Bull Environ Contam Toxicol (2009) 82:610–615
DOI 10.1007/s00128-009-9654-3

Hydrolysis and Photolysis of Diacylhydrazines-Type Insect Growth Regulator JS-118 in Aqueous Solutions Under Abiotic Conditions

J.-Y. Hu · C. Liu · Y.-C. Zhang · Z.-X. Zheng

Received: 22 September 2008 / Accepted: 9 January 2009 / Published online: 23 January 2009

Abstract JS-118 is a diacylhydrazines-type insect growth regulator which is now used extensively in China. The hydrolysis and photolysis of the pesticide JS-118 in aqueous solutions have been assessed under natural and controlled conditions in this project. Hydrolysis experimental results show that JS-118 is quite stable in aqueous solutions in dark, with no significant variations be observed in degradation under various conditions. Abiotic hydrolysis is relatively unimportant compared to photolysis. The rate of photodecomposition of JS-118 in aqueous solutions follows first-order kinetics both in UV radiation and natural sunlight. The degradation rates are faster under UV light than sunlight, with the half-lives ($t_{1/2} = \ln 2/k$) of 6.00–10.85 min and 6.63–10.16 day, respectively. Under UV light, two major photoproducts are detected, and tentatively identified according to HPLC-MS spectral information as *N*-*t*-butyl-*N*-(3,5-dimethylbenzoyl) and 3,7-dimethyl-benzoatedihydrofuran. The corresponding photolysis pathways of JS-118 are also proposed. The results obtained indicate that direct photoreaction is an important dissipation pathway of JS-118 in natural water systems.

Keywords Insecticide JS-118 · Hydrolysis · Photolysis · Photoproducts · Aquatic

The use of agricultural pesticides has increased dramatically during the past few decades and has consequently led to increasing concern about the environmental fate of these substances. To evaluate the fate of pesticides in the environment, the influences of both abiotic and biotic factors should be taken into account. Among the abiotic chemical factors affecting the behavior of pesticides, hydrolysis and photochemical reactions are important. In the surface layers of aquatic systems, hydrolysis and photochemical reactions can play dominant roles in the conversion and degradation of pesticides. Diacylhydrazines are non-steroidal molting hormone agonists that have insecticidal activity. To date four compounds, tebufenozide (RH-5992), methoxyfenozide (RH-2485), chromafenozide (ANS-118), and halofenozide (RH-0345) are currently used as insecticides (Nakagawa et al. 2005). Figure 1a shows the common structure of them.

The insecticide JS-118 [*N*′-*t*-butyl-*N*′-(3,5-dimethylbenzoyl)- (2,7-dimethyl-benzodihydrofuran) methylbenzohydrazine, CAS NO. 467427-81-1] is a recently introduced diacylhydrazines-type insect growth regulator to control *Lepidoptera*. It was developed by Jiangsu Pesticide Research Institute China in 1990s, has been granted patents in China (ZL01181611.9). It was to be commercialized as a *leptidopteran*-specific insecticide under the trade name Fuxian which was 10% suspensoid of JS-118 (Zhang 2005). This insecticide induces premature molting and causes the death of insects by mimicking their hormone (Mao et al. 2004), and has been extensively used in China in recent years. The chemical structure of JS-118 is illustrates in Fig. 1b, and it is a diacylhydrazine derivative containing furan.

Although JS-118 is used on an extensive scale in China, studies on the environmental behavior of the pesticide are scarce. To our knowledge, no data were available about hydrolysis and photolysis of other diacylhydrazines-type insect growth regulator in scientific literature. Understanding of aquatic fate is a building block for a complete environmental safety assessment of pesticides. Detailed

J.-Y. Hu (✉) · C. Liu · Y.-C. Zhang · Z.-X. Zheng
School of Applied Science, University of Science and Technology Beijing, 100083 Beijing, China
e-mail: jiyehu@sas.ustb.edu.cn

