Journal of Hazardous Materials 192 (2011) 1260–1266

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Simulation and quantification of the natural decay of a typical endocrine disrupting chemical Atrazine in an aquatic system

K.Y. Lin, W. Chu*

Department of Civil and Structural Engineering, Research Centre for Urban Environmental Technology and Management, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong

ARTICLE INFO

Article history:
Received 20 January 2011
Received in revised form 24 May 2011
Accepted 14 June 2011
Available online 8 July 2011

Keywords:
Atrazine
Endocrine disrupting chemicals
Natural decay
Abiotic degradation

ABSTRACT

The degradation of Atrazine (ATZ) in an outdoor environment was investigated by varying the ATZ concentration and pH levels and then cross-checked with temperature and sunlight information. The overall decay rate constant of ATZ in outdoor is slower in neutral pH and faster at extreme pH levels, while parallel tests show that higher ATZ concentration leads to slower decay rate constant. Two abiotic mechanisms including direct photolysis and hydrolysis were identified and studied in the laboratory as a comparison. Hydrolysis was found to be a slow process but it is a continuous process, which is critical as the sunlight intensity is weak. Effect of temperature on the hydrolysis was also studied. A model incorporating ATZ decay rate constants, pH levels and temperatures was proposed. Photolysis, though, is a non-continuous process in the environment. It is a fast and dominant process, which contributes 82–45% (depending on pH levels) of overall ATZ decay at outdoor. In natural environment, humic acid can act as photosensitizer and enhance photolysis of ATZ at low concentration (<10 mg/L); while at high concentration of humic acid, retardation of ATZ decay was observed likely due to the scavenging of radicals and light attenuation.

1. Introduction

Endocrine disrupting chemicals (EDC) are major environmental concerns due to their adverse effect on wildlife and human beings. Atrazine (ATZ), 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine, has been chosen in this study because it has become a widely used herbicide for agricultural and forestry purpose since 1950s. It is classified as a possible human carcinogen by U.S. EPA. Several studies have also suggested that ATZ is an endocrine disruptor. Besides its endocrine disrupting property, ATZ is a water-quality concern also because of its persistence in water and soil. For example, even four years after a large-scale accidental leakage in Liaoning Province of China that took place in 1997, ATZ could still be detected in the agro ecosystem of the affected area [1]. Higher solubility of ATZ also makes it easy to find its way into ground water and the aquatic environment.

Although the use of ATZ has been restricted in Switzerland for years, it is still used extensively and has been detected in water bodies, both marine and rivers, around the world. In 2009, U.S. EPA announced the launch of a new evaluation of the human health effects of ATZ. To fully understand the effect of ATZ on water quality, it is important to know the nature of ATZ when it reaches the aquatic system.

ATZ is very persistent in natural environment once applied [2]. The water solubility of ATZ is 33 mg/L and its soil sorption coefficient Koc is low, at about 100 mL/g, which makes the ATZ likely to be washed off from the soil to the surface water after storms [3,4]. The half-life of ATZ in soil is 60 days and once it is in surface water, the half-life increased significantly due to reduced microorganisms [4].

Several recent studies show that ATZ causes sexual abnormalities in aquatic animals. It is a potent endocrine disruptor that both chemically castrates and feminizes larval and adult male amphibians [5–8]. It was also reported that ATZ retards development and delays metamorphosis at ecologically relevant concentrations [5].

The maximum contamination level (MCL) for ATZ in drinking water established by the USEPA and HKEPA is 3 μg/L and 2 μg/L, respectively. In Hong Kong, ATZ has been detected in Shing Mun Reservoir and Lam Chuen River, especially after seeding season [9]. ATZ has also been found in various marine water in Hong Kong including Ma Wan Village, Hoi Ha Wan and Kat O, where all three locations are pristine coral reef sites and ATZ was reported to reduce the viability of coral reefs [10].

ATZ was also detected in many rivers and reservoirs in China. Its usage in China has been increasing by 20% each year since 1980 [11]. China is now one of the biggest manufacturers and consumers

* Corresponding author. Tel.: +1 852 2766 6075; fax: +1 852 2334 6389.
E-mail address: cewchu@polyu.edu.hk (W. Chu).

0304-3894/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2011.06.042

Table 1
Weather conditions of irradiation duration.

Irradiation duration	Average UV index					Average temperature (°C)				
	Mar	Apr	May	Jun	Jul	Mar	Apr	May	Jun	Jul
March 6–July 8, 2009	5.4	2.9	4.0	3.4	5	19.8	22.0	25.5	28.1	28.7
May 11–July 8, 2009	–	–	3.5	3.4	5	–	–	26.2	28.1	28.7
May 20–July 8, 2009	–	–	2.4	3.4	5	–	–	25.6	28.1	28.7

of ATZ in the world and ATZ contamination were also reported with concentration as high as 26.1 μg/L in a large area of Yang River and Guanting Reservoir [12].

In natural environment, degradation of ATZ involves microbial and abiotic pathway which includes hydrolysis and photolysis. Hydrolysis is affected by several parameters such as temperature, pH, and the presence of catalysts. Generally, hydrolysis is enhanced by extreme pH and temperature.

