

Evaluation of parameters influencing removal efficiencies for organic contaminant degradation in advanced oxidation processes

Julie R. Peller, William J. Cooper, Kenneth P. Ishida and Stephen P. Mezyk

ABSTRACT

Advanced oxidation processes, based on hydroxyl radical chemistry, can be used to successfully destroy chemical contaminants in waters intended for reuse. In determining the effectiveness of these radical oxidative degradations and transformations in water, both reaction rate constants and compound removal efficiencies must be considered. Removal efficiencies are defined as the number of contaminant molecules transformed per 100 hydroxyl radicals reacting. Hydroxyl radical reaction efficiencies have been determined for bisphenol A, caffeine, DEET, and sulfamethazine in different qualities of treated and model laboratory wastewaters. While these four contaminants show similar hydroxyl radical reaction rate constants, their removal efficiencies in deionized water varied significantly at 76 ± 7 , 92 ± 8 , 95 ± 9 , and $56 \pm 7\%$, respectively. Model wastewater studies showed that dissolved oxygen did not appreciably influence these values, and low levels of dissolved organic matter (DOM) reduced the removal efficiencies by an average of approximately 20%. However, the combination of solution alkalinity and DOM had a significant impact in reducing hydroxyl radical reaction efficiencies, although not always in a linear, additive, fashion. These results imply that the effective implementation of advanced oxidation technologies in wastewater treatments might be enhanced by prior removal of organics or alkalinity.

Key words | advanced oxidation, bisphenol A, caffeine, DEET, removal efficiencies, sulfamethazine

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INTRODUCTION

Many wastewater treatment plants and water utilities are considering water reuse as a planning option to deal with the shortage of potable water associated with climatic change, increasing population, and/or the overall desire for an alternative sustainable water supply (Vorosmarty *et al.* 2000; Al-Jayyousi 2003). However, reclamation facilities are challenged with a vast array of water contaminants due to the widespread use of chemicals in modern society (Petrovic *et al.* 2003). Pharmaceuticals, pesticides, personal care products, and other organic chemicals are introduced into treatment

facilities or washed into natural waters on a daily basis (Kolpin *et al.* 2002; Lindqvist *et al.* 2005). Agricultural runoff and industrial wastewaters also contribute contaminants to natural waters and the chemical load encountered by the water treatment plants (Pendersen *et al.* 2005). Many of these chemicals are classified as endocrine disruptors or carcinogens.

Wastewater intended for reuse requires the application of additional treatment(s) to ensure the quantitative removal of low concentrations of organic contaminants.

While post-secondary (or tertiary) treatments such as nutrient removal and membrane filtration have become integral to many wastewater processes, these methods (with the exception of reverse osmosis) are unable to adequately eliminate many dissolved chemical contaminants. Therefore, treatment using advanced oxidation processes (AOPs) may be necessary in the future (Parsons 2005). These processes, such as UV/hydrogen peroxide or ozone/hydrogen peroxide, form highly reactive hydroxyl radicals ($\bullet\text{OH}$), which can destroy a wide variety of organic contaminants in solution (Andreozzi *et al.* 1999; von Sonntag 2008). However, the efficiency of these processes can be highly variable depending on their location in the treatment train and the inherent water quality. In addition to anthropogenic chemicals, dissolved matter (both inorganic and organic) is ubiquitous in natural and treated wastewaters, and affects the chemistry that takes place in water treatment (Westerhoff *et al.* 2007).

The usefulness of an AOP in wastewater treatment depends upon how efficiently $\bullet\text{OH}$ reactions destroy the chemical contaminants present. To date, numerous reaction rate constants have been determined for these reactions. Most are fast, near diffusion controlled, with values between 10^9 and $10^{10} \text{ M}^{-1}\text{s}^{-1}$ (Buxton *et al.* 1988). Reaction rate constants and associated transient absorption spectra offer information on $\bullet\text{OH}$ oxidations occurring in both laboratory grade and real-world waters, and can be used to evaluate differences in reaction pathways. For example, the initial step of $\bullet\text{OH}$ reactions often involves addition to an electron-rich site. In the case of aromatic contaminants such as bisphenol A (BPA), the hydroxyl radical adds to an aromatic ring to form a transient cyclohexadienyl radical (as shown in Figure 1), which is readily detected using transient UV

absorption (Peller *et al.* 2009). The time-dependent changes in the transient absorption spectra provide insight into the subsequent chemistry that occurs. In a treated wastewater matrix, the initial $\bullet\text{OH}$ reaction with BPA was followed by another fast chemical transformation, observed as the formation of a second transient absorption peak, which differed from its chemistry in pure water (Peller *et al.* 2009).

Rate constants alone, however, do not provide a complete accounting of the effectiveness or efficiency of the hydroxyl radical in organic contaminant transformations in water solutions of varying quality. While the reaction rate constant for the $\bullet\text{OH}$ with BPA falls in the predicted range for aromatic compounds ($(6.9 \pm 0.2) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$), the hydroxyl radical-mediated removal of BPA in high-purity water measured in steady state radiolysis experiments occurs with only 76% efficiency (Peller *et al.* 2009). The removal efficiency is defined as the number of contaminant molecules destroyed per 100 hydroxyl radical reactions generated in solution. When this efficiency is multiplied by the pure water measured rate constant ($0.76 \times 6.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), an effective contaminant removal value of $5.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ is generated. This latter rate constant would be the correct value required for any kinetic modeling studies (Crittenden *et al.* 1999).

