

Nitrate-Induced Photolysis in Natural Waters: Controls on Concentrations of Hydroxyl Radical Photo-Intermediates by Natural Scavenging Agents

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The importance of the principal natural scavenging agents for hydroxyl radicals ($\cdot\text{OH}$) was evaluated, and a general framework was developed to predict the significance of nitrate-induced, $\cdot\text{OH}$ -mediated degradation of aquatic contaminants. Rate constants for $\cdot\text{OH}$ scavenging by dissolved organic matter (DOM) from five surface water sources were in a narrow range ($2.3 \pm 0.77 \times 10^4$ (mg of C/L) $^{-1}$ s $^{-1}$), which is similar to previously reported values and suggests that the importance of DOM as a $\cdot\text{OH}$ sink can be estimated simply from the dissolved organic carbon (DOC) concentration of a water. Scavenging of $\cdot\text{OH}$ by carbonate and bicarbonate is generally less important, but these ions can be the major cause of $\cdot\text{OH}$ scavenging in low DOC, high alkalinity waters. Use of the framework is illustrated by predicting levels of $\cdot\text{OH}$ and half-lives of the corn herbicide acetochlor in waters ranging from pristine to highly influenced by agricultural activities.

Introduction

Nitrate was regarded for many decades as an ion with only a biological role in aquatic systems. Its production and loss processes were thought to be mediated almost exclusively by microorganisms: formation by bacterial nitrification and loss by planktonic assimilation and bacterial denitrification. It is one of the weakest ligands known; all its salts are very soluble; and it participates in no acid–base equilibria within the pH range of natural systems. It is the thermodynamically stable redox state for nitrogen in oxic systems and is not subject to chemical reduction by any of the common reducing agents in water. In brief, it was assumed to be nearly chemically inert in natural aquatic systems.

Some 25 years ago, however, nitrate was found to be photoreactive (1, 2). Its photolysis produces the hydroxyl radical, $\cdot\text{OH}$, an extremely reactive oxidant (3) and one of the principal intermediates in natural water photochemistry. Increasing nitrate levels in many surface waters provided motivation for examining this oxidation pathway. Previous work has shown that nitrate is the primary source of $\cdot\text{OH}$ in natural waters, but $\cdot\text{OH}$ is also consumed rapidly by natural scavengers. $\cdot\text{OH}$ concentrations thus depend on the chemical composition of a water. In general, the rate of change in $[\cdot\text{OH}]$ can be described as

$$d[\cdot\text{OH}]/dt = R_{p,\cdot\text{OH}} - R_{s,\cdot\text{OH}} = \sum k_j[P]_j - \sum k_i[S]_i[\cdot\text{OH}]$$

where $R_{p,\cdot\text{OH}}$ is the rate of $\cdot\text{OH}$ production, $R_{s,\cdot\text{OH}}$ is the scavenging rate of $\cdot\text{OH}$, P is a reactant that produces $\cdot\text{OH}$, and S is a scavenger of $\cdot\text{OH}$. To predict the availability of $\cdot\text{OH}$ for oxidation of pollutants, we determined the effects of the major scavenging agents in freshwaters—carbonate forms and dissolved organic matter (DOM)—on $[\cdot\text{OH}]$.

Studies were done generating $\cdot\text{OH}$ by nitrate photolysis under a UV light source and sunlight. Scavenging of $\cdot\text{OH}$ by carbonate forms was generally less important than scavenging by dissolved organic matter (DOM) in surface waters. Rate constants for $\cdot\text{OH}$ scavenging by five DOM sources were in a narrow range, suggesting that the importance of DOM as a $\cdot\text{OH}$ sink can be estimated simply from the dissolved organic carbon (DOC) concentration of a water. On the basis of this information, we developed a framework to predict the significance of nitrate-induced, $\cdot\text{OH}$ -mediated degradation of aquatic contaminants. Use of the framework is illustrated by predicting levels of $\cdot\text{OH}$ and half-lives of the herbicide acetochlor in natural waters that range from pristine to heavily impacted by agricultural activities.

Background

Hydroxyl radical ($\cdot\text{OH}$) can be produced by several mechanisms, including photolysis of hydrogen peroxide, ozone, nitrate, nitrite, dissolved organic matter and FeOH^{2+} and reaction of Fe^{2+} with H_2O_2 (the Fenton reaction), but several studies have pointed to nitrate as the key source of $\cdot\text{OH}$ in natural waters (for a review, see ref 3). Consumers of $\cdot\text{OH}$ in water include natural organic matter, carbonate forms, and bromide (in seawater).

The reactivity of $\cdot\text{OH}$ has been widely studied. It reacts fairly nonselectively with organic compounds by hydrogen abstraction or hydroxyl addition. Buxton et al. (4) compiled a list of rate constants for reactions of $\cdot\text{OH}$ with more than 1200 compounds. Second-order rate constants for reaction with organic compounds are in the range of 10^7 – 10^{10} M $^{-1}$ s $^{-1}$. Haag and Yao (5) measured rate constants for reaction of $\cdot\text{OH}$ with several drinking water contaminants and estimated others from structure–activity relationships. They concluded that $\cdot\text{OH}$ is relatively nonselective toward C–H bonds and least reactive with aliphatic polyhalogenated compounds. For the 39 compounds they studied, the smallest rate constant was 10^7 M $^{-1}$ s $^{-1}$; the highest were close to diffusion-controlled limits ($\sim 10^{10}$ M $^{-1}$ s $^{-1}$). Reaction with $\cdot\text{OH}$ has been studied as a potential degradation pathway for polychlorinated biphenyls (PCBs) in water; half-lives due to reaction with $\cdot\text{OH}$ were estimated to be on the order of days if particle-bound PCBs react with $\cdot\text{OH}$ (6). Later studies found that reaction rates of PCB congeners decrease as chlorine content increases and that sorption of more hydrophobic congeners to particulate matter significantly slows transformation rates (7).

Several studies have examined the role of nitrate as a source of $\cdot\text{OH}$ in natural waters (8–12). Haag and Hoigné (8) ruled out H_2O_2 as the dominant $\cdot\text{OH}$ precursor in Greifensee, Switzerland, and suggested that the dominant source was nitrate. Kochany and Maguire (11) found that photodegradation of quinoline, a polycyclic aromatic nitrogen heterocycle produced by fossil fuel combustion, was accelerated by the addition of NaNO_3 to water. The most comprehensive study of nitrate photolysis was by Zepp et al. (12), who proposed a simple model to estimate $[\cdot\text{OH}]_{ss}$ for noon, midsummer sun at the surface of water bodies.

