

# Photodegradation of Atrazine IN WATER



**WATER**  
Waste Water

## Author Details

Hashem, F.H.Hafez and Wolfram, H.P.Thiemann  
Plant Protection Dept., Faculty of Agric., Minia, Egypt  
Physical and Environm. Chemistry, Bremen Univ., Germany  
Tel: 086-357799 or 086-362182 and Fax No: 086-357799 or 086-362182.  
Email: hashemfouad@yahoo.com

Photodegradation experiments of atrazine were carried out under UV light ( $\lambda$  254 nm, 24h), sunlight (one month, 8h/day), and in the dark conditions in a variety of waters. Residue analysis of this compound in the water samples was determined using high performance liquid chromatography (HPLC). The Photodegradation rate was followed first-order kinetics with different rate constants ( $k$ ) and high  $r^2$  values. The loss of atrazine in the water samples under dark conditions was negligible. Whereas, the Photodegradation of the compound in water was higher after exposure to UV light than that under sunlight conditions. The Photodegradation rate of atrazine in different waters after exposure to either UV light or sunlight decreased in the following order: river water > canal water > distilled water. HPLC analysis showed that there were at least three different photoproducts of atrazine in water extracts after exposure to UV light, while only two photoproducts were detected in the water extracts under sunlight conditions.

## INTRODUCTION

The s-triazine herbicides are among the most widely used pesticides. Atrazine, simazine and propazine, as well as the mono-N-dealkylated metabolites have been detected in ground water (EPA, 1990; Isensee *et al.*, 1990; Adams and Thurman, 1991). These compounds are nonvolatile and highly water soluble (usually in acid or base) and are inefficiently recovered from environmental matrices (Nash, 1990). Its widespread use has resulted in the detection of it in rivers, lakes (Goolsby *et al.*, 1993; Tierney *et al.*, 1993), and their sediments (Spalding *et al.*, 1994). Most of atrazine and simazine would be transported in the water phase of runoff; however, some will still be adsorbed to fine clay and silt particles (Ghadiri and Rose 1991). Their concentrations in surface water and groundwaters, when detected, are usually around 100 ng litre<sup>-1</sup> or less, although levels over 1  $\mu$ g litre<sup>-1</sup> have been reported (SAC Scientific, 1987). In studies using river water, a half-life of approximately one month for atrazine has been measured (Glottfely *et al.*, 1984). A considerably longer half-life of five months was estimated for atrazine added to lake enclosures (Hamilton *et al.*, 1989). Similar half-lives (nine months) were obtained for simazine in a lake study in America (Jenkins and Buikema, 1990). Degradation of these compounds can occur via biotic and abiotic (hydrolysis and Photodegradation) processes. Generally, hydrolysis and Photodegradation are the major chemical transformation pathways of a pesticide in aqueous solution. Among these, Photodegradation is known to be the important degradation pathway for atrazine and simazine in water under normal conditions (Comber, 1999). Photodegradation experiments have included irradiation in sunlight, at 254nm using a mercury lamp, and at greater than 340nm using a xenon lamp, to mimic natural radiation more closely (Kearney *et al.*, 1984; Pelizzetti *et al.*, 1991). This paper concentrates on the Photodegradation of atrazine in different sources of water under UV light (using a low-pressure Hg lamp at 254 nm), sunlight (wavelength between 300-400 nm), and in the dark conditions.

## MATERIALS AND METHODS

**Water sources:** The types of water used in this experiment were distilled water (pH 7.0, double distilled in the laboratory), canal water (collected from El-Ibrahiemeya canal in Minia region) and river water (collected from Nile River, in Minia region, Upper Egypt). The chemical and physical properties of the water samples are reported in Table 1. All water samples were filter-sterilized by passage through a 0.1- $\mu$ m filter paper (Whatman No.42, 60-mm diameter), and stored in the dark prior to use in experiments.

**Chemicals:** Merck Corp.Germany provided technical samples of atrazine (99% purity). All the organic solvents used in this study were of HPLC grade.

