Photoinduced Degradation of Carbaryl in a Wetland Surface Water

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The photoinduced degradation of carbaryl (1-naphthyl-*N*-methyl carbamate) was studied in a wetland's surface water to examine the photochemical processes influencing its transformation. For this particular wetland water, at high pH, it was difficult to delineate the photolytic contribution to the overall degradation of carbaryl. At lower pH values, the extent of the degradation attributable to indirect pathways, that is, in the presence of naturally occurring photosensitizers, increased significantly. Moreover, the photoenhanced degradation at the lower pH values was found to be seasonally and spatially dependent. Analysis of water samples revealed two primary constituents responsible for the observed indirect photolytic processes: nitrate and dissolved natural organic matter (NOM). Nitrate in the wetland appears at high concentrations (≥ 1 mM) seasonally after the application of fertilizers in the watershed and promotes contaminant destruction through the photochemical production of the hydroxyl radical (HO$^\bullet$). The extent of the observed indirect photolysis pathway appears to be dependent upon the concentration of nitrates and the presence of HO$^\bullet$ scavengers such as dissolved NOM and carbonate alkalinity. Paradoxically, during low-nitrate events (<50 μM), NOM becomes the principal photosensitizer through either the production of HO$^\bullet$, direct energy transfer from the excited triplet state, and/or production of an unidentified transient species.

KEYWORDS: Photolysis; carbaryl; natural organic matter; nitrate

INTRODUCTION

Photolysis may be an important degradative pathway for many agrochemicals in surface waters. Many of these chemicals are organic contaminants that can be potentially degraded by both direct and indirect photolysis (*1–5*). Field studies conducted in streams and rivers located in Iowa have shown that an increase in the number of sunlight hours (from winter to summer) results in a significant increase in the overall transformation coefficient (by as much as a factor of 4) for atrazine (*1*). The photolytic degradation of several pesticides (and daughter products) was significant in rice fields, and the effect was attributed to the concentration of contaminants in surface microlayers (*6*) and photosensitized reactions (*7*). Finally, simulations modeling the fate of phenylurea herbicides in lake water suggested that photosensitized transformation of phenyl-urea herbicides promoted by natural organic matter is an important removal mechanism (*8*).

To date we are unaware of any study that has focused on the photolytic fate of agrochemicals in wetlands. Wetlands (in comparison to other water bodies) are rich in photosensitizers such as natural organic matter (NOM) and nitrates. Both of these substances are capable of absorbing sunlight and inducing the transformation of organic compounds via indirect pathways (*5,*

9, 8). NOM is a poorly defined matrix of labile and nonlabile organic substances that are capable of acting as photosensitizers through the direct reaction of excited states with contaminants (*10–12*) or by the production of reactive intermediates (*5, 13*). Nitrate and nitrite are other photosensitizers in natural waters and are considered to be important precursors in the photoproduction of the hydroxyl radical (HO$^\bullet$) (*14–17*). Whereas nitrate levels are typically low in many natural waters (<10 μM), they are often elevated in wetlands receiving agricultural runoff after precipitation events (*17*). Thus, indirect photolysis may be an important degradative pathway in these wetlands for those contaminants that are incapable of absorbing solar radiation.

This research investigates the photochemical processes occurring in the surface water of a wetland and how they influence the degradation of the pesticide carbaryl (1-naphthyl-*N*-methyl carbamate). This compound was chosen because it is a widely used phenyl *N*-methyl carbamate insecticide in Ohio and across the United States (*18*) that undergoes direct and indirect (through its reaction with HO$^\bullet$) photolysis (*7, 19–22*). Specific objectives of this research were to quantify the levels of NOM and nitrate present in the target wetland and to elucidate the role that these constituents play in the indirect photolysis of carbaryl.

MATERIALS AND METHODS

Reagents and Materials. All chemicals and reagents were purchased commercially and used without further purification. Purchases were as follows: carbaryl from Chem Services (99%; West Chester, PA);

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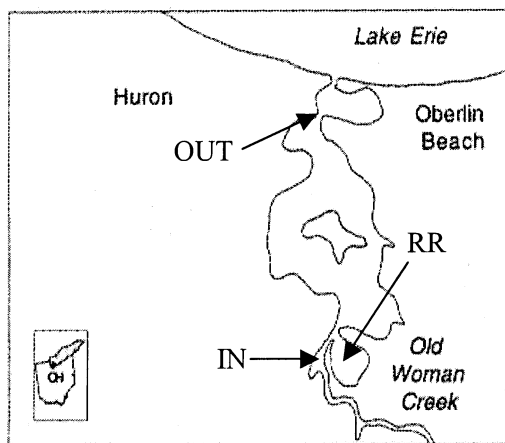
Photoinduced Degradation of Carbaryl

J. Agric. Food Chem., Vol. 50, No. 23, 2002 **6759**

Figure 1. Map of Old Woman Creek Estuarine Reserve (OWC), Huron, OH. Water samples were obtained from the inlet (IN), railroad (RR), and outlet (OUT).

1-naphthol (99%), *p*-nitroanisole (97%), and pyridine (99%) from Aldrich (Milwaukee, WI); chemical reagents (potassium dihydrogen phosphate, potassium phosphate, sodium borate, and trace metal grade sulfuric acid) and HPLC solvents of the highest purity from Fisher Scientific (Chicago, IL). All glassware was acid-washed and rinsed several times with Milli-Q water (Millipore Corp., Bedford, MA).