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Because of the high reactivity and nonselectivity of $\cdot\text{OH}$, its importance as an oxidant in natural waters is controlled primarily by factors other than its reactivity toward target compounds. Availability of $\cdot\text{OH}$ for reaction with organic pollutants depends on concentrations of naturally occurring scavengers of $\cdot\text{OH}$ as well as species that produce it photochemically. Concentrations of $\cdot\text{OH}$ thus will be greatest in surface waters with high insolation and high nitrate and low scavenger concentrations. Regarding the main $\cdot\text{OH}$ scavengers in freshwater, Zepp et al. (12) found a value of 2.6×10^4 ($\text{mg of C/L}^{-1} \text{ s}^{-1}$ for k_{DOM} , the rate constant for scavenging of $\cdot\text{OH}$, by DOM from Greifensee; others have reported values of k_{DOM} in the range of $1\text{--}5 \times 10^4$ ($\text{mg of C/L}^{-1} \text{ s}^{-1}$ for different DOM sources (8, 13–15). Chen and Hoffman (16) reported rate constants for the reaction of CO_3^{2-} and HCO_3^- with $\cdot\text{OH}$ of 4.2×10^8 and $1.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, respectively.

Methods

Analytical Methods. $[\cdot\text{OH}]_{\text{ss}}$ was measured indirectly from the rate of disappearance of the probe compound, 1-chlorobutane (butyl chloride), which reacts rapidly with $\cdot\text{OH}$ ($k_{\text{OH}} = 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [8, 12]) to form various products. Butyl chloride was measured by headspace gas chromatography, as in other studies (8). Because of the volatility of butyl chloride, care was taken to prevent its loss. The 70-mL quartz bottles used for incubations were completely filled with surface water or Milli-Q filtered water. Quartz stoppers were coated with high vacuum grease, and the bottles were capped without headspace. Just before irradiation, a small volume of saturated butyl chloride solution proportional to the capped bottle volume was injected below the water surface to yield 1.8 mM of butyl chloride. After irradiation, 20 mL of the sample was transferred to 25-mL headspace bottles, which were capped immediately, injected with an internal standard (10 mL of saturated amyl chloride solution), and placed in a 80°C water bath for 30 min. A 100-mL sample of headspace gas was injected onto a 2-m SP-30 packed column at 100°C in a HP 5890A gas chromatograph with FID detector and N_2 carrier gas. All analyses were performed in duplicate. The relative standard deviation for butyl chloride measurement was 3%.

Dissolved organic carbon (DOC) of water samples was determined by UV–persulfate oxidation to CO_2 in a Dohrmann DC-80 carbon analyzer with a Horiba PIR-2000 IR detector. The analyzer was calibrated with potassium hydrogen phthalate. Aliquots of water samples used in irradiation experiments were frozen and analyzed later for nitrate with a Dionex DX-100 ion chromatograph. Quality control standards from the U.S. EPA used to evaluate bias gave an error of 6.0%. Color was measured spectrophotometrically on unfiltered, centrifuged samples using a Bausch and Lomb Spectronic 1001 at 420 nm against standardized platinum–cobalt reference solutions (Fischer Scientific).

Aquatic humic matter (AHM) was extracted from surface waters by the DEAE–cellulose method (17); 20 g of DEAE–cellulose was mixed with 150 mL of 0.01 M KCl to make a slurry and adjusted to pH 6 with HCl and NaOH. The slurry was poured into a glass column and allowed to settle, after which the KCl solution was drained from the column. The desired volume of filtered water sample, adjusted to pH 6, was passed through the column, and the effluent DOC was measured to determine efficiency of DOC retention by the column. AHM retained on the column was eluted with 0.1 M NaOH and collected when the eluate appeared colored. The DOC of the filtered water sample was measured before passage through the column. The maximum possible recovery of DOC in AHM extracts was determined from the initial DOC and the volume ratio of lake water (V_i) passed through the column and AHM extract (V_e). Actual recovery

was determined from the measured DOC of AHM extracts. Before use in experiments, AHM extracts were adjusted to pH 6–7 by hydrochloric acid.

Experimental Procedures. Samples were irradiated both in sunlight and in the laboratory. Experiments with artificial media used Milli-Q filtered water with added nitrate; 1.0 mg/L octanol was added as an $\cdot\text{OH}$ scavenging agent to maintain a steady-state concentration of $\cdot\text{OH}$. Controls containing only Milli-Q filtered water and probe were irradiated and otherwise treated the same as the rest of the bottles in each experiment. A medium-pressure quartz mercury vapor lamp was the UV source in the laboratory. The lamp was immersed in a borosilicate glass well (Ace Glass) through which tap water was passed to keep the lamp cool. The glass well filtered out wavelengths $< 280 \text{ nm}$. The bottles (3 cm diameter) were placed on a revolving turntable apparatus to ensure that each received the same light intensity. A fan kept the temperature of the bottles below 25°C during irradiation. In sunlight, the quartz bottles were set outside upside down on a rack. The bottles were rotated to maintain constant UV intensity. The time of day for sunlight experiments varied, but began after 9 a.m., ended before 5 p.m., and usually included noon sunlight.

The importance of carbonate and bicarbonate as scavengers of $\cdot\text{OH}$ was determined by varying concentrations of dissolved inorganic carbon (DIC; added as NaHCO_3) in Milli-Q water containing 1.43 mM nitrate (20 mg/L as N). DIC concentrations ranged from 0.2 to 48 mg/L (16–4000 mM in DIC), covering the range of most natural waters. Concentrations of HCO_3^- and CO_3^{2-} formed by dissolution of NaHCO_3 were calculated from the DIC and pH measured before irradiation. Rate constants for reaction of CO_3^{2-} and HCO_3^- with $\cdot\text{OH}$ were used to account for the relative effect of each ion on $[\cdot\text{OH}]_{\text{ss}}$.

The effect of concentration and source of dissolved organic matter (DOM) on $[\cdot\text{OH}]_{\text{ss}}$ was examined by irradiating five surface waters (described below) with nitrate added at 1.43 mM (20 mg/L as N). DOC levels of the waters ranged from 2.4 to 7.5 mg of C/L, and color ranged from 5 to 107 PCU. Two experiments were done under the UV lamp, and three were done under sunlight. Irradiation times were 3–4 h in the lab and 5–6 h in sunlight. For all samples except one, the effective nitrate concentration was 20 mg/L as N, i.e., ambient nitrate was negligible. A river water sample (see below) had a high ambient concentration reflecting agricultural runoff. Experiments with AHM extracts from the waters used Milli-Q water spiked with nitrate also at 1.43 mM (20 mg/L as N); AHM was added at concentrations of 2–24 mg/L as C.