The explanation for less than 100% $\bullet\text{OH}$ transformation efficiency in pure water might be due to different factors, such as ineffective initial reactions, radical combination or repair reactions of the transient radicals which might regenerate the parent compound, or alternative radical pathways. Experiments are currently underway to understand the lower efficiency reactions.

The measured $\bullet\text{OH}$ efficiency with BPA in a secondary-treated wastewater matrix was substantially lower (34%)

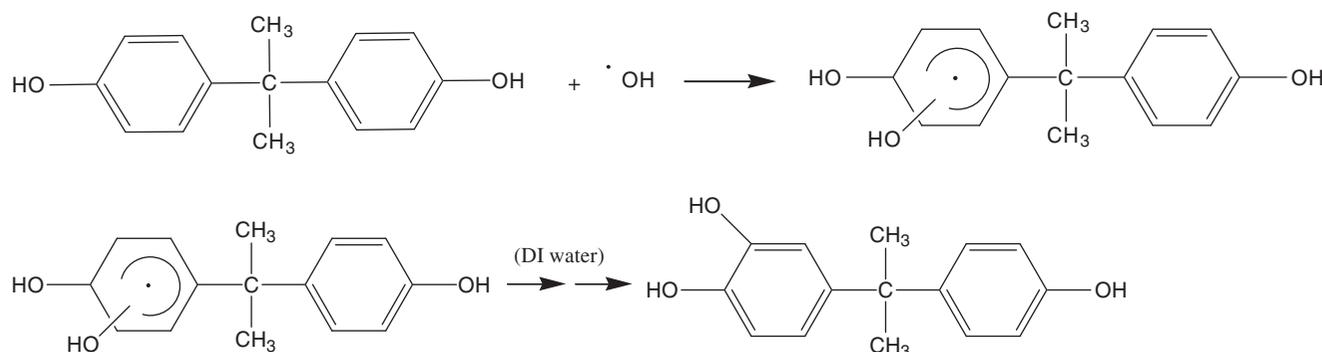
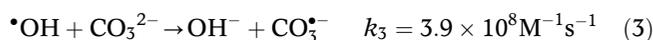


Figure 1 | Reaction of the hydroxyl radical with bisphenol-A to form a transient cyclohexadienyl species and ultimate conversion to a dihydroxylated ring species.

than in deionized water, as expected, due to $\bullet\text{OH}$ reactions with other water constituents. Correspondingly, this would give an even lower effective removal value of $(0.34 \times 6.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}) = 2.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for BPA in this water quality. Thus, two important questions arise for the use of an AOP to remove unwanted chemicals: what is the *effective* contaminant removal value (measured rate constant multiplied by the inherent destruction efficiency for the $\bullet\text{OH}$ reaction in a particular water matrix) and what is the effect of additional dissolved substances on this value?

Dissolved substances such as inorganic bicarbonate and carbonate ions and organic matter (DOM) are ubiquitous in natural waters and most treated wastewaters and their role in hydroxyl radical based AOP chemistry must be considered. Both bicarbonate and carbonate react readily with the hydroxyl radical to produce the carbonate radical anion, $\text{CO}_3^{\bullet-}$ (Weeks & Rabani 1966; Buxton *et al.* 1988) which is also a reactive species known to participate in aquatic oxidation reactions (Behar *et al.* 1970; Huang & Mabury 2000; Canonica *et al.* 2005; Busset *et al.* 2007; Mazellier *et al.* 2007).



Dissolved organic matter also reacts readily with the hydroxyl radical, with a reported average rate constant of

$2.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Westerhoff *et al.* 2007). The natural organic content of waters varies according to geography, and the rate constants for non-isolated effluent organic matter from treated wastewater effluents with the hydroxyl radical correspondingly fluctuate (Rosario-Ortiz *et al.* 2008; Gonsior *et al.* 2011). As the hydroxyl radical can react via different reaction pathways and/or with different dissolved species depending upon the water matrix, it is essential that quantitative efficiency investigations be performed in the actual treated wastewater solution.

This study was designed to provide a more thorough understanding of hydroxyl radical-mediated oxidation processes in complex, real-world, water matrices utilizing frequently detected contaminant chemicals of varying structures. Experimental hydroxyl radical reaction efficiencies were determined for: BPA (bisphenol A), caffeine, DEET (*N,N*-Diethyl-*meta*-toluamide), and sulfamethazine (shown in Figure 2) in both laboratory-grade and real-world water matrices.

METHODS

Chemicals

Most chemicals used in this study were obtained from the Aldrich Chemical Company at the highest purity available and used as received. Characterized Suwannee River DOM, Suwannee River fulvic acid Standard II and Suwannee River

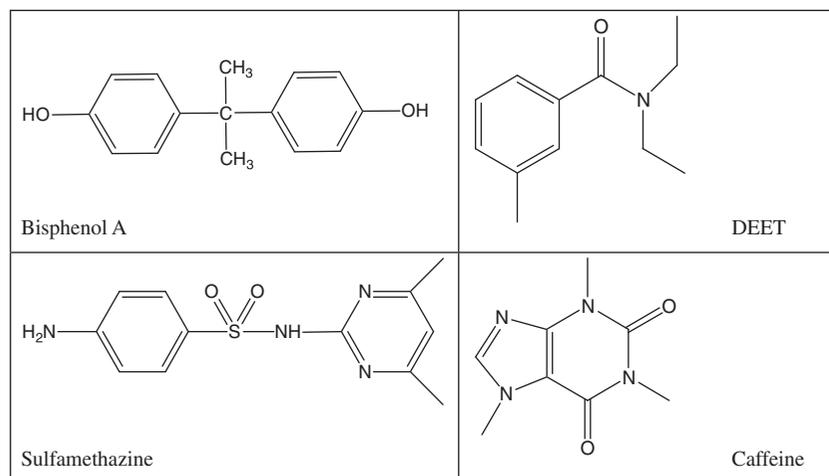


Figure 2 | Structures of model organic contaminants.

