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Photodegradation of atrazine in water

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ABSTRACT

Photodegradation studies of atrazine were carried out under UV radiation (λ 254 nm, 24 h), sunlight (one month, 8 h / day) or dark conditions in different types of water. Residue analysis of the compound in the different water samples was done using high performance liquid chromatography (HPLC). The rate of photodecomposition in different water samples 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 dissipation of the compound after exposure to UV radiation was found to be higher than that under sunlight conditions. The photodegradation rate of atrazine in different types of water after exposure to either UV radiation or sunlight was decreased in the following order: river water > canal water > distilled water. HPLC analysis showed unknown peaks in river and canal water either expossed to UV radiation or sunlight.

Keywords: Atrazine, photodegradation, river water, canal water.

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 and Adams and Thurman, 1991). These compounds are nonvolatile and highly water soluble and are inefficiently recovered from environmental matrices (Nash, 1990). The widespread use of this group of herbicides has resulted in their detection in rivers and lakes (Goolsby *et al.*, 1993 and 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 on fine clay and silt particles (Ghadiri and Rose, 1991). Their concentrations in surface water and groundwaters are usually around 100 ng / l or less, although levels over 1 µg / l have been reported (SAC Scientific, 1987). In studies using river water, a half-life of approximately one month for atrazine has been measured (Glotfelty *et al.*, 1984). A considerably longer half-life, about five months, was estimated for atrazine added to lake enclosures (Hamilton *et al.*, 1989). On the other hand, the half-life value for simazine was found to be nine months in lake water 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 pesticides 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 included irradiation in sunlight, at 254 nm using a mercury lamp, and at greater than 340 nm using a xenon lamp, to mimic natural radiation (Kearney *et al.*, 1984 and Pelizzetti *et al.*, 1991). Our research is dealing with the photodegradation of atrazine in different sources of water under UV radiation (using a low- pressure mercury lamp at 254 nm), sunlight (wavelength between 300-400 nm), and the dark conditions.

MATERIALS AND METHODS

Water sources: The types of water used in this experiment were double distilled water, canal water (collected from El-Ibrahiemeya canal, Minia region) and river water (collected from Nile River, 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-μm filter paper (Whatman No.42, 60-mm diameter), and stored in the dark prior to use.

Chemicals: Atrazine; (2-chloro-6-(ethylamino)-4-isopropylamino-1,3,5-triazine), 99 % technical grade sample was provided by Merck Corp, Germany. All the organic solvents used in this study were of HPLC grade.

Table (1): Chemical and physical properties of different types of water[a]

Property	*River water*	*Canal water*
pH	8.5	7.6
Cl^- (mg / l)	88.0	35.2
Hardness (mg $CaCO_3$/ l)	143.0	295.0
$SO4^{--}$(mg / l)	62.6	14.0
Ca^{++} (mg / l)	101.0	60.4
Na^+(mg / l)	30.0	7.5
K^+(mg / l)	15.5	3.1
Mg^{++}(mg / l)	99.4	33.0
Conductivity (μohms/ cm^2)	1190.0	828.0
DOC[b] (mg / l)	0.21	0.28

[a] Measured by the Water Science Dept. Bremen University, Germany.
[b] Dissolved organic carbon

Treatment of water: Atrazine was dissolved in methanol and added to the samples of each water type to give a final concentration of 5 mg / l.

Photodegradation procedures: In order to assess the significance of light on the degradation of atrazine in water, different sources of water, i.e. distilled water, canal water and river water samples spiked with atrazine at 5 mg / l were irradiated by using a low-pressure mercury lamp or sunlight.

1-Ultraviolet radiation (UV): Aqueous solutions (150 ml each) of atrazine spiked samples from distilled water, canal water, and river water were transferred to a 200-ml pear-shaped necked flask and irradiated to UV light at 254 nm for 24 hr. 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 (15 ml) at 0, 4, 8, 12, 16, 20, and 24 hr of irradiation was withdrawn in triplicate, extracted and analyzed by HPLC.

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

Extraction procedures: Solid phase extraction (SPE) is a commonly method used to extract and purify herbicides from water (Johnson *et al.*, 1991). 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_{18}) 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 2 ml of methanol. The collected eluates were evaporated to dryness under nitrogen stream. The residues were dissolved in 1 ml of methanol and then analyzed using HPLC.

High-Performance Liquid Chromatography: The analysis of atrazine using HPLC in different sources of water was carried out according to the method of Steinheimer (1993) and Lerch and Donald (1994). A Waters Associates HPLC system was consisted of two Model 510 pumps operated at a 1 ml / min 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, 5μm, 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 μl injection loop was used for all HPLC separations. Under these conditions, the retention time of atrazine was 13.7 minute. The average of recovery percentages of atrazine were 98.3, 95 and 93.7 % in distilled water, canal water and river water, respectively. Results were corrected according to the average of recovery.

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 ($t_{½}$) was calculated from the rate constant (k) as follow:

$$t_{½} = 0.693/k$$

RESULTS AND DISCUSSION

Hydrolysis of atrazine in the dark:

The hydrolysis of atrazine in different sources of water under dark conditions showed that the loss of the compound was negligible during the time course of experiments. The half-lives were calculated and given in Tables 2 and 3. These results confirm previous findings which should that the hydrolysis of atrazine is negligible in the dark conditions (Sinclair and Lee, 1992 and Evgenidou and Fytianos, 2002).