Sampling Locations. Five surface waters with widely differing chemical characteristics were sampled to obtain different types of dissolved organic matter (DOM). Based on various lake and watershed characteristics, we inferred the likely origin of DOM in the waters. Some waters contained mostly allochthonous (terrestrial) DOM; others mostly contained autochthonous DOM produced by phytoplankton in the water body. Lake Nichols and Vandercook Lake are small seepage lakes (no surface inlets or outlets) in northern Wisconsin (Vilas County). Watersheds of these lakes are forested, scarcely populated, and have highly permeable soil. The lakes have low ionic strength and low levels of alkalinity, nutrients, and DOC (Table 1). Mann Creek, also in Vilas County, WI, is a highly stained (humic-rich), low alkalinity creek that drains a marsh. The Blue Earth River drains an agricultural watershed in southern Minnesota; its hard water is enriched with nutrients, including nitrate, and pesticides. The river was sampled at the Rapidan Dam, near Mankato. Lake Minnetonka, a large, productive hardwater lake surrounded by residential areas west of Minneapolis, MN, was sampled at Wayzata Bay. Samples were collected at the

TABLE 1. Chemical Characteristics of Water Bodies

water body	NO ₃ ⁻ (mg of N/L)	alkalinity (μequiv/L)	pH	color PCU	DOC (mg/L)	AHM ^a (% DOC)	PCU/(mg of C/L)	
							color/ DOC	color/ AHM
Blue Earth River	8.80	2300	8.4	22	4.19	42	5.3	7.4
Mann Creek	0.13	100	7.5	107	6.97	80	15.4	20.8
Lake Minnetonka	0.27	2650	8.4	13	7.45	41	1.8	2.5
Lake Nichols	0.13	27	5.9	33	6.23	57	3.7	8.0
Lake Vandercook	0.15	27	6.1	5	2.36	25	2.1	5.1

^a Percent of original DOC extracted as aquatic humic material.

surface in 20-L polyethylene bottles that had been washed, rinsed with deionized–distilled water, soaked in 10% HNO₃ overnight, and rinsed with Milli-Q water three times. Samples were stored at 4 °C and filtered within 24 h through 0.4-μm polycarbonate filters.

Results

Verification of Pseudo-First-Order Conditions. Rates of •OH reaction are first order with respect to [•OH] and the species with which it reacts. Under constant light intensity, [•OH] reaches a steady state, and loss of probe can be expressed as

$$-d[P]/dt = k_p[•OH]_{ss}[P] = k_{exp}[P] \quad (1)$$

or

$$\ln([P]/[P]_0) = -k_{exp}t \quad (2)$$

where k_p is the rate constant for probe reaction with •OH ($M^{-1}s^{-1}$); k_{exp} is a measured pseudo-first-order rate constant (s^{-1}); $[P]$ is probe concentration (M); t is time. To verify that pseudo-first-order conditions held for our measurements, Milli-Q water was irradiated with 1.07 mM (15 mg/L as N) nitrate and 1 mg/L 1-octanol, a scavenger added to maintain a steady-state [•OH]. A plot of $\ln([P]/[P]_0)$ vs time over the 3.5-h laboratory experiment yielded a straight line ($r^2 = 0.987$). In subsequent experiments with both lab light and sunlight, pseudo-first-order conditions were assumed to apply, and only one time period was used for irradiation to reduce the number of measurements. Experimental rate constants, k_{exp} , were calculated from eq 1, and [•OH]_{ss} was determined from the ratio k_{exp}/k_p .

Effect of [NO₃⁻] on [•OH]_{ss} and Rate Constant for •OH Production. To determine the relationship between nitrate concentration and [•OH]_{ss}, nitrate was added at concentrations from 0.143 to 1.43 mM (2–20 mg/L as N) to Milli-Q water containing 1 mg/L 1-octanol. A plot of [•OH]_{ss} vs [NO₃⁻] (Figure 1) yielded a straight line ($r^2 = 0.9986$). Other experiments with [NO₃⁻] up to 20 mg N/L in deionized and lake water also yielded linear relationships with both sunlight and the UV lamp (18). In contrast, Zepp et al. (12) found that [•OH]_{ss} reached a plateau at [NO₃⁻] > 5 mg/L at high light intensities, possibly a result of quenching of •OH by nitrite. To obtain sufficient decrease in probe concentration in irradiation times of a few hours, we added nitrate at 0.7–1.4 mM (10–20 mg/L as N) in all subsequent experiments and extrapolated results to ambient levels. It was assumed that, at [NO₃⁻] = 0 in distilled water, [•OH]_{ss} = 0 M.

To determine the rate of •OH production, $R_{p,OH}$, from nitrate for the intensity of our lamp, we used data from experiments in which only nitrate, 1-octanol, and butyl chloride were added to pure water. Under these conditions

$$d[•OH]/dt = R_{p,OH} - R_{s,OH} = k_{NO_3}[NO_3^-] - k_{oct}[octanol][•OH] \quad (3)$$

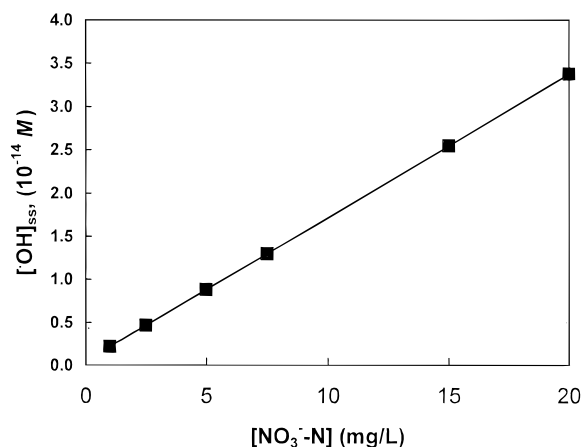


FIGURE 1. Relationship between [•OH]_{ss} and nitrate concentration for irradiation by UV lamp in laboratory.

where $R_{s,OH}$ is the scavenging rate of •OH; k_{NO_3} is the observed rate constant of •OH formation from nitrate (a function of light intensity); and k_{oct} is the rate constant for •OH reaction with octanol, $6 \times 10^9 M^{-1}s^{-1}$ (7). If [NO₃⁻] and light intensity are constant, a steady state is reached where the production rate equals the scavenging rate of •OH, and

$$k_{NO_3} = k_{oct}[octanol][•OH]_{ss}/[NO_3^-] \quad (4)$$

For known nitrate and octanol concentrations and [•OH]_{ss} computed from eq 1, k_{NO_3} can be determined. The mean value of k_{NO_3} for laboratory experiments conducted over 10 months was $6.6 \times 10^{-7} s^{-1}$ with a relative standard deviation of 38%. The relatively large uncertainty probably reflects variations in intensity of the UV source over this period.