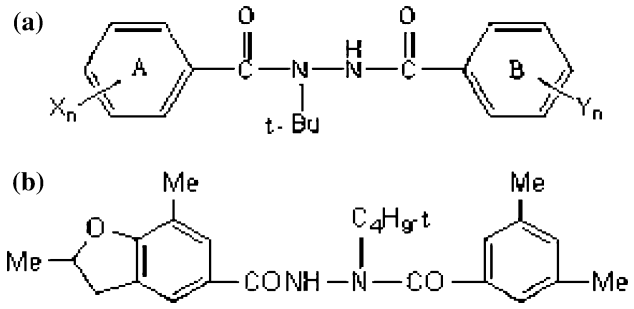

Fig. 1 Chemical structures of diacylhydrazines (**a**) and JS-118 (**b**)

knowledge of hydrolysis and photolysis of pesticides is pertinent in designing experiments to obtain reliable rate constants for use in assessing the fate and transport of pesticide pollutants in aquatic ecosystems (Ramesh and Balasubramanian 1999). In this project, the degradation kinetics and the main photoproducts in aqueous solutions in controlled and natural conditions were evaluated by using the HPLC-UV, HPLC-MS. The corresponding photolysis pathways were also proposed.

Materials and Methods

Residue analysis grade JS-118 was supplied by Jiangsu Pesticide Research Institute China. Water for HPLC was obtained with a Milli-Q water purification system (Millipore). HPLC grade methanol was procured from Dikma Limited (China). SPE columns were Dikma Limited Preparation Products (C-18, 500 mg, 3 mL).

Five buffer solutions (pH at 2.0 ± 0.1, 4.5 ± 0.1, 7.4 ± 0.1, 9.2 ± 0.1, and 12.3 ± 0.1) were used to study the aqueous degradation of JS-118. The procedures followed for their preparation according to the reference (Morrica et al. 2001).

To study the influence of natural water constituents on photodegradation, lake water was collected from Guishui Lake located at the suburb of Beijing, China. The lake (area 550 km^2, maximum depth 20 m) is a slightly eutrophic lake, and its water quality is affected by agricultural effluents and wastes. Natural water was sampled by dipping a clean stainless steel can into top the 1 m of water until the can was full. Samples were sub-sampled prior to beginning the experiment for measurements of dissolved total organic carbon (TOC), total suspended solids (TSS), pH, and electrical conductivity (EC). Data are as follow: TOC, 20.1 mg/L; TSS, 19.4 mg/mL; pH, 8.0; EC, 2.12 mS/cm.

To avoid microbial degradation, buffer solutions and natural water were sterilized by filtration and all glass apparatuses by autoclaving for 20 min at 121°C. Aseptic techniques were adopted throughout the study to maintain sterility.

High performance liquid chromatograph (Agilent 1100) equipped with an analytical column (250 mm × 4.6 mm I.D., 5 μm ODS) attached to a UV detector. The chromatographic conditions used for the analysis of JS-118 residues were as follows: the mobile phase was methanol–water (80 + 20, v/v) with a total flow of 1.0 mL/min. The injection volume was 20 μL; Detection was performed at 230 nm. Under these conditions, the retention time of JS-118 was about 6.3 min. All measurements were carried out at room temperature. For HPLC-MS analysis, Agilent 6130 single Quad MSD system was employed. Acquisition parameters were as follows: Column, Agilent Zorbax SB-Aq, 2.1 mm × 100 mm, 1.8 μm. Flow rate, 0.2 mL/min. Temperature 25°C. Mobile phase, A-0.1% formic acid; B methanol, A:B = 30:70 Gas flow, 8 mL/min. Gas temperature, 350°C Capillary voltage, 3 kV Fragmentor, 70.

Photolysis experiments for the aqueous solutions were carried out in XPA (II) photolysis reactor made in Nanjing, China, equipped with Philips HPK 300 W high-pressure mercury lamp. The lamp was jacketed with a water-cooled Pyrex filter. The tap water cooling circuit maintained the temperature at 30–35°C.

Sunlight conditions Photolysis under sunlight was conducted from July to August 2008, in Beijing. The sunlight intensity at 300–400 nm wavelength was 502, 1,838,350 mW/cm^2 at the beginning, middle, and the end of the day, respectively.

Triplicate 200.0 mL buffer solution samples, each containing 1.0 mg/L of JS-118, were obtained by adding appropriate volume of the stock solution into the buffer solutions. The treated buffer solutions were stored in the dark at ambient temperature (25 ± 2°C) in Erlenmeyer flasks. Another sets of triplicate 200.0 mL buffer solution samples containing 1.0 mg/L of the pesticide, was stored in the dark at 50 ± 2°C to test the effects of temperature on hydrolysis. In all trials, the pH of each sample was periodically measured and did not vary by >0.1 unit. Experimental bottles were left static in the laboratory and shaken very 8–12 h. Initially, the starting concentration was determined. Samples (5 mL) were drawn out from each bottle at day 5, 10, 20, 30, 40, 60 and 90. Samples were treated followed the sample preparation procedure below.

