

PhotoFate: A New Approach in Accounting for the Contribution of Indirect Photolysis of Pesticides and Pharmaceuticals in Surface Waters

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A new approach was developed to account for the contribution of indirect photolysis of pesticides and pharmaceuticals in which laboratory test conditions are similar to those prevalent in the aqueous environment. Rates of photolysis as a function of water composition were investigated for several aquatic contaminants. Using the laboratory-based test system, PhotoFate, the dependence of phototransformation rates on concentrations of natural water constituents that are radical producers and scavengers (nitrate, colored dissolved organic matter, bicarbonate) was studied. Mean half-lives of the model compounds in the presence of water constituents were compared to their direct photolysis half-lives to assess the contribution of photosensitized reactions to their fate in surface waters. Reactions mediated by $\cdot\text{OH}$ were predominant in waters with high nitrate concentrations. Colored dissolved organic matter (cDOM) acted mainly as a radiation filter and had a more important role in scavenging radicals than in their production. However, in low nitrate waters, the contribution of cDOM-derived reactive intermediates to the degradation of parent compounds became more apparent.

Introduction

There have been increasing public and scientific concern about the appearance of trace amounts of pesticides and, more recently, pharmaceuticals that occur in surface water and groundwater (1–3). The aquatic fates of these contaminants are often unknown, but direct and indirect sunlight-induced photochemical reactions may contribute to the transformation of these compounds in natural waters. Since these photoinduced transformations can occur simultaneously in natural waters, it is necessary to consider both processes when investigating the photochemical behavior and the environmental half-life of organic contaminants.

Indirect photolytic reactions are thought to proceed due to the presence of chemical transients such as hydroxyl, alkyl peroxy, and carbonate radicals, singlet oxygen, aqueous electrons, and colored dissolved organic matter (cDOM) in its excited triplet state. Previous research has suggested that the sunlight-induced hydroxyl radical ($\cdot\text{OH}$), produced predominantly through the photolysis of nitrate and cDOM, may play a significant role in the phototransformation of

TABLE 1. Concentrations and Rate Constants of Reactive Transients in Natural Surface Waters

species	concentration (M)	rate constant ($\text{M}^{-1}\text{s}^{-1}$)
$\cdot\text{OH}$	10^{-14} – 10^{-18} ^{a,b}	10^7 – 10^{10} ^c
$\cdot\text{OOR}$	10^{-9} ^d	10^3 ^e
$\cdot\text{CO}_3^-$	10^{-13} – 10^{-15} ^f	10^6 – 10^7 ^g
$^1\text{O}_2$	10^{-14} ^h	10^7 ⁱ
$\text{e}^-_{(\text{aq})}$	10^{-17} ^j	10^{10} ^k

^a Reference 9. ^b Reference 10. ^c Reference 11. ^d Reference 12. ^e Reference 13. ^f Reference 14. ^g Reference 15. ^h Reference 16. ⁱ Reference 17. ^j Reference 18. ^k Reference 19.

organic compounds in natural waters because it is known to be the most reactive with electron-rich aromatic organic compounds due to its electrophilicity and nonselectiveness (4–6). Carbonate radicals ($\cdot\text{CO}_3^-$), generated from the reaction of $\cdot\text{OH}$ with either carbonate or bicarbonate ions, react rapidly with sulfur-containing compounds and electron-rich compounds such as anilines and phenols and have been shown to play a significant role in limiting the persistence of sulfur-containing pesticides such as fenthion, thioanisole, and dibenzothiophene (7, 8). Because they are more selective than $\cdot\text{OH}$, the steady-state concentrations of $\cdot\text{CO}_3^-$ are higher than those for $\cdot\text{OH}$ (see Table 1) (9–19). Alkyl peroxy radicals ($\cdot\text{OOR}$) may be produced through the reaction of ground-state oxygen with excited cDOM chromophores, and singlet oxygen ($^1\text{O}_2$) may be formed upon the absorption of sunlight by cDOM and subsequent energy transfer to ground-state oxygen ($^3\text{O}_2$) (20, 21). Short-lived triplet states of cDOM ($^3\text{cDOM}^*$) may contribute significantly to the loss of phenols through electron abstraction, hydrogen transfer, or both (22). The aqueous electron ($\text{e}^-_{(\text{aq})}$) is a highly reactive and strongly reducing species and has previously been reported to be produced upon the photolysis of cDOM in sunlit natural waters and scavenged by nitrate (18, 23–25).

Although the nonselective and reactive $\cdot\text{OH}$ is thought to play a significant role in limiting the persistence of many chemical pollutants, the other more selective reactive intermediates may contribute to the degradation of chemicals that are not efficiently removed by the $\cdot\text{OH}$ pathway. The ability of each reactive transient to contribute toward the systematic self-cleansing of sunlit natural waters by reacting and subsequently degrading a compound depends on the steady-state concentration of the reactants, which arise as a result of a balance between their rates of production and rates of consumption. This in turn is likely to be affected by the composition of natural water, particularly in the concentrations of nitrate, cDOM, and bicarbonate/carbonate. In a survey of lakes, rivers, and ponds, humic substances in natural waters were found to be present at concentrations ranging from 0.3 to 30 mg of C/L (26). Nitrate and bicarbonate, also considered principal components of surface water, are present with concentrations ranging from 3 to 323 μM and 0.4 to 4.4 mM, respectively, as determined from a survey of several water bodies in the Great Lakes region (14).