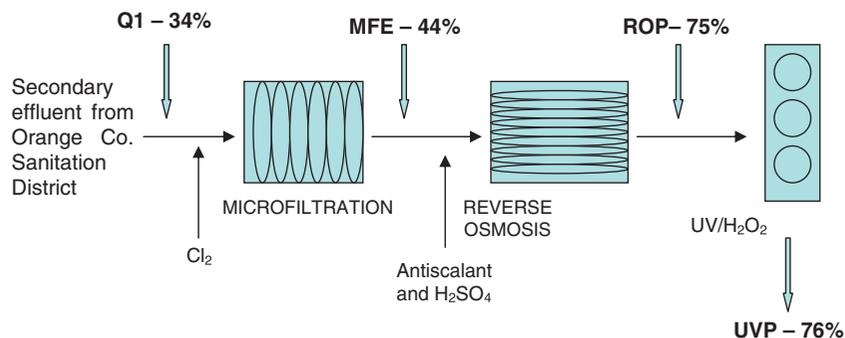


Figure 3 | Sampling sites and corresponding removal efficiencies for hydroxyl radical-mediated bisphenol-A oxidations in different levels of treated wastewater from the Orange County Water District, Fountain Valley, CA, USA.

natural organic matter (NOM) were supplied by the International Humic Substances Society. Solutions were made using high purity water produced from a Millipore Milli-Q[®] system or in treated wastewater of differing quality (see Figure 3 for sampling sites and Table 1 for individual water quality parameters) provided by the Orange County Water District, Fountain Valley, CA, USA. Solutions were either pre-saturated with high purity N₂O to remove the dissolved oxygen and ensure only oxidizing conditions, or where indicated, a 4:1 gas mixture of N₂O and O₂ was utilized to mimic hydroxyl radical chemistry occurring in the presence of typical atmospheric oxygen content in waters.

Steady state radiolysis experiments

Radiation chemistry techniques were used to quantitatively form hydroxyl radicals in a variety of aqueous solutions

spiked individually with these model contaminants. The irradiation of solution samples was performed using a Gammacell 220 ⁶⁰Co γ irradiator housed at the Radiation Laboratory, University of Notre Dame, Notre Dame, IN, USA. During the dates of irradiation, the average dose rate was 0.0441 kGy min⁻¹.

Solutions of bisphenol A, caffeine, DEET and sulfamethazine were prepared in deionized water and in the different quality of treated wastewaters (Q1, MFE, ROP, UVP; see Table 1) at typical concentrations of 50 μ M. It is worthwhile to note that the 50 μ M average concentration was dictated by the limitations imposed by the available irradiations dose rates and the analytical analyses. While lower, closer to real-world concentrations were preferred for the study, in order to measure the first 30% of the oxidative destruction, the radiation doses required solute concentrations around 50 μ M. These solutions were subjected to different time

Table 1 | Summary of constituent parameters for Orange County Water District treated and laboratory model wastewater qualities used in this study

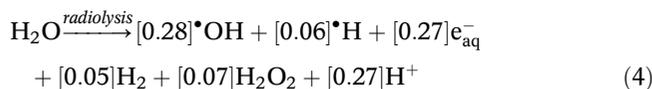
	Water description	TOC (mg L ⁻¹) Average	HCO ₃ ^a (mg L ⁻¹) Average	pH range
UVP	Advanced oxidation product containing H ₂ O ₂ ; most extensively treated waste water	0.2	13	6.1–6.5
ROP	Reverse osmosis permeate	0.2	15	5.7–6.7
MFE	Microfiltration effluent; chlorination prior to the filtration	11	340	6.8–8.0
Q1	Secondary treated wastewater; no disinfection (no chlorine); least treated	13	350	7.5–8.2
MilliQ Water		<0.005	0	7.0
DI water + DOM	SRFA, fulvic acid, 10 mg L ⁻¹	10	0	4–5.5
DI water + NaHCO ₃	10 mM NaHCO ₃	<0.002	610	7–10
DI + DOM + NaHCO ₃	10 mg L ⁻¹ SRFA, 10 mM NaHCO ₃	10	610	7–8.5

TOC: total organic carbon; DI: deionized; DOM: dissolved organic matter; SRFA: Suwannee River fulvic acid.

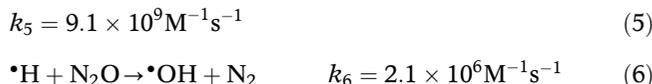
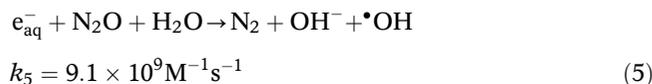
^aCarbonate (CO₃²⁻) levels were <0.6 mg L⁻¹ for natural wastewaters, or as dictated by solution pH (see Equation (1)).

intervals of ^{60}Co gamma irradiation, which corresponded to specific irradiation doses.

In the γ -irradiation of water solutions containing low solute concentrations ($<0.1\text{ M}$), radicals and other species are formed according to the following reaction (Buxton *et al.* 1988).