Collection and Characterization of Wetland Raw Water. The field site selected for sampling was Old Woman Creek Estuarine Reserve (OWC), which is a 30 ha wetland located on the south shore of Lake Erie, 5 km east of Huron, OH (**Figure 1**). Approximately 69 km^2 of agricultural land drains into OWC's basin and, subsequently, it receives a significant amount of suspended solids and pesticides (D. Baker, personal communication). Sampling sites were chosen at the inlet (IN), interior [railroad (RR)], and outlet (OUT) of the wetland. Samples were collected in June (which corresponded to the time of spring runoff: Kreiger, personal communication), August, and September of 1998. Raw water samples were collected in 4-L amber glass jugs, placed on ice, and transported to The Ohio State University (OSU). Samples were stored at 4 °C until use.

Wetland water samples were filtered with glass fiber filters (Gelman A/E) prior to analysis and use. Samples were analyzed for total organic carbon (TOC) using a Shimadzu TOC 5000 analyzer. Samples were analyzed for nitrate, nitrite, chloride, and sulfate via ion chromatography (IC) (Dionex DX-500 IC, Sunnyvale, CA).

The light-absorbing properties of the NOM were assessed by UV−vis spectrophotometry (Varian Cary 1). Samples were scanned in a quartz cuvette from 200 to 600 nm. The collected absorptivities were used to calculate attenuation coefficients and light-screening factors appropriate for each natural water sample. The screening factor (S_λ) is used to quantify the effect of light attenuation by natural waters on the direct photolysis rate. Application of S_λ to rate coefficients measured in distilled water can yield an *upper-limit* estimate of an expected direct photolysis rate coefficient in a given natural water under identical irradiation conditions. The wavelength-specific light-screening factor, S_λ, can be calculated from

$$S_\lambda = \frac{1 - 10^{-\alpha_\lambda l}}{2.303\alpha_\lambda l} \quad (1)$$

where *l* is the path length of the test tubes used for the experiments [1.12 cm (*23*)] and α_λ is the light attenuation coefficient for natural water constituents (the measured absorbance for a given wavelength when the cuvette path length is 1.0 cm). This equation is valid only in systems in which the attenuation due to the natural water constituents is much greater than the attenuation of the contaminant [ϵ (M^{-1} cm^{-1}) × [C] (M)] of interest. Because a polychromatic light source was used to irradiate the natural water samples, an overall screening factor, $S_{\Sigma\lambda}$, for all of the wavelengths that could be absorbed by carbaryl (290−

370 nm) was calculated. First, S_λ was determined from the measured absorbance at each wavelength of interest ($\lambda = 290-370$ nm). A value of 1.0 for S_λ indicates that light was not significantly attenuated by sample. The resulting values were plotted versus wavelength and fitted with a polynomial function (least squares, Microsoft Excel) to yield an equation that adequately (R^2's = 0.99) described the screening factor as a function of the wavelength in this range. This was done for each natural water sample in which an experiment was run. These equations were then integrated and evaluated from $\lambda = 290-370$ nm. The determined areas were then normalized to the area expected if no screening was occurring to yield the overall screening factor ($S_{\Sigma\lambda}$).

Photolytic Reactions. Photochemical experiments were conducted using a merry-go-round reactor equipped with a xenon arc lamp (450-W) housed in a borosilicate immersion well (Ace Glass, Vineland, NJ), which screened out light with $\lambda < 290$ nm. Light intensity was monitored with chemical actinometry (*p*-nitroanisole/pyridine system) (*23*) and found to be 99.4% of summer sunlight (35 °C) measured in Columbus, OH, at a latitude of 40° N. During the course of the experiments, the measured radiant emittance of the lamp varied no more than 5%. Therefore, we assumed a constant irradiance in our photoreactor and compared observed rate coefficients directly without the incorporation of a correction term for variable light intensity.

Reaction mixtures were prepared according to the following procedure. An aliquot of carbaryl stock solution (0.01 M in acetonitrile) was plated-out onto a graduated storage bottle. All traces of acetonitrile were evaporated under a gentle stream of argon because indirect photolytic processes can generate intermediates that may react with the acetonitrile (Canonica, personal communication). A predetermined volume (for a desired concentration of ∼5 μM carbaryl) of natural water sample or buffered Milli-Q water (Millipore Corp.) was added to the storage bottle and equilibrated for a few minutes. The reaction solution was pipetted into Pyrex culture tubes (13 × 100 mm), and the tubes were placed either in the photoreactor for irradiation (operated at 40 °C) or in a temperature-controlled water bath for the dark control (also at 40 °C). Test tubes were completely filled as a precaution to avoid extra losses to the headspace due to Henry's law partitioning. To distinguish between direct and indirect photolytic mechanisms and a base-promoted dark reaction, reactions were carried out at the pH of the natural water sample and in samples that had been pH-adjusted to ∼4.3. Test tubes were sacrificed periodically, and 20 μL of 2 N HCl was added to each sample tube to reduce the pH to ∼2.3, which completely quenched any dark reaction.

