# Atrazine Photolysis: Mechanistic Investigations of Direct and Nitrate-Mediated Hydroxy Radical Processes and the Influence of Dissolved Organic Carbon from the Chesapeake Bay

ALBA TORRENTS,<sup>†</sup> BRENT G. ANDERSON,<sup>†,‡</sup> SUSANNA BILBOULIAN,<sup>†,‡</sup> W. EDWARD JOHNSON,<sup>‡</sup> AND CATHLEEN J. HAPEMAN<sup>\*,‡</sup>

Environmental Engineering Program, Department of Civil Engineering, University of Maryland, College Park, Maryland 20742, and Environmental Chemistry Laboratory, Natural Resources Institute, Agricultural Research Service, U.S. Department of Agriculture, Beltsville, Maryland 20705

Direct and nitrate-mediated hydroxy radical photoprocesses were examined with respect to atrazine

(2-chloro-4-ethylamino-6-isopropylamino-s-triazine) transformation. Irradiation ( $\lambda > 290$  nm) of aqueous solutions of atrazine in the presence of nitrate, which generates •OH, yielded 20% of 6-amino-2-chloro-4-isopropylamino-s-triazine (CIAT), 10% of 6-amino-2-chloro-4-ethylamino-s-triazine (CEAT), 6% of 4-acetamide-2-chloro-6-isopropylamino-striazine (CDIT), 3% of 4-acetamide-2-chloro-6-ethylaminos-triazine (CDET), 16% of chlorodiamino-s-triazine (CAAT), and 3% of hydroxy atrazine (OIET, 4-ethylamino-6-isopropylamino-2-hydroxy-s-triazine) at 87% atrazine conversion. Direct photolysis of atrazine was much slower and at 23% atrazine conversion gave rise to 14% OIET and ca. 9% of chloroalkyloxidized or chlorodealkylated compounds with the ratio of the reaction rate constants equal to 0.14 (k<sub>direct</sub>/ kindirect). Results also suggest that OIET was not the product of a hydroxy radical process. The efficiency of the hydroxy radical process decreased more than 85%, with increasing DOC obtained from the surface layer of the Chesapeake Bay. However, only a slight decrease (<15%) in efficiency was observed for direct photolysis, suggesting that in the presence of surface layer DOC direct photolysis may become more important relative to the •OH processes.

## Introduction

The environmental fate of pesticides is determined by various transport and transformation processes. Solar irradiation can initiate important transformation pathways in the atmosphere and at the soil and water surfaces via direct or indirect processes (1-3). In direct photolysis, the substrate absorbs UV–visible light energy and undergoes transformation,

whereas during indirect photolysis a species other than the substrate absorbs the light. The excited species can then transfer the energy directly to the substrate (sensitization), undergo electron transfer with the substrate, or cause a series of reactions with the subsequent formation of oxidants such as singlet oxygen, hydroxy radical, and alkylperoxy radicals (4-9).

Irradiation of nitrate, which is present in many natural waters, has been shown to give rise to 'OH (6, 9-11). The concentrations of nitrate in the Chesapeake Bay (located in the Mid-Atlantic region of the United States) fluctuate seasonally and spatially and are moderated by biological and chemical processes with influences from anthropogenic activities. For example, in the Wye River, an Eastern Shore tributary of the Chesapeake Bay, nitrate levels range from <14  $\mu$ M NO<sub>3</sub> during May through August up to 100  $\mu$ M NO<sub>3</sub> in January (*12, 13*). Nitrate concentrations at midbay were observed at 36  $\mu$ M NO<sub>3</sub> in January 1991 and 0.3  $\mu$ M NO<sub>3</sub> in August 1991 (*14*).

Atrazine (CIET, Table 1) is a widely used herbicide in many regions of the United States and is commonly found throughout the entire hydrological cycle. Concentrations of atrazine in the Chesapeake Bay and its 3000 square miles of watershed have at times exceeded the U.S. EPA maximum contaminant level of 0.01  $\mu$ M during the spring and early summer (*15*). Atrazine has also been observed in other surface waters. For example, average levels of 0.02  $\mu$ M have been found during post-planting season in streams of the midwestern United States (*16*) and up to 0.002  $\mu$ M in a Swiss lake (*17*).