The numbers in brackets are the G-values (yields) of each species in $\mu\text{mol Gy}^{-1}$ of deposited energy. In N_2O -saturated solutions, completely oxidizing conditions are established since hydrated electrons, e_{aq}^- and some hydrogen atoms, $\bullet\text{H}$, are converted to hydroxyl radicals according to the following reactions (Buxton *et al.* 1988):



Based on experimental measurements, the total hydroxyl radical yield for N_2O -saturated conditions is $0.59\ \mu\text{mol J}^{-1}$ (Buxton & Stuart 1995).

HPLC analyses

The quantitative loss of the contaminant compounds and the formation of intermediates was followed using a Waters HPLC system (Millennium 2010, Waters 717 plus Autosampler, Waters 600 Controller Solvent Pump) equipped with a Supelco Discovery[®] C18 column, $5\ \mu\text{m}$ ($250\ \text{mm} \times 4.6\ \text{mm}$). A solvent flow of $0.85\ \text{mL min}^{-1}$ utilized three solvents: water, methanol, and 1% acetic acid solution. In the analyses of BPA solutions, the initial solvent mixture consisted of 70% methanol and 30% water. Using a gradient curve, the solvent mixture changed to 30% methanol, 68% water and 2% acetic acid solution at the 13 minute mark. The solvent switched back to the original flow by 16 minutes. The same solvents were utilized in the analyses of the other compounds, with slight variations in the gradients. A photodiode array detector monitored the 200–400 nm range.

Removal efficiency determinations

The determination of hydroxyl radical reaction efficiencies involves the quantitative measurement of the absolute change in contaminant concentration with absorbed radiation dose (Mezyk *et al.* 2007). In order to avoid significant interferences from intermediate reaction products, which often effectively compete for hydroxyl radicals, only data for total contaminant loss of $\leq 15\text{--}30\%$ were used. Initial slope values were obtained by fitting the experimental data to a quadratic equation, where the linear coefficient of this fit corresponds to the best-fit initial slope (see Figure 4). The initial slope value is then divided by $0.59\ \mu\text{mol J}^{-1}$, which corresponds to the total $\bullet\text{OH}$ yield under N_2O -saturated conditions (Buxton & Stuart 1995) and multiplied by 100 to get percentage efficiency. Using this methodology, for $50\ \mu\text{M}$, nitrous oxide-saturated solutions of bisphenol A in deionized water, a contaminant removal reaction efficiency of $76 \pm 7\%$ was determined (see Figure 4).

RESULTS AND DISCUSSION

Hydroxyl radical removal efficiencies

The reaction rate constants and hydroxyl radical removal efficiencies for the contaminants of interest in this study are

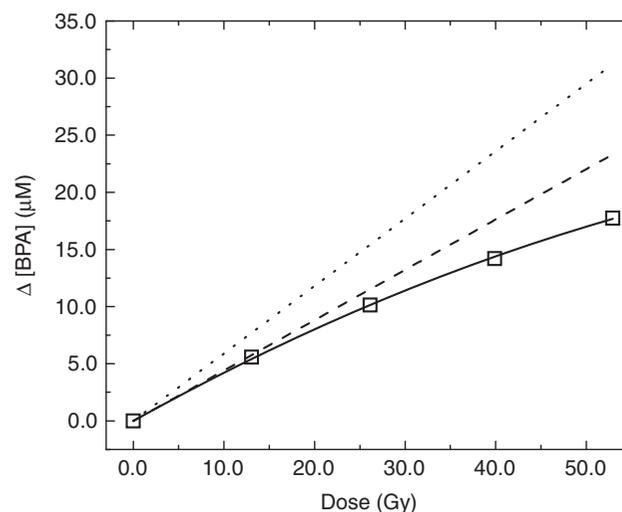


Figure 4 | Efficiency evaluation for the hydroxyl radical reaction and $50\ \mu\text{M}$ BPA in deionized water. The solid line is the quadratic fit to the data, with dashed line corresponding to initial slope from the fitted linear coefficient. The slope of dashed line is $0.45 (\pm 0.04)\ \mu\text{M/Gy}$, which converts to $76 (\pm 7)\%$ efficiency. The dotted line corresponds to the theoretical 100% efficiency line.

Table 2 | Contaminant rate constants and removal efficiencies for hydroxyl radical reactions in deionized water and three treated wastewaters (Average contaminant concentration = 50 μM).

Solution/contaminant	Bisphenol A	Caffeine	Sulfamethazine	DEET
Rate constant in DI water ($\text{M}^{-1}\text{s}^{-1}$)	$6.9 (\pm 0.2) \times 10^9$	$6.9 (\pm 0.4) \times 10^9$	$8.3 (\pm 0.8) \times 10^9$	$4.9 (\pm 0.2) \times 10^9$
Deionized water	$76 \pm 7\%$	$92 \pm 8\%$	$56 \pm 7\%$	$95 \pm 9\%$
Q1 (secondary treated wastewater)	$34 \pm 2\%$		$29 \pm 7\%$	$42 \pm 8\%$
Microfiltration effluent	$44 \pm 5\%$	$34 \pm 9\%$	$32 \pm 9\%$	$42 \pm 8\%$
Reverse osmosis permeate	$75 \pm 5\%$	$80 \pm 9\%$	$53 \pm 4\%$	$81 \pm 10\%$
10 mg L^{-1} fulvic acid	$71 \pm 5\%$	$64 \pm 1\%$		$71 \pm 4\%$
10 mg L^{-1} humic acid		$75 \pm 3\%$		$78 \pm 5\%$
10 mg L^{-1} natural organic matter (pH value)		$68 \pm 1\%$	$54 \pm 7\%$ (5) $52 \pm 8\%$ (7)	$80 \pm 4\%$
10 mM NaHCO_3 (pH value)	$56 \pm 3\%$ (8.4) $73 \pm 5\%$ (7) $76 \pm 6\%$ (10)	$70 \pm 4\%$ (7) $72 \pm 4\%$ (8.4)	$36 \pm 2\%$ (8.4)	$85 \pm 10\%$ (5 mM NaHCO_3 , pH 8)
10 mM NaHCO_3 (pH value) + 10 mg L^{-1} DOM	$25 \pm 2\%$ (8.4) $37 \pm 4\%$ (7)	$58 \pm 2\%$ (7)	$29 \pm 10\%$ (8)	$65 \pm 3\%$ (8) (5 mM NaHCO_3 , pH 8)