Effect of Carbonate and Bicarbonate on [•OH]_{ss}. If the only scavengers of •OH present are carbonate species, then

$$[•OH]_{ss} = k_{NO_3}[NO_3^-]/\{k_{CO_3^{2-}}[CO_3^{2-}] + k_{HCO_3^-}[HCO_3^-]\} \quad (5)$$

and a plot of $1/[•OH]_{ss}$ vs $k_{CO_3^{2-}}[CO_3^{2-}] + k_{HCO_3^-}[HCO_3^-]$ at constant light and nitrate should yield a straight line. This plot (Figure 2) is linear at DIC ≥ 0.7 mg/L but for unknown reasons deviates from linearity, with higher than expected [•OH]_{ss} at very low DIC. The extrapolated y-intercept value yields the steady-state •OH concentration that should be obtained when carbonate forms are absent, and other experimental conditions (light intensity, nitrate concentration, and concentrations of other scavengers—in this case, butyl chloride) remain constant. Figure 2 indicates that scavenging by carbonate species at DIC concentrations typical of most natural waters can be quantified from measured values of any two of the following: pH, alkalinity, and DIC, from which concentrations of HCO₃⁻ and CO₃²⁻ can be calculated.

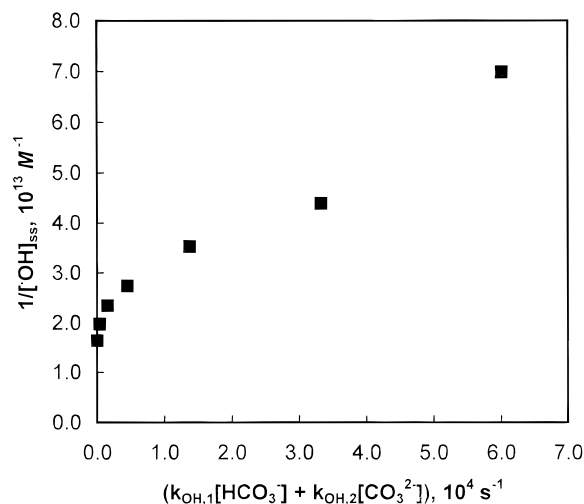


FIGURE 2. Relationship between $[\text{OH}]_{\text{ss}}^{-1}$ and concentrations of bicarbonate and carbonate multiplied by respective rate constants for reaction with $\cdot\text{OH}$.

TABLE 2. $\cdot\text{OH}$ Scavenging Rate Coefficients for DOM and AHM Extracts

water body	$[\text{OH}]_{\text{ss}}^a$ (M)	k_{DOM} (mg of C/L) $^{-1}$ s $^{-1}$	k_{AHM} (mg of C/L) $^{-1}$ s $^{-1}$
Blue Earth River	8.4×10^{-15}	2.8×10^4	2.9×10^4
Mann Creek	3.8×10^{-15}	3.3×10^4	1.4×10^4
Lake Minnetonka	6.1×10^{-15}	1.4×10^4	1.0×10^4
Lake Nichols	1.0×10^{-14}	1.8×10^4	1.5×10^4
Lake Vandercook	1.5×10^{-14}	2.6×10^4	1.9×10^4
average	8.8×10^{-15}	2.4×10^4	1.7×10^4
SD	4.4×10^{-15}	0.8×10^4	0.7×10^4

^a Results from laboratory incubations for the listed waters; values used to calculate k_{DOM} .

Effect of DOM on $[\text{OH}]_{\text{ss}}$. Dissolved organic carbon and color levels varied among the five water sources (Table 1). The ratio of color to DOC was greater in the extracts than in the raw water samples, indicating (as expected) that extraction recovered more humic material and less hydrophilic material. The percent DOC recovered by extraction ranged from 25% for autochthonous DOM from Lake Vandercook to 80% for allochthonous DOM from Mann Creek.

If all types of DOM scavenge $\cdot\text{OH}$ at equal rates, $[\text{OH}]_{\text{ss}}$ should be inversely proportional to the DOC concentration of a water sample. This was generally true, and the water with the lowest DOC produced the highest $[\text{OH}]_{\text{ss}}$ (Table 2). However, Mann Creek produced the lowest $[\text{OH}]_{\text{ss}}$ even though it had a slightly lower DOC than Lake Minnetonka, which yielded a 60% higher value of $[\text{OH}]_{\text{ss}}$. In addition, Lake Nichols produced a higher $[\text{OH}]_{\text{ss}}$ than the Blue Earth River, although the latter sample had significantly higher nitrate (because of high ambient levels) and lower DOC levels.

The discrepancy in $[\text{OH}]_{\text{ss}}$ between Mann Creek and Lake Minnetonka probably reflects differences in the nature and origin of DOM in the two waters. The latter contains DOM primarily of autochthonous origin and is not highly colored. The highly colored DOM of Mann Creek undoubtedly absorbed some UV light, lowering the amount available for absorption by nitrate. Light absorption by DOM also may produce $\cdot\text{OH}$ (19), but overall, DOM probably has a negative effect on $[\text{OH}]_{\text{ss}}$ because of radical scavenging and light attenuation. The discrepancy between the Blue Earth River and Lake Nichols probably reflects scavenging by carbonate species in the Blue Earth River. The river has a high alkalinity (~2300 mequiv/L), about 85 times that of the lake (27 mequiv/L).

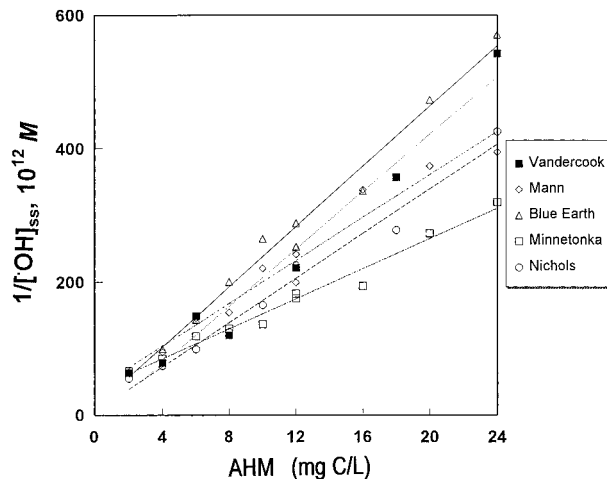


FIGURE 3. Relationship between $1/[\text{OH}]_{\text{ss}}$ and concentration of AHM (expressed in mg of C/L) extracted from the surface waters. (Irradiation conditions described in text.)