All samples from time courses were assayed by HPLC for the parent compound and the detectable derivative (1-naphthol). A direct aqueous injection (25 μL) from each vial was made into the HPLC, and analytes were separated using a 300 × 3.9 mm Novapak (Waters) column and detected using a programmable fluorescence detector (Waters 470). The mobile phase for the analysis was 40% acetonitrile/60% of a 1% (v/v) glacial acetic acid buffer (v/v), and the flow rate was 1.0 mL/min. The program for the detector was as follows: initial through 8.9 min, λ_{exc} = 282 nm, λ_{em} = 330 nm for carbaryl (RT = 7.8 min); 8.9 min through 11 min, λ_{exc} = 292 nm, λ_{em} = 462 nm for 1-naphthol (RT = 9.7 min). Preliminary work in our laboratory has shown that this analytical approach is highly sensitive and provides linear detection over several decades of analyte concentration.

Data Analysis. Kinetic data from photolytic time courses were analyzed using Scientist for Windows v. 2.01 (MicroMath Scientific Software, Salt Lake City, UT). Observed rate constants (k_{obs}) for carbaryl degradation were determined from least-squares fit (Powell algorithm) of the observed kinetic data to the pseudo-first-order kinetic model.

We assumed in this study that three basic processes contribute to carbaryl's degradation: (1) a dark reaction, that is, base-catalyzed hydrolysis, (2) direct photolysis, and (3) indirect photolysis. The terms for these processes may be collected into an overall rate expression for the degradation of the pollutant of interest. Thus, the contribution of any known process to the observed first-order rate coefficient for carbaryl's degradation (k_{obs}) may be quantified by comparing the relevant pseudo-first-order rate coefficient for the process in question

6760 *J. Agric. Food Chem.,* Vol. 50, No. 23, 2002

Miller and Chin

Table 1. Water Quality Characteristics for Water Samples Taken from Old Woman Creek (OWC) in June, August, and September of 1998

sample	pH[a]	TOC (mM)	ϵ at 280 nm[b] $(M^{-1}\,cm^{-1})$	$S_{\Sigma\lambda}$[c] (at 290–370 nm)	specific conductivity (μS/cm)	alkalinity (mM CaCO$_3$)	nitrate (mM)
inlet							
June	7.65	0.595 (0.072)[d]	307	0.874	425	0.838	1.01
Sept	7.78	0.436 (0.033)	242	0.940	540	1.55	0.0274
railroad							
June	NA[e]	0.588 (0.089)	333	0.841	NA	NA	0.790
Aug	7.71	0.558 (0.120)	219	0.917	437	1.55	0.0131
Sept	7.80	0.534 (0.072)	288	0.914	411	1.34	0.0295
outlet							
June	8.09	0.514 (0.310)	242	0.931	396	1.18	0.154
Sept	7.96	0.181 (0.078)	166	0.980	274	0.839	0.0185

[a] pH measured at field site. [b] ϵ = calculated molar absorptivity for various OWC waters (corrected for nitrate absorption). [c] Calculated overall screening factor, $S_{\Sigma\lambda}$. [d] Values in parentheses represent %CV for replicate samples. [e] Data not available.

(e.g., k_{direct} or Σk_i) to the sum of the relevant degradation rate coefficients (i.e., Σk_j):

$$k_{obs} = \Sigma k_j = k_{OH^-}[OH^-] + k_{direct} + \Sigma k_i[\text{transient}]_i \qquad (2)$$

where k_{OH^-} is the second-order rate constant for the base-promoted elimination reaction, k_{direct} corresponds to the rate coefficient for the direct photolysis, and Σk_i are the second-order rate constants for any reactive transient species i that results in the indirect photolysis of carbaryl. For simplicity, $\Sigma k_i[\text{transient}]_i$ will be referred to as the pseudo-first-order indirect photolytic rate coefficient $k_{indirect}$ throughout the remainder of this paper. For these systems, k_{OH^-} can be determined from Arrhenius data published in the literature (*24–26*), and k_{direct} can be reasonably predicted from its measurement in buffered control solutions. Using these two values and application of the screening factor for a given sample, the contribution to k_{obs} from the indirect processes can easily be calculated from the difference.

We anticipate the results from such analysis will provide some general trends regarding the reactivity of the water constituents in inducing indirect photolysis of carbaryl. Caution must be used, however, when these results are extrapolated to natural environments. First, using the Pyrex immersion well and tubes results in the attenuation of light in the wavelength region between 290 and 350 nm. This attenuation is greatest at 290 nm and decreases with increasing wavelength (e.g., approximately 70 and 95% of the light is *transmitted* at 320 and 350 nm, respectively). Thus, in natural systems, reaction rates may be accelerated due to a higher intensity of light in these photoreactive regions. The use of tubes for the photoreactions can accelerate measured rates of photolysis for a given solution when compared to a flat water body (*24*) and can introduce error in the determination of screening factors because the curved geometry of tubes refracts and reflects light incongruently causing a variation in the light field (*23*). Furthermore, the temperatures in natural systems are not expected to reach the temperatures that were measured in the photoreactor. Due to the inability to vary the temperature of the photoreactor, we were unable to determine the Arrhenius parameters for the reactions; hence, it is difficult to surmise the effect of lower temperatures on the reaction rates. Although beyond the scope of the current study, such parameters should eventually be determined.