Since the steady-state concentrations of the reactants are predominantly a reflection of the concentrations of nitrate, cDOM, and bicarbonate levels, the resultant rate of indirect photolysis and fate of an organic pollutant could vary as a function of the composition of water. However, little research has been conducted in studying the simultaneous interaction between organic contaminants with a range of excited-state species produced by photochemical reactions involving

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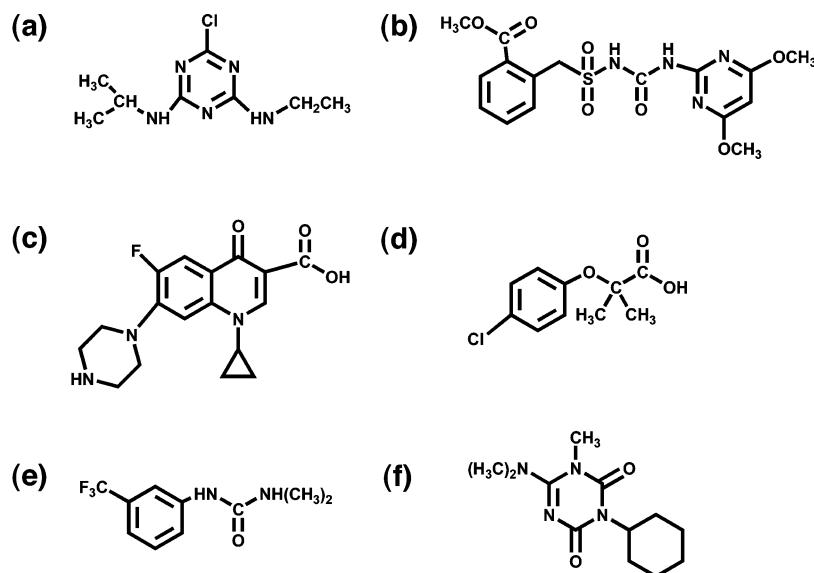


FIGURE 1. Structures of model compounds: (a) atrazine; (b) bensulfuron methyl; (c) ciprofloxacin; (d) clofibric acid; (e) fluometuron; (f) hexazinone.

nitrate, cDOM, and bicarbonate and the effect of a change in concentration of those species on the environmental fate of a pollutant (10, 27).

In this study, a well-defined laboratory-based test system developed by our group, PhotoFate, is used to investigate the aquatic fate of several chemical pollutants in test solutions containing natural radical-producing and -scavenging agents. PhotoFate is a systematic multivariate approach that can be used to assess important contributory loss processes in the overall fate of a chemical in sunlit surface waters. Ratios of the constituents in synthetic mixtures are varied in a combinatorial approach and environmentally relevant and realistic mixtures are chosen and used to investigate the synergistic or inhibitory effects that multiple water constituents can have on influencing the photochemical fate of organic contaminants. The number of possible permutations is dependent on the number of constituents and the concentration levels used. In this study, nitrate, cDOM and bicarbonate are the chosen synthetic field water (SFW) constituents and the concentration levels used are listed in the Experimental Section. Due to space limitations in the photosimulator used in this study, 16 of the possible combinations that are still environmentally realistic and representative of the variability and complexity of natural waters were selected to demonstrate the variation in photo-degradation kinetics when the ratios of these constituents are changed. To illustrate the utility of PhotoFate the pesticides atrazine (ATR), bensulfuron methyl (BSM), fluometuron (FLU), and hexazinone (HEX), the pharmaceutical ciprofloxacin (CPX), and the pharmaceutical metabolite clofibric acid (CLO) were chosen as model compounds since their presence has reportedly been detected in lakes and rivers and because they represent a range of chemical structures (see Figure 1) (3, 28–32). Although direct photolysis and microbial degradation of several of the chosen test probes have been studied, the contribution of indirect photolysis to their environmental fate is largely unknown.

The laboratory conditions used in this approach are more similar to those prevalent in the aqueous environment than the EPA guideline for indirect photolysis testing in which test solutions contain only a single reactive transient precursor (50 mg of C/L of cDOM) (33). The primary advantages of using the PhotoFate approach are as follows: (1) presence of multiple reactive transient precursors and scavengers; (2) production of multiple reactive intermediates; (3) capability

of studying competition kinetics of reactive intermediates; (4) ability to assess the influence of cDOM shading.

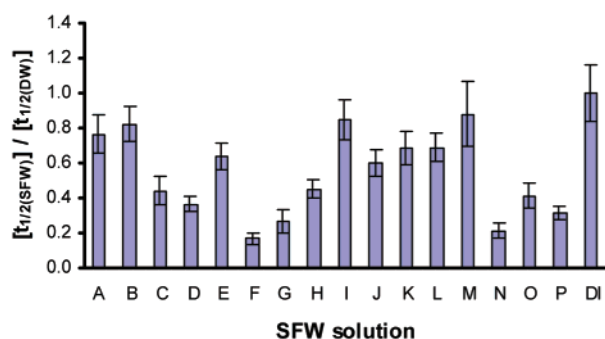
The objective of this study was to use PhotoFate to demonstrate that the extent of the photoinduced degradation of target contaminants can vary significantly depending on the water constituents present in solution. It is our hypothesis that the observed rates of degradation are dependent on the composition of water. Future characterization of PhotoFate will include the measurement of aqueous oxidants produced in each of the SFW solutions, a study of reaction pathway differences, and a comparative study of the toxicological effects of direct and indirect photochemical degradation products.

Experimental Section

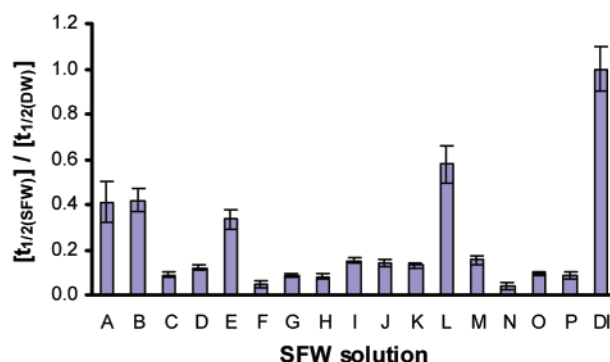
Chemicals. All chemicals were analytical reagent grade and were used as received. ATR (98.8%) was obtained from Supelco (Bellefonte, PA); CPX (99%) was purchased from Interchem (Paramus, NJ); CLO (97%), acetic acid, sodium bicarbonate, potassium nitrate, *p*-nitroanisole, and humic acid were purchased from Aldrich (Oakville, ON). FLU and BSM (98 and 99%, respectively) were obtained from Chem Service (West Chester, PA), and HEX (98%) was obtained from DuPont (Wilmington, DE). Phosphoric acid was obtained from BDH (Toronto, ON, Canada), and pyridine was purchased from ACP (Montreal, PQ, Canada). HPLC grade acetonitrile (>99%) was purchased from Fisher (Toronto, ON, Canada) or Caledon (Georgetown, ON, Canada). For all the model compounds, analytical standard solutions were made in acetonitrile and stored in the dark at a temperature of 3 °C. Stock experimental solutions of each test compound were prepared by dissolving the compound directly in Barnstead E-pure water with a resistance of 18 MΩ·cm⁻¹; no organic solvent was used.

