

Protecting Public Health – UV Disinfection of Drinking Water
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Introduction

Atrazine

Atrazine is an s-triazine solid organic herbicide used for weed control throughout the mid-western United States. It is the most widely used herbicide in the U.S. It is used under a variety of names including Weedex A and Primatol and Candex. Its potential health effects are numerous. Short-term effects include low blood pressure, muscle spasms, weight loss, congestion of heart, lungs, and kidneys, and even adrenal gland damage. Long-term health effects can be severe. They include retinal and muscle degeneration, cardiovascular damage and potentially cancer. (Ground)

The Office of Pesticide Programs of the USEPA has recently downgraded atrazine from a “possible” to a “not likely” human carcinogen. (USEPA) While atrazine is applied mainly in the mid-west, it is detected in drinking water throughout the United States. Rivers, rain, and fog transport it.

The US EPA has set regulations regarding atrazine. The regulations in the US were set at 3 ug/L as an average annual concentration in 1991. A one-day health advisory level of 100 ug/L has also been set. Average concentrations in water vary from season to season. From 1993 to 1998 the maximum seasonal mean was at 61.6 ug/L and the average annual levels were 18.9 ug/L. (USEPA) These values are above the USEPA regulations and therefore the surface and ground water must be treated. The US EPA has approved of granular activated charcoal as a treatment method. (Ground) Irradiation by Ultra Violet light is also a promising technology on target to be approved by the EPA in the near future. In addition to degrading organics, UV light has successfully deactivated *Cryptosporidium* oocysts and *Giardia* oocysts and leaves no disinfection byproducts that are often a problem in highly chlorinated water. For these reasons, it is currently highly researched for drinking water treatment. (Dussert)

Ultraviolet Light

Ultraviolet light includes UVA (320-400 nm), UVB (280-320 nm) and UVC (200-280 nm). The UVC range is deemed the germicidal range because it is able to inactivate viruses and bacteria. Photochemical reactions occurring with the organic pesticides can only take place if the UV light is absorbed. The amount of light absorbed by the solution is given in the following equation.

Equation: $F_{\lambda} = 1 - T_{\lambda}$

where...

F_{λ} = The fraction of light absorbed at a wavelength

T_{λ} = transmittance at a wavelength

To find the amount of light absorbed by a specific component of the solution the following equation is utilized.

$X_i = (e_i c_i) / a$ where...

X_i = The fraction of light absorbed by a specific substance

ϵ_i = the substance's molar absorption coefficient
 c_i = concentration of the substance
 a = total absorption coefficient

From there, it is necessary to determine the rate of the photochemical reaction. This is given by the following equation.

$$R_c = G F_c \phi_c / V \quad \text{where...}$$

R_c = rate of the photochemical reaction of a component

G = photon flow

F_c = fraction of light absorbed by the component

ϕ_c = quantum yield

absorbed photons that result in a chemical reaction of the component / total absorbed photons

V = Volume of Reactor

In low concentrations, the rate constant follows first order kinetics. This equation can be used to solve for the quantum yield.

$$K_1 = (G \phi_c / V) * \ln(10) \epsilon_i l$$

Ultra-violet light can degrade atrazine directly and indirectly. Directly, the UV light energy reacts with organics degrading them into byproducts. Indirectly, the UV light reacts with an oxidant such as hydrogen peroxide, forming OH radicals. The OH radicals then oxidize organics degrading them into byproducts. The ideal end products of the oxidation are carbon dioxide, water, and mineral acids. (Bolton, p.16-17)

Previous Research

In deciding what variables would be tested and what methods would be effective, the literature on atrazine and ultraviolet degradation was researched. Numerous studies relevant to this research involved the use of natural sunlight, UV light, numerous oxidants, and variables such as pH, water quality, and temperature.

Natural Sunlight:

Numerous studies have investigated the effect of light and hydroxyl radicals on atrazine degradation. As described above, light can directly degrade atrazine. It is of interest to research the effect of natural sunlight on the degradation of herbicides. Water in the natural environment such as in lakes and rivers will be degraded at a slow rate due to solar light. Pelizzetti et. al. (Identification) degraded 3 2-chloro-s-triazine herbicides including atrazine with TiO₂ under solar light and UV light with near solar wavelengths of 300-800 nm (Photocatalytic).