Photolysis is possible in water; however, only wavelengths above 290 nm are available in natural environment due to the ozone layer absorption in the upper atmosphere. ATZ absorbs sunlight weakly at wavelengths longer than 290 nm, but the sunlight in the near UV range is still adequate to break various covalent bonds in organic molecules homolytically. Direct photolysis of pesticides at the low concentration found in environmental waters mostly obeys pseudo first-order expression [13].

However, different wavelengths may result in different intermediates, e.g. 2-hydroxy-4-(isopropylamino)-6- (ethylamino)-s-triazine (OIET) is the only intermediate when ATZ exposed to 254 nm [14], while additional intermediates 2-hydroxy-4-(ethylamino)-6-amino-s-triazine (OEAT), 2-hydroxy-4-(isopropylamino)-6-amino-s-trazine (OIAT), 2-hydroxy-4, 6-diamino-*s*-triazine(OAAT), 2-chloro-4-(isopropylamino)-6-amino-s-triazine (CIAT), 2-chloro-4-(ethylamino)-6-amino-s-triazine (CEAT), and chlorodiamino-s-triazine (CAAT) can be observed at the wavelength > 290 nm [15].

The aim of this project is to study the decay kinetics of ATZ in an outdoor environment. In this study, non-biological degradation of ATZ was investigated. The experiments were carried out in outdoor conditions on a rooftop. Laboratory studies were performed to evaluate the contribution of various factors responsible for the degradation of ATZ. The presence of humic acid in the natural water could accelerate the rate of photolysis due to the sensitization process [16]. Therefore, its effect on photolysis was investigated in this study as well.

2. Experimental

2.1. Materials

All the chemicals used in this study were of HPLC-grade and were used as received without further purification. The mobile phase containing acetonitrile and water (from Fisher Scientific UK Ltd.) used for LC analysis in this study was degassed before used. Nonlabeled ATZ at 99% purity was purchased from RdH Laborchemikalien GmbH & Co. Humic Acid, HA, as a sodium salt was purchased from Acros.

All indoor photochemical reactions were carried out in a Rayonet™ photochemical reactor RPR-200, manufactured by the Southern New England Ultraviolet Company. Refrigerator and ovens with preset temperatures were used for the investigation of the temperature effect on ATZ degradation. Samples collected from different reactions were analyzed by HPLC using a Restek 5 μm 4.6 (ID) × 250 mm Pinnacle™ Octyl Amine column. The maximum absorption wavelength of ATZ was determined and selected at 221 nm. The mobile phase consisted of 60% acetonitrile with 40% de-ionized distilled water (DDW) was delivered at a flow rate of 1.0 mL/min, which results in an ATZ peak at 4.7 min.

2.2. Methods

ATZ samples were prepared by dissolving ATZ in DDW. The pH level was then adjusted using sulfuric acid and/or sodium hydroxide.

2.2.1. Outdoor test

The investigation of ATZ degradation in the outdoor environment was carried out on the rooftop of our laboratory. 10 mL of tested solutions were placed in small quartz tubes, which were then sealed and placed in open racks. The set-up was then placed in open area on the rooftop without shading accessories. The tests were carried out over a period of 4 months from March 6, 2009 to July 8, 2009 with different ATZ concentrations (6.9–46.4 μM) and/or pH levels (2–12). All the tests were duplicated. The maximum and minimum air temperature during this period was 32.6 °C and 15.9 °C, respectively. Weather conditions including average temperature and UV index over the irradiation duration were listed in Table 1.

2.2.2. Hydrolysis of ATZ

Hydrolysis process was simulated in the laboratory at 20 °C. ATZ samples with an initial concentration of 13.9 μM at pH levels of 2, 3, 4, 9 and 12 were performed in pyrex glass tubes. The tubes were then capped and wrapped with aluminum foil to minimize the possible photodegradation and bioreaction.

To examine the effect of temperature on the hydrolysis of ATZ, 13.9 μM of ATZ in pyrex glass tubes were capped and wrapped with aluminum foil and placed at different temperatures of 4, 20, 30 and 70 °C under different pH levels (2 and 6).

2.2.3. Photolysis of ATZ

Photolysis of ATZ using artificial UV lamps was also performed in the laboratory to simulate outdoor photodegradation. About 100 mL of ATZ samples with initial concentration of 13.9 μM were prepared in a quartz beaker and placed in the Rayonet™ Photoreactor with magnetic stirring at room temperature (20 °C). Samples were exposed to different ultraviolet wavelengths at either 300, 350 or 419 nm with six UV lamps. For the 300 nm tests, the effects of varying solution pH levels (from 2 to 12) were conducted as well.

The effect of humic acid (HA) on the photolysis of ATZ at 300 nm was examined using 13.9 μM ATZ solutions in the presence of 10, 20, 50 and 100 mg/L HA in the Rayonet™ Photoreactor.

3. Results and discussion

3.1. Outdoor test

The degradation of ATZ in an outdoor environment was performed by varying pH levels and ATZ concentration. Three outdoor exposure tests with different reaction conditions (pH and $[ATZ]_0$ were ranged from 2 to 12 and 6.9 to 46.4 μM, respectively) were conducted from 6 March to 8 July (Table 2). The degradation of ATZ generally follows pseudo first-order decay kinetics. Since sunlight

Table 2
Experimental setup of outdoor test.