Rate constants for $\cdot\text{OH}$ scavenging by the five DOM sources were calculated by assuming that DOM, carbonate, and bicarbonate were the only scavengers in the water. At steady state, the $\cdot\text{OH}$ scavenging rate, $R_{s,\text{OH}}$, is

$$R_{s,\text{OH}} = \{k_{\text{DOM}}[\text{DOM}] + k_{\text{CO}_3^{2-}}[\text{CO}_3^{2-}] + k_{\text{HCO}_3^-}[\text{HCO}_3^-]\}[\text{OH}]_{\text{ss}} = k_{\text{NO}_3^-}[\text{NO}_3^-] \quad (6)$$

or

$$k_{\text{DOM}} = \{k_{\text{NO}_3^-}[\text{NO}_3^-]/[\text{OH}]_{\text{ss}} - k_{\text{CO}_3^{2-}}[\text{CO}_3^{2-}] - k_{\text{HCO}_3^-}[\text{HCO}_3^-]\}/\text{DOM} \quad (7)$$

Using published values of $k_{\text{CO}_3^{2-}}$ and $k_{\text{HCO}_3^-}$ (16) and the average value of $k_{\text{NO}_3^-}$ for our experimental conditions ($6.6 \times 10^{-7} \text{ s}^{-1}$), we calculated k_{DOM} from measured DOC, $[\text{NO}_3^-]$, alkalinity, pH, and $[\text{OH}]_{\text{ss}}$. Resulting values range from 1.4×10^4 to 3.3×10^4 (mg of C/L) $^{-1} \text{ s}^{-1}$ (Table 2).

The relationship between [AHM] and $[\text{OH}]_{\text{ss}}$ was similar for all sources; $[\text{OH}]_{\text{ss}}$ decreased in nonlinear fashion as [AHM] increased. The relationship between [AHM] and $[\text{OH}]_{\text{ss}}$ was analyzed the same way as the data for DIC. If AHM is the only scavenger and nitrate the only source of $\cdot\text{OH}$, then $[\text{OH}]_{\text{ss}}$ is given by

$$[\text{OH}]_{\text{ss}} = k_{\text{NO}_3^-}[\text{NO}_3^-]/k_{\text{AHM}}[\text{AHM}] = \text{constant}/[\text{AHM}] \quad (8)$$

where k_{AHM} is the average rate constant for reaction of AHM with $\cdot\text{OH}$. Plots of $1/[\text{OH}]_{\text{ss}}$ vs [AHM] (expressed as DOC) should yield straight lines with slopes proportional to k_{AHM} . Slopes of such plots (Figure 3) ranged from 1.1×10^{13} to 2.3×10^{13} (mean = 1.8×10^{13} and relative standard deviation = 23%). We expected that the slopes would be correlated with color of the AHM extract. Lake Minnetonka AHM had the lowest color and the smallest slope, but the extract from Mann Creek, which had more than twice the color of the other extracts, had the second smallest slope (1.6×10^{13}). Color thus is not an accurate predictor of $\cdot\text{OH}$ scavenging rates by AHM. Nonetheless, the results show that $[\text{OH}]_{\text{ss}}$ for a given source is inversely proportional to [AHM].

From eq 8, $k_{\text{AHM}} = \text{slope} \times k_{\text{NO}_3^-}[\text{NO}_3^-]$. Comparison of values for k_{AHM} and k_{DOM} (Table 2) indicates that DOM in the original water scavenged $\cdot\text{OH}$ somewhat more efficiently than the extracted AHM, at least on a mass concentration basis. However, because the number of samples is small, the means

are not statistically different ($p > 0.1$, paired t-test). A possible explanation for the differences between k_{DOM} and k_{AHM} is that the extracts were more colored than the original water samples, and the AHM may have contributed to $\cdot\text{OH}$ production upon absorption of UV light. This would have resulted in higher production rates than we calculated, leading to underestimates of k_{AHM} . It also is possible that the structural components in AHM simply are less reactive on average than the more diverse array of structures in raw DOM.

Values of k_{DOM} varied among the five waters by a factor of only 2.4; mean = 2.3×10^4 (mg of C/L) $^{-1}$ s $^{-1}$; standard deviation (SD) = 0.77×10^4 (mg of C/L) $^{-1}$ s $^{-1}$ (CV = 30%). AHM extracts yielded k_{AHM} values that varied by a factor of 2.9; mean k_{AHM} = 1.65×10^4 (mg of C/L) $^{-1}$ s $^{-1}$, SD = 0.72×10^4 (mg of C/L) $^{-1}$ s $^{-1}$ (CV = 37%). Although the DOM samples varied greatly in color and origin, efficiency in scavenging $\cdot\text{OH}$ was similar among all sources. Thus, it may be adequate to use the average k_{DOM} [2.3×10^4 (mg of C/L) $^{-1}$ s $^{-1}$] to estimate $\cdot\text{OH}$ scavenging by DOM in surface waters.

This conclusion is supported by values of k_{DOM} that have been reported by other workers. For example, DOM from Greifensee, Switzerland, yielded k_{DOM} = 2.5×10^4 (mg of C/L) $^{-1}$ s $^{-1}$ in experiments where $\cdot\text{OH}$ was generated by nitrate photolysis (12). Several workers have obtained k_{DOM} values for $\cdot\text{OH}$ generated by ozone photolysis. For example, Hoigné and Bader (13) and Haag and Hoigné (8) reported that k_{DOM} was 2.5 – 4.0×10^4 (mg of C/L) $^{-1}$ s $^{-1}$ for Swiss lake water. Haag and Yao (14) reported a value of $(3.8 \pm 2.1) \times 10^4$ (mg of C/L) $^{-1}$ s $^{-1}$ for 11 U.S. surface waters (seven from California) and 4.0×10^4 (mg of C/L) $^{-1}$ s $^{-1}$ for Aldrich humic acid. Westerhoff et al. (15) recently reported a value of $(2.9 \pm 0.4) \times 10^4$ (mg of C/L) $^{-1}$ s $^{-1}$ for isolates of dissolved organic matter from nine surface waters from around the United States, as well as values of 3.1 and 6.8×10^4 (mg of C/L) $^{-1}$ s $^{-1}$ for standard Suwanee River fulvic and humic acid, respectively. There is some uncertainty in comparing k_{DOM} values for reaction with $\cdot\text{OH}$ obtained from ozone decomposition measurements with values found using nitrate as the $\cdot\text{OH}$ source because the former method relies on an estimated value for η , the efficiency of $\cdot\text{OH}$ production from ozone, and various workers have used different values for η . Nonetheless, it is gratifying that the two approaches and a wide range of water samples yield such similar results.