Other OH radicals with UV:

In addition to direct photolysis, numerous studies were conducted with indirect photolysis. Ozone was added to the solution in research by both Adams et. al. and Acero et. al. Beltran et. al. used hydrogen peroxide as an oxidant with a low-pressure mercury

vapor lamp. Hydrogen peroxide was also used by Chan et. al. who found an increase in degradation of atrazine with the hydrogen peroxide.

Combinations of oxidants were used in numerous studies. Pratap et. al. degraded atrazine in a bench-scale Fenton electrochemical system. Hydrogen peroxide produced hydroxyl radicals when reacting with electro-chemically generated ferrous iron. UV light was also used in the degradation process. It was found that adding hydrogen peroxide in smaller doses over a period of time was more successful in degrading the atrazine than adding it all at once in the beginning.

Zwiener et. al. used UV, O₂ and ozone in the combinations of UV/O₂ and UV/O₂/O₃ to degrade atrazine and parathion-methyl in a pilot plant for drinking water treatment. The rate of photodecomposition for atrazine was not increased with the UV/O₂/O₃ combination in the pilot plant. Field experiments were also conducted in a large-scale plant. The ozone dose rates were smaller and the residence time shorter than in the pilot plant. A conclusion was reached that as the ozone dose and radiant power increased, the degradation rate increased. In the field plants, a flow rate of 70 m³/h of raw water resulted in a degradation of atrazine below the threshold of .1 ug/L. Medium pressure mercury vapor lamps at 220 to 440 nm were used. Nelieu et. al. used aqueous ozone treatment in conjunction with hydrogen peroxide to degrade atrazine.

pH Effects:

Previous studies such as “Photochemical Processes for Atrazine Degradation: Methodological Approach” by V. Hequet et. al. have found little effect of pH, just a slight increase in efficiency with a pH of 8 vs. pH 6 when using both hydrogen peroxide and titanium dioxide.

Nelieu et. al. found that the amount of degradation was affected by the initial pH of the system using O₃ and H₂O₂. A pH of 7.5 – 8 was found to be optimal because of the higher O₃ and H₂O₂ dissociation rates and therefore higher amounts of OH radicals.

Water Quality:

The influence of water quality was investigated with little observed difference by using natural water versus DI water in the degradation of atrazine by Hequet et. al. Beltran et. al. tested numerous variables including humic substances, which absorb radiation and scavenge hydroxyl radicals, bicarbonate ions, which do not affect the atrazine degradation rate, and the initial concentration of atrazine. Both methods degraded 99% of the atrazine within 15 minutes. The rate was increased with the addition of H₂O₂.

Durand et. al. used both distilled water and artificial seawater with humic acids spiked with .1 ppm atrazine. Methanol was added for solubility reasons. Hydroxyatrazine was broken down in salt but not regular water. A faster degradation occurred in salt water than regular water.

Byproducts:

The degradation by different treatments resulted in different resultant and intermediate byproducts. Some of the degradation byproducts for different treatments in published in the literature follow.

Hequet et. al. found the main products to be hydroxyatrazine and the minor products to be OHDEA and OHDIA when oxidized by *titanium dioxide and UV light*. Nelieu et. al. found ammeline as the major end product and 2 chloro -4, 6 diamino -s-triazine when atrazine was degraded by *aqueous ozone treatment with hydrogen peroxide*. The new intermediate products found were amino-aldehydes and carbinolamine. Acero et. al. found two new imide groups that were products of a given *ozone* process with OH radicals.

When atrazine was degraded with only *ozone*, Zwiener et. al. detected the degradation product desethylatrazine as 30% of the initial atrazine concentration. When used in combination of *UV/O₂/O₃*, no more than 2% of the original concentration was desethylatrazine. The primary degradation product of atrazine from *ozone treatment* was found to be deethylatrazine (CIAT). 7 others were detected including CEAT, CAAT, DIAT, and CDAT. The first condition set up contained zero hydroxyl radicals, a low pH and high alkalinity. The degradation products from this setup were dealkylation byproducts such as amide. The second setup included hydroxyl radical forms, a high pH, low alkalinity and the presence of H₂O₂. Additional s-triazine hydroxy analogues were detected. Temperature was found to not play a role.