**Table 1. Chemical and physical properties of different types of water<sup>a</sup>**

Property	River water	Canal water
pH	8.5	7.6
CL <sup>-</sup> (mg litre <sup>-1</sup> )	88.0	35.2
Hardness (mg CaCO <sub>3</sub> litre <sup>-1</sup> )	143.0	295.0
SO <sub>4</sub> <sup>-2</sup> (mg litre <sup>-1</sup> )	62.6	14.0
Ca <sup>+2</sup> (mg litre <sup>-1</sup> )	101.0	60.4
Na <sup>+</sup> (mg litre <sup>-1</sup> )	30.0	7.5
K <sup>+</sup> (mg litre <sup>-1</sup> )	15.5	3.1
Mg <sup>+2</sup> (mg litre <sup>-1</sup> )	99.4	33.0
Conductivity ( $\mu$ ohms cm <sup>-2</sup> )	1190.0	828.0
DOC <sup>b</sup> (mg litre <sup>-1</sup> )	0.21	0.28

<sup>a</sup> Measured by the Water Science Dept. Bremen University, Germany.

<sup>b</sup> Dissolved organic carbon

**Treatment of water:** The method of Comber, 1999 was used in this experiment. Solutions of atrazine dissolved in methanol were prepared and added to the samples of each water type to give a final concentration of 5mg litre<sup>-1</sup>.

**Photodegradation procedures:** In order to assess the significance of light on the Photodegradation of atrazine in water, experiments were conducted in distilled water, canal water and river water under either UV or sunlight conditions.

**Ultraviolet light (UV):** Aqueous solutions (150 mL) of atrazine in (distilled water, canal water, and river water, 5ppm) were transferred to a 200-mL pear-shaped necked flask and irradiated to UV light (24h) with a low-pressure Hg lamp emitting at 254nm in the main. The lamp was inserted into the solution through the neck of the reaction flask, and the apparatus was placed in a dark room. Temperature control (25°C) was maintained with water circulation. A magnetic stirrer was used to agitate the solutions during exposure. Aqueous solution samples of atrazine were kept in darkness to serve as control. An aliquot (15mL) at 0,4,8,12,16,20, and 24 h of irradiation was withdrawn in triplicate, extracted and analysed by HPLC.

**Sunlight:** Spiked samples of different waters were exposed to sunlight in the glass vessels over a period of approximately one month (about 8 h per day in September 2001). The control experiment was conducted in a similar manner in the dark for all the treatments to ensure that a given product was derived only by photochemical processes. At various time intervals of irradiation, spiked water samples in triplicate were taken for extraction and analysis.

**Extraction procedures:** Solid phase extraction (SPE) is commonly used to extract and purify herbicides from water (Johnson *et al.*, 1991; Adams and Randtke, 1992). Before extraction, each water sample was adjusted to pH 7.0-7.5 by dropwise addition of phosphoric acid, as needed. Spiked water samples (20 ml-each) were added onto octadecyl (C<sub>18</sub>) SPE cartridges preconditioned with sequential volumes of methanol and distilled water. After addition of the samples, the cartridges were washed with 4ml of distilled water, dried and eluted with 2ml of methanol. The collected elutes were evaporated to dryness under nitrogen stream. The residues were dissolved in 1 ml of methanol and analysed by HPLC.

**High-Performance Liquid Chromatography:** HPLC is successful for determination of atrazine herbicide residues and its degradation products in water (Lerch and Donald, 1994). In this study, the analysis of atrazine in different sources of water was carried out according to the method of Steinheimer (1993). A Waters Associates HPLC system was consisted of two Model 510 pumps operated at a 1ml min<sup>-1</sup> flow rate, a WISP 710 B automatic injector, Lambda-Max Model 480 UV detector set to 220 nm, and M 730 integrator. A LiChrospher 100 RP-18 column, 5 $\mu$ m, 125 x 4 mm was used. The HPLC column was cleaned with 100% acetonitrile. The eluant comprised a ratio of 65:35 acetonitrile and double distilled water, degassed with helium, and a 25  $\mu$ L injection loop was used for all HPLC separations. Under these conditions, the retention time of atrazine was 13.7 min. The average of recovery percentages of atrazine were 98.3%; 95%; and 93.7% in distilled water, canal water and river water, respectively.