Comparison of DOC and Carbonate Species as $\cdot\text{OH}$ Scavengers. In freshwater, the rate of scavenging of $\cdot\text{OH}$ ($R_{\text{S},\text{OH}}$) is expressed by eq 6. Relative contributions of each term to $R_{\text{S},\text{OH}}$ can be calculated for a water from measurements of DOC, alkalinity, and pH. A few examples are described below. The National Surface Water Survey (NSWS) sampled over 1000 lakes as part of the National Acid Precipitation Assessment Program (20). The purpose of the survey was to determine the chemical status of surface waters in acid-sensitive regions of the United States. Mean values of NSWS lake data for the above variables are as follows: DOC = 4.8 mg/L, alkalinity = 280 mequiv/L, and pH = 6.8, from which mean $[\text{HCO}_3^-]$ and $[\text{CO}_3^{2-}]$ are found to be 2.8×10^{-4} and 8.9×10^{-8} M, respectively. Using published values of $k_{\text{CO}_3^{2-}}$ and $k_{\text{HCO}_3^-}$ (16) and our mean value of k_{DOM} , we calculate pseudo-first-order losses of $\cdot\text{OH}$ for each scavenger as $k_{\text{CO}_3^{2-}}[\text{CO}_3^{2-}] = 40$ s $^{-1}$, $k_{\text{HCO}_3^-}[\text{HCO}_3^-] = 4 \times 10^3$ s $^{-1}$, and $k_{\text{DOM}}[\text{DOC}] = 1.1 \times 10^5$ s $^{-1}$. For these low alkalinity waters, DOM thus is the most important scavenger of $\cdot\text{OH}$; bicarbonate causes only ~3% of the scavenging, and carbonate is insignificant.

In contrast, for a high alkalinity water such as the Blue Earth River (DOC = 4.2 mg/L, alkalinity = 2300 mequiv/L, and pH = 8.4), we find $[\text{HCO}_3^-] = 2.2 \times 10^{-3}$ M, and $[\text{CO}_3^{2-}] = 2.8 \times 10^{-5}$ M. Using the measured value of k_{DOM} for the river (Table 2) and published values of $k_{\text{CO}_3^{2-}}$ and $k_{\text{HCO}_3^-}$, we find $k_{\text{CO}_3^{2-}}[\text{CO}_3^{2-}] = 1.2 \times 10^4$ s $^{-1}$; $k_{\text{HCO}_3^-}[\text{HCO}_3^-] = 3.4 \times 10^4$ s $^{-1}$; and $k_{\text{DOM}}[\text{DOC}] = 1.2 \times 10^5$ s $^{-1}$. In this case, bicarbonate

TABLE 3. Calibration of Laboratory Light Conditions to Sunlight

date	water body ^a					
	1	2	3	4	5	6
Section A: $[\cdot\text{OH}]_{\text{ss}}$, Laboratory Incubations, 10^{-15} M						
6/04	11		3.9	6.5	9.9	
6/20	18	8.4	3.8	5.7	11	15
av	14	8.4	3.8	6.1	10	15
Section B: $[\cdot\text{OH}]_{\text{ss}}$, Sunlight Incubations, 10^{-15} M						
6/10	6.4	3.0	1.3	3.3	2.8	6.4
6/13	8.0	4.5				6.0
6/25	7.3	3.9			6.0	
Section C: $R_i = [\cdot\text{OH}]_{\text{ss,uvlamp}}/[\cdot\text{OH}]_{\text{ss,sun}}^b$						
6/10	2.2	2.8	2.9	1.9	3.6	2.4
6/13	1.8	1.9				2.6
6/25	2.0	2.2			1.7	
Section D						
	$R_{i,\text{ave}}$	I_{sun}^c		I_{uvlamp}^c		
6/10	2.64	1.23		3.24		
6/13	2.08	1.37		2.86		
6/25	1.95	1.39		2.71		
av	2.22 ± 0.36	1.330 ± 0.088		2.94 ± 0.27		

^a Water body 1, deionized water with 1 mg/L octanol; 2, Blue Earth River; 3, Mann Creek; 4, Lake Minnetonka; 5, Lake Nichols; 6, Lake Vandercook; 1.43 mM nitrate added to all samples. ^b R_i calculated from average $[\cdot\text{OH}]_{\text{ss}}$ for laboratory incubations in Section A. ^c I_{sun} = broadband sunlight intensity (cal cm $^{-2}$ min $^{-1}$) from Climatology Observatory, University of Minnesota, St. Paul (Ruschy, D., personal communication). I_{uvlamp} calculated from $R_{i,\text{ave}} I_{\text{sun}}$.

and carbonate together account for 28% of the $\cdot\text{OH}$ scavenging. Similar calculations for the other waters in our study indicate that carbonate forms accounted for ~34% of $\cdot\text{OH}$ scavenging in Lake Minnetonka but were insignificant in the other waters.

Normalization to Sunlight Conditions. Three experiments were done to normalize laboratory results to sunlight conditions. If other factors are constant, rates of $\cdot\text{OH}$ production and $[\cdot\text{OH}]_{\text{ss}}$ are proportional to light intensity. The intensity ratio of the two light sources for each experiment thus is $R_i = I_{\text{uvlamp}}/I_{\text{sun}} = [\cdot\text{OH}]_{\text{ss,uvlamp}}/[\cdot\text{OH}]_{\text{ss,sun}}$ (Table 3). Values of $[\cdot\text{OH}]_{\text{ss}}$ for sunlight are average values, because solar intensity was not constant over the 5–6-h irradiation periods. The measured solar intensity, I_{sun} for the date and time of each experiment was obtained from the climatological observatory at the University of Minnesota in St. Paul. Calculated values of R_i indicate that the UV lamp was about twice as intense as June mid-day sunlight in Minnesota. Multiplying the ratio $[\cdot\text{OH}]_{\text{ss,uvlamp}}/[\cdot\text{OH}]_{\text{ss,sunlight}}$ by I_{sun} yields I_{uvlamp} . For three measurement dates in June 1996, I_{uvlamp} calculated this way had a mean of 2.94 cal cm $^{-2}$ min $^{-1}$ and a relative standard deviation of 9% (Table 3).