Pratap et. al. detected the atrazine degradation products DEIA, DEA, OA, and 2 other unidentified peaks using *Fenton Electrochemical Treatment*. Chan et. al. identified cyanuric acid as the resultant degradation product of atrazine treated with *low pressure UV light and hydrogen peroxide*. Cyanuric acid is less toxic than atrazine and can be removed by charcoal treatment, important to know for water treatment processes. The degradation product deisopropyl was also tested.

From the above literature, there seemed to be a lack of research on the effect of temperature on the degradation of atrazine and the formation of its degradation byproducts with direct and indirect photolysis. There is also limited literature on the use of medium pressure UV light alone and used in conjunction with hydrogen peroxide. We decided to conduct experiments investigating these parameters because we felt there would be an important correlation. The result of this research aids drinking water treatment plants that utilize medium pressure UV light and hydrogen peroxide treatment as well as those plants considering this options. The degradation products formed and the rate they are formed can help decide which process to use depending on the temperature of the water being treated.

Also, when dissolved nitrate in the water is irradiated, it forms OH radicals. These OH radicals oxidize atrazine increasing the rate of degradation. Experiments investigating the effect of nitrate on the degradation of atrazine were conducted using competition kinetics with Octanol. Interesting results were obtained which are out of the scope of this paper.

Materials and Methods

Reagents and Solutions: All chemicals were analytical grade and were used as received. Experiments were conducted in 1mM phosphate buffer at pH 7 with varying amount of H₂O₂. A stock solution of 135 µM atrazine (ATZ) was prepared by adding the solid (Supelco) to deionized water, stirring overnight, and filtering (.45 µm). The stock solution was added into the petri dish for a diluted concentration of 5 uM. A 120 mL solution was made in the petri dish (area = 34.2 cm²).

Photolysis Experiments: Photolysis was performed with a 1 kW medium pressure Hg lamp (ozone-free, Hanovia #6806A441). A Varian Spectrophotometer was used to measure the absorbance of the solution at all times during the irradiation process. The incident irradiance is the sum of all the wavelengths from the MPUV. This is the amount of UV light that reaches the surface of the petri dish. The solution in the petri dish is constantly stirred to homogenize the UV light irradiance throughout the solution. The total average irradiance was the sum of the average wavelengths calculated factoring the spectrophotometer determined absorbance spectrum of the solution. For solution with no hydrogen peroxide, the incident irradiance was approximately 2.5 mW/cm² to produce the average radiance of 2.35 mW/cm². For solutions with hydrogen peroxide, incident irradiance of 2.71 mW/cm² was applied to produce the average radiance of approximately 2.35 mW/cm².

Actinometry: Actinometry and radiometer readings were used to determine the administered UV dose. Reference: Environmental Science & Technology. 2003 ASAP Article DOI: 10.1021/es025814p.

Temperature Control: A HAAKE K20 temperature control (ReFR: R134a) with a copper coil was used as the temperature control apparatus. The model has an immersion bath with circulating cooling. The coil was placed around the petri dish to main constant temperature.

ATZ Analysis: Atrazine was analyzed by C-18 reversed phase HPLC (Prostar system, Varian Scientific Instruments, Inc.) With 50 µL injections, a mobile phase of 50% methanol was increased to 62% linearly over 15 minutes for the 0 ppm H₂O₂. A mobile phase of 20% methanol constant for 4 minutes, then increased linearly to 70% over 15 minutes was used for the 10 ppm H₂O₂ runs. .01M phosphate buffer at a pH of 6 was used with the methanol in all cases. The flowrate in all cases was 1-mL min⁻¹, absorbance detection at 220 nm. These HPLC methods were chosen after working with methods used in the literature and altering them to attain readable peaks on the chromatographs. The ATZ detection limit was 2 nM.

Results and Discussion

Atrazine was first degraded with MPUV as the only treatment. Three degradation byproducts were present and one identified as hydroxyatrazine. First order k constants were determined and Arrhenius plots created to predict effects at varying temperatures.

Atrazine was then degraded with UV light in conjunction with hydrogen peroxide at 10 ppm. First order kinetics were applied and k constants determined for atrazine. The degradation byproducts were looked at and future work will aim to identify and map out their degradation train.

