbance detection, for DOM reacted by sonolysis (panel a) or radiolysis (panel b). In both panels, curve 3 is the difference between the HPSEC UV-A chromatograms for the unreacted (curve 1) and reacted DOM (curve 2).

by sonolysis or radiolysis appear in the Supporting Information. We present HPSEC chromatograms here rather than molecular weight distributions for two reasons: Differences in the impacts on DOM of sonolysis and radiolysis were seen in the HPSEC chromatograms, and there can be significant error in the comparison of molecular weight data from optical and DOC detector channels (54). Upon reaction of the DOM by either technique, the DOM HPSEC chromatograms were shifted toward longer retention times, indicating that the DOM was decreased in average molecular weight. Weight average molecular weight (M_w) data, calculated from the 254 nm absorption channel, is shown in the Supporting Information.

Figure 3 (panel a) shows a 254 nm absorbance HPSEC chromatogram for the DOM solution prior to reaction (curve 1), a chromatogram of the same solution following reaction by sonolysis to a point at which the 280 nm absorbance had fallen to $\sim 10\%$ of its initial value, and the calculated difference between these final and initial chromatograms (curve 3). Figure 3 (panel b) presents similar data for DOM reacted to a similar extent, in terms of absorbance bleaching, by radiolysis. Curves 3 in both panels a and b of Figure 3 indicate that both reactions substantially decreased the UV-A absorbance of high molecular weight molecules and that any lower molecular weight molecules that were produced in the degradation of the large molecules were not significantly light-absorbing at 254 nm.

Figure 4 presents HPSEC DOC chromatographic data in a manner analogous to that of Figure 3 for the HPSEC UV-A data. In curve 3 of Figure 4 (panel a), it can be seen that over an extended period of sonolysis the greatest amount of mineralization occurred in the high molecular weight DOM fraction and that there was a substantial gain of mass in the intermediate to low molecular weight fraction. The HPSEC DOC difference chromatogram for radiolysis, i.e., curve 3 of Figure 4 (panel b), shows that the high molecular weight DOM fraction similarly lost the greatest amount of carbon but that there was only a minor gain in the intermediate to lower molecular weight fraction, due to mineralization.

Whereas the sonolysis HPSEC UV-A difference chromatogram indicates that the material produced in solution through the sonolysis of high molecular weight molecules was not significantly light-absorbing at 254 nm, the sonolysis HPSEC DOC difference chromatogram allows the molecular

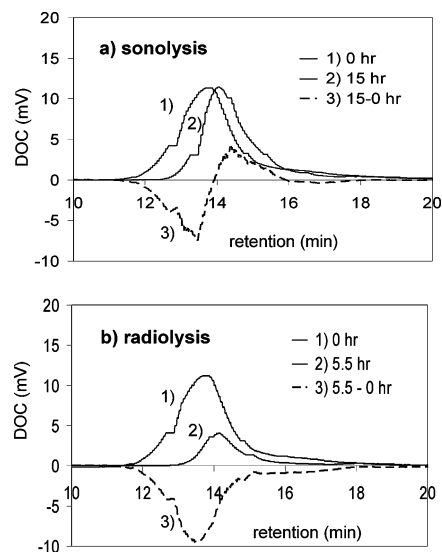


FIGURE 4. HPSEC "difference" chromatograms, from the DOC detection channel, for DOM reacted by sonolysis (panel a) or radiolysis (panel b). In both panels, curve 3 is the difference between the HPSEC DOC chromatograms for the unreacted (curve 1) and reacted DOM (curve 2).

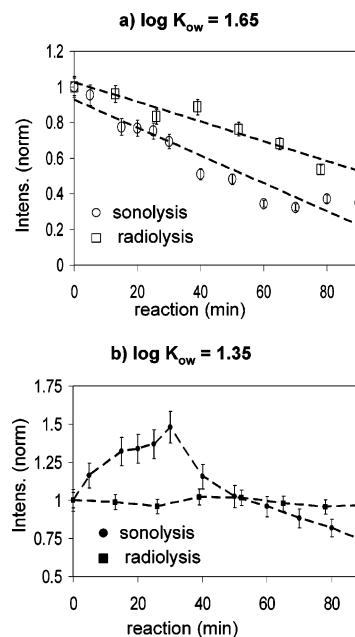


FIGURE 5. The 254 nm absorbance detector signals at $\log K_{ow}$ values 1.65 (panel a) and 1.35 (panel b) for DOM reacted by sonolysis (circles) or radiolysis (squares). Error bars are estimated as $\pm 5\%$ of the detector signal, from Namjesnik-Dejanovic and Cabaniss (9).

weight of these products to be estimated. These results illustrate the utility of using online [DOC] analysis in conjunction with optical detectors in the application of HPSEC in studies in which DOM is degraded.