Analytical Methods. UV–visible absorption spectra were recorded using a Hewlett-Packard 8452A diode array spectrophotometer (see Figure 1 in Supporting Information). The HPLC analyses were performed using a Waters 600S chromatograph fitted with a reversed-phase column (Alltima C-18 5 μm 250 × 4.6 mm; Alltech) at room temperature. A 20-μL injection of each sample was done in duplicate using a Waters 717 autosampler. Detection was performed with a Waters 996 photodiode array detector. A flow rate of 1 mL/min was used for all analyses. Mobile-phase composition and wave-

(a) Bensulfuron methyl



(b) Hexazinone



pH	8.1	10	8.2	7.9	10	7.9	10	10	10	7.9	8	10	9.7	7.9	7.9	9.9	5.5
HCO ₃ ⁻ (mM)	0.8	5	0.8	0.8	5	0.8	5	5	5	0.8	0.8	5	5	0.8	0.8	5	0
cDOM (mg C/L)	0.7	7	67	7	7	0.7	0.7	67	67	0.7	67	0.7	67	7	67	7	0
NO ₃ ⁻ (μM)	8	8	8	81	81	806	806	806	8	81	81	81	81	806	806	806	0
SFW	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	DI

FIGURE 2. Half-lives in SFW normalized to direct photolysis of model compounds: (a) bensulfuron methyl; (b) hexazinone in SFW solutions A–P. Error bars represent standard deviation of $N = 6$ or 9 measurements.

lengths used for quantification are outlined in Table 1 in Supporting Information. cDOM concentrations were determined using a Tekmar Dohrmann Phoenix 8000 TOC Analyzer.

Synthetic Field Water Solutions. A concentrated cDOM stock solution was prepared according to the EPA method [OPPTS 835.5270] (33). The concentrations used were 8, 81, and 806 μ M for nitrate, 0.8 or 5 mM for bicarbonate, and 0.7, 7, and 67 mg of C/L for cDOM (see Figure 2 for concentrations in each SFW solution). Direct photolysis solutions for each compound were also prepared consisting of only the model compound in deionized water. The final concentration of the solutions was 5 and 10 μ M for the pesticides and pharmaceuticals, respectively. These concentrations did not approach the solubility limits of the compounds.

Photoreaction Setup. Photochemical experiments were conducted in a Suntest CPS photosimulator equipped with a Xe lamp as the UV radiation source and special glass filters restricting the transmission of wavelengths below 290 nm. However, even with the presence of these filters there was a slight bleed of wavelengths below 290 nm, thus introducing systematic error. This becomes important for compounds, such as ATR and BSM in this study, that absorb weakly above 280 nm as direct photolysis rates subsequently become overemphasized. The lamp was set to maximum intensity (765 W/m²). Cold water flowed through the bottom of the photosimulator to maintain the internal temperature at ~ 27 °C. The SFW solutions were contained in randomly arranged quartz cylindrical tubes (20 mm \times 40 mm; ~ 12.6 mL), which were covered by a quartz plate (20 cm \times 17.5 cm) to minimize evaporation during irradiation. *p*-Nitroanisole (PNA) and pyridine were the chemical actinometers used in this study.

Irradiation of SFW Solutions in the Photosimulator. Each solution was equally divided between 3 cylindrical tubes for a total of 24 indirect photolysis, 3 direct photolysis, and 3 actinometry solutions, arranged randomly in the photoreactor (see Figure 2 in Supporting Information for setup). In each run, the 24 indirect photolysis tubes consisted of either 8 solutions in group 1 (A–H) or group 2 (I–P) in triplicate. Five time points were sampled over the irradiation

period for each compound. Each experiment was carried out until degradation to at least one half-life was achieved. Each run was repeated at least once for a total of $N = 6$ or 9. The samples were quantitatively analyzed by HPLC immediately for the amount of compound of interest remaining in the solution after irradiation based on external calibration. Pseudo-first-order rate constants, k_{obs} , for the model compounds were obtained by linear regression of logarithmic concentration values determined as a function of time.

Dark control experiments of the test probes in each SFW solution were conducted concurrently with irradiation experiments. Sample aliquots of dark controls were taken at the same time points as those for irradiation experiments. Additional control experiments included the direct photolysis of the test compounds in buffer solutions at pH 5.5, 7, and 10 to investigate pH dependence of direct photolysis.

Results and Discussion

Evaluation of PhotoFate as a Test System for Direct and Indirect Photolysis. *Actinometry.* The loss of PNA followed pseudo-first-order kinetics as indicated by correlation values (R^2) of 0.99 or better. Prior to starting SFW irradiation experiments, actinometry was conducted in 24 quartz reaction vessels to assess the uniformity of light distribution across the floor of the sunlight simulator and to ensure measured rate constants were independent of the placement of reaction vessels in the photoreactor. Relative error was typically low (1%) for the $N = 24$ measurements made, indicating that the intensity of light emitted from the Xe lamp was consistent for the duration of the experiment. Over the course of this study, actinometry experiments were conducted simultaneously with the irradiation of SFW solutions in the photoreactor. The half-life of PNA was determined for each irradiation experiment, and half-lives from consecutive experiments were compared to determine whether any variation in light intensity occurred over the course of the entire study. The mean half-life of PNA was calculated (191 min), and the low relative standard deviation of 6% for $N = 26$ experiments indicated the Xe lamp intensity

TABLE 2. Half-Lives of the Model Compounds in SFW Solutions A–P and in Deionized Water