RESULTS AND DISCUSSION

Natural Water Characteristics. Several water quality parameters [e.g., pH, TOC (a measure of the NOM content), nitrate, and alkalinity] were measured for the OWC samples (**Table 1**). The UV–vis absorption spectrum for each OWC sample was also recorded (**Figure 2**). The spectra of the June samples were dominated by the presence of nitrate (see insert in **Figure 2A**) as expected on the basis of the measured concentrations of nitrate in these samples (**Table 1**). For the August and September samples (**Figure 2B**), spectra more characteristic for NOM present in natural water samples were
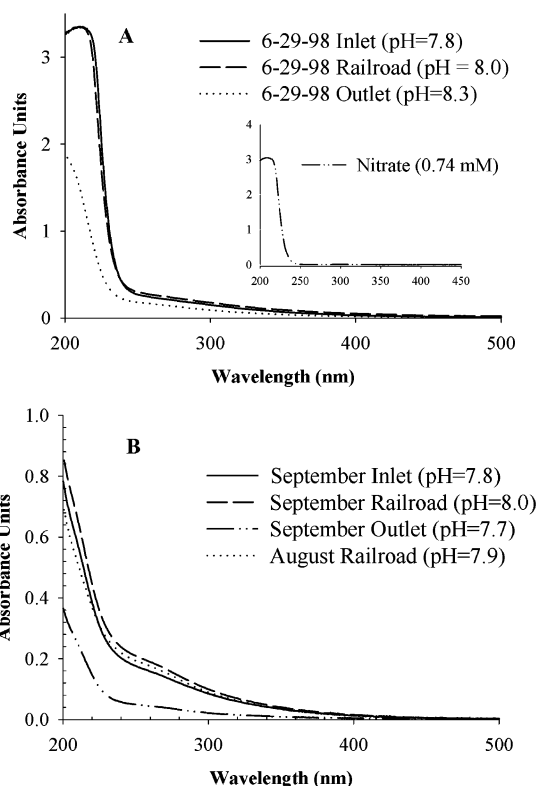

Figure 2. UV–vis for OWC water samples collected on June 29, 1998 (A), August 24, 1998 (B), and September 8, 1998 (B).

obtained. Thus, in this wetland NOM and nitrate appear to be the important photosensitizers with significant amounts of the latter occurring seasonally.

Kinetic Time Courses. The results from the time courses run in these experiments were treated according to pseudo-first-order kinetics, and the models fit reasonably well having an R^2 > 0.99 for all reactions. According to the analysis of the data, the contribution from the elimination pathway was large in the unaltered samples and accounted for the largest percentage (ranging from 46 to 73%) of the overall reaction in the presence of light (**Table 2**; **Figure 3**). This result is not unexpected because carbaryl is known to undergo a significant base-catalyzed elimination reaction at pH values >7 (*24, 27, 28*). The light-induced degradation of carbaryl, however, in the higher pH samples was not insignificant. In fact, light was found to promote the transformation by 37–117% for the natural water samples (**Table 2**). Thus, the presence of light did enhance carbaryl's degradation. The only daughter product observed and quantified under our analytical conditions was 1-naphthol

Photoinduced Degradation of Carbaryl

J. Agric. Food Chem., Vol. 50, No. 23, 2002 **6761**

Table 2. Rate Coefficients Measured and Total Mass Balances Calculated for the Degradation of Carbaryl in Old Woman Creek Wetland Water Samples in the Dark and Light

| description | pH[a] | k_{obs} (min^{-1}) × 10^3 | | | | | |
		dark[b]	% mass balance[c]	light[b]	% mass balance[c]	k_{direct}[d]	corrected[e]
inlet							
June	4.37	0.04 ± 0.02	98	2.73 ± 0.05	25	0.12	2.69 ± 0.05
	7.86	2.97 ± 0.15	96	4.56 ± 0.17	24	1.5	1.59 ± 0.23
Sept	4.32	0.12 ± 0.05	95	0.86 ± 0.05	64	0.13	0.74 ± 0.07
	7.85	2.40 ± 0.11	94	3.28 ± 0.11	34	1.6	0.88 ± 0.15
railroad							
June	4.38	0.14 ± 0.05	93	2.32 ± 0.08	33	0.12	2.18 ± 0.10
	7.93	2.71 ± 0.16	98	4.46 ± 0.19	20	1.7	1.75 ± 0.25
Aug	4.37	0.03 ± 0.03	99	1.10 ± 0.05	58	0.13	1.06 ± 0.04
	7.96	1.73 ± 0.08	94	3.75 ± 0.10	25	2.0	2.02 ± 0.13
Sept	4.31	0.13 ± 0.08	94	1.25 ± 0.09	50	0.13	1.12 ± 0.12
	8.02	3.36 ± 0.13	92	4.95 ± 0.15	20	2.3	1.59 ± 0.12
outlet							
June	4.34	0.12 ± 0.05	94	1.37 ± 0.06	50	0.13	1.25 ± 0.08
	8.2	4.32 ± 0.31	98	6.73 ± 0.28	9	2.4	2.41 ± 0.42
Sept	4.31	0.05 ± 0.02	97	0.48 ± 0.02	75	0.14	0.43 ± 0.03
	7.76	1.94 ± 0.13	96	3.10 ± 0.133	39	1.14	1.16 ± 0.19
buffer							
phosphate	4.35	0.12 ± 0.05	90	0.24 ± 0.04	87	0.14	0.12 ± 0.06
borate	7.99	2.16 ± 0.13	92	4.32 ± 0.14	20	2.3	2.16 ± 0.19