	Date	Tested pH	$[ATZ]_0$
Test 1	March 6–July 8, 2009	2, 5, 7, 9, 12	46.4 μM
Test 2	May 12–July 8, 2009	2, 5, 7, 9	13.9 and 6.9 μM
Test 3	May 20–July 8, 2009	2, 3, 4	13.9 and 6.9 μM

is only available for several hours within 1 day (24 h), corrections are to be performed and discussed later.

At outdoor, direct photolysis and hydrolysis are the two major processes responsible for ATZ decay. The photolysis of ATZ by sunlight (UV) is a fast but non-continuous reaction, while hydrolysis is a slow but continuous process. This makes ATZ decay at outdoor complicated. The normal time scale is not suitable for analyzing the kinetic data; therefore, the decay data needs to be adjusted by the UV exposure. The proposed approach is to correlate the decay rate constants with the accumulated UV radiation rather than using the total reaction time at outdoor, because the amount of UV radiation varied every day during the tested period. The daily mean UV index (UVI) provided by The Hong Kong Observatory (HKO) is used as an indicator of the strength of UV radiation. The HKO updates UVI every 15 min for about 12 h per day (6 am to 6 pm). Accumulated UV index is therefore calculated by summing up the daily mean UVI.

Correlations between accumulated UVI and total reaction time for different reaction conditions can be resolved (see Fig. 1 for the case of Test 3, pH 2 and 6.9 μM). As the total reaction time divided by the total accumulated UVI, it gives a unit index (UI). The UI can then be multiplied by the accumulated UVI of the sample and a corrected reaction time that is normalized to the sunlight exposure can be achieved. This correction can be used for adjusting the pseudo first-order rate calculation by converting the reaction time into a UVI adjusted time. The result is that the decay rate constant fits the first-order decay rate constant model better by using adjusted time than the unadjusted time (Fig. 2).

The results of outdoor tests are summarized in Fig. 3, where all the tests show the same trend with a $k_{outdoor}$ that is lower at neutral pH levels and higher at both acidic and basic conditions. This is likely due to the higher hydrolysis rate at extreme-ends of pH levels, which will be discussed in detail later.

Previous studies reported no degradation of ATZ in aqueous or buffer solution at neutral pH when samples were placed in amber [17] or colorless [18] glass, which would filter out UV radiation that could provide energy for degradation. Quartz vessels were used in this experiment to mimic the natural environment as much as possible.

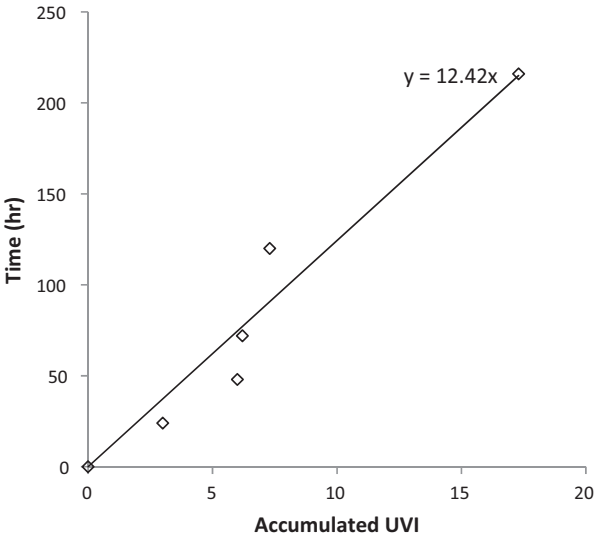

Fig. 1. Correlation of time and accumulated UVI (Test 3, pH 2, $[ATZ]_0$ = 6.9 μM).

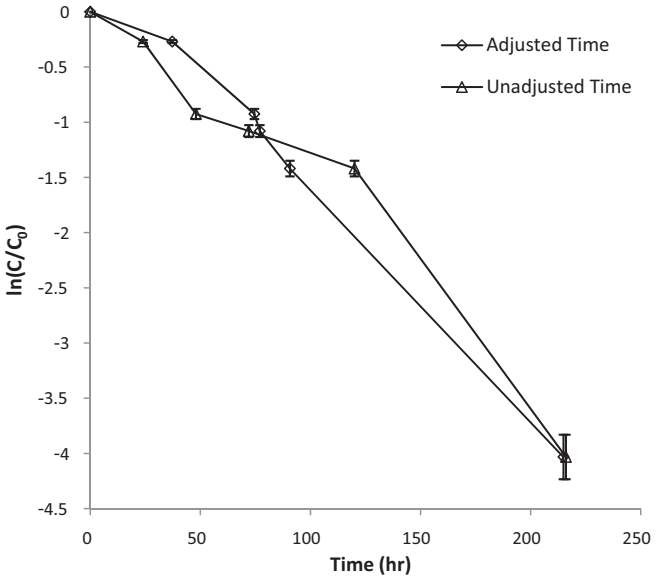

Fig. 2. Decay rate constant of ATZ (Test 3, pH 2, $[ATZ]_0$ = 6.9 μM) with respect to adjusted and unadjusted time.