A solid phase extraction (SPE) method has been developed to allow purification and low-concentration experiment. C-18 cartridges (3 mL, 500 mg) were conditioned with methanol (5 mL), followed by distilled water (5 mL). Immediately after, the solutions (5 mL) was removed and passed through the cartridge at a flow rate of ~1 mL/min. After loading, the analytes were eluted with methanol (2 mL). The eluate was dried under a gentle stream of nitrogen. The residue was re-constituted in mobile phase (1 mL) for HPLC analysis.

Kinetic studies of photodegradation were performed with high-pressure mercury lamp (HPK 300 W) in water-cooled quartz housing from Philips (The Netherlands) with a prominent emission band around 254 nm and several above 290 nm. Samples were placed in a quartz or Pyrex glass cuvette. Experiments were conducted at room temperature. The concentration of pesticide JS-118 in aqueous solutions (buffer solutions and natural water) was 10 mg/L in order to facilitate the identification of intermediate products. At specific time intervals (2 min), samples of 2 mL were withdrawn from the reactor and analyzed after direct injection for HPLC or HPLC-MS. Each series of photodegradation experiments was conducted in two replicates and accompanied by dark reaction controls.

For sunlight experiment, the initial concentration of JS-118 in aqueous solutions (buffer solutions and natural water) was 1 mg/L being close to the natural environmental conditions. Samples (5 mL) were drawn out from

Table 1 Dissipation of JS-118 at 25 ± 2–50 ± 2°C in aqueous buffer solutions

Residue (μg/mL) (n = 3)[a]										
25 ± 2°C						50 ± 2°C				
Days	pH 2.0	pH4.5	pH7.4	pH9.2	pH12.3	pH2.0	pH4.5	pH7.4	pH9.2	pH12.3
0	0.90 ± 0.01	1.00 ± 0.02	0.98 ± 0.01	0.97 ± 0.02	1.00 ± 0.03	0.97 ± 0.01	1.00 ± 0.01	0.99 ± 0.01	1.00 ± 0.01	0.99 ± 0.01
5	1.01 ± 0.01	1.00 ± 0.02	0.98 ± 0.02	0.98 ± 0.02	1.00 ± 0.02	0.98 ± 0.01	0.995 ± 0.01	0.94 ± 0.03	1.00 ± 0.01	0.99 ± 0.01
10	0.99 ± 0.02	0.97 ± 0.01	0.98 ± 0.03	0.99 ± 0.01	1.01 ± 0.03	0.98 ± 0.01	0.987 ± 0.01	0.99 ± 0.01	1.02 ± 0.01	0.98 ± 0.02
20	0.96 ± 0.01	1.01 ± 0.01	0.99 ± 0.03	0.99 ± 0.03	0.99 ± 0.01	0.99 ± 0.01	0.98 ± 0.01	0.99 ± 0.01	0.99 ± 0.02	0.99 ± 0.01
30	0.98 ± 0.01	0.98 ± 0.02	1.01 ± 0.02	0.99 ± 0.02	0.97 ± 0.01	0.98 ± 0.03	0.98 ± 0.01	0.99 ± 0.01	0.99 ± 0.01	1.00 ± 0.01
40	1.03 ± 0.02	0.97 ± 0.01	0.98 ± 0.01	0.99 ± 0.02	1.00 ± 0.01	0.96 ± 0.01	0.98 ± 0.03	0.97 ± 0.01	1.00 ± 0.03	0.99 ± 0.01
60	0.99 ± 0.01	1.01 ± 0.01	0.98 ± 0.03	1.00 ± 0.03	1.00 ± 0.02	0.96 ± 0.01	1.00 ± 0.01	0.95 ± 0.03	0.97 ± 0.01	0.99 ± 0.01
90	0.97 ± 0.03	1.00 ± 0.02	0.99 ± 0.01	0.99 ± 0.01	0.97 ± 0.02	0.99 ± 0.01	0.99 ± 0.02	0.99 ± 0.01	1.00 ± 0.01	1.00 ± 0.03