summarized in Table 2. The three contaminants BPA, caffeine, and sulfamethazine were specifically chosen, since their hydroxyl radical reaction rate constants are very similar ($\sim 7\text{--}8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), even though the structures are variable. A slightly lower rate constant is reported in the literature for DEET ($4.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) (Song et al. 2009).

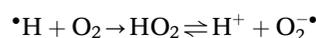
The removal efficiency involves the direct measurement of the loss of the organic contaminant in the water solution, and is, therefore, the most applicable assessment of AOP effectiveness. While the experimental reaction efficiencies were expected to correspond to measured rate constants, this did not occur. From the data given in Table 2, a few trends are evident. While caffeine and DEET have greater than 90% removal in high-quality deionized water, the removal efficiencies for BPA (76%) and sulfamethazine (56%) are considerably lower. The contaminant removal efficiencies determined in ROP water are nearly equivalent to those in deionized water, but a consistent reduced effectiveness was found for all of the model contaminants in waters of lower quality. The decreased efficiency of the hydroxyl radical in solutions containing significant concentrations of dissolved substances is expected, as many of these species successfully compete for the hydroxyl radical or alter $\bullet\text{OH}$ -contaminant reaction pathways. Figure 3 shows the removal efficiencies determined for BPA for

different quality wastewaters at various points in a treatment process.

In order to gain further insight into the real-world water reaction efficiencies, experiments were also performed using model wastewater containing varying levels of the most prevalent dissolved components: oxygen, DOM, and bicarbonate.

Effects of molecular oxygen

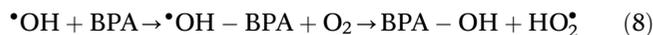
Since the production of hydroxyl radicals by AOPs will always occur in the presence of oxygen, experiments were performed utilizing mixed $\text{N}_2\text{O}/\text{O}_2$ conditions. Several BPA solutions were saturated with a 4:1 (v/v) mixture of $\text{N}_2\text{O}/\text{O}_2$, which still gives quantitative $\bullet\text{OH}$ radical production as well as a real-world dissolved oxygen level of $2.5 \times 10^{-4} \text{ M}$ (8 mg L^{-1}). With this gas mixture, most of the formed hydrogen atoms will react to form $\bullet\text{HO}_2$ radicals, which are in equilibrium with the deprotonated form $\text{O}_2\bullet$ (Buxton et al. 1988).



$$k_7 = 1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}; \text{p}K_7 = 4.8 \quad (7)$$

More importantly, though, the yield of the hydroxyl radicals remains essentially the same (0.56 $\mu\text{mol}/\text{Gy}$), while

the yield of $\bullet\text{HO}_2/\text{O}_2^-$ is negligibly small ($\sim 0.06 \mu\text{mol}/\text{Gy}$). This $\bullet\text{OH}/\text{O}_2$ mixture potentially allows for the following additional stabilization reaction to occur:



However, the calculated removal efficiencies for these mixed gas systems were within experimental error of the values for only N_2O -saturated solutions (see Table 3). Detailed analyses of the HPLC chromatograms revealed a greater number of oxidized intermediates formed in the mixed gas solutions, attributed to the products formed through additional radical reactions that take place with molecular oxygen. However, the equal removal efficiencies of the solutions saturated with the $\text{N}_2\text{O}/\text{O}_2$ clearly indicate that the data generated from N_2O -saturated conditions are directly transferable to real-world (aerated) AOP remediation conditions.

Effects of DOM

In order to simulate the distinct effects of the dissolved organic matter present in treated wastewaters, 10 mg/L of Suwannee River fulvic acid (SRFA) was added to the individual organic contaminant solutions. For BPA, an average removal efficiency of $71 \pm 5\%$ was determined, within experimental error for the value in deionized water ($76 \pm 7\%$). A more extensive study was performed for caffeine and DEET where, in addition to SRFA, isolates of humic acid and natural organic matter, NOM were utilized. The efficiencies of the hydroxyl radical reactions with these compounds in the presence of the DOM are also summarized in Table 2.