Many reports have been published describing the photolysis of atrazine (18-23). Dechlorination, dealkylation, and alkyl chain oxidation have all been observed in these studies. The resulting products OIET, OEAT, OIAT, CEAT, CIAT, and CDIT have also been observed in surface waters and rainwater (24-28). However, the differences in direct versus photoinitiated hydroxy radical processes have not been thoroughly described. This lack of mechanistic understanding has led to some confusion in describing the processes causing the appearance of these products in the environment. For example, the appearance of the dechlorination product OIET has recently been attributed to a hydroxy radical process (24, 25) but in a non-photolytic hydroxy radical system, OIET was not observed (29, 30).

The aim of this work is to evaluate and discern the mechanisms involved in the photolytic fate of atrazine. Direct and indirect photolysis, using nitrate as a precursor for 'OH, and the products of these processes will be elucidated and compared to other hydroxy radical processes. The relative rates of the different mechanisms will be determined so as to more accurately evaluate the impact of each on the overall fate. In addition, dissolved organic carbon (DOC) not only can serve as a hydroxy radical scavenger but also can absorb UVlight (5-9). The influence of DOC on the various processes will also be examined. The DOC used in this study was obtained from the surface layer of the Chesapeake Bay since phototransformation and photoinitiated 'OH processes are most likely to occur in the upper portion of surface waters.

## Materials and Methods

**Standards and Reagents.** Atrazine, CEAT, CIAT, OAAT, OEAT, OIAT, OIET, and OOAT were obtained gratis from Ciba, Plant Protection Division (Greensboro, NC). CAAT and OOOT were purchased from Aldrich (Milwaukee, WI). CDIT, CDET, CDDT, and CDAT were synthesized according to procedures discussed previously (*29*). Ultra-purified water (18 MΩ/cm,

<sup>\*</sup> Corresponding author e-mail: chapeman@asrr.arsusda.gov; fax: (301)504-5048.

<sup>&</sup>lt;sup>†</sup> University of Maryland.

<sup>&</sup>lt;sup>‡</sup> U.S. Department of Agriculture.

#### TABLE 1. List of Triazine Compounds

acronym	compound
CAAT	chlorodiamino-s-triazine
CDAT	6-amino-4-acetamido-2-chloro-s-triazine
CDDT	2-chloro-4,6-diacetamido-s-triazine
CDET	4-acetamido-2-chloro-6-ethylamino-s-triazine
CDIT	4-acetamido-2-chloro-6-isopropylamino-s-triazine
CEAT	6-amino-2-chloro-4-ethylamino-s-triazine
CIAT	6-amino-2-chloro-4-isopropylamino-s-triazine
CIET	atrazine (2-chloro-4-ethylamino-6-isopropylamino-s- triazine)
OAAT	ammeline (diaminohydroxy-s-triazine)
OEAT	4-ethylamino-6-amino-2-hydroxy-s-triazine
OIAT	6-amino-4-isopropylamino-2-hydroxy-s-triazine
OIET	hydroxy atrazine (4-ethylamino-2-hydroxy-6- isopropylamino-s-triazine)
00AT 000T	ammelide (aminodihydroxy-s-triazine) cyanuric acid (trihydroxy-s-triazine)





Modulab, Type I HPLC, Continental Water System Corp., San Antonio, TX) was used in all dilutions except as indicated.

Collection and Analysis of DOC. Samples of DOC were obtained near the mouth of Patapsco River in the upper bay from the bow of the R/V Aquarius, University of Maryland, in September 1993 using 47 cm<sup>2</sup> stainless steel wire screens attached to nylon lines. This technique generally collects the top 100–450  $\mu$ m (31). The screens were lowered to the water surface, retrieved, and drained into a 4-L stainless steel pressure filtration can (Millipore, Milford, MA). The 4-L can was subsequently pressurized with nitrogen gas (10 psi), forcing the contents through a 90-mm-diameter stainless steel filter head (Millipore) containing three stacked filters in the following order: Whatman GF/D (nominal 1.7  $\mu$ m pore size pre-combusted at 450 °C, glass fiber), Whatman GF/F (nominal 0.7  $\mu$ m pore size pre-combusted glass fiber), and a 0.45-µm pore size silver membrane filter (Hytrex Filter Division, Osmonics, Inc., Minnetonka, MN). The filtrate was collected in a 4-L brown glass bottle, stored on ice, and transported back to the laboratory for analysis.