[a] JS-118 concentrations are denoted as the means ± standard deviation (for n = 3). The statistical difference is indicated at the significance level of $p < 0.05$, calculated using *t*-test

Table 2 Photodegradation kinetic parameters

Distilled water			Buffer solutions								
			pH = 4.5			pH = 7.4			pH = 9.2		
$k \times 10^2$ (min^{-1})	$t_{1/2}$ (min)	R^2	$k \times 10^2$ (min^{-1})	$t_{1/2}$ (min)	R^2	$k \times 10^2$ (min^{-1})	$t_{1/2}$ (min)	R^2	$k \times 10^2$ (min^{-1})	$t_{1/2}$ (min)	R^2
11.6	6.00	0.94	6.39	10.85	0.99	8.86	7.82	0.99	7.58	9.14	0.99

Rate constants (*k*), correlation coefficients (R^2), and half-lives ($t_{1/2}$) of the studied JS-118 in distilled water and in buffer solutions under UV light

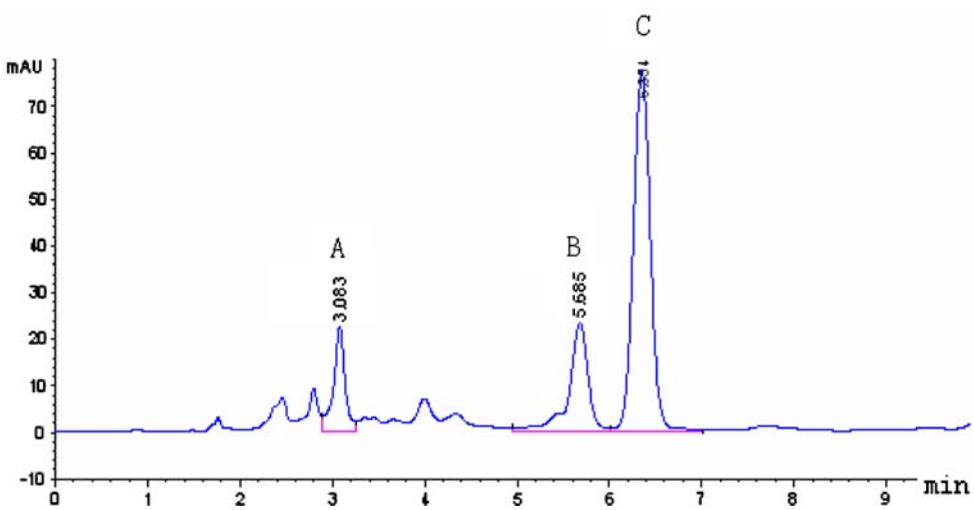

Fig. 2 HPLC chromatogram of two products (*A* and *B*) and parent pesticide JS1I8 (*C*)