Changes in DOM Hydrophobicity Distributions. DOM hydrophobicity distribution analyses were performed using a previously reported method (9). Extended reaction by either technique did not substantially shift the position of the main $\log K_{ow}$ distribution peak (Supporting Information). Sonolysis and radiolysis however differed in their effects on the DOM polarity distributions for reactions times less than 90 min. Detector intensities at the two specific $\log K_{ow}$ values of 1.35 and 1.65 are plotted as a function of reaction time in panels a and b of Figure 5 for sonolysis and radiolysis, respectively. Whereas the $\log K_{ow}$ value 1.65 lies on the hydrophobic tail

of the distribution, the log K_{ow} value of 1.35 lies approximately on the center of the main distribution peak. During the first 30 min of the sonolysis reaction the detector signal at log K_{ow} = 1.65 decreased steadily while the intensity at log K_{ow} = 1.35 increased to a maximum. This suggested that, in this first reaction phase, DOM molecules of the hydrophobic (high log K_{ow}) tail of the DOM polarity distribution were converted to molecules having average values of hydrophilicity. A similar effect was not observed upon radiolysis. This property of sonolysis may be of interest to engineers seeking to design AOPs in which the most hydrophobic components of DOM are rapidly degraded to more hydrophilic products.

Comparison of Changes in Molecular Size and Hydrophobicity. The observation that the position of the main of the RP-HPLC peak did not shift substantially during these reactions suggests that the average hydrophilicities of the bulk of the DOM molecules did not change significantly despite undergoing substantial decreases in size. Namjesnik-Dejanovic and Cabaniss (9) reported that DOM hydrophilicity is correlated more strongly with the O/C elemental ratio than with other DOM parameters such as ^{13}C NMR aromaticity. These results hence suggest that the DOM molecules had nearly constant O/C ratios prior to and throughout these reactions. This further can be taken to suggest that the rates of loss and gain of oxygen-rich hydrophilic groups were comparable during the reactions.

The observation, by RP-HPLC, that the relative hydrophilicities of the bulk of the DOM molecules did not change substantially during these reactions agrees with the observation that the rate of DOC loss decreased by only a small amount during sonolysis. It is presumed that the DOM aromaticity decreased substantially in the sonolysis reaction, due to major decreases in the 280 nm absorbance but only a minor decrease in [DOC]. The observation that the position of the main peak of the polarity distribution did not move substantially upon either reaction hence may support the hypothesis that DOM hydrophilicity does not depend significantly on aromaticity.

Implications. $\cdot\text{OH}$ radicals presumably are uniformly distributed in natural surface waters, due to random spatial distribution of $\cdot\text{OH}$ sources such as nitrate ions and collisions of $\text{Fe}(\text{II})$ ions and H_2O_2 molecules. $\cdot\text{OH}$ concentrations however decrease with depth in sunlit natural waters, due to decreasing radiation penetration (20). Whereas in sonolysis hydrophobic and hydrophilic solutes encounter differing $\cdot\text{OH}$ concentrations (33), all solutes in γ -irradiated solutions are exposed to uniform concentrations of $\cdot\text{OH}$. Radiolysis is hence likely superior to sonolysis for studies of natural DOM- $\cdot\text{OH}$ reactions. The intrinsic selectivity in sonolysis toward the degradation of hydrophobic solution components may be of interest to researchers who wish to probe the consequences of the more-or-less selective elimination of the most hydrophobic components of DOM on its reactions such as toxic metal complexation or interaction with hydrophobic organic compounds (HOCs). In engineering, the selectivity of sonolysis toward hydrophobic components of aqueous solutions may be of interest in the design of AOPs for decontamination of field waters containing HOCs that are complexed or partitioned within hydrophobic DOM domains (55, 56). This latter area is one in which further investigation is needed.

Acknowledgments

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Supporting Information Available

Experimental method of the application of the terephthalate $\cdot\text{OH}$ dosimeter in the sonolysis and radiolysis chambers, production of 2-hydroxyterephthalate in the sonolysis and radiolysis chambers, 254 nm absorbance SEC chromatograms for DOM reacted by sonolysis and radiolysis, fluorescence channel SEC chromatograms for DOM reacted by sonolysis and radiolysis, SEC chromatograms from online DOC detection for DOM reacted by sonolysis and radiolysis, weight average molecular weight of DOM reacted by sonolysis and radiolysis as a function of reaction time, and RP-HPLC polarity (log K_{ow}) distributions for DOM reacted by sonolysis and radiolysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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