[a] Values are the average pH. [b] Values following the ± are the 95% confidence levels. [c] Calculated as the sum of all quantifiable species measured at the end of the time course divided by initial carbaryl concentration. [d] Values predicted from $S_{\Sigma\lambda} \times k_{direct}$ (predicted from linear regression of measured k_{direct} vs [OH–]). [e] Rate constants were corrected for the dark reactions. Values following the ± are the propagated errors from data manipulation.
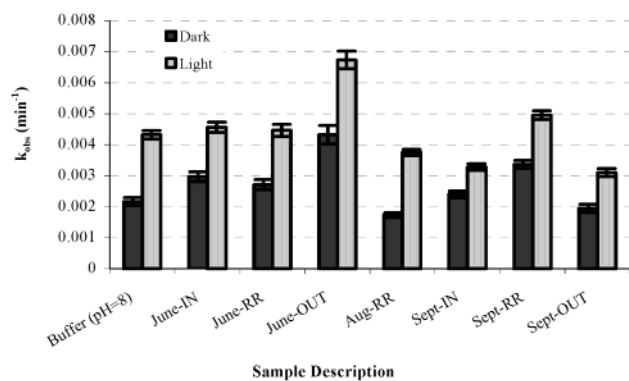
Figure 3. Photoinduced degradation of carbaryl in OWC wetland water samples at their natural pH (∼8). Error bars represent the 95% CI.
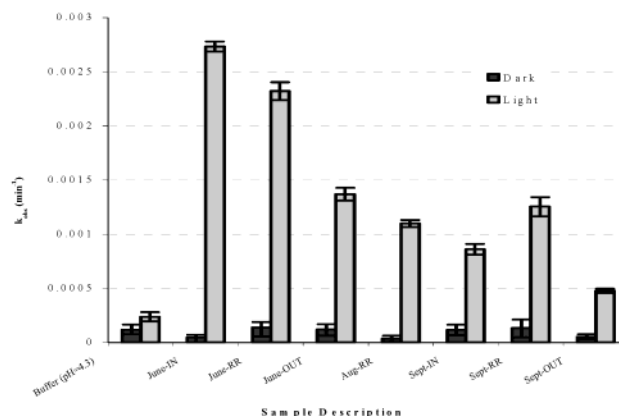
Figure 5. Photoinduced degradation of carbaryl in pH-adjusted (∼4) water samples. Error bars represent the 95% CI.
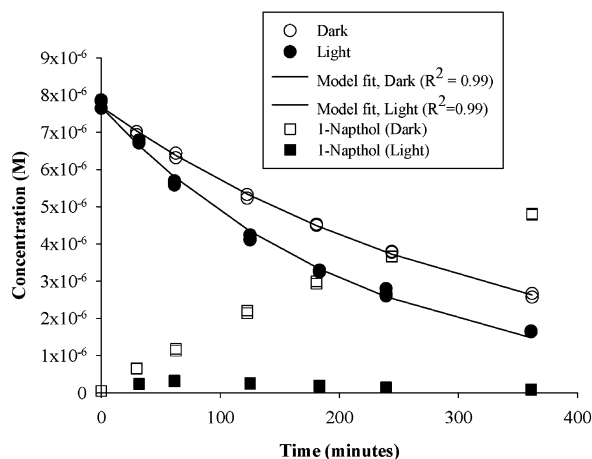
Figure 4. Photoinduced degradation of carbaryl in OWC water sampled from the inlet site on June 29, 1998, at ambient pH (∼8).

(**Figure 4**). In the dark reactions, 1-naphthol accumulated in the reaction solution resulting in good mass balances (**Figure 4**; **Table 2**), suggesting that 1-naphthol was the major product. Conversely, in the photoexperiments, 1-naphthol behaved as a photoreactive intermediate and never accumulated to levels observed in the dark (**Figure 4**; **Table 2**), suggesting that other unidentified products were produced and not detected using our analytical procedure.

In the pH-adjusted natural water sample, the reaction in the light accounted for 87−98% of the overall reaction (**Figures 5** and **6**; **Table 2**). The daughter product, 1-naphthol, was not detected under our analytical conditions; hence, resulting mass balances were poor as they were based on this one derivative. The dark reaction was relatively insignificant at the lower pH experiments (**Figure 6**) and accounted for as little as 1% to, at most, 13% of the overall reaction. Thus, for the purposes of this paper, the role of both the direct and indirect photolytic pathways for carbaryl is evaluated at the lower pH value.