SFW	mean $t_{1/2}$					
	atrazine (h)	bensulfuron methyl (h)	ciprofloxacin (min)	clofibric acid (h)	fluometuron (h)	hexazinone (h)
A	180 ± 11	72 ± 5	5.3 ± 0.1	17.9 ± 0.2	63 ± 6	382 ± 73
B	241 ± 14	77 ± 1	4.2 ± 0.8	18.0 ± 0.4	107 ± 27	386 ± 30
C	106 ± 4	41 ± 6	19 ± 2	9.5 ± 0.1	50 ± 18	82 ± 9
D	97 ± 3	34 ± 3	6.5 ± 0.5	16.4 ± 0.7	42 ± 2	110 ± 29
E	186 ± 25	60 ± 1	3.0 ± 0.9	18.1 ± 0.3	68 ± 10	309 ± 29
F	37 ± 1	16 ± 3	2.6 ± 0.8	14.0 ± 0.6	9 ± 3	41 ± 14
G	40.6 ± 0.4	25 ± 5	8.2 ± 0.6	17 ± 1	15 ± 3	81 ± 3
H	97 ± 5	42 ± 2	18.9 ± 0.5	11.4 ± 0.7	35 ± 20	76 ± 10
I	168 ± 29	79 ± 4	23 ± 2	14.7 ± 0.5	28.7 ± 0.1	141 ± 4
J	125 ± 19	56 ± 3	7.5 ± 0.2	15.7 ± 0.2	44 ± 3	133 ± 7
K	113 ± 3	64 ± 5	18.3 ± 0.1	12.4 ± 0.8	29 ± 7	122 ± 6
L	118 ± 8	64 ± 4	11 ± 1	19 ± 1	44 ± 9	537 ± 58
M	175 ± 24	82 ± 14	25.5 ± 0.2	15.3 ± 0.5	42 ± 3	144 ± 13
N	21 ± 2	20 ± 3	11.7 ± 0.1	11.4 ± 0.4	26 ± 9	37 ± 15
O	59 ± 1	39 ± 5	17 ± 2	10.6 ± 0.3	26 ± 2	88 ± 4
P	37 ± 3	29 ± 1	13 ± 2	15.7 ± 0.6	23 ± 2	81 ± 12
DI	208 ± 33	94 ± 11	13 ± 3	19.3 ± 0.5	67 ± 11	928 ± 88

remained relatively constant over the duration of the study.

Accuracy and Precision. PhotoFate offered the capability to determine precision in the photolysis experiments by conducting replicate measurements. For actinometry experiments, degradation rate constants of PNA were reproducible with a relative error of less than 1% for the $N = 3$ measurements made in one experiment. Average half-lives of the model compounds in deionized water and SFW solutions are listed in Table 2. The relative error for direct and indirect photolysis of all test probes was less than 15% and typically was between 3 and 6%.

Accuracy of the rates of degradation of each compound with and without the presence of nitrate, bicarbonate, and cDOM was more difficult to judge since there is little known literature available for comparison. However, the degradation of ATR in water has been extensively researched, and our experimentally obtained direct photolysis rate of $0.0034 \pm 0.0005 \text{ h}^{-1}$ is in good agreement with the rate of $0.0040 \pm 0.0006 \text{ h}^{-1}$ obtained by Torrents et al. using a Suntest CPS photoreactor as well (34). The accuracy of the rates of degradation obtained for the test probes in the SFW solutions could be assessed if results from the comparison of photolysis experiments in field water samples and SFW solutions with similar amounts of nitrate, cDOM and bicarbonate were available.

Photolysis of Model Compounds. Experimental data indicated that photolysis in deionized water generally proceeded slower than photolysis in the SFW solutions. Since all of the test compounds absorb little or no radiation in the actinic portion of the solar spectrum, direct photodegradation reactions were expected to proceed relatively slow. No loss of the model compounds was observed in the dark control experiments indicating degradation was photoinduced, and any loss of parent compound that occurred was not by microbiological, thermal, or hydrolytic means. Dark controls for the pH control experiments also indicated that the test compounds were stable in the dark between pH 5.5 and 10. Although hydrolytic degradation at low pH (<5) could be important for some of the test compounds, this was not investigated as the test solutions were all pH 5.5 or above.

Results from pH control experiments suggested that in the range of pH 5.5–10 there was no observable effect on measured rate constants of direct photolysis for CPX, CLO, FLU, and HEX. However, a decrease in k_{obs} for the direct photodegradation of ATR and BSM was observed with pH increase. Although the contribution of direct photolysis to k_{obs} in SFW could be reduced above pH 5.5, the k_{obs} in SFW

solutions above this pH were still faster than that in deionized water alone, suggesting that indirect photolysis reactions made an even greater contribution to the degradation of ATR and BSM in these matrixes.

To illustrate the variation in half-lives of each model compound in SFW solutions containing different concentrations of SFW constituents, the half-life in each SFW solution was normalized to the direct photolytic half-life of that compound (e.g., $[t_{1/2}(\text{SFW})]/[t_{1/2}(\text{deionized water})]$). The normalized half-lives of BSM and HEX in each SFW solution are shown as representative examples in Figure 2 to illustrate the impact of the presence of the SFW constituents and the extent of variability depending on their concentrations. Also, for each test probe, a mean half-life in SFW for the entire suite of solutions was normalized to the half-life by direct photolysis of that compound ($\text{mean}[t_{1/2}(\text{SFW})]/[t_{1/2}(\text{deionized water})]$), and the overall contribution of the presence of multiple water constituents on the loss process in sunlit freshwater systems is illustrated in Figure 3. The variation bars for the mean half-life in SFW of each compound in the figure represent the spread of the half-lives of that compound in the suite of SFW solutions.

The mean half-lives of CPX and CLO in SFW were not significantly different from the direct photolytic half-lives of these compounds. In contrast, in SFW half-lives of hexazinone were on average 5 times shorter. Mean half-lives of ATR, FLU, and BSM in SFW were roughly half of that in deionized water. CLO photolysis rates appeared to be the least dependent on water quality; but the lower degree of variation in half-lives of a pollutant may not be an inherent characteristic of rapid direct photolysis in general, because although CPX had a relatively short half-life in deionized water ($13 \pm 2 \text{ min}$), considerable variability in its half-lives was observed in the SFW matrixes.

Of all the test probes, HEX photolyzed the slowest whether by direct or indirect means. The lower reactivity of hexazinone was also observed in a previous study where its unreactivity was attributed to the reduced presence of olefinic character relative to more reactive pesticides, with hydrogen abstraction being the primary mode of attack by $\cdot\text{OH}$ (35).