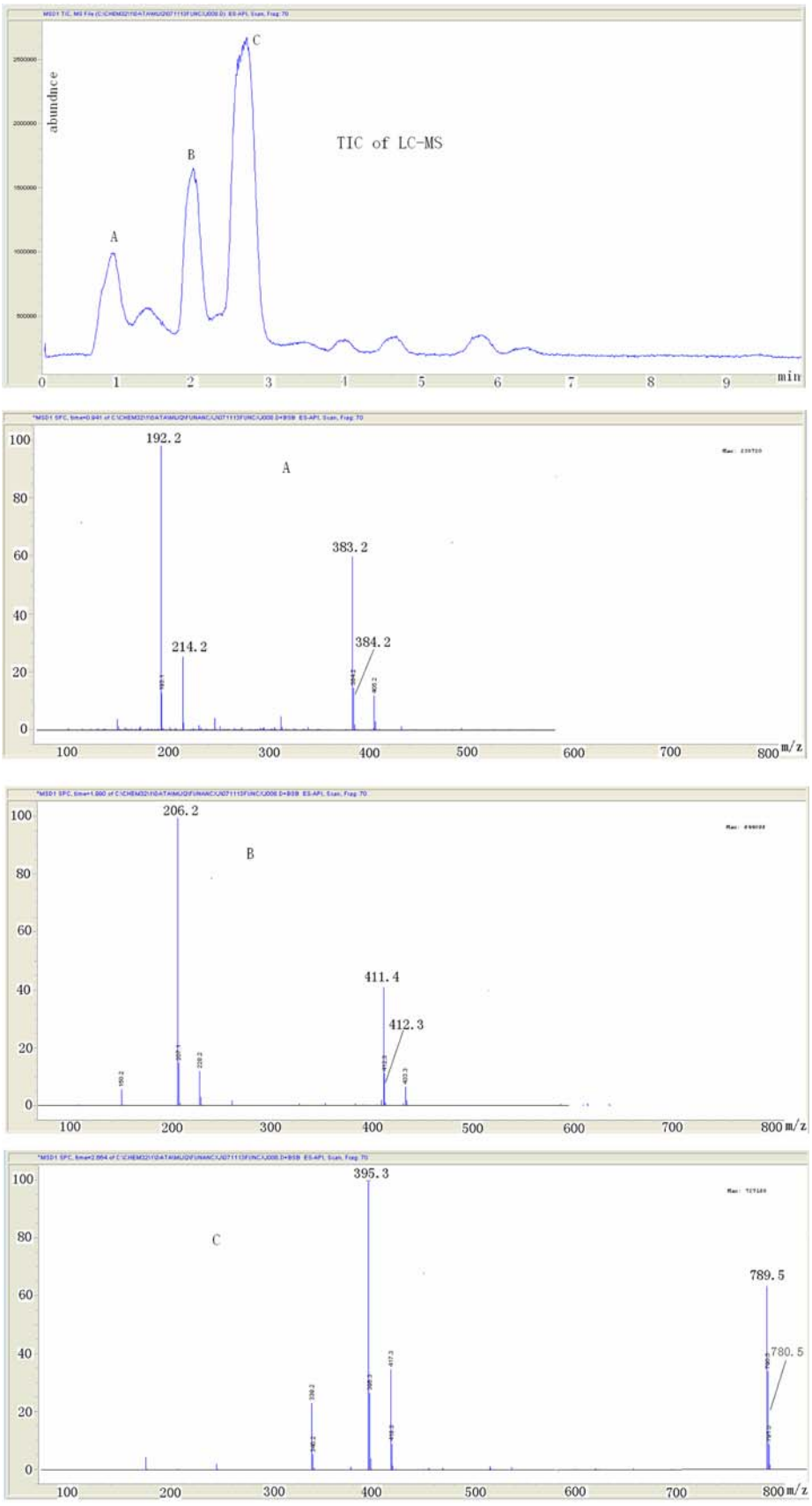

Fig. 3 TIC of LC-MS chromatogram and MS spectrum of **a**, **b**, and **c**

each bottle at day 1, 2, 3, 5, 7, 10 and 15 day. Samples were treated followed the SPE (C-18) sample preparation procedure above.

Results and Discussion

The degradation of JS-118 in aqueous solution in the absence of light at ambient temperatures (25 ± 2 or 50 ± 2°C) was monitored at different pH values. Data observed at different pH and temperatures are presented in Table 1. No significant variations can be observed in degradation with respect to pH and temperature. The results indicate that JS-118 has substantial chemical stability in the buffer solutions.

This also means that the hydrolytic processes of JS-118 during the course of the photolysis experiment can be ignored.

Under UV light, the kinetics of the investigated pesticide follows an apparent first-order degradation model. Table 3 lists the values of k and the linear regression coefficients for first-order kinetics of the photodegradation of the studied compound. The half-lives could be determined from the equation: $t_{1/2} = \ln 2/k$. The investigated pesticide was sufficiently degraded in aqueous solutions under UV light. The half-lives ranged from 6.00 to 10.85 min for the studied pesticide in the examined waters (distilled water and buffer solutions) Table 2.

Special attention was paid to the photoproducts. Aqueous solutions of JS-118 were irradiated under UV light, and samples were taken at regular time intervals. Two photoproducts have been always found at any time intervals besides JS-118 in HPLC chromatogram (see Fig. 2). From the TIC of LC-MS, the two photoproducts also have been observed (see Fig. 3).

The degradation products were tentatively identified by studying their mass spectra. From Fig. 3a was identified as 3,7-dimethyl-benzoatedihydrofuran, according to its mass spectrum, with an ion peak at m/z 192 ($M + 1$), and m/z 383 is its proton ion of hydrogen bond dimer (191 × 2+1). Figure 3b was identified as: *N*-*t*-butyl-*N*-(3,5-dimethyl-benzoyl), according to its mass spectrum with a molecular ion peak at m/z 206 ($M + 1$), m/z 411 is its proton ion of hydrogen bond dimer (205 × 2+1). Figure 3c is the LC-MS spectrum of parent pesticide JS-118, a molecular ion peak is at m/z 395 ($M + 1$).