Spatial and Temporal Trends. The maximum photodegradation due to indirect processes occurs in the June inlet water, which had the highest amount of nitrate (**Table 1**). Carbaryl transformation is less in the June railroad and outlet samples but still corresponds to the amount of nitrate present in the samples (**Figure 7**). Interestingly, the other samples, from August and September, show light-promoted degradation even
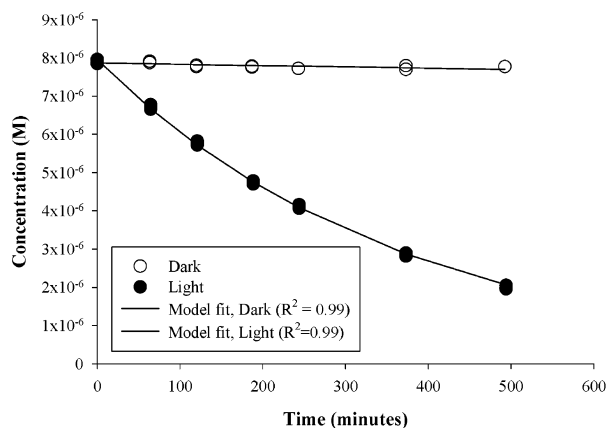
6762 *J. Agric. Food Chem.,* Vol. 50, No. 23, 2002

Miller and Chin

Figure 6. Photoinduced degradation of carbaryl in the OWC June 29, 1998, inlet water in pH-adjusted (4.37) water samples.
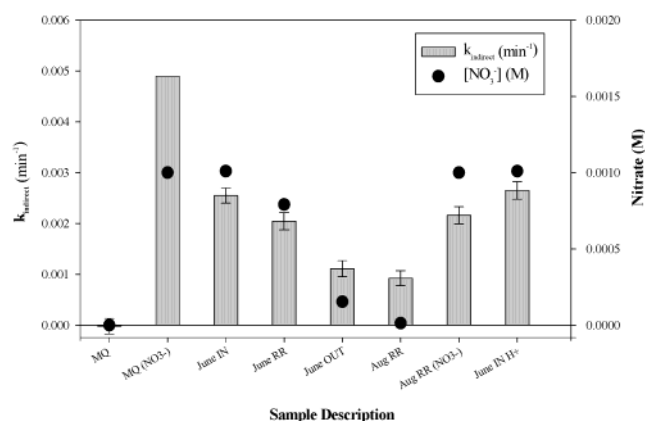

Figure 7. Correspondence of nitrate level to the indirect photolytic rate coefficient for carbaryl degradation in the pH-adjusted samples. Plot shows the spatial and temporal trends of nitrate levels. Error bars represent the propagated error (95% CI).
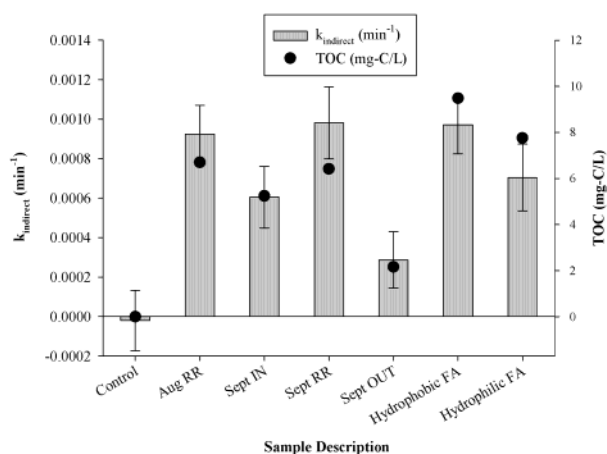

Figure 8. Comparison of the indirect photolytic rate coefficient for the degradation of carbaryl in low nitrate (<50 mM), pH-adjusted OWC samples. Hydrophobic and hydrophilic samples were obtained by dissolving XAD-8 and -4 isolates in buffered Milli-Q water. Error bars represent the propagated error (95% CI).

though they have significantly less nitrate (**Figure 8**). The September outlet sample showed the least light-promoted degradation and contained the least amount of nitrate and TOC (**Table 1**).

Possible reasons for the large range of reactivity in the pH-altered samples should be interpreted within the context of the water samples. Analysis of the surface water revealed at least

two classes of constituents that may act as photosensitizers: nitrate and natural organic matter. Multiple regression of the lower pH data indicated a significant relationship between k_{obs}, TOC, and nitrate level [k_{obs} (min^{-1}) = 1.67[NO$_3^-$] + 1.27 × [TOC M−C/L] + 1.95 × 10^{-4}; n = 12; R^2 = 0.97). Although this relationship provides no information regarding the mechanisms of the indirect photolysis, it does show that the rate of reaction of carbaryl is positively correlated to the levels of both nitrate and NOM present in the natural water samples.

Nitrates as Photosensitizers. Control photolysis experiments were performed to confirm the influence of nitrate photochemistry on the photoinduced degradation of carbaryl in our samples. Photoreactions were performed in phosphate-buffered ([PO$_4^{3-}$]$_T$ = 3.0 mM; pH 4.35) Milli-Q water. At this pH, H$_2$PO$_4^{2-}$ phosphate is not predicted to be an important quencher of HO$^\bullet$ with a reported rate constant of 1 × 10^5 M^{-1} s^{-1} (29). In these "clean" experiments, the effect of adding 1.0 mM nitrate to the solution enhanced the photolytic reaction by a factor of 41 compared to the Milli-Q control. Experiments with pH-adjusted OWC water also showed that when a low-nitrate sample (August RR) was "spiked" with NO$_3^-$ to levels observed in the June IN (1 mM), the indirect photolysis component increased to a level similar to that observed in the June IN sample (**Figure 7**). Zepp et al. (17) showed that when the total scavenger concentration was constant for a given water sample, the rate coefficient measured for the nitrate-induced photooxidation of nitroanisole and nitrobenzene was directly proportional to the amount of nitrate added. Assuming that a similar linear relationship exists in this experiment, we attribute 57% of the overall observed rate coefficient to a nitrate-promoted process by subtracting the $k_{indirect}$ of the reaction *without* the added nitrate from that measured for the reaction performed in the nitrate-spiked water. This value is similar to that predicted on the basis of the multiple regression for this water, where nitrate photolysis should account for almost 65% of the predicted overall reaction.