**Data Analysis:** The first-order kinetic equation was used to depict the Photodegradation of atrazine residues in different sources of water. The integrated form of the first-order kinetic equation (Atkins, 1994) is:

$$C=C_0e^{-kt}$$

Where  $t$  is time,  $C$  is the atrazine concentration at time  $t$ ,  $C_0$  is the atrazine concentration at time 0 and  $k$  is the rate constant. The half-life ( $t_{1/2}$ ) was calculated from the rate constant ( $k$ ) as follow:

$$t_{1/2} = \ln(2)/k \text{ or } t_{1/2} = 0.693/k$$

## RESULTS AND DISCUSSION

### Hydrolysis of atrazine in the dark:

The hydrolysis of atrazine conducted in different sources of water under dark conditions showed that the loss of the compound was negligible during the course of experiments. The half-lives were calculated and given in Tables 2 and 3. These results confirm previous findings that the hydrolysis of atrazine is negligible in the dark conditions (Erickson and Lee, 1989; Sinclair and Lee, 1992).

### Photodegradation of atrazine:

The Photodegradation rate of atrazine in different waters was followed first-order kinetics with different rate constants ( $k$ ) and high  $r^2$  values (Tables 2 and 3). The Photodegradation rate in water samples was higher after exposure to UV light than that under sunlight conditions. Also, the results indicated that the rate of atrazine Photodegradation decreased in the following order: river water > canal water > distilled water (Figure 1). Estimated from the half-life values given in Tables 2 and 3, the Photodegradation of atrazine in canal and river water was about 4-4.5 times and 5-8 times under sunlight and UV light, respectively as rapid as that in distilled water. These results indicated that the chemical and physical properties of both canal and river water, including DOC may be responsible for accelerating the Photodegradation of atrazine. It is clear in the case of distilled water, which does not contain any concentration of these properties, so the rate of Photodegradation was lowest. This result confirmed several suggestions that natural waters contain a variety of dissolved colloidal and suspended organic and mineral constituents from soil. Also, a part of the pesticides present in the aquatic systems will be associated with these materials (Mathew and Khan, 1996). In addition, atrazine is soil-applied pesticide with a relative high sorption affinity for soil and various soil organic and mineral constituents (Mersie and Seybold, 1996; Li *et al.*, 1996). Therefore, Kochany, 1992; Katagi, 1993 suggested that these constituents may accelerate the photodegradation by energy transfer reactions, by photoinduced oxidation, or by efficient light scattering. On the other hand, it could be also noticed from our results that the spiked water samples exposed to UV light with 254 nm exhibited shorter half-lives of atrazine degradation in different waters compared with those exposed to sunlight (300-400 nm, approximately) and recorded longer half-lives (Tables 2 and 3). These results confirmed those of Kearney *et al.*, 1984 who suggested that irradiation of atrazine at 254 nm using a low-pressure mercury lamp, in combination with ozonation, reduced the half-life to a matter of minutes, even at atrazine concentrations of 1000 mg litre<sup>-1</sup>. Also, Comber 1999 suggested that at environmentally realistic conditions with water at around pH 7.0, in the absence of any photo-sensitizers, Photodegradation of atrazine be mainly initiated by light with wavelengths of less than 300nm. Conversely, the calculated half-life for the photo-reaction of atrazine with hydroxy radicals in clean water was 340 days for light above 290nm (Mansour *et al.*, 1985). Therefore, the proportion of Photodegradation will be dependent on the intensity and wavelength of radiation. Overall, temporal variations in the rate of Photodegradation as the intensity of solar radiation changes on a seasonal basis can therefore be expected in natural waters. For example, simazine and atrazine present in low-pH waters during the summer months will persist for a matter of days, compared with months for triazines in higher pH waters during the winter months (Comber, 1999).