3.1.1. Effect of temperature and sunlight intensity

ATZ decay at outdoor with different initial concentrations of 13.9 μM and 6.9 μM were studied and compared in both Test 2 and Test 3. Given the same pH and concentration, the decay rate constants of Test 2 are generally higher than Test 3 (Fig. 3). This is likely due to different outdoor temperature and sunlight intensity. By comparing the climatic data for the tested period of Test 2 and 3 provided by The Hong Kong Observatory, it is clear to note that both the temperature and the UV radiation during Test 2 are higher than that of Test 3. The average temperature and mean UVI of Test 3 (May 20–May 29) is 25.6 °C and 2, respectively; while that of Test 2

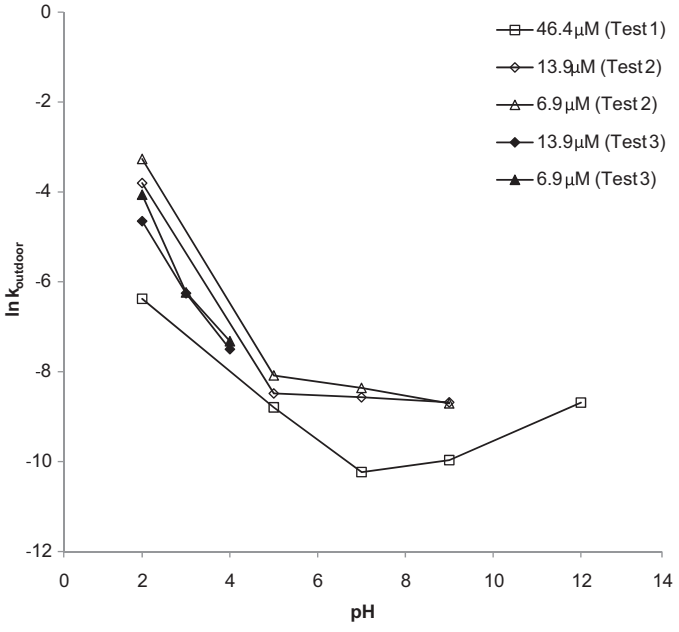

Fig. 3. Effect of pH on decay rate constant (with respect to adjusted time) of ATZ at outdoor (The errors of all data points are within ±5%).

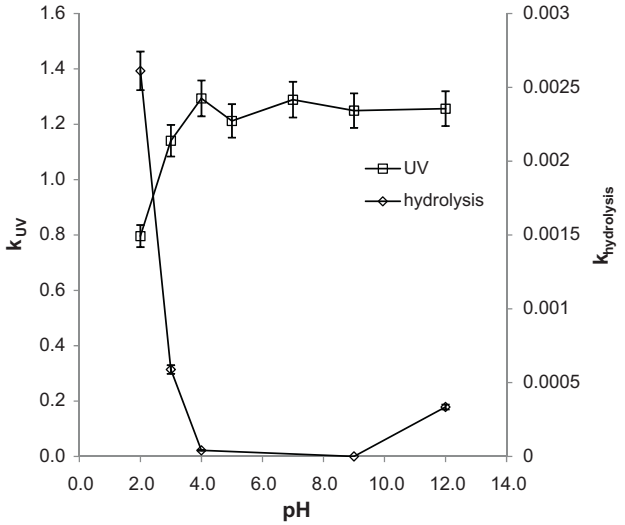

Fig. 4. Decay rate constant of hydrolysis and UV experiment ($[ATZ]_0$ = 13.9 μM).

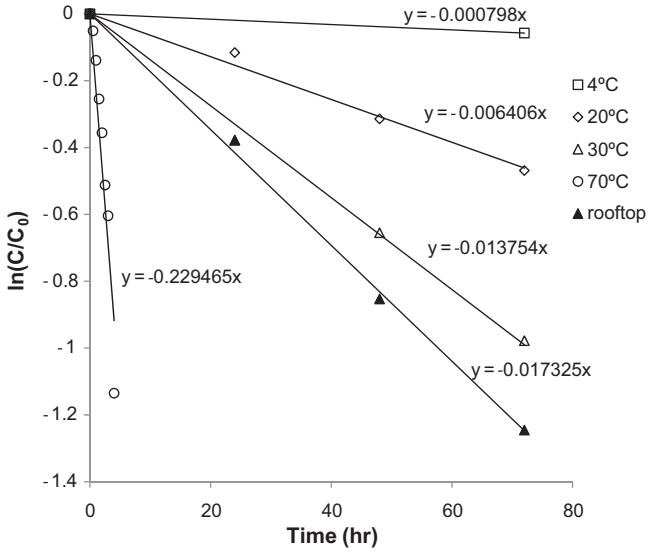

Fig. 5. Effect of temperature on the hydrolysis of ATZ ($[ATZ]_0$ = 13.9 μM, pH = 2) (the errors of all data points are within ±5%).

is 27.9 °C and 5, respectively. Therefore, higher temperature and/or UV radiation leads to higher decay rate, and the contribution of each parameter are to be quantified in laboratory study.