Direct Photolysis

Graph 1 shows the kinetics of atrazine under direct photolysis. Atrazine, at low concentrations, follows pseudo first order kinetics.

$$\ln [ATZ(0)] = \ln[ATZ(t)] + kt \quad \text{where...}$$

ATZ(0)= the initial concentration of atrazine

[ATZ(t)]= the concentration of atrazine at a time t corresponding to a UV dose

k= the pseudo first order rate constant

t*= the time corresponding to a UV dose.

Graph 1: Kinetics of ATZ Direct Photolysis

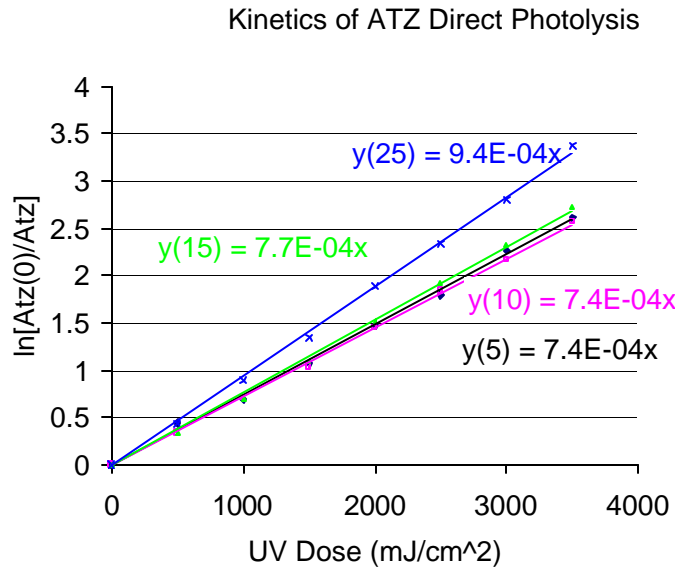


Table 1: k constants for ATZ Direct Photolysis

Temperature (Degrees C)	k (cm ² /mJ)
5	7.4 E-04
10	7.4 E-04
15	7.7 E-04
25	9.4 E-04

Table 1 summarizes the rate constants for the direct photolysis of atrazine at the varying temperatures. These rate constants can now be used to form Arrhenius' Equation.

Arrhenius Equation: $\ln k = A - E_a/RT$ where...

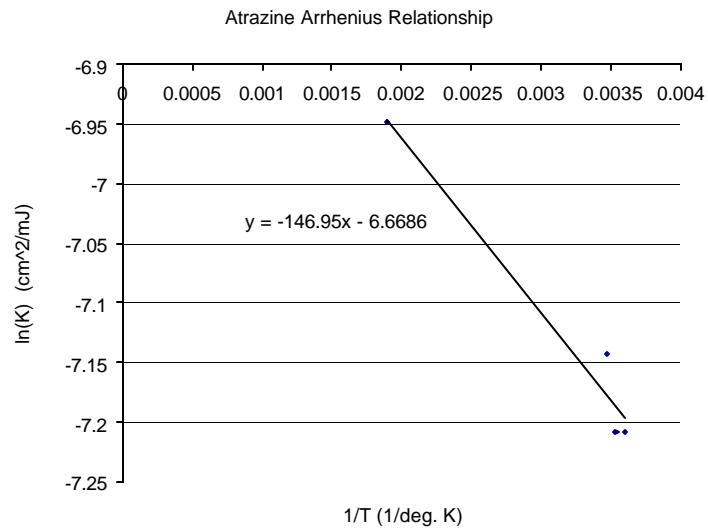
A= pre-exponential factor

E_a = activation energy

R= constant (.0823)

T= temperature in degrees Kelvin.

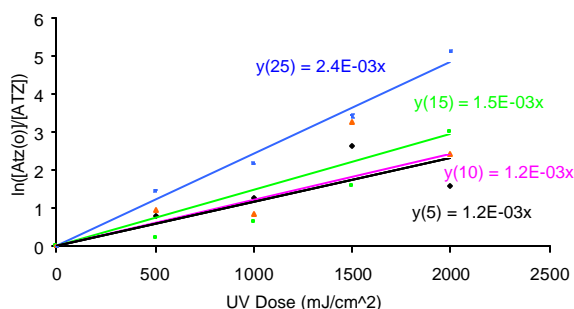
A graph of the $\ln(k)$ vs. $1/T$ produces a linear graph with slope of E_a/R .
Multiplying this by the R constant provides a slope of the activation energy. As shown in the below graph, the slope of 146.95 when multiplied by $R=.08314 \text{ J}/(\text{mol} \cdot \text{K})$ gives an activation energy of 12 J.