Table 3 | Calculated removal efficiencies for the radiolytic oxidation of BPA under conditions of N_2O and $\text{N}_2\text{O}/\text{O}_2$ (4/1) saturation

50 μM BPA solutions	Removal efficiency: N_2O -saturated	Removal efficiency: $\text{N}_2\text{O}/\text{O}_2$ (4/1)
Deionized water	$76 \pm 7\%$	$71 \pm 2\%$
10 mgL^{-1} DOM	$71 \pm 5\%$	$66 \pm 5\%$
UVP treated wastewater	$76 \pm 2\%$	$73 \pm 5\%$
ROP treated wastewater	$75 \pm 5\%$	$71 \pm 5\%$
MFE treated wastewater	$44 \pm 5\%$	$37 \pm 2\%$
Q1 treated wastewater	$34 \pm 2\%$	$34 \pm 3\%$

Dissolved organic matter is a complex mixture of natural organic compounds including carboxylic acids, phenolic aromatics, and polyphenols. It has been shown that dissolved organic matter reacts readily with the hydroxyl radical, with an average rate constant of $2.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Westerhoff *et al.* 2007). The average value for non-isolated effluent organic matter was reported as $8.6 \times 10^8 \text{ M}_c^{-1} \text{ s}^{-1}$, where M_c is defined as the DOM molarity for moles of carbon, assuming 12 g of C/mole C (Rosario-Ortiz *et al.* 2008). If DOM functioned solely as a competitor for hydroxyl radicals, a consistent change in removal efficiency for each contaminant would be observed. However, for BPA and sulfamethazine, no significant decrease in the reaction efficiency was measured in the presence of 10 mg/L SRFA, whereas substantial decreases were observed for caffeine and DEET. For BPA and sulfamethazine, this suggests that some of the radicals produced from the DOM and $\bullet\text{OH}$ reactions are capable of further degrading BPA molecules. This additional reaction pathway is supported by the HPLC data shown in Figure 5(a), where the formation of the hydroxylated-BPA intermediate (the smaller HPLC peak) occurs to a significantly greater extent in the presence of fulvic acid (Figure 5(b)).

While small variations in the hydroxyl radical removal efficiencies for the different organic carbon isolates were found for the four contaminants, the differences are somewhat compound-dependent and variable. The average decrease in removal efficiencies for the 50 μM contaminant concentrations, in the presence of 10 mg L^{-1} of organic carbon, was around 20% (see Table 2). It is also worth noting that the pH of the contaminant solutions with dissolved DOM fell in the range of 4.5–6.0, consistent with some wastewater effluents (Table 1). To eliminate potential pH effects in the decreased removal efficiencies some DOM solutions of sulfamethazine were run at an adjusted pH of 7, but no change in removal efficiency was observed (Table 2).

Effects of bicarbonate and pH

The range of pH values for the treated wastewater solutions in this study was relatively large, 5.7–8.2; therefore, the laboratory prepared solutions also covered a wide pH range (Table 1). Since treated wastewaters and natural waters vary

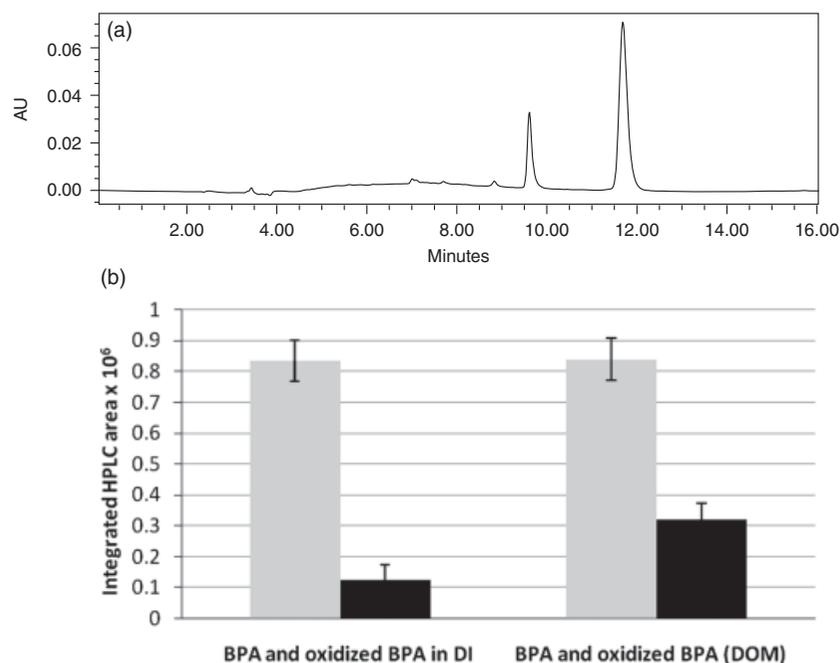


Figure 5 a) HPLC chromatogram of irradiated 50 μM BPA solution, 10 mgL^{-1} DOM in DI water (N_2O -saturated) at 276 nm after a radiation dose of 0.05 kGy. The large peak represents BPA (~ 12 min) and the peak at ~ 9.6 min represents hydroxylated BPA. b) HPLC peak integration areas. The first bar of each set represents the average integrated area of the BPA peak and the second, smaller bar represents the integrated area of the hydroxylated BPA peak for DI water and DI water containing DOM, respectively.

greatly in solution pH, experiments were performed and monitored with both natural pH solutions and in buffered solutions.