3.1.2. Effect of ATZ concentration

Test 2 and 3 as shown in Fig. 3 are used to study the effect of initial concentration, where the climatic conditions are exactly the same. At pH 2, $k_{outdoor}$ of 6.9 μM ATZ is 1.7 and 1.8 times higher than that of 13.9 μM ATZ for Test 2 and Test 3, respectively. The decay rate constant appears to be inversely proportional to the ATZ concentration. However, this difference becomes less significant as the pH increases, as shown in Fig. 3, the gap between $k_{outdoor}$ of 6.9 μM and 13.9 μM narrows down as the pH increase and finally merged (i.e. no difference) at pH 9. The effect of ATZ concentration is therefore dependent on the pH level in the outdoor environment.

The two main decay mechanisms in outdoor, photolysis and hydrolysis of ATZ, were further studied in the laboratory to quantitatively determine their contribution to the overall decay rate. Since the decay of ATZ with initial concentration 13.9 μM gives relatively fast and stable results comparing to the others, it was selected as the initial concentration for the laboratory study.

3.2. Hydrolysis of ATZ

Hydrolysis basically depends on the solution's pH levels. To minimize the side reaction by indoor light and heat, the tests were conducted in the dark at room temperature with an initial ATZ concentration of 13.9 μM.

At pH 9, the decay rate constant is insignificant. No decay was observed even after 28 days (Fig. 4). The hydrolysis rate of ATZ is lowest at pH 9, and then increases as the pH either increased or decreased. This is likely due to the acid/base catalyzed hydrolysis process, in which the acid catalyzed hydrolysis is more significant, and the pattern is similar to that of outdoor study (Fig. 3). Therefore, a model of acid-catalyzed ATZ hydrolysis was established. The plot of ln k versus pH was found to give a linear correlation as below:

$$\ln k_{hydrolysis} = -2.077\ pH - 1.597 \quad (1)$$

Rearranging Eq. (1) gives:

$$k_{hydrolysis} = 0.202e^{-2.077\,pH}\ (\text{as pH} \le 4) \quad (2)$$

Using Eq. (2), the ATZ hydrolysis rate constant becomes predictable at a given acidic condition.

3.2.1. Effect of temperature on hydrolysis

The temperature effect on ATZ decay was also investigated. In general, the reaction rate increases with the increment of temperature, and the degradation is characterized by pseudo first-order kinetics. At 4 °C, the decay rate constant was very slow at around 7.98×10^{-4} h^{-1}. The decay rate constant increases to 0.0064, 0.0138 and 0.2295 h^{-1} as the temperature increases to 20, 30 and 70 °C, respectively (Fig. 5).

Assuming higher temperature does not induce an alteration on the ATZ molecule, Arrhenius equation was used to describe the effect of temperature on ATZ decay (Eq. (3)) with a θ as a temperature characteristic constant:

$$k_2 = k_1\theta^{(T_2-T_1)} \quad (3)$$

If the decay rate constant at 20 °C is used as a reference point, Eq. (3) becomes:

$$k_T = k_{20}\theta^{(T-20)} \quad (4)$$

To determine the value of θ specific to the decay of ATZ, $\log(k_T/k_{20})$ was plotted versus $T-20$, the resulting slope will be $\log\theta$, and θ can be calculated as 1.094. Therefore, the relationship between temperature and decay rate constant of ATZ can be characterized by the following equation:

$$k_T = k_{20}1.094^{T-20} \quad (5)$$

Since all the hydrolysis experiments were conducted at air-conditioned room temperature, at around 20 °C, $k_{hydrolysis}$ is equivalent to k_{20} under various pH levels. By incorporating Eqs. (2) into (5), the relationship among pH (under tested acidic range), temperature, and a temperature-corrected hydrolysis rate constant can be established through the following equation:

$$k_{(hydrolysis,\ temperature)} = 0.2025e^{-2.077pH^*}1.094^{T-20} \quad (6)$$

The decay rate constants of ATZ for pH ranging from 4 to 9 were found to be close to 0. It has been well established that ATZ is resistant to hydrolysis at neutral pH range [18]. Under these circumstances, both the k_{20} and $k_{(hydrolysis,temperature)}$ will be close to zero.

To verify this model, an ATZ solution at pH 5.8 was allowed to decay at 70 °C in an oven. Plugging in 5.8 for pH and 70 for T into

Table 3
Contribution of hydrolysis (temperature-corrected) on the decay rate constant of ATZ at outdoor.

Test	pH	$k_{(hydrolysis,temperature)}$	$k_{outdoor}$	$k_{(hydrolysis,temperature)}/k_{outdoor}$
2	2	0.00646551	0.022313	0.29
3	2	0.00525851	0.009567	0.55
	3	0.00080292	0.001925	0.42
	4	0.00010061	0.000555	0.18

Eq. (6), the model predicts the decay rate constant to be 0.00007 h^{-1}, which confirms with the experimental data (the actual decay rate constant is close to zero).

The decay rate constant of ATZ on rooftop (in dark) is found higher than that of 30 °C (Fig. 5). Using Eq. (5), the average T of the rooftop case is calculated to be 31 °C, which is very close to the average temperature at 29.5 °C during the tested period from July 20 to July 23, 2009.