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). Its degradation rate in water samples was found to be higher after exposed to UV light than that under sunlight conditions. The rate of atrazine photodecomposition was decreased in the following order: river water > canal water > distilled water (Fig. 1). From the half-life values given in Tables 2 and 3, it can be seen that 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 degradation process depends on the constitution of the water soursces. The presence of dissolved organic carbon in canal and river water samples may be responsible for accelerating the photodegradation process of atrazine. In the case of distilled water, which does not contain any of this property, therefore, the rate of photodegradation was the 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 and Li *et al.*, 1996). Kochany (1992) and 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 radiation at 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 / l. Also, Comber (1999) suggested that at environmentally realistic conditions with water at around pH 7.0, in the absence of any photo-sensitisers, photodegradation of atrazine be mainly initiated by light with wavelengths of less than 300 nm. Conversely, the calculated half-life for the photo-reaction of atrazine with hydroxy radicals in clean water was 340 days for light above 290 nm (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, simasine 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).

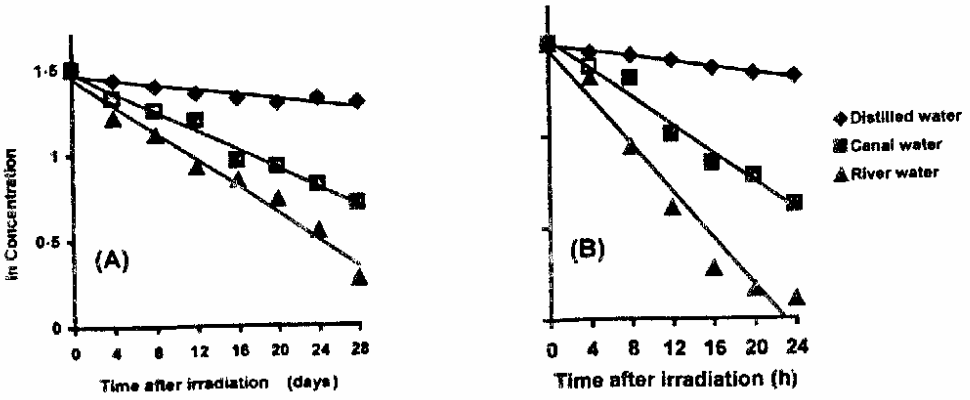

Fig. (1): Photodegradation of atrazine in different types of water under (A): sunlight and (B): UV light conditions.

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:

Based on the findings of Kolpin and Kalkhoff (1993) who reported that the major product of atrazine had formed abiotically via photodegradation in water and stream water. 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. Recently, Konstantinou *et al.*, (2001) who indecated that the major photodegradation products of s-trazines which identified by using GC-MS techniques in various natural water and soils were the hydroxy and dealkylated derivatives. Our HPLC results indecated three unknown peaks

were found in the extracts of analysis for atrazine in different water in the extracts of river or canal water after exposure to UV light. While, only two unknown peaks for the compound were detected in the water extracts under sunlight conditions (Fig. 2).

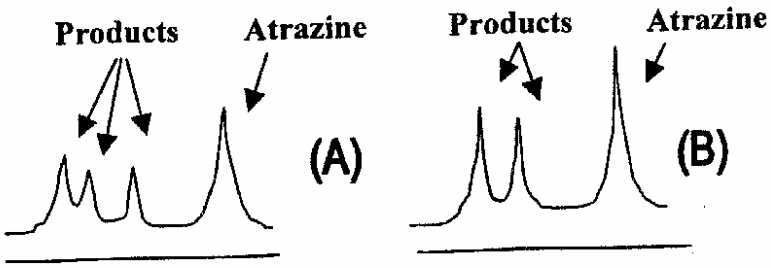

Fig. 2. HPLC chromatograms of atrazine and its degradation products after exposure to (A): UV light ; (B): sunlight

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التحطم الضوئي للأترازين في الماء

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تم دراسة التحطم الضوئي لمبيد الحشائش الأترازين في ثلاثة مصادر مائية مختلفة(ماء مقطر، ماء ترعة، ماء نهر) وذلك بعد تعريض عينات الماء المعاملة بالمبيد لكل من الأشعة فوق البنفسجية (٢٤ ساعة على درجة حرارة ٢٥° م) وأشعة الشمس (٨ ساعات/ يوم لمدة شهر في سبتمبر ٢٠٠١)، بالإضافة إلى معاملة الكونترول(تحت ظروف الظلام). وقد تم تحليل متبقيات المبيد من العينات المأخوذة على أزمنة مختلفة من التعريض باستخدام جهاز التحليل الكروماتوجرافى HPLC . وقد أوضحت النتائج أن التحليل المائي للأترازين تحت ظروف الظلام كان ضئيلا، بينما كان التحطم الضوئي للمركب أعلى عند التعريض للأشعة فوق البنفسجية بالمقارنة عند التعريض لأشعة الشمس. أوضحت النتائج المتحصل عليها كذلك أن معدل التحطم الضوئي للمركب في المصادر المائية المختلفة تحت ظروف التعريض لأى من الأشعة فوق البنفسجية وأشعة الشمس كان كما يلي : ماء النهر > ماء الترعة > الماء المقطر ومن ناحية أخرى أوضحت نتائج التحليل الكروماتوجرافى بجهاز ال HPLC ظهور ثلاثة نواتج تحطم ضوئي للأترازين في مستخلصات ماء النهر أو ماء الترعة وذلك بعد التعريض للأشعة فوق البنفسجية ، بينما تم ظهور ناتجين فقط للمركب بعد التعريض لأشعة الشمس.