Nitrate is capable of producing HO$^\bullet$ with quantum yields ranging from 9 × 10^{-3} to 17 × 10^{-3} when irradiated at wavelengths between 290 and 330 nm (15, 17, 30, 31). Under constant irradiation, the HO$^\bullet$ generated is scavenged by other water constituents, which results in a low, steady-state concentration. Both NOM and carbonate species (HCO$_3^-$ and CO$_3^-$) are important scavengers of HO$^\bullet$ in natural waters (32−35). In considering just the concentrations of nitrate measured in this study [(1.3−1.01) × 10^{-3} M], the production (noonday sunlight at 40° N latitude) of steady-state concentrations of HO$^\bullet$ in the OWC water at the natural pH of the wetland in the presence of these scavengers is predicted to be relatively high ($\sim$10^{-15}−10^{-17} M) (eq 13-62 from ref 33) when compared with that measured in other water bodies ($\sim$10^{-18}−10^{-16} M) (17).

Preliminary calculations (independent of the multiple regression) were performed to ascertain how much of the observed light-promoted degradation of carbaryl in the pH-altered samples was due to nitrate photochemistry. The effect on scavenging by carbonate species is expected to be negligible at the lower pH used in this study. It was assumed that NOM was the dominant HO$^\bullet$ scavenger with a second-order rate constant of 1.4 × 10^4 L/mg-C/s (reported for a similar NOM) (34). The HO$^\bullet$ production rate measured for our photoreactor was found to be 3.1 × 10^{-13} M HO$^\bullet$/s per μM nitrate (36). We estimated the [HO$^\bullet$]$_{ss}$ for all of the water samples at pH 4.3 to range from 4 × 10^{-17} to 3 × 10^{-15} M depending on the levels of nitrate and TOC in the system (**Table 3**). Indeed, White (36) measured steady-state concentrations of 3.0 × 10^{-18} and 1.1 × 10^{-15} M [HO$^\bullet$]$_{ss}$ for low-nitrate (2.6 μM) and high-nitrate (580 μM) OWC

Photoinduced Degradation of Carbaryl

J. Agric. Food Chem., Vol. 50, No. 23, 2002 **6763**

Table 3. Predicted $[HO^\bullet]_{ss}$ for Water Samples Taken from Old Woman Creek (OWC) in June, August, and September of 1998 in the pH-Adjusted Water

sample	pH^a	TOC (mM)	nitrate (mM)	$[HO^\bullet]_{ss}$	k_{pred} (min^{-1})	% k_{pred} of $k_{corrected}$
inlet						
June	4.37	0.595 $(0.072)^b$	1.01	3.1×10^{-15}	6.4×10^{-4}	24
Sept	4.32	0.436 (0.033)	0.0274	1.2×10^{-16}	2.3×10^{-5}	3.2
railroad						
June	NA^c	0.588 (0.089)	0.790	2.5×10^{-15}	5.1×10^{-4}	23
Aug	4.37	0.558 (0.120)	0.0131	4.3×10^{-17}	8.8×10^{-6}	0.8
Aug^d	4.35	0.558 (120)	1.01	3.3×10^{-15}	6.7×10^{-4}	29
Sept	4.31	0.534 (0.072)	0.0295	1.0×10^{-16}	2.1×10^{-5}	1.8
outlet						
June	4.34	0.514 (0.310)	0.154	5.5×10^{-16}	1.1×10^{-4}	9.0
Sept	4.31	0.181 (0.078)	0.0185	1.3×10^{-16}	3.8×10^{-5}	9.0

^{a} Average pH measured in samples. ^{b} Values in parentheses represent %CV for replicate samples. ^{c} Data not available. ^{d} Sample spiked with nitrate to a level of 1 mM.

water samples, respectively. These values are comparable to the calculated values of 5.3×10^{-18} and 1.6×10^{-15} M for these specific samples and corroborates our estimates for our water samples.

Using the reported $HO^\bullet$ bimolecular rate constant of 3.4×10^9 M^{-1} s^{-1} for carbaryl (*7*), we predicted that reaction of carbaryl with $HO^\bullet$ generated from NO_3^- photolysis alone should account for <1−24% of the overall photolysis at pH 4 (**Table 3**). Similarly, when applied to the control experiments performed with the August RR water (low nitrate containing OWC water spiked with nitrate to a level of 1 mM), only 29% of the rate coefficient could be accounted for by nitrate-promoted processes (**Table 3**). Although this is less than the expected impact (a 57% contribution), it is still reasonable given the uncertainties in the NOM-scavenging rates and the second-order rate constant for the carbaryl hydroxyl radical reaction. For example, Westerhoff et al. (*37*) reported a range of k_{DOC} values for various NOMs that differed by as much as a factor of 3 and correlated reactivity to the origin of the NOM material. These variations could result in 1−3 times difference in calculated half-lives for a contaminant of interest.