DOC concentrations were measured on an Oceanographic International Model 700 total organic carbon analyzer (College



FIGURE 1. Product profile of direct photolysis of 30  $\mu$ M atrazine. Each data point represents an average of three experiments with duplicates; standard deviations are <0.2  $\mu$ M.



FIGURE 2. Comparison of atrazine (30  $\mu$ M) degradation: (1) direct photolysis (no nitrate or *t*-butanol), (2) indirect photolysis (804  $\mu$ M nitrate, no *t*-butanol), (3) direct photolysis with •OH quenched (30 mM *t*-butanol, no nitrate), (4) indirect photolysis with •OH quenched (804  $\mu$ M nitrate and 30 mM *t*-butanol).

Station, TX) using the persulfate oxidation method (*32*). Several different samples were analyzed in triplicate, and the sample with the highest concentration (5.3 ppm DOC) was used in all experiments. UV spectra of the isolated DOC as well as atrazine and atrazine with nitrate were obtained on a Shimadzu UV160 UV/vis recording spectrophotometer (Columbia, MD). The UV spectrum of DOC (5 ppm) showed a typical maximum at 205 nm (0.8 au) which rapidly decayed to 225 nm (0.08 au) with some tailing to 350 nm (<0.01 au).

**General Procedure for Photolytic Experiments.** Photolytic studies were conducted using a Suntest CPS machine (Heraeus DSET Laboratories, Inc., Phoenix, AZ) equipped with a xenon lamp and special glass filters restricting the transmission of wavelengths below 290 nm. An average irradiation intensity of ca. 450 W/m<sup>2</sup> was maintained throughout the experiments and was measured by internal radiometer, which was calibrated annually by the manufacturer. Chamber and black panel temperature were monitored using thermocouples supplied by the manufacturer; the temperature of samples was maintained at room temperature. Solutions were irradiated in identical 15-mL quartz tubes sealed with Teflon caps. Initial pH was ca. 6.5 and did not change over the course of the reaction. (The pH of the Chesapeake Bay ranged from 6.5 to 7.2.) In some experiments, samples were





FIGURE 3. Product profile of indirect photolysis of 30  $\mu$ M atrazine (804  $\mu$ M nitrate present). Each data point represents an average of three experiments with duplicates; standard deviation are <0.2  $\mu$ M. To make the figure clearer, OEAT and OIAT have been excluded as they were formed and did not accumulate to quantities more than 0.02  $\mu$ M.

purged prior to irradiation with argon for ca. 15 min to remove oxygen. Approximately  $200 \,\mu$ L of each solution were removed at selected intervals and analyzed by HPLC. Irradiations were carried out for ca. 60 h.

**Photolytic Experiments with Atrazine.** Concentrations of nitrate and atrazine in the mainstem of the Chesapeake Bay range from 0.3 to 100  $\mu$ M and from 0.005 to 0.01  $\mu$ M, respectively (*12–15*). This is very near the limit of detection by HPLC for the triazines, which is the preferred analysis method for many of the transformation products. Therefore, experiments were conducted at higher than normal levels while maintaining an excess of nitrate to triazine and at similar ratios to that found in the Chesapeake Bay. A stock solution of atrazine was prepared by adding 32.4 mg of atrazine to 1 L of ultra-pure water. A total of 250 mL was removed and

amended with 85.7 mg of NaNO<sub>3</sub>. These two stock solutions and a third stock solution of 5.3 ppm DOC were used to prepare samples for irradiation. Final concentrations were 30  $\mu$ M atrazine, 0 or 800  $\mu$ M NaNO<sub>3</sub>, and 0–4.2 ppm DOC. Duplicate samples were irradiated, and each experiment was conducted several times. In some experiments, final solutions contained 30  $\mu$ M atrazine, 0 or 800  $\mu$ M NaNO<sub>3</sub>, 3 or 30 mmol of *tert*-butanol to serve as a 'OH scavenger, and no DOC.