The effect of the bicarbonate ion on the hydroxyl radical-mediated oxidation of BPA was studied individually to elucidate its impact. When sodium bicarbonate (10 mM) was added to a 50 μM contaminant solution, the resulting solution pH was 8.4. Hydroxyl radical-initiated oxidations of BPA were performed at this natural solution pH and also at pH 7 and 10, adjusted by the addition of either HClO_4 or NaOH . The measured removal efficiencies are summarized in Table 2. Although the initial $\bullet\text{OH}$ radical yield is effectively the same over the pH range 3–10 (Buxton *et al.* 1988), the average value for the degradation of BPA in the presence of 10 mM NaHCO_3 at pH 8.4, $56 \pm 3\%$, was measurably lower than the reaction efficiency for BPA in deionized water at pH 7.0, $76 \pm 7\%$, and similar to the difference ($\sim 20\%$ decrease) measured for DEET, caffeine, and sulfamethazine in the presence of 10 mM bicarbonate. However, when the pH of these carbonate-containing BPA solutions was adjusted to a higher (pH 10) or to a neutral value, the removal efficiencies increased ($76 \pm 6\%$, $73 \pm 5\%$, respectively) and

were comparable to those of BPA in deionized water ($76 \pm 7\%$). In contrast, the removal efficiencies for caffeine/bicarbonate solutions showed no change when adjusted to neutral pH.

In the case of BPA with 10 mM bicarbonate at pH 7, a chemical pathway similar to the pure BPA in deionized water was observed, as evidenced by the equivalent reaction efficiency and the HPLC chromatograms for stable products, which were similar for both. Alternatively, at pH 8.4 and 10, the oxidation reactions in the presence of bicarbonate follow different chemical pathways that are void of the main stable intermediate, the hydroxylated BPA. At higher pH (\sim pH 10), more carbonate is present and the carbonate radical anion forms to a greater extent (Equation (3)). More importantly, the concentration of deprotonated BPA also increased (pK_a BPA = 9.6, 10.2). The phenoxide ion of BPA can react via electron transfer with both carbonate and hydroxyl radicals, as shown in Figure 6, leading to different, stable intermediate products (Leopoldini *et al.* 2004; Neta & Grodkowski 2005; Peller & Kamat 2005; Priyadarsini *et al.* 1998). The greater efficiency of the higher pH solutions is likely attributed to the higher rate of reaction for carbonate

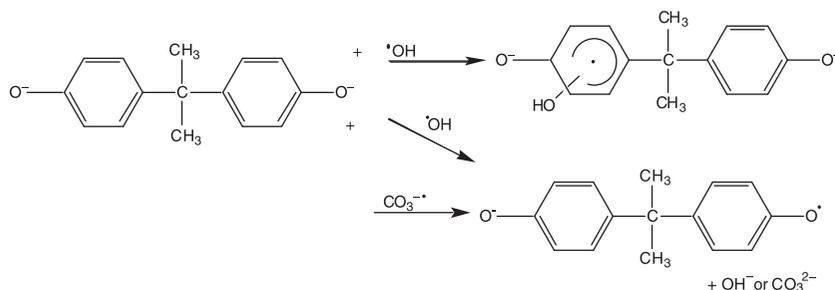


Figure 6 | Reaction pathways for bisphenol A with hydroxyl and carbonate anion radicals in higher pH solutions, ~ 10 .

with the phenoxide ion, which would minimize the occurrence of second-order carbonate radical recombination.

Effects of DOM + bicarbonate

Since real-world waters contain both bicarbonate and DOM, a model 50 μM BPA solution was prepared with 10 mM NaHCO_3 and 10 mg L^{-1} DOM (fulvic acid) in deionized water. At the unadjusted pH (~ 8.4) of this solution, the average removal efficiency was determined to be only $25 \pm 2\%$, a drastically lower value than determined for either individual component. For this combined solution adjusted to pH 7.0, the efficiency was again noticeably low ($37 \pm 4\%$). These low removal efficiencies are similar to the values determined for the lesser treated wastewater solutions, Q1, and MFE (Table 2).

These experiments demonstrated that, individually, DOM and bicarbonate ions lower $\bullet\text{OH}$ removal efficiencies on average by 20%. However, in the presence of both of these prominent dissolved components of real world waters, the drop in $\bullet\text{OH}$ efficiency is *at least* additive ($\sim 40\%$) but dependent upon the contaminant as noted in the $\bullet\text{OH}$ reaction studies with BPA. The impact of both dissolved species shows sharp similarities to the reactivity of the organic contaminant in the less extensively treated wastewaters.

CONCLUSIONS

For AOP treatment optimization, experimentally determined removal efficiencies must be properly combined with measured rate constants before being incorporated into computer modeling codes. These preliminary data utilizing four representative organic contaminants demonstrate that one cannot

necessarily assume a relative rates partitioning distribution of $\bullet\text{OH}$ reactions; instead, real-world water $\bullet\text{OH}$ efficiency measurements need to be made for accurate large-scale predictions. Based on the results of this work, for the quantitative removal of organic contaminants, pre-removal of either DOM (through filtration) or bicarbonate (through pH adjustment) would substantially improve AOP remediation efficiency, especially for contaminants similar in structure to BPA.

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REFERENCES

- Al-Jayyousi, O. R. 2003 Greywater reuse: towards sustainable watermanagement. *Desalination* **156**, 181–192.
- Andreozzi, R., Caprio, V., Insola, A. & Marotta, R. 1999 Advanced oxidation processes (AOP) for water purification and recovery. *Catal. Today* **53**, 51–59.
- Behar, D., Czapski, G. & Duchovny, I. 1970 Carbonate radical in flash photolysis and pulse radiolysis. *J. Phys. Chem.* **74**, 2206–2210.
- Busset, C., Mazellier, P., Sarakha, M. & De Laat, J. 2007 Photochemical generation of carbonate radicals and their reactivity with phenol. *J. Photochem. Photobiol. A* **185**, 127–132.
- Buxton, G., Greenstock, C., Helman, W. P. & Ross, A. B. 1988 Critical review of rate constants for reactions of hydrated electrons,