Natural Organic Matter. Our multiple regression analysis indicated that NOM plays an important role in carbaryl photodegradation. In the low nitrate containing samples (September and August), up to 73% of the light-promoted degradation could be attributed to NOM. Furthermore, even though there was 2 orders of magnitude less nitrate present in the September and August samples in comparison with the June samples, there was not a corresponding decrease in the measured photolysis rate. These results support the theory that NOM is both an important photosensitizer and a scavenger of reactive intermediates and photons (*3, 4, 8, 10, 11, 13, 32, 38*), resulting in very low steady-state concentrations of reactive species in natural surface waters (*39*).

The observed NOM photoenhancement could be due to several possibilities including (1) NOM triplet states reacting with ground-state carbaryl through energy or electron-transfer processes (*8, 10−12*); (2) excited-state NOM reacting with oxygen to form reactive oxygen species (ROS) that, in turn, react with carbaryl; (3) carbaryl forming charge-transfer (CT) complexes with NOM; or (4) the interaction of metals (associated with organic ligands or free species in the water column) in promoting Fenton- or photo-Fenton-type chemistry.

CT complexes result in an association that could cause a red shift in the absorption spectrum of carbaryl. After excitation,

electron transfer would be facilitated by the proximity of the donor (carbaryl) and acceptor (NOM) and result in the degradation of the carbaryl. Such a complex could explain observations of fluorescence quenching of carbaryl by NOM (*40*); however, Wenska et al. (*41*) reported weak carbaryl CT complexes in the ground state with nucleic acids. These workers observed that the fluorescence quenching due to the formation of CT complexes (static quenching) was minimal in comparison to that occurring through dynamic processes. Dynamic quenching could be an alternative explanation for the results observed by Fang et al. (*40*), who did not measure fluorescence lifetimes for their experiments.

Although the possibility exists that CT complexes may influence the reactivity of carbaryl with NOM, we doubt that the interaction occurs via partitioning to the NOM phase. If one considers reported literature values for K_{OC} measured for soil organic matter (229−575 L/kg) (*42*), the K_{DOC} (the partition coefficient between carbaryl and NOM) values should be smaller, and as a result, a negligible amount of carbaryl would be bound to the NOM phase. To illustrate this point, we used the highest K_{OC} determined from soil organic matter (575 L/kg) and estimated that *at most* 0.4% of the carbaryl is associated with the organic matter levels measured in the natural water samples. Thus, it appears highly unlikely that CT complexes play an important role.

The observed promotion in the degradation of carbaryl by NOM at low pH most likely results from metal mediation and/or the photoproduction of ROS. An argument can be made that trace metals, free and associated with organic matter, could be the primary photoreactive reagents present in solution. The observed pH dependency is consistent with the literature, where numerous photochemical processes were promoted by free and/or complexed iron (*43−47*).

To test the role of iron or other trace metals in these reactions, the most reactive water, the June inlet water, was passed through a column packed with a cation-exchange resin (proton saturated) to remove any free or weakly complexed (labile) metals from the water sample. The effluent (June IN H+) was collected, and the pH of the effluent was raised to 4.35. Some of the NOM was lost to the resin (~16%), but we observed no change in nitrate levels. In the case that free or labile metals were responsible for the observed reaction in the original sample, the removal of these species from the water should result in sample that would exhibit decreased reactivity in the photodegradation of carbaryl. No statistically significant difference was found between our reported k_{obs} for this sample and that observed for the pH-adjusted June inlet sample (**Figure 7**). When k_{obs} is normalized to the TOC, however, the photoenhancement in the June IN H+ sample is 24% higher than that in the June inlet sample. Thus, it appears that "free or labile" metals do not play an important role in these experiments. Indeed, the increase in reactivity could be caused by the removal of additional NOM that could have scavenged photolytically generated ROS. Finally, control experiments using XAD-8/4 OWC isolates, that is, the fulvic acid components of the NOM phase, showed the same level of photoenhancement as samples containing low nitrate. These results corroborate the H+-saturated raw water experiments because the isolation method removes all free and labile metals (*48, 49*).

NOM and nitrate in conjunction acted as photosensitizers that resulted in the indirect photolytic degradation of carbaryl. We suspect that the principal pathway occurs through the generation of ROS, which in turn are capable of reacting with the target pesticide. The identities of these ROS are unknown, but on the

6764 *J. Agric. Food Chem.,* Vol. 50, No. 23, 2002

Miller and Chin

basis of previous work by others (*7, 15, 50*), we believe that OH$^\bullet$ may be an important phototransient. Although we have demonstrated that free and labile metals do not appear to play an important role, this does not rule out the possibility that strongly bound metals are more photoreactive. This role of strong metal−NOM complexes needs further investigation.

ACKNOWLEDGMENT

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Photoinduced Degradation of Carbaryl

J. Agric. Food Chem., Vol. 50, No. 23, 2002 **6765**

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