**Photolytic Experiments with CEAT and CIAT.** Stock solutions of CEAT, CIAT, and NaNO<sub>3</sub> were prepared by adding 4.8, 6.2, and 66.1 mg, respectively, to 500 mL of deionized water. Dilutions were prepared, affording samples that contained 33  $\mu$ M CIAT; 33  $\mu$ M CIAT with 800  $\mu$ M NaNO<sub>3</sub>; 28  $\mu$ M CEAT; and 28  $\mu$ M CEAT with 800  $\mu$ M NaNO<sub>3</sub>. Duplicate samples of all four dilutions were irradiated. In another set of experiments, dilutions resulted in two solutions: the first containing 26  $\mu$ M CIAT, 28  $\mu$ M CEAT, and 800  $\mu$ M NaNO<sub>3</sub>. Duplicate samples were irradiated.

**HPLC Analysis.** Irradiated samples were analyzed directly by HPLC employing two Gilson Model 303 HPLC pumps (Middleton, WI) equipped with a Gilson Model 116 UV detector (210, 225, and 235 nm monitored). Separations were achieved using a sequence of linear gradients, 0% (4 min), 0-12% (3 min), 12-60% (5 min), and 60% (7 min) acetonitrile in phosphoric acid buffer (pH 2) at a flow rate of 1.5 mL/min on a Beckman C-18 (ODS, 5  $\mu$ m), end-capped, 4.6 mm × 25 cm steel-jacketed column. Identification was established by comparison of the retention times and the UV spectra obtained using the above gradient and a second LC system: two Waters 510 pumps (Milford, MA) equipped with a Waters 996 photodiode array detector, a 712 autosampler, and Waters Millennium software.

#### Results

**Direct Photolysis of Atrazine.** Direct photolysis of atrazine has been shown previously to proceed via excitation of the triazine followed by dechlorination and hydroxylation. Dealkylation of OIET was also observed (Scheme 1) (18-20). Excitation of atrazine in ultra-pure water under simulated



FIGURE 4. Product profile of (a) direct photolysis (no nitrate present) and (b) indirect photolysis (804  $\mu$ M nitrate present) of CIAT. Note different y-axis scales. Each data point represents an average of three experiments with duplicates; standard deviation are <0.2  $\mu$ M.

solar irradiation afforded 14% OIET, 4% CDIT, 1% CIAT, 4% CDET, and <1% CEAT with 76% atrazine remaining (reaction time = 60 h); no hydroxy dealkylated products (OEAT, OIAT, and OAAT) were detected (Figure 1). A solution of 20  $\mu$ M OIET was irradiated under the exact same conditions as atrazine, and no detectable loss of OIET was observed over a 60-h period.

The appearance of the chlorodealkylated (CEAT and CIAT) and chloroalkyloxidized (CDET and CDIT) products was somewhat unexpected since these compounds were the principle products of •OH systems (*20, 22, 23, 29, 30, 33*), although CIAT and CEAT were observed when using acetone as a photosensitizer (*21*). To eliminate •OH as a possible reactant, *t*-butanol, a •OH scavenger, was added to the system. No differences in the product ratio or the rate of atrazine loss were observed between the *t*-butanol system and the system without *t*-butanol (Figure 2). Another possible oxidant is singlet oxygen (*22*); however, no changes in the rate or the product ratios were found when irradiation was conducted on argon-purged solutions.