General Trends in Photolysis Rates as a Function of SFW Constituent Concentrations. Nitrate photolysis results in the production of $\cdot\text{OH}$; in SFW matrixes containing high nitrate concentrations, k_{obs} were generally greater, which suggested the loss of parent compound was predominantly the result of reaction with $\cdot\text{OH}$. In SFW matrixes with low cDOM concentrations (0.7 mg of C/L), the relationship

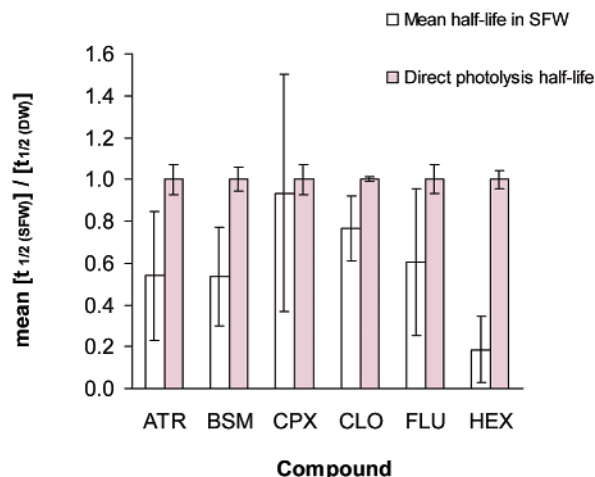


FIGURE 3. Comparison of the mean photolytic half-life in SFW normalized to direct photolysis for the model compounds. Variation bars for all normalized photolytic half-lives in SFW represent the spread of half-lives in the entire suite of solutions. Error bars for direct photolysis half-lives represent the relative standard deviation of $N = 6$ or 9 measurements.

between nitrate concentration and k_{obs} was directly proportional and positively correlated ($R^2 > 0.99$) (See Figure 3a,b in Supporting Information.). Although a positive correlation was still observed in SFW matrixes with higher cDOM concentrations, the degree of correlation and the linearity of the relationship decreased, with $R^2 < 0.97$ typically observed in the presence of 7 mg of C/L and $R^2 < 0.60$ typically observed for SFW matrixes containing 67 mg of C/L (See Figure 3a,b in Supporting Information). Also, a change in the relationship between nitrate concentration and k_{obs} was observed at the two bicarbonate concentrations that were used. The increase in bicarbonate concentration from 0.8 to 5 mM resulted in a pH increase from 8 to 10 in the SFW matrix. The magnitude of the slope of the plots generally decreased with more alkaline pH. This observation suggests half-lives were prolonged due to increased $\cdot\text{OH}$ scavenging by bicarbonate/carbonate and nitrite at high pH. At elevated pH, carbonate becomes an important scavenger of $\cdot\text{OH}$ due to the change in distribution of bicarbonate/carbonate ions. In fact, the presence of more carbonate ions enhances $\cdot\text{OH}$ scavenging ability of bicarbonate carbonate ions 28 times (10). In addition, nitrate photolysis changes above pH 8 with the increased production of nitrite, which also acts as a scavenger of $\cdot\text{OH}$ (36).

Although cDOM photolysis also results in $\cdot\text{OH}$ production, increasing cDOM concentrations often resulted in longer half-lives in this study. Some studies have concluded that cDOM photolysis is considered a minor contribution to the concentration of $\cdot\text{OH}$ that occurs in natural waters (37, 38), but more recent observations suggest that cDOM is a significant source of $\cdot\text{OH}$ (6, 39). The results from this study suggest that this constituent had a more important role in inhibiting the loss of the parent compound and this inhibition could be a result of either sorption of the contaminant (40, 41), radical scavenging, or light attenuation. However, cDOM-mediated reactive intermediates may still play a role in limiting the persistence of a pollutant.

What became apparent with changing the concentration of cDOM while the concentration of the other constituents were held constant is that there were complex relationships that existed between photolysis rates and the concentration of the SFW components. A description of the role of cDOM in PhotoFate is given below followed by a detailed description of the trends observed for each model compound.

Role of cDOM. ATR, BSM, CPX, CLO, and FLU absorb some radiation in the wavelength region emitted by the lamp

source, and this wavelength range overlaps with the region of cDOM absorption; thus, screening by cDOM could be significant for both direct photolysis (Figure 1 in Supporting Information) and indirect photolysis. Light screening factors, $S(\lambda)$, calculated for each SFW solution ranged from 0.152 to 0.975 at a depth of 3 cm in the reaction vessels (See Table 2 in Supporting Information). Thus, the average photon fluence rate when 0.7–67 mg of C/L was included in the matrix was between 15.2 and 97.5% of the near-surface photon fluence rate, indicating direct and indirect photodegradation rate constants could be reduced as much as 85% when 67 mg of C/L of cDOM is present in the matrix.

The influence of light attenuation by natural substances in water has been considered previously (42). A method for assessing photosensitized processes in natural waters that involves disentangling competitive absorption from indirect photochemical processes has been previously described (43, 44). Since photolysis rates are directly related to light intensity, a reduction in intensity through light attenuation produces a proportional decrease in direct photolysis rates if no indirect photochemical processes are involved. Observed photolysis rate coefficients are compared to those predicted on the basis of competitive light absorption by natural water, and sensitization factors may be determined through the ratio relating predicted photolysis rates based on light attenuation to those determined experimentally.

Using the equations described by Miller et al. (43), sensitization factors were calculated for each SFW solution (see Table 2 in Supporting Information). The attenuation coefficients at 312 nm for the SFW solutions ranged from 0.08 to 2.2 cm^{-1} , and SFW solutions with higher attenuation coefficients appeared visually darker than solutions with lower attenuation coefficients. An inverse relationship between attenuation coefficient and predicted ratio of photolysis rate constants in SFW to that in distilled water was observed. The predicted ratios of photolysis rate constants ranged from 0.02 to 0.9; all values were less than 1, implying that the presence of natural water constituents was expected to retard photolysis rates due to light attenuation. However, most of the observed ratios were greater than 1; thus, photolysis rates actually accelerated in these solutions due to sensitization processes that were occurring although the humic matter present absorbed much of the radiation. Furthermore, calculated sensitization factors for each model compound suggested that sensitization was observed in all SFW solutions for hexazinone and in most of the SFW solutions for the other model compounds (see Table 2 in Supporting Information).