In addition, Eq. (6) was used to determine the contribution of temperature-corrected hydrolysis in the decay of ATZ at outdoor using a mean temperature. For example, according to the Hong Kong Observatory, the average temperature during the tested period (May 20–May 29, 2009) for Test 3 at pH 2 is 25.6 °C (varied from 20 to 30.9 °C) so the decay rate constant is determined to be 0.00526 h^{-1}. Table 3 shows that the $k_{outdoor}$ is generally higher than the hydrolysis rate and only 18–55% of $k_{outdoor}$ is contributed by hydrolysis. The lowest contribution of hydrolysis was found at pH 4 (18%), this is because the decay rate constant decreases exponentially as pH approaches to neutral (Eq. (2)), where the temperature effect is insignificant as well.

3.3. Photolysis of ATZ

Besides hydrolysis, photolysis is another expected mechanism for ATZ decay at outdoor. As hydrolysis only accounts for 18–55% of $k_{outdoor}$ under various conditions, the remaining 45–82% of $k_{outdoor}$ is likely contributed by UV irradiation, which increases the decay rate constants of outdoor experiment significantly ranging from 81.9% to 451.6%.

UVA (400–320 nm) and UVB (320–280 nm) are the two main ultraviolet ranges present in natural environment. To determine the contribution of photolysis, ATZ was exposed to artificial UV lamps at 300, 350 and 419 nm in laboratory. The experiments were carried out at pH 2, where the decay rate was most significant at outdoor. It is interesting to note that 82% of ATZ was decayed at 300 nm in 2 h, while no ATZ decay was observed for 350 and 419 nm, even up to 8 h of exposure. This is consistent with a previous study, in which only wavelengths below 300 nm are energetic enough for degradation of ATZ [19].

Since photolysis of ATZ was only observed at 300 nm, this wavelength was used exclusively for the indoor study. The result shows that the decay rate constant increases slightly from 0.80 to 1.14 h^{-1} as pH levels increased from 2 to 3, while a further increase of pH (from 4 to 12), the decay rate constants varied between 1.21 and 1.29 h^{-1}.

Among the pH tests, the results of pH 9 provide some insights for quantifying the contribution of k_{UV} to $k_{outdoor}$. $k_{hydrolysis}$ of pH 9 is found to be close to 0 h^{-1}, while $k_{outdoor}$ of pH 9 with the same initial ATZ concentration (13.9 μM) is 0.000170 h^{-1}. Under these circumstances, the ATZ decay can be assumed to be solely resulted from UV radiation, in which k_{UV} at pH 9 was determined to be 1.25 h^{-1} in laboratory test. In other words, the performance of sunlight at outdoor is only 0.0136% of that in the photoreactor for degrading ATZ. Although UV radiation at outdoor exerts a considerable effect on the decay rate constant, the level of $k_{outdoor}$ is significantly smaller than k_{UV} for all pH levels. This is likely due to the following reasons:

First, the availability of UV radiation at outdoor is normally less than 12 h a day (around 6 am to 6 pm), while the hydrolysis takes place 24 h a day regardless of the presence of sunlight.
Secondly, the spectrum of the 300 nm UV lamp is not exactly the same comparing to the available sunlight at UV range, in addition, the former has a much higher intensity than the latter. To verify this, some measurement works were conducted. The highest UV intensity measured outdoor was 2551 μW/cm^2 while the UV intensity measured in photoreactor was 2221 μW/cm^2. At first glance, the UV intensity of both is about the same. However, the range and energy distribution of the irradiance of sunlight and UV lamps are different. The above readings, therefore, have to be readjusted.

According to the spectrum of UV radiance at different wavelengths provided by The National Oceanic and Atmospheric Administration, most of the UVA rays can reach the Earth's surface while some of the UVB rays are filtered by the ozone layer. Noon is the time of the day when the amount of UVB rays that reach the Earth's surface is at the maximum, assuming a typical sunlight spectrum can be used for this condition.

The light meter used for measuring UV intensity is sensitive to both UVA and UVB range, and the reading is a summation of intensity detected from 290 nm to 390 nm (in the unit μW/cm^2). As the measured intensity 2551 μW/cm^2 (at outdoor) is the integrated area underneath the curve from 290 to 390 nm. The maximum intensity, x, can be determined by using Eq. (7). Assuming each nanometer of wavelength received the maximum intensity from 320 nm to 390 nm (UVA range) while the integrated area underneath 290 nm to 320 nm (UVB range) is about 2/3 of that maximum intensity:

$$(390 - 320) * x + (320 - 290) * \frac{2}{3} * x = 2551 \quad (7)$$

x is therefore determined to be 28 μW/(cm^2 nm).

The same rationale can be applied to the 300 nm lamp. The energy distribution of the RMR-3000 Å UV lamps used in this experiment was provided by manufacturer, and the maximum intensity from the photoreactor is determined to be 79 μW/(cm^2 nm).

By incorporating the above two curves, the comparison of the UV irradiation between the 300 nm UV lamps and sunlight is possible. The shaded area in Fig. 6 indicates the amount and spectrum of radiation co-exist in both the systems. It is clear that sunlight has lower intensity comparing to that of a 300 nm lamp.

From Fig. 6, it can also be noted that 300 nm lamp has small leakages at UVC range (250–290 nm), which is not normally observed in the ambient environment. Previous study has proposed that decay pathway above 290 nm is very different from that below [15]. This also contributes to the different performance of photolysis between indoor and outdoor.