**Photoinitiated Nitrate-Mediated Hydroxy Radical Process.** Irradiation of aqueous atrazine solutions containing nitrate, in which 'OH is readily generated, afforded alkyl oxidation and/or removal of the alkyl moiety. At 87% atrazine conversion (60-h irradiation), the reaction gave rise to 6% CDIT, 20% CIAT, 3% CDET, 10% CEAT, 1% CDAT, and 16% CAAT (Scheme 2 and Figure 3). Also formed were the dechlorinated compounds OIET, OEAT, and OIAT at 3%, <0.1%, and <0.1%, respectively. During the initial stages of the reaction (i.e., less than 24 h), the products CDIT, CIAT, CDET, and CEAT accounted for over 95% of the atrazine degraded. Over this time period, dealkylation was favored by 1.4 over alkyl oxidation as determined by the ratio of the concentrations of CIAT and CEAT divided by the sum of the concentrations of CDIT and CDET, i.e., ([CIAT] + [CEAT])/([CDIT] + [CDET]). Attack on the ethyl group was 1.7 times as likely to occur as attack on the isopropyl as determined from the ratio ([CIAT] + [CDIT])/([CEAT] + [CDET]).

While several groups observed the formation of OIET in other hydroxy radical systems such as TiO<sub>2</sub> and Fenton's reagent (23, 33), OIET was not observed in non-photolytic ozonation systems (29, 30). To determine if •OH was involved in the formation of OIET, atrazine solutions containing nitrate and *t*-butanol were irradiated and compared to atrazine solutions containing nitrate only (indirect photolysis), t-butanol only (direct photolysis), and neither nitrate nor t-butanol (direct photolysis). Interestingly, as Figure 2 indicates, the rate of atrazine degradation in the nitrate/tbutanol system was the same as the rate of direct photolysis. Furthermore, the product profile of the nitrate/t-butanol system was very similar to the product profile for direct photolysis as presented in Figure 1 (data not shown). This strongly suggests that OIET is the result of a direct photolytic process (i.e., excitation of the triazine) rather than a 'OH product.

**Relative Rates and Reactivity.** Simultaneous irradiation of atrazine with and without nitrate was carried out. The observed rate constants calculated from first-order rate plots were  $0.0040 \pm 0.0006$  and  $0.029 \pm 0.002$  h<sup>-1</sup> (x = 7) for direct and indirect photolysis, respectively, with the ratio of rate constants ( $k_{\text{direct}}/k_{\text{indirect}}$ ) equal to  $0.14 \pm 0.02$  (Figure 2).

To obtain additional mechanistic information, CIAT and CEAT were irradiated with and without nitrate, separately and together. Essentially no differences in the rates of degradation or the product ratios were observed between the reactions conducted in separate tubes and those in the same reaction vessel. Direct photolysis of CIAT at 24% conversion afforded 10% OIAT, 1% CDAT, and 5% CAAT while



FIGURE 5. Product profile of (a) direct photolysis (no nitrate present) and (b) indirect photolysis (804  $\mu$ M nitrate present) of CEAT. Note different y-axis scales. Each data point represents an average of three experiments with duplicates; standard deviation are <0.2  $\mu$ M.



FIGURE 6. CEAT versus CIAT degradation without (direct photolysis) and with nitrate (indirect photolysis).

direct photolysis of CEAT at 24% conversion gave rise to 5% OEAT, 1% CDAT, and 5% CAAT. Photolysis of CIAT in the presence of nitrate gave rise to 2% CDAT, 43% CAAT, and 5% OIAT at 60% conversion, while irradiation of CEAT in the presence of nitrate at 77% conversion afforded 7% CDAT, 55% CAAT, and 2% OEAT (Figures 4 and 5). The observable rate constants were calculated from first-order rate plots:  $k_{\text{CEAT}}$ , direct =  $k_{\text{CIAT}, \text{ direct}} = 0.004 \text{ h}^{-1}$ ,  $k_{\text{CEAT}, \text{ indirect}} = 0.026 \text{ h}^{-1}$ , and  $k_{\text{CIAT}, \text{ indirect}} = 0.016 \text{ h}^{-1}$  (Figure 6). Again, attack at the ethyl carbon was favored 1.6 over the isopropyl.