- hydrogen atoms and hydroxyl radicals (OH/O⁻) in aqueous solution. *J. Phys. Chem. Ref. Data* **17**, 513–886.
- Buxton, G. V. & Stuart, C. R. 1995 Re-evaluation of the thiocyanate dosimeter for pulse radiolysis. *J. Chem. Soc. Faraday Trans.* **91**, 279–281.
- Canonica, S., Kohn, R., Mac, M., Real, F. J., Wirz, J., & Von Guten, U. 2005 Photosensitizer method to determine rate constants for the reaction of carbonate radical with organic compounds. *Environ. Sci. Technol.* **39**, 9182–9188.
- Crittenden, J. C., Hu, S. M., Hand, D. W. & Green, S. A. 1999 A kinetic model for H₂O₂/UV process in a completely mixed batch reactor. *Wat. Res.* **33**, 2315–2328.
- Gonsior, M., Zwartjes, M., Cooper, W. J., Song, W., Ishida, K. P., Rosso, D., Hertkorn, N. & Schmitt-Kopplin, P. 2011 Molecular characterization of effluent organic matter identified by ultrahigh resolution mass spectrometry. *Water Research* (submitted).
- Huang, J. & Mabury, S. A. 2000 The role of carbonate radical in limiting the persistence of sulfur-containing chemicals in sunlit natural waters. *Chemosphere* **41**, 1775–1782.
- Kolpin, D. W., Furlong, E. T., Meyer, M. T., Thurman, E. M., Zaugg, S. D., Barber, L. B. et al. 2002 Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000: A national reconnaissance. *Environ. Sci. Technol.* **36**, 1202–1211.
- Leopoldini, M., Marino, T., Russo, N. & Toscano, M. 2004 Antioxidant properties of phenolic compounds: H-atom versus electron transfer mechanism. *J. Phys. Chem. A* **108**, 4916–4922.
- Lindqvist N., Tuhkanen T. & Kronberg L. 2005 Occurrence of acidic pharmaceuticals in raw and treated sewages and in receiving waters. *Wat. Res.* **39**, 2219–2228.
- Mazellier, P., Busset, C., Delmont, A. & De Laat, J. 2007 A comparison of fenuron degradation by hydroxyl and carbonate radicals in aqueous solution. *Water Res.* **41**, 4585–4594.
- Mezyk, S. P., Neubauer, T., Cooper, W. J. & Peller, J. R. 2007 Free-radical-induced oxidative and reductive degradation of sulfa drugs in water: absolute kinetics and efficiencies of hydroxyl radical and hydrated electron reactions. *J. Phys. Chem. A* **111**, 9019–9024.
- Neta, P. & Grodkowski, J. 2005 Rate constants for reactions of phenoxy radicals in solution. *J. Phys. Chem. Ref. Data* **34**, 109–199.
- Parsons, S. 2005 *Advanced Oxidation Processes for Water and Wastewater Treatment*. IWA Publishing, London.
- Peller, J. & Kamat, P. V. 2005 Radiolytic transformations of chlorinated phenols and chlorinated phenoxyacetic acids. *J. Phys. Chem. A* **109**, 9528–9535.
- Peller, J., Mezyk, S. P. & Cooper, W. J. 2009 Bisphenol A reactions with hydroxyl radicals: Diverse pathways determined between deionized water and tertiary treated wastewater solutions. *Res. Chem. Intermed.* **35**, 21–34.
- Pendersen, J. A., Soliman, M. & Suffet, I. H. 2005 Human pharmaceuticals, hormones and personal care product ingredients in runoff from agricultural fields irrigated with treated wastewater. *J Agric Food Chem.* **53**, 1625–1632.
- Petrovic, M., Gonzales, S. & Barcelo, D. 2005 Analysis and removal of emerging contaminants in wastewater and drinking water. *Trends Anal. Chem.* **22**, 685–696.
- Priyadarsini, K. I., Guha, S. N. & Rao, M. N. A. 1998 Physio-chemical properties and antioxidant activities of methoxy phenols. *Free Radic. Biol. Med.* **24**, 933–941.
- Rosario-Ortiz, F. L., Mezyk, S. P., Doud, D. F. R. & Snyder, S. A. 2008 Quantitative correlation of absolute hydroxyl radical rate constants with non-isolated effluent organic matter bulk properties in water. *Environ. Sci. Technol.* **42**, 5924–5930.
- Song, W., Cooper, W. J., Peake, B. M., Mezyk, S. P., Nickelson, M. G. & O'Shea, K. E. 2009 Free radical destruction of N,N-diethyl-m-toluamide (DEET) in aqueous solution. *Water Res.* **43**, 635–642.
- von Sonntag, C. 2008 Advanced oxidation processes: mechanistic aspects. *Water Sci. Technol.* **58**, 1015–1021.
- Vorosmarty, C. J., Green, P., Salisbury, J. & Lammers, R. B. 2000 Global water resources: vulnerability from climate change and population growth. *Science* **289**, 284–288.
- Weeks, J. L. & Rabani, J. 1966 Pulse radiolysis of deaerated aqueous carbonate solutions. 1. Transient optical spectrum and mechanisms. 2. pK for OH radicals. *J. Phys. Chem.* **70**, 2100–2106.
- Westerhoff, P., Mezyk, S. P., Cooper, W. J. & Minakata, D. 2007 Electron pulse radiolysis determination of hydroxyl radical rate constants with Suwannee River fulvic acid and other dissolved organic matter isolates. *Environ. Sci. Technol.* **41**, 4640–4644.

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