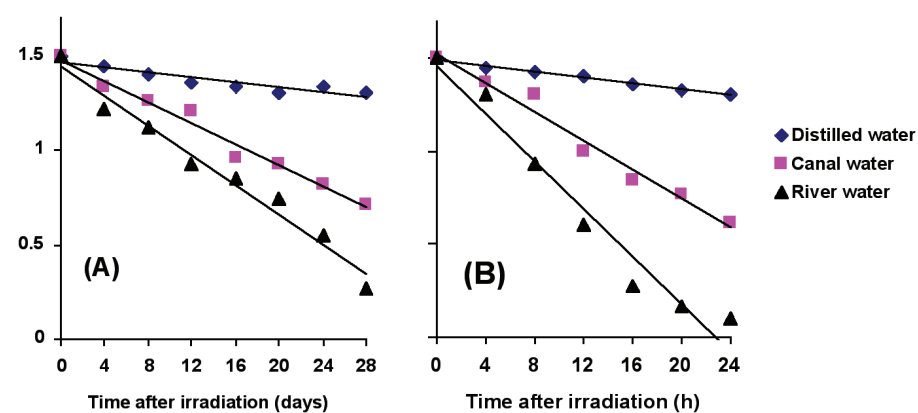


Figure 1. Photodegradation of atrazine in different types of water under (A): sunlight and (B): UV light conditions.

Table 2. Rate constant ( $k$ ) and half-life ( $t_{1/2}$ ) values of atrazine in different sources of water under sunlight and dark conditions.

Water source	Sunlight			Dark		
	$k$	$r^2$	$t_{1/2}$ (days)	$k$	$r^2$	$t_{1/2}$ (days)
Distilled water	0.007	0.86	99.00	0.005	0.99	138.60
Canal water	0.028	0.98	24.75	0.006	0.97	115.50
River water	0.039	0.98	17.77	0.007	0.99	99.00

Table 3. Rate constant ( $k$ ) and half-life ( $t_{1/2}$ ) values of atrazine in different sources of water under UV light and dark conditions.

Water source	UV light			Dark		
	$k$	$r^2$	$t_{1/2}$ (h)	$k$	$r^2$	$t_{1/2}$ (h)
Distilled water	0.008	0.99	86.63	0.0045	0.98	154.00
Canal water	0.039	0.98	17.80	0.0057	0.93	121.58
River water	0.064	0.96	10.83	0.0068	0.95	101.90

### HPLC analysis:

The results of HPLC analysis for atrazine in different water extracts showed different photoproducts for the compound under either UV light or sunlight conditions. At least three photoproducts for atrazine were presented in the extracts of river or canal water after exposure to UV light. While, only two photoproducts for the compound were detected in the water extracts under sunlight conditions (Figure 2). These unknown products could not be identified because of their low levels and unavailability of reference standards. Several authors demonstrated in their studies that hydroxyatrazine was the major product of atrazine had formed abiotically via Photodegradation in water and stream water (Durand *et al.*, 1991; Kolpin and Kalkhoff, 1993). Also, Lerch and Donald, 1994 found that three hydroxylated atrazine degradation products (HADPs), hydroxyatrazine (HA), deethylhydroxyatrazine (DEHA), and deisopropylhydroxyatrazine (DIHA), were detected in laboratory water and stream water samples.

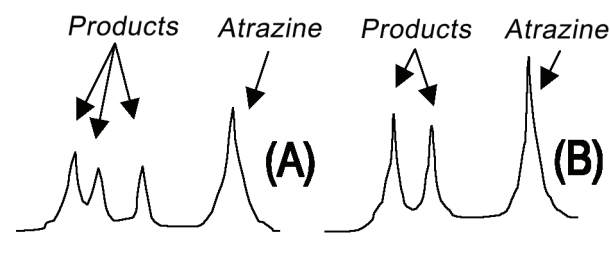


Figure 2. HPLC chromatograms of atrazine and its degradation products after exposure to (A): UV light ; (B): sunlight

## CONCLUSION

The Photodegradation experiments of atrazine in different sources of water indicated that this compound was more susceptible for Photodegradation under UV light than that under sunlight. The loss of the compound was negligible in the dark conditions. The Photodegradation rate decreased in the following order : river water > canal water > distilled water. The results of HPLC analysis showed that three and two different photoproducts of atrazine were detected in water extracts after exposure to UV light and sunlight, respectively.

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