3.4. Effect of humic acid on the photolysis of ATZ

Humic substances arise from microbial degradation of plants and are ubiquitous in natural water bodies. It is therefore important to understand their effects on the degradation of ATZ. In this study, humic acid was used to quantify such an effect. It was found that 10 mg/L humic acid increases the decay rate constant of 13.9 μM ATZ when exposed to UV 300 nm at pH 2 comparing to that without the humic acid. However, excess humic acid (higher than 10 mg/L) will decrease the decay rate, see Fig. 7. This observation is consistent with previous studies. It was suggested that low level of humic acid can act as photosensitizer and radical precursor in the presence of

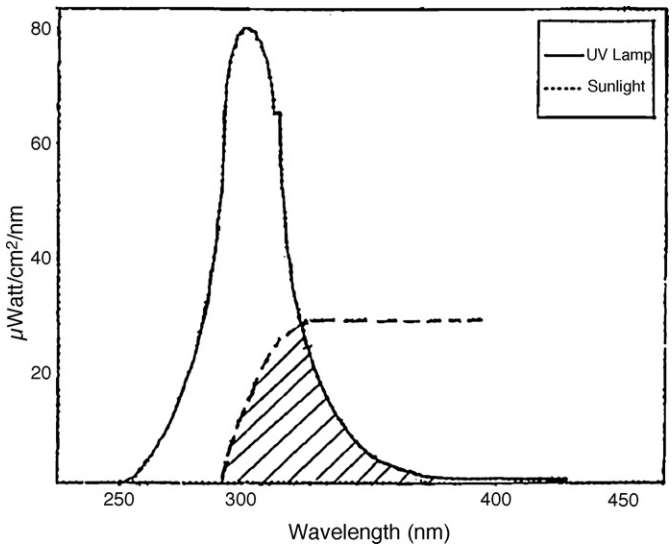

Fig. 6. Amount of UV radiation effective on ATZ decay in sunlight.

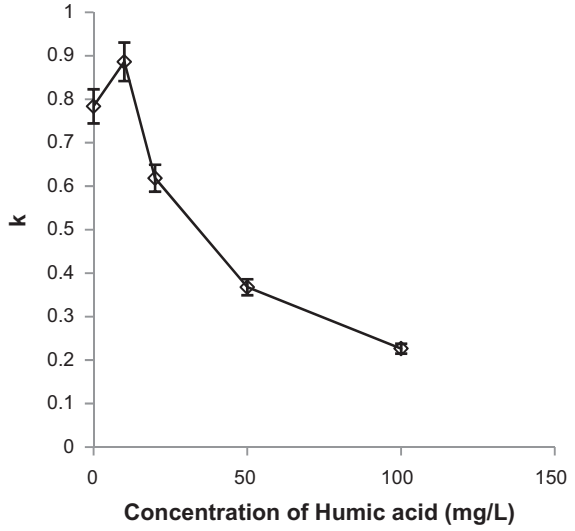

Fig. 7. Effect of humic acid on the photolysis of ATZ ($[ATZ]_0$ = 13.9 μM, pH = 2).

UV radiation. However, in the presence of high concentration of humic acid, the above effects become minor and the excess humic acid might scavenge radicals and resulted in quenching effect of the system [20]. In addition, light attenuation effect (i.e. incident light absorption by humic materials rather than the ATZ) may also contribute to the slowdown of the ATZ decay.

4. Conclusion

Study of the degradation of endocrine disruptors in a closed-to-natural environment is helpful to the understanding of their effects on water quality. Two abiotic degradation mechanisms, photolysis and hydrolysis of ATZ including temperature effect, have been studied. The contribution of each was further investigated in the laboratory.

- Hydrolysis is a slow process but it dominates the outdoor process in terms of reaction time, while photolysis is a faster path but only available for several hours a day in the outdoor environment. The real photolysis time at outdoor was therefore adjusted by using accumulated UV index to determine the pseudo first-order decay rate constant.
- Decay rate constant of ATZ was found to be slowest at neutral pH and fastest in extreme pH levels. The effect of concentration on decay rate constant of ATZ is pH-dependent. Increase in sunlight radiation and/or temperature also resulted in an increase in the decay rate constant of ATZ.
- The effect of hydrolysis on the decay of ATZ was further studied in laboratory (indoor). It was found that the trend of decay is similar to that at outdoor with decay rate constant slowest at neutral and faster at extreme pH levels.
- Effect of temperature on hydrolysis of ATZ was also investigated and found critical. A mathematical model incorporating ATZ decay rate constants, pH levels and temperatures was established quantitatively. Depending on pH levels, the hydrolysis contributes to 18–55% of overall outdoor decay, where the remaining is therefore resulted from the photolysis.
- No decay of ATZ was observed at wavelengths longer than 300 nm. The results of indoor photolysis using 300 nm UV lamps showed that the photolysis is lower at pH 2, which is different from the outdoor observation. This is likely due to the different intensity and spectrum distribution between sunlight and UV lamps as discussed in the paper.
- The effect of humic acid on photolysis of ATZ was found to have two distinct stages. A rate enhancement was observed at lower humic acid level, while the increase of humic acid will retard the photolysis. This is resulted from a balance among the various characteristics of photosensitizer, radical precursor, light attenuator and quencher of humic acid.