Laboratory data for $[\cdot\text{OH}]_{\text{ss}}$ thus could be normalized to any desired sunlight condition (in cal cm $^{-2}$ min $^{-1}$) by the relationship: $[\cdot\text{OH}]_{\text{ss,sun}} = [\cdot\text{OH}]_{\text{ss,uvlamp}} I_{\text{sun}}/2.94$. This was used to correct lab-measured values of $k_{\text{NO}_3^-}$ (mean = 6.6×10^{-7} s $^{-1}$) to sunlight conditions. The average solar intensity for June in St. Paul, MN (45°0' N latitude), is 530 cal cm $^{-2}$ day $^{-1}$ or 0.37 cal cm $^{-2}$ min $^{-1}$ averaged over 24 h. For this intensity, the whole-day rate constant for $\cdot\text{OH}$ production by nitrate photolysis at the surface of a water body ($k_{\text{NO}_3^-, \text{sun}}$) is 6.6×10^{-7} s $^{-1} \times 0.37/2.94 = 8.3 \times 10^{-8}$ s $^{-1}$ or 7.2×10^{-3} day $^{-1}$. This result is virtually the same as the value of 7.3×10^3 day $^{-1}$ for midsummer conditions at this latitude reported by Zepp et al. (12) based on the computer model GCSolar.

Environmental Significance. Values of $[\cdot\text{OH}]_{\text{ss}}$ were estimated for several natural waters, including those studied above, for June mid-day (10 a.m. to 2 p.m.) sunlight (Table

TABLE 4. Calculated Values of $[\cdot\text{OH}]_{\text{ss}}$ and $t_{1/2}$ for Acetochlor in Some Natural Waters

water body ^a	surface				whole water column			
	June mid-day		annual average		June mid-day		annual average	
	$[\cdot\text{OH}]_{\text{ss}}$ (M)	$t_{1/2}$ (days)	$[\cdot\text{OH}]_{\text{ss}}$ (M)	$t_{1/2}$ (days)	$[\cdot\text{OH}]_{\text{ss}}$ (M)	$t_{1/2}$ (days)	$[\cdot\text{OH}]_{\text{ss}}$ (M)	$t_{1/2}$ (days)
Blue Earth River	9.9E-16	1.1	1.7E-16	6.3	5.5E-17	19	9.3E-18	110
Lake Minnetonka	3.1E-17	34.1	5.4E-18	200	9.0E-19	1200	1.5E-19	7000
Lake Nichols	2.5E-17	42.1	4.3E-18	250	2.0E-18	530	3.5E-19	3100
Lake Superior	2.1E-16	5.0	3.5E-17	30	1.0E-18	1000	1.7E-19	6100
San Joaquin River, CA	1.9E-16	5.5	3.7E-17	29	1.1E-17	100	2.1E-18	520
Camp 13, Slough, CA	1.0E-15	1.0	2.0E-16	5.3	2.9E-17	37	5.5E-18	190

^a Nitrate, DOC, alkalinity, and pH values used to estimate $[\cdot\text{OH}]_{\text{ss}}$ from Table 1 for first three waters; values for last three waters reported in ref 17; data for California waters from C. R. Kratzer, USGS, Sacramento, CA, personal communication; $k_{\text{NO}_3^-}$ adjusted to account for differences in latitude among the waters.

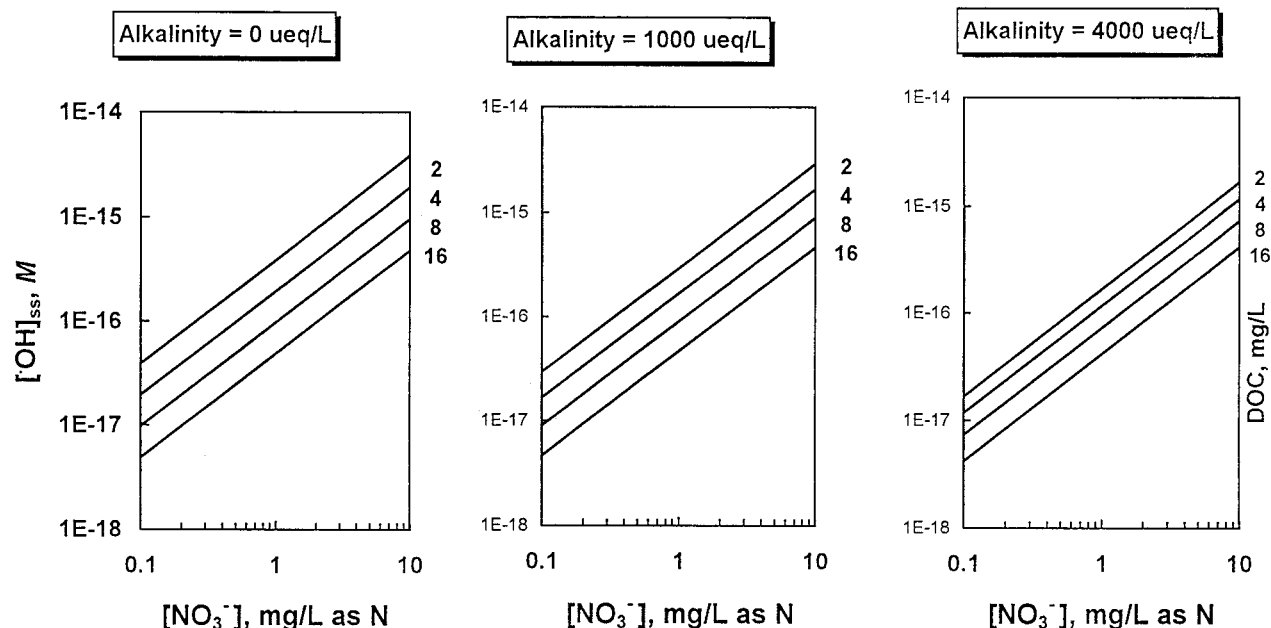


FIGURE 4. Graphical model to predict $[\cdot\text{OH}]_{\text{ss}}$ at 45° N latitude for June mid-day conditions at the water surface. Values of NO_3^- , DOC, and alkalinity represent ranges for most surface waters.