Indirect Photolysis

When hydrogen peroxide is irradiated, it is degraded into OH radicals. These OH radicals degrade the atrazine. This process is called indirect photolysis. The rate constant k, determined from the slope of the below graph is a combination of the indirect and direct rate constants. The direct rate constants are actually lower than the rate constants found from the direct photolysis experiments because not all of the light is available for absorption. The hydrogen peroxide in the solution absorbs some of the UV light to form the OH radicals. This absorbed light is therefore not available for the atrazine. The amount of light absorbed by the hydrogen peroxide will be ignored for this

Kinetics of ATZ Photolysis with Hydrogen Peroxide (10 ppm)



research as it is small enough to be deemed negligible.

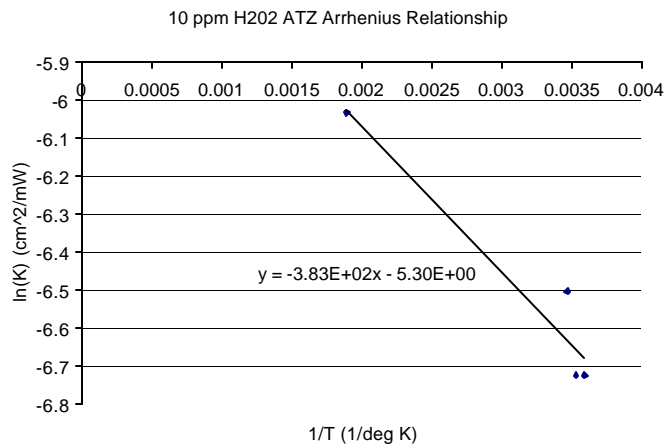
Graph 2 shows the kinetics of atrazine under indirect photolysis. Again, because atrazine is at a low concentration it follows pseudo first order kinetics.

$$\ln [ATZ(0)] = \ln[ATZ(t)] + kt *$$

T (deg. C)	kt	kd	ki
5	12 *10 ⁻⁰⁴	7.4 *10 ⁻⁰⁴	4.6 *10 ⁻⁰⁴
10	12 *10 ⁻⁰⁴	7.4 *10 ⁻⁰⁴	4.6 *10 ⁻⁰⁴
15	15 *10 ⁻⁰⁴	7.9 *10 ⁻⁰⁴	7.1 *10 ⁻⁰⁴
25	24 *10 ⁻⁰⁴	9.6 *10 ⁻⁰⁴	14.4 *10 ⁻⁰⁴

The above table provides a summary of kt: the total rate constant or slope of the above graph, kd: the direct rate constant previously determined from the direct photolysis experiments, and ki: the indirect constant, roughly determined by subtracting the direct rate constant from the total rate constant.

The total rate constant can be used similarly to how the direct rate constant was previously used to form an Arrhenius equation which is a function of temperature. The graph below shows the natural log of the total rate constant versus 1 over the temperature in degrees Kelvin. The negative slope was determined to be 383. This multiplied by the R constant of .08314 J/mol*K provides an activation energy of 32 J.