Although half-lives were directly influenced by nitrate and bicarbonate concentrations, whatever influence cDOM had on lifetime seemed to depend on one or both of the other two constituent concentrations. In low-nitrate and -bicarbonate matrixes, although photolysis rates actually accelerated with increasing cDOM levels, this does not suggest that light attenuation is unimportant; the observations suggest that sensitized reactions can still play an important role in the photodegradation of organic pollutants in the presence of humic matter which act to attenuate light at the wavelengths that many compounds absorb at. Research by Brezonik et al. showed that in low-alkalinity waters, cDOM is the most important scavenger of $\cdot\text{OH}$ with bicarbonate and carbonate accounting for only 3% of the scavenging (10). Thus, secondary radicals resulting from the reaction between cDOM and $\cdot\text{OH}$ could have played a role in providing an alternate pathway for the loss of all the model compounds in SFW solutions where the concentration of the nonselective and highly reactive $\cdot\text{OH}$ was low (45). In addition, as suggested by Schindelin et al. (27) and Gerecke et al. (45), if the contributions of non-cDOM-derived reactive intermediates are considered negligible because of their low steady-state

concentrations in irradiated water, other species such as cDOM-derived reactive intermediates (e.g., $^1\text{O}_2$, $^{\bullet}\text{OOR}$, $^3\text{cDOM}^*$) could likely be involved in the transformation of the parent compound. Alternatively, in SFW matrixes with higher nitrate and bicarbonate concentrations, the production of reactive intermediates with greater oxidation potential (e.g., $^{\bullet}\text{OH}$ and $^{\bullet}\text{CO}_3^-$) would increase. The contribution of cDOM-derived reactive intermediates would become less apparent, and light attenuation by humic molecules would result in a deceleration of photolysis rates.

It is known from previous studies that $^{\bullet}\text{CO}_3^-$, $^1\text{O}_2$, and $^{\bullet}\text{OOR}$ react selectively with sulfur-containing compounds. Since BSM was the only sulfur-containing compound in this study, it is possible that these photooxidants could have some role in the sensitized reactions that occur to degrade this chemical. Also, in SFW matrixes where steady-state concentrations of $^{\bullet}\text{CO}_3^-$ are low, the potential contribution of $^1\text{O}_2$ and $^{\bullet}\text{OOR}$ to BSM degradation would become more apparent. The measurement of the concentrations of the reactive transient species is currently being done to verify this.

The apparent change in the influence of cDOM was only observed for compounds for which indirect photolysis had a significant contribution to the loss of that compound in an aqueous setting.

Influence of SFW Constituents on the Half-Lives of the Test Probes Atrazine, Fluometuron, and Hexazinone. ATR is a triazine herbicide that is used to control broadleaf and grassy weeds in corn, sugarcane, sorghum, pineapple, Christmas trees, and other crops (46). There has been a great deal of research involving the environmental fate of ATR since it is widely used in treating crops and it is the second most common pesticide found in private and community wells. Torrents et al. (34) reported an increase in the photolysis rate coefficient of ATR from 0.0040 ± 0.0006 to $0.029 \pm 0.002 \text{ h}^{-1}$ following the addition of 1 mM NaNO_3 to deionized water using the same photosimulator as the one used in the current study (34). Previous photolytic work by Schmitt et al. has shown that the fulvic acid (5 mg of C/L) alone will decrease the half-life of ATR by direct photolysis from 66.08 to 49.62 h when solutions were irradiated by a high-pressure Hg vapor lamp (47).

FLU is applied for weed control in sugarcane and cotton plants and is highly persistent, with a half-life of 110–144 weeks in water (48). Aquatic fate studies of FLU have mostly been focused on direct photolysis with exact photolytic conditions rarely reported (49). FLU has been found to be stable in water at 20 °C from pH 1 to 13 (50). However, under natural sunlight, a 10 ppm aqueous solution of FLU had a direct photolytic half-life of 1.2 days (50). Data from our experiments indicate this compound is susceptible not only to indirect photolysis in all the SFW solutions where pH ranged from 8 to 10 but also by direct photolysis in deionized water, which was pH 5.5.

HEX is applied to control weeds in sugarcane, pineapples, and lucerne, although it is mainly used for noncrop areas (50). Fate studies have shown sunlight may break down the compound by photodegradation, although this loss occurred very slowly under natural sunlight; 70% remained after 5 weeks in standard reference water (51). The same study found 49% of the parent compound remained after 5 weeks when its degradation in field water was investigated, suggesting that the components found in field water increased the rate of degradation of a compound.

In this study, ATR half-lives ranged from 21 ± 2 (SFW N: 806 μM nitrate; 7 mg of C/L cDOM; 0.8 mM bicarbonate) to 241 ± 14 h (SFW B: 8 μM nitrate; 7 mg of C/L cDOM; 5 mM bicarbonate) while the half-life of this compound by direct photolysis alone was 208 ± 33 h.

FLU half-lives ranged from 9 ± 3 (SFW F: 806 μM nitrate; 0.7 mg of C/L cDOM; 0.8 mM bicarbonate) to 107 ± 27 h (SFW B: 8 μM nitrate; 7 mg of C/L cDOM; 5 mM bicarbonate), while the half-life of this compound by direct photolysis was 67 ± 11 h. It is unclear why the loss of FLU by direct photolysis occurred at a faster rate than its loss in SFW solution B. Shading by humic material may not be the primary reason for this observation, since the calculated $S(\lambda)$ suggest there is typically more light penetration in solutions with cDOM concentrations of 7 mg of C/L ($S(\lambda) = 0.883$) compared to solutions with 67 mg of C/L ($S(\lambda) \approx 0.15$) at a depth of 3 cm. Similar results were obtained with replicate trials, and it remains unclear why the loss of this model compound occurred at a slower rate in the presence of reactive intermediates than in their absence.

Half-lives of HEX in the SFW solutions ranged from as low 37 ± 15 (SFW N: 806 μM nitrate; 7 mg of C/L; 0.8 mM bicarbonate) to 537 ± 58 h (SFW L: 81 μM nitrate; 0.7 mg of C/L cDOM; 5 mM bicarbonate). The half-life of HEX by direct photolysis alone was 928 ± 88 h. Half-lives in SFW were dramatically reduced, which suggests reactive intermediates generated upon irradiation could react with and degrade HEX. Thus, indirect photolysis could potentially dominate the degradation of this otherwise relatively persistent organic pollutant.