**Effect of DOC.** The effect of surface layer DOC on direct and indirect atrazine photolysis was examined using various concentrations of DOC. The product profile of direct photolysis was very similar to that obtained in the absence

irradiation versus 1.4 in the absence of DOC. At this same point, the ratio dechlorination/(dealkylation + alkyl oxidation) was 0.15 as compared to 0.029 in the absence of DOC. This provides further evidence that OIET formation is not a hydroxy radical process. A plot of ln *k* versus ln [DOC], where *k* is the observed rate constant from first-order rate plots, clearly indicated the dependence of indirect photolysis on the [DOC];  $k_{4.2 \text{ ppm DOC}}/k_{no DOC} = 0.20$  (Figure 7). Direct photolysis was affected less by the increase in concentration of surface layer DOC;  $k_{4.2 \text{ ppm}}$ 

of DOC. In the nitrate and DOC system, alkyl oxidation was

favored over dealkylation, and the relative ratio of dechlorination byproduct (OIET) to all other products increased.

For example, in the presence of nitrate and 3.2 ppm DOC, the

ratio of dealkylation to alkyl oxidation was 0.67 at 24-h

### Discussion

 $poc/k_{no DOC} = 0.83.$ 

The ratio of products formed upon direct and indirect irradiation are significantly different. Results from this study strongly suggest that the formation of OIET is not a hydroxy radical process. This further implies that the observation of OIET in surface waters is due to the absorption of light energy by atrazine itself (direct photolysis), photosensitization, metalassisted hydrolysis or biotic processes. In addition, since no effect was observed on direct photolysis degradation rate relative to ethyl or isopropyl substitution, the rate-determining step must not involve the alkyl group, further supporting that dechlorination is the major degradation pathway in direct photolysis. And, the rate-determining step in the photoinitiated nitrate-mediated hydroxy radical system must therefore involve the alkyl group for exactly the opposite



FIGURE 7. Effect of DOC concentration (ppm) on atrazine degradation with (direct photolysis) and without nitrate (indirect photolysis), where k (h<sup>-1</sup>) is the observable rate constant from first-order rate plots.

reason—a difference was observed in the rate of degradation between CEAT and CIAT. These data also suggest that a sterically controlled mechanism is operational in the 'OH process rather than an electronically controlled one, because the more hindered isopropyl hydrogen was less reactive than ethyl (*34*). In an electronically controlled mechanism, attack at the isopropyl would be more favored since the C–H bond of the CH(CH<sub>3</sub>)<sub>2</sub> is somewhat weaker than the C–H bond of CH<sub>2</sub>CH<sub>3</sub> (*30*).

In the presence of nitrate, where 'OH are readily formed, faster degradation of atrazine was observed as compared to direct photolysis in distilled water. Natural waters, however, generally contain significant concentrations of DOC. In other studies, the rate of direct photolysis of atrazine was found to increase 3-fold when conducted in the presence of humic acid with a concomitant increase in deamination presumably through photosensitization (*35*). The addition of humic material was shown not only to increase the rate of atrazine photolysis and the rate of OIET formation but also to increase dealkylation and alkyl oxidation, indicating both an increase in photosensitization and an increase in 'OH processes (*36*).

In the current study, indirect photolysis decreased substantially whereas only a slight decrease was observed in the direct photolysis reactions with increasing DOC concentration. These data, in contrast with the earlier studies, indicate that the DOC in this study does not effectively compete with atrazine for UV light but does efficiently scavenge 'OH. Indeed, the UV spectrum shows that DOC from the surface layer does not effectively absorb UV light, indicating low aromatic or conjugated character. This further suggests that a significant concentration of structural components susceptible to hydroxy radical attack, such as alkyl hydrogens, maybe present in this DOC.

This study demonstrates that much knowledge can be obtained by determining degradation products, their relative ratios, and the mechanisms that lead to their formation. DOC concentration and presumably the type of functional groups and aromaticity present in the DOC will also influence the photoprocesses differently. Clearly, in this study direct photolysis becomes more important while 'OH processes contribute less to the photolytic fate of atrazine as surface layer DOC concentrations increase, but this was not the case for all types of DOC. Thus, to predict accurately the photolytic fate of atrazine and other organic pollutants in surface water, the differences in direct versus indirect processes should be delineated as well as the influence of diverse structural properties of DOC.

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