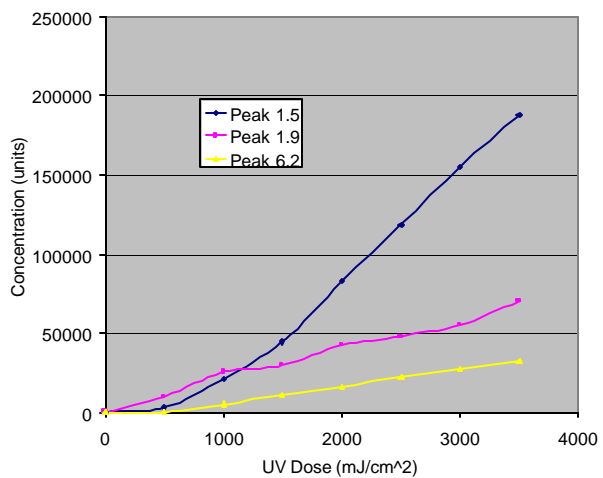


As can be seen from the graphs below, numerous degradation byproducts form when atrazine is oxidized. Some peaks were labeled A and others B. These were given these labels after analyzing their concentration changes with increasing UV Dose. Peaks labeled A increased immediately after the UV was applied and continued to increase throughout the irradiation process. A Peaks are therefore considered to be direct degradation products of the degradation of atrazine by UV light and hydrogen peroxide. Those labeled B have more sporadic changes in concentration. Some of these increase and then decrease. These may be direct degradation products that then degrade again. Some form after a significant amount of UV is applied. These could be secondary products resulting from the degradation of primary degradation products. Further analysis of these peaks is necessary to determine which secondary products arise from which primary products. This is out of the scope of this research but is interesting for future study.

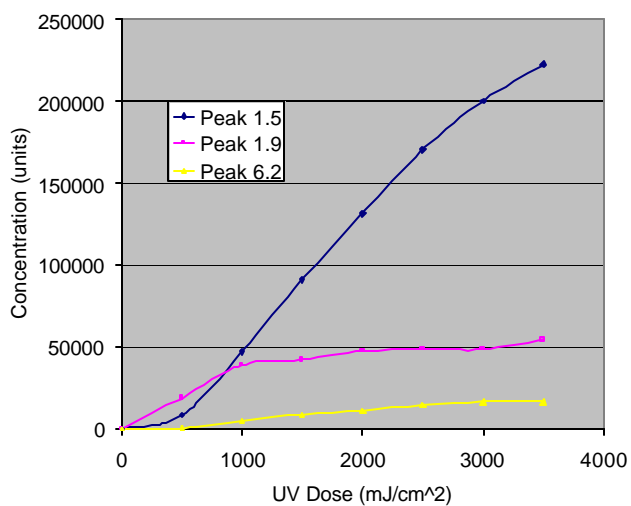
The effect of temperature is noticed on the degradation byproducts. The peaks are shifted slightly to the left and up. This indicates that more degradation byproducts are forming at lower temperatures. This is expected because more atrazine is degraded at these higher temperatures. For example at 5 degrees, Peak 1.5 reaches a concentration of 50,000 units at a UV Dose of approximately 1500 mJ/cm². At 25 degrees C, Peak 1.5 reaches that same concentration of 50,000 units at only 1000 mJ/cm². This indicates that at higher temperatures more degradation byproducts will form.

From a standard, hydroxyatrazine was found to have a retention time of 4.5 min. B Peaks occur at both 4.3 minutes and 4.7 minutes. It is highly likely that one of these is hydroxyatrazine. Another possibility is that hydroxyatrazine split into 2 forming both of the peaks. This can be determined from further analysis of the spectrum of both the 4.3 min and 4.7 min peaks.

5 Deg.C A Peaks



25 Deg. C A Peaks



Conclusions

In this study, atrazine was first degraded directly by Medium Pressure UV light. Hydroxyatrazine was identified as the main degradation product with 2 unknown minor products. The first order kinetic rate constants were determined for atrazine and its main degradation byproduct hydroxyatrazine at a variety of temperatures. These constants were then used in the Arrhenius equation to determine the activation energy of the process.

Next, atrazine was degraded indirectly with OH radicals produced from treatment with hydrogen peroxide and Medium Pressure UV light. HPLC chromatograms showed numerous peaks yet to be identified. It is suspected that either Peak 4.3 or Peak 4.7 or both are hydroxyatrazine. The first order rate constant was determined for atrazine and broken down into its direct and indirect kinetic constants. Arrhenius' equation was used to determine the activation energy. The effect of temperature on the degradation byproducts of atrazine was recognizable. Higher concentrations of the degradation byproducts formed at lower UV doses when irradiated at higher temperatures. This is due to the increased rate of degradation of atrazine at those temperatures. This information could all be used for water treatment plants that utilize MPUV treatment alone or with hydrogen peroxide in part to treat organic pesticides.

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