Increasing nitrate concentrations decreased the half-life of ATR, FLU, and HEX, which suggests $^{\bullet}\text{OH}$ produced from nitrate photolysis aided in their degradation (see Figure 4a for a representative example using ATR). However, as the bicarbonate concentration and subsequent alkalinity increased, half-lives were prolonged, which is suggestive of increased $^{\bullet}\text{OH}$ scavenging by bicarbonate/carbonate and nitrite ions (Figure 4b). Although secondary radicals, such as $^{\bullet}\text{CO}_3^-$, may also play a role in degrading these pesticides, their oxidation potential is less positive than that of $^{\bullet}\text{OH}$ (52). Thus, $^{\bullet}\text{OH}$ is the suspected reactive intermediate inducing the degradation of these compounds. The data suggest carbonate species behave primarily as scavengers of OH rather than promoters of photoreactions degrading the target compounds through carbonate radical reactivity.

While the photolysis rate constant, k_{obs} , of these three pesticides appeared to be directly related to the concentration of nitrate and bicarbonate, how cDOM influenced k_{obs} appeared to depend on the concentration of nitrate in the SFW matrix. When nitrate was present at low concentrations (8 μM), increases in cDOM concentrations resulted in shorter half-lives. However, in solutions containing high amounts of nitrate (806 μM), the opposite effect was observed; an increase in concentrations of cDOM resulted in a longer half-lives. With nitrate concentrations at an intermediate level (81 μM), changes in the concentration of cDOM did not cause half-lives to fluctuate significantly. As discussed earlier, calculated $S(\lambda)$ values suggest less light penetration is observed in solutions containing more cDOM. However, light attenuation alone does not explain the observations made since different trends for half-lives were seen with increasing cDOM concentrations at the three nitrate concentrations used in the SFW solutions.

Although cDOM shading may have also occurred with the other model compounds used in this study, its effect seemed to be experienced to a greater degree by HEX because its loss appeared to be more heavily dependent on the contribution of indirect photolysis.

Bensulfuron Methyl. BSM is a sulfonylurea herbicide developed by DuPont and registered for use on paddy rice (53). The dissipation of BSM in California rice fields and its persistence in soil has been studied (54), and several photodegradation studies have also been done for this compound (55, 56).

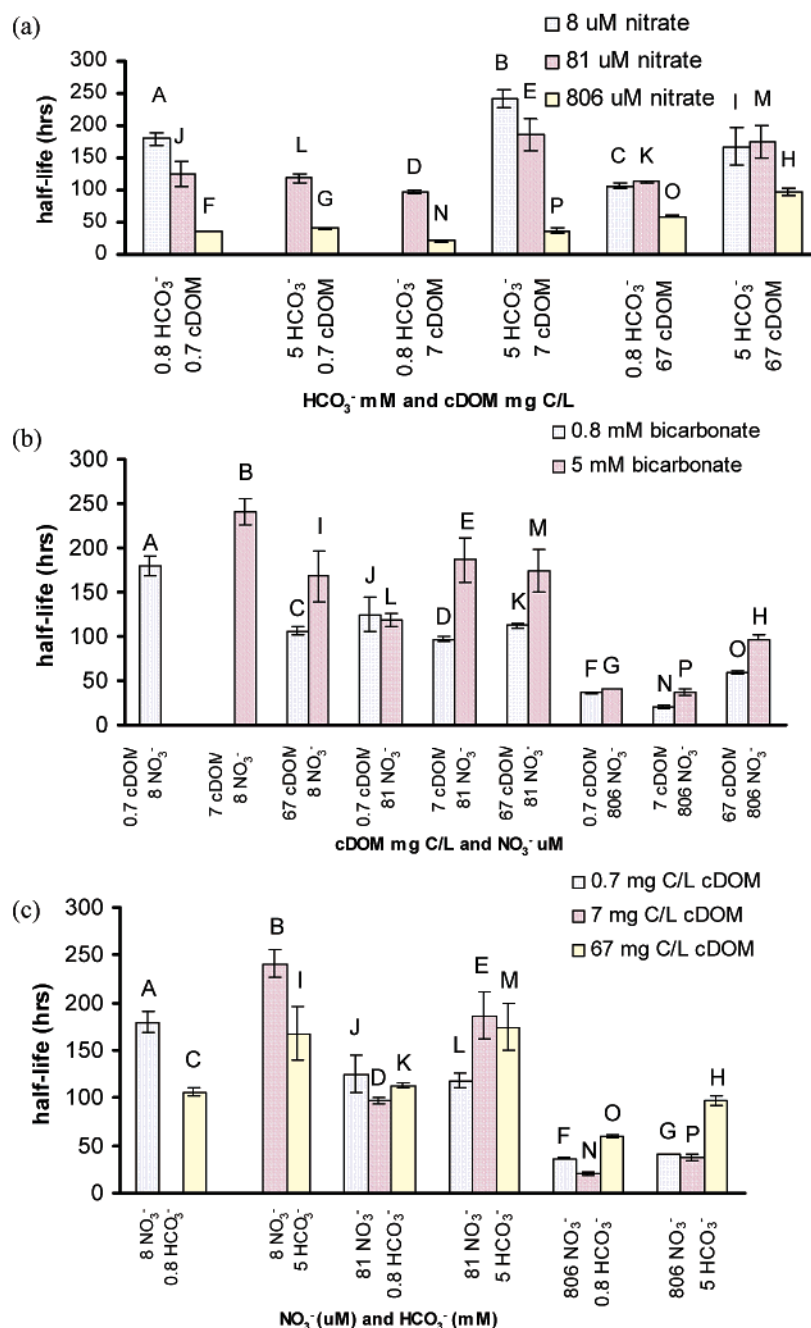


FIGURE 4. Half-life of atrazine as a function of (a) nitrate concentration (μM), (b) bicarbonate concentration (mM), and (c) DOC concentration (mg C/L). Error bars represent the standard deviation of $N = 9$ measurements.