Acknowledgment

The authors appreciate the financial support from the Hong Kong Polytechnic University (GU-590).

References

[1] Q. Li, Y. Luo, J. Song, L. Wu, Risk assessment of Atrazine polluted farmland and drinking water: a case study, Bull. Environ. Contam. Toxicol. 78 (2007) 187–190.
[2] D.W. Kolpin, E.M. Thurman, S.M. Linhart, The environmental occurrence of herbicides: the importance of degradates in ground water, Arch. Environ. Contam. Toxicol. 35 (1998) 385–390.
[3] R.L. Becker, D. Herzfeld, K.R. Ostlie, E.J. Stamm-Katovich, Pesticides—Surface Runoff, Leaching, and Exposure Concerns, University of Minnesota, Minnesota Extension Service AG-BU-3911, Minneapolis, 1989, p. 32.
[4] D.A. Goolsby, W.A. Battaglin, E.M. Thurman, Occurrence and transport of agricultural chemicals in the Mississippi River Basin, July through August 1993 in: U.S. Geological Survey Circular 1120-C, 1993.
[5] J.A. Carr, A. Gentles, E.E. Smith, W.L. Goleman, L.J. Urquidi, K. Thuett, R.J. Kendall, J.P. Giesy, T.S. Gross, K.R. Solomon, G. Van Der Kraak, Response of larval *Xenopus laevis* to Atrazine: assessment of growth, metamorphosis, and gonadal and laryngeal morphology, Environ. Toxicol. Chem. 22 (2003) 396–405.
[6] T.B. Hayes, P. Case, S. Chui, C. Duc, C. Haeffele, K. Haston, M. Lee, M. Vien Phoung, Y. Marjuoa, J. Parker, M. Tsui, Pesticide mixtures, endocrine disruption, and amphibian declines: are we underestimating the impact? Environ. Health Perspect. 114 (2006) 40–50.
[7] A. Reeder, G. Foley, D. Nichols, L. Hansen, B. Wikoff, S. Faeh, J. Eisold, M. Wheeler, R. Warner, J. Murphy, V. Beasley, Forms and prevalence of intersexuality and effects of environmental contaminants on sexuality in Cricket Frogs (*Acris crepitans*), Environ. Health Perspect. 106 (1998) 261–266.
[8] L. Tavera-Mendoza, S. Ruby, P. Brousseau, M. Fournier, D. Cyr, D. Marcogliese, Response of the amphibian tadpole (*Xenopus laevis*) to Atrazine during sexual differentiation of the testis, Environ. Toxicol. Chem. 21 (2002) 527–531.
[9] Z. Cai, D. Wang, W.T. Ma, Gas chromatography/ion trap mass spectrometry applied for the analysis of triazine herbicides in environmental waters by an isotope dilution technique, Anal. Chim. Acta 503 (2004) 263–270.
[10] C.M. Shaw, P.K.S. Lam, J.F. Mueller, Photosystem II herbicide pollution in Hong Kong and its potential photosynthetic effects on corals, Mar. Pollut. Bull. 57 (2008) 473–478.
[11] F. Shu, Prediction and analysis of Chinese pesticides market for the year 2002, Pestic. Sci. Admin. 23 (2002) 42–46.
[12] R. Jin, J. Ke, Impact of Atrazine disposal on the water resources of the Yang River in Zhangjiakou Area in China, Bull. Environ. Contam. Toxicol. 68 (2002) 893–900.

[13] T. Hedlund, R. Russell, C. Youngson, The rates of photodecomposition of picloram in aqueous systems, in: Fate of Organic Pesticides in the Aquatic Environment, American Chemical Society, 1972, pp. 159–172.
[14] B.E. Pape, M.J. Zabik, Photochemistry of bioactive compounds. Photochemistry of selected 2-chloro- and 2-methylthio-4,6-di(alkylamino)-S-triazine herbicides, J. Agric. Food Chem. 18 (1970) 202–207.
[15] A.J. Cessna, M.L. Homer, E.M. Janis, C.B. Orvin, Nonbiological degradation of triazine herbicides: photolysis and hydrolysis, in: The Triazine Herbicides, Elsevier, San Diego, 2008, pp. 329–353.
[16] F.H. Frimmel, D.P. Hessler, Photochemical degradation of triazine and anilide pesticides in natural waters, in: G.R. Helz, R.G. Zepp, D.G. Crosby (Eds.), Aquatic and Surface Photochemistry, Lewis Publishers, Boca Raton, 1994, pp. 137–147.
[17] S.B. Lartiges, P.P. Garrigues, Degradation kinetics of organophosphorus and organonitrogen pesticides in different waters under various environmental conditions, Environ. Sci. Technol. 29 (1995) 1246–1254.
[18] H. Prosen, L. Zupancic-Kralj, Evaluation of photolysis and hydrolysis of Atrazine and its first degradation products in the presence of humic acids, Environ. Pollut. 133 (2005) 517–529.
[19] S.D.W. Comber, Abiotic persistence of Atrazine and simazine in water, Pestic. Sci. 55 (1999) 696–702.
[20] K.H. Chan, W. Chu, Effect of humic acid on the photolysis of the pesticide Atrazine in a surfactant-aided soil-washing system in acidic condition, Water Res. 39 (2005) 2154–2166.