4). The calculations do not account for light attenuation by the water and thus represent surface concentrations. Analytically determined data were used when available. Among the waters, $[\cdot\text{OH}]_{\text{ss}}$ ranged from 3×10^{-17} M for waters low in nitrate with medium DOC, such as lakes Minnetonka and Nichols, to 10^{-15} M for waters high in nitrate such as the Blue Earth River. The San Joaquin River, though it contains four times the nitrate concentration of Lake Superior, yields nearly the same surface $[\cdot\text{OH}]$, reflecting the low DOC and low alkalinity of the lake. However, the depth of a water body also must be considered. The great mean depth of Lake Superior causes average whole-lake $\cdot\text{OH}$ concentration to be about 200 times less than its surface concentration (18). Annual average surface concentrations of $\cdot\text{OH}$ were estimated for the same waters using annual average values of $k_{\text{NO}_3^-}$ calculated from Zepp et al. (12). For northern water bodies, a production rate of zero was assumed during winter due to ice cover. Calculated values are in the range 2×10^{-16} to 4×10^{-18} M (Table 4) or roughly one-sixth of the June mid-day values.

To examine the significance of the calculated $\cdot\text{OH}$ levels in degrading organic pollutants, the half-life of the herbicide acetochlor due to reaction with $\cdot\text{OH}$ was calculated for the same water bodies from $t_{1/2} = \ln(0.5)/k_{\text{a,OH}} \times [\cdot\text{OH}]_{\text{ss}}$, where $k_{\text{a,OH}} = 7.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ is the second-order rate constant for reaction of acetochlor with $\cdot\text{OH}$ (21). The half-life of acetochlor during June mid-day sun at the water surface

(Table 4) ranges from ~ 1 to 42 days (i.e., ~ 24 –1000 h) of June mid-day sun. The near-surface half-life of acetochlor over the whole year, based on the annual average $[\cdot\text{OH}]$, ranges from about 5 to 250 days.

Depth-averaged $\cdot\text{OH}$ production rates by nitrate photolysis can be estimated (12) by

$$v(Z) = v(0)(1 - e^{-K_R Z})/ZK_R \quad (9)$$

where $v(0)$ is the surface $\cdot\text{OH}$ production rate, $k(0)_{\text{NO}_3^-}[\text{NO}_3^-]$; Z is the mean depth of the water body, assuming it is completely mixed; and K_R is the diffuse light attenuation coefficient measured by a Robertson meter (22). For most surface waters, K_R ranges from about 1 to 10 m^{-1} , and $v(Z)$ is effectively $v(0)/ZK_R$. A reasonable correlation was found between $1/K_R$ and Z_{SD} , the Secchi disk transparency of a water (18):

$$1/K_R = 0.11Z_{\text{SD}}, \quad r^2 = 0.78 \quad (10)$$

Average $[\cdot\text{OH}]_{\text{ss}}$ and $t_{1/2}$ values for acetochlor were calculated for June mid-day sunlight conditions and annual average conditions for the entire water column of the same waters on which surface calculations were done (Table 4). Mean depth was used for Z , when available, and the water was assumed to be completely mixed. Due to lack of data,

a few mean depths and transparencies were estimated. For relatively shallow water bodies such as the Blue Earth River, Lake Nichols, and the San Joaquin River, average $[\cdot\text{OH}]$ in the water column is 1/20–1/30 of the surface concentration. Light attenuation in natural water bodies thus reduces the overall significance of $\cdot\text{OH}$ oxidation. For example, the annual average $t_{1/2}$ for acetochlor in the Blue Earth River due to reaction with $\cdot\text{OH}$ is only ~ 6 days at the surface but 114 days for the entire water column. Nonetheless, half-lives of acetochlor still are ~ 100 days for mean annual light conditions and < 20 days for June mid-day sunlight in some waters.

Model of Surface $[\cdot\text{OH}]_{\text{ss}}$ at 45°N Latitude. The relationships described above were used to construct a simple graphical model to estimate $[\cdot\text{OH}]_{\text{ss}}$ over the range of nitrate, DOC, and alkalinity values found in surface waters. Plots of surface $[\cdot\text{OH}]_{\text{ss}}$ at 45°N latitude are shown in Figure 4 as a function of nitrate over the range of 0.1–10 mg/L as N for levels of DOC ranging from 2 to 16 mg/L and three levels of alkalinity (range 0–4000 mequiv/L). To produce these plots, we used $k_{\text{NO}_3^-, \text{sun}} = 2.5 \times 10^{-7} \text{ s}^{-1}$, which applies to June mid-day sunlight at this latitude (12). The possibility that $\cdot\text{OH}$ may be produced directly by photolysis of DOM itself was not considered in developing Figure 4, and thus actual values of $[\cdot\text{OH}]_{\text{ss}}$ may be higher. It is apparent that DOM has a greater scavenging effect on $[\cdot\text{OH}]_{\text{ss}}$ than alkalinity. At alkalinity values typical of hard waters (> 1000 mequiv/L) and relatively low DOM (< 4 mg of C/L), the effect of DIC is noticeable. To estimate the annual average surface $[\cdot\text{OH}]_{\text{ss}}$ at 45°N latitude, the value of $[\cdot\text{OH}]_{\text{ss}}$ in Figure 4 should be reduced by a factor of about 6 (12); see calculations in Table 4. To estimate the annual average $[\cdot\text{OH}]_{\text{ss}}$ at 45°N latitude for the entire water body, the latter value should be reduced again by a factor of $0.11Z_{\text{SD}}/Z_{\text{mean}}$ (eq 10).

According to Figure 4, maximum surface $[\cdot\text{OH}]_{\text{ss}}$ at 45°N ranges from less than 10^{-17} to $\sim 4 \times 10^{-15} \text{ M}$ for levels of nitrate, DOC, and alkalinity present in most surface waters. Averaged over the whole year, surface $[\cdot\text{OH}]$ ranges from $\sim 7 \times 10^{-16}$ to $1 \times 10^{-19} \text{ M}$. This range of $[\cdot\text{OH}]_{\text{ss}}$ results in a very wide range of potential half-lives for compounds that react with $\cdot\text{OH}$. For example, $t_{1/2}$ for this range of $[\cdot\text{OH}]_{\text{ss}}$ ranges from $\sim 4.6 \text{ h}$ to 29 years for the herbicide acetochlor. Thus, it is apparent that the parameters examined in this paper (DOC and alkalinity) must be known to estimate the rate at which a pollutant in surface water reacts by $\cdot\text{OH}$ -mediated processes.

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