In the SFW solutions, BSM half-lives ranged from 16 ± 3 (SFW F: $806 \mu\text{M}$ nitrate; 0.7 mg C/L cDOM ; 0.8 mM bicarbonate) to $82 \pm 14 \text{ h}$ (SFW M: $8 \mu\text{M}$ nitrate; 67 mg C/L ; 5 mM bicarbonate). The half-life of this compound by direct photolytic means was $94 \pm 11 \text{ h}$.

Increasing the concentration of nitrate resulted in shorter half-lives, and increasing the concentration of bicarbonate prolonged the half-life of BSM. The rate constant for the reaction between $\cdot\text{OH}$ and BSM has been previously determined to be $2.6 \times 10^{13} \text{ M/h}$, which suggests that this photooxidant could play an important role in limiting the persistence of this chemical (55). cDOM did not appear to influence the lifetime of this model compound to a large degree, although an increase in cDOM concentration generally increased the lifetime of BSM. It appears cDOM was more important as an inner filter and in the scavenging of radicals that had a role in BSM degradation than in their

production. However, different trends were exhibited when the alkalinity if the SFW solution changed. Like the observations made for ATR, FLU, and HEX, in less alkaline solutions (0.8 mM bicarbonate) a change in the role of cDOM was observed with different nitrate ion concentrations. While an increase in cDOM concentrations at low nitrate levels ($8 \mu\text{M}$) shortened the half-life of BSM, an increase in the presence of high nitrate concentrations ($806 \mu\text{M}$) had the opposite effect; half-lives lengthened as cDOM concentrations increased (see Figure 4a in Supporting Information). A different observation was made in more alkaline solutions (5 mM bicarbonate); increasing the concentration of cDOM resulted in longer half-lives (see Figure 4b in Supporting Information).

Ciprofloxacin. CPX is a synthetic fluoroquinolone antibiotic that has a broad spectrum of Gram-negative and Gram-positive antibacterial activity and is commonly used in human and veterinary medical treatment (57). In a recent USGS

survey of 139 U.S. streams, this drug was present at a median concentration of 0.02 $\mu\text{g/L}$ (3). There have been extensive studies investigating the photodegradation of CPX and its binding to clay minerals (41, 58). The family of fluoroquinolone antibacterial agents is known to be photosensitive, but the studies completed to date have not examined degradation kinetics in an environmental setting.

The half-life of CPX by direct photolysis was found to be 13 ± 2 min, and the half-life ranged from 3 ± 1 (SFW F: 806 μM nitrate; 0.7 mg of C/L cDOM; 0.8 mM bicarbonate) to 25.5 ± 0.2 min (SFW M: 81 μM nitrate; 67 mg of C/L; 5 mM bicarbonate).

There was a relatively small difference between k_{obs} in SFW matrixes and k_{obs} in deionized water for CPX, which suggests direct photolysis accounts for most of the photo-transformation of this compound in sunlit surface waters.

Increasing concentrations of nitrate in the SFW matrixes did not appear to accelerate the photodegradation of this pharmaceutical. Slightly slower rates of photodegradation of CPX were observed in SFW matrixes with greater amounts of bicarbonate.

Clofibric Acid. CLO, produced in the low-kiloton range per annum, is mainly used in the ethyl ester form as a human blood lipid regulator where CLO is the effective metabolite (59). CLO was first identified in effluents from wastewater treatment plants 20 years ago, and in 1991, the metabolite was detected in surface waters, groundwater, and drinking water in and around the city of Berlin (32, 60). There is a limited amount of literature surrounding the transformation of CLO in the presence of reactive intermediates in aquatic systems.

The half-life of CLO by direct photolysis was 19.3 ± 0.5 h, and the half-lives in the presence of SFW constituents ranged from 9.5 ± 0.1 (SFW C: 8 μM nitrate; 67 mg of C/L cDOM; 0.8 mM bicarbonate) to 19 ± 1 h (SFW L: 81 μM nitrate; 0.7 mg of C/L cDOM; 5 mM bicarbonate). Because of the relatively small difference between k_{obs} in SFW solutions and deionized water for clofibric acid, indirect photolysis probably does not make a large contribution to the photolytic loss of this compound in the aquatic environment. Also, changes to the amount of the SFW constituents present did not appear to cause degradation rates to vary significantly.

An inconsistent trend was observed with increasing nitrate concentrations; increasing nitrate concentration generally accelerated the degradation of CLO, although not to a great extent. Similarly, although bicarbonate inhibited the loss of CLO, this was not to a significant degree. Regardless of the amount of nitrate present, increasing the cDOM concentration seemed to generally shorten the half-lives by some extent.

•OH versus Other Reactive Transients. The observations made suggested that •OH-mediated processes were generally predominant in the PhotoFate system. Although other reactive transient species may have been formed, their contribution to the loss of the parent compounds may not have been apparent when the steady-state concentration of •OH was high. The oxidation potential of the nonselective and reactive •OH has been determined to be more positive than the other reactive intermediates (52). In future work, compounds that could react more selectively with the other transients could be examined using PhotoFate. To characterize the SFW solutions, the concentrations of the reactive intermediates present in the SFW matrixes are currently being quantified using probe molecules and our findings will be reported in a future paper.

The results from this investigation not only clearly showed that the presence of nitrate, bicarbonate, and cDOM could have a large impact on the rate of degradation of the parent compound, but also the change in water composition could result in a variation in the lifetime of a pollutant. Thus, the EPA guideline for testing the persistence of chemicals is

inadequate as the only condition for indirect photolysis testing is the presence of 50 mg of C/L of cDOM. In addition to acting as a light attenuator, this particular constituent has a dual role of being a source and sink for •OH, $^1\text{O}_2$, and •OOR, and cDOM's influence appears to depend on the concentration of nitrate and the subsequent steady-state concentration of •OH in surface water. Also, results from the use of a single reactive transient precursor in indirect photolysis testing of aquatic contaminants may not be a correct reflection their fate in real natural water systems where multiple reactive intermediate precursors are present. The EPA guideline does not take into account potential nitrate–cDOM and bicarbonate–cDOM interactions that could subsequently change how cDOM influences indirect photodegradation rates. PhotoFate may provide a more robust and powerful means of evaluating aqueous persistence.

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Supporting Information Available

Additional tables and figures as noted in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Note Added after Asap

This paper was released ASAP on 1/24/2003 with errors in Figure 1. The correct version was posted on 2/3/2003.

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