Based on the structures of photoproducts, two possible photodegradation pathways were proposed for JS-118 in aqueous solution under UV irradiation, Fig. 4.

Under exposure to sunlight, the degradation of JS-118 in natural water, distilled water and buffer solution samples followed a first-order kinetics according to linear regression analysis, with R^2 ranging from 0.98 to 0.99 and the half-lives ($t_{1/2} = \ln 2/k$) from 6.63 to 10.16 day. Table 3 lists the values of k and the linear regression coefficients for kinetics of the photodegradation of JS-118 under solar light.

Photochemical reactions are affected by changes in sunlight intensity and wavelength associated with season and time of day, amount of dissolved and particulate substances and presence of photosensitizers (Castillo et al. 1997). The kinetics was faster in natural water than distilled water. This may be explained that in natural water dissolved total organic carbon (TOC) which absorbs a large portion of photons is a potential photosensitizer.

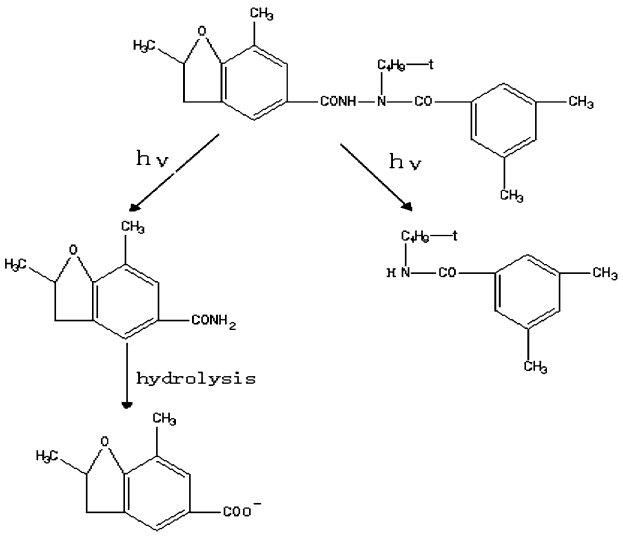

Fig. 4 Proposed path ways of JS-118 under UV irradiation

Table 3 Photodegradation kinetic parameters

Natural water			Distilled water			Buffer solutions								
						pH = 4.5			pH = 7.4			pH = 9.2		
$k \times 10^2$ (day^{-1})	$t_{1/2}$ (day)	R^2	$k \times 10^2$ (day^{-1})	$t_{1/2}$ (day)	R^2	$k \times 10^2$ (day^{-1})	$t_{1/2}$ (day)	R^2	$k \times 10^2$ (day^{-1})	$t_{1/2}$ (day)	R^2	$k \times 10^2$ (day^{-1})	$t_{1/2}$ (day)	R^2
10.45	6.63	0.98	8.63	8.03	0.99	11.65	5.95	0.99	8.21	8.44	0.99	6.82	10.16	0.99

Rate constants (k), correlation coefficients (R^2), and half-lives ($t_{1/2}$) of the studied JS-118 in natural water, distilled water and buffer solutions under solar light

The photolysis rates of JS-118 in buffer solutions depended on the pH value, and the half-life being 5.95 day at pH 4.5, 8.44 day at pH 7.4, and 10.16 day at pH 9.2.

Conclusions

The hydrolysis and photolysis studies carried out on JS-118 in aqueous solution have enabled us to better understand the behavior of this insecticide as well as other diacylhydrazines in the environment.

Results obtained in this study demonstrate that the dark hydrolysis of JS-118 in aqueous solution is negligible with respect to the photochemical decomposition.

The rate of photodecomposition of aqueous solutions follows first-order kinetics both in UV radiation and natural sunlight. The degradation rates are faster under UV light than sunlight, with the half-lives ($t_{1/2} = \ln 2/k$) 6.00–10.85 min and 6.63–10.16 day, respectively. In the case of UV radiation, two major photoproducts was detected and tentatively identified as *N*-*t*-butyl-*N*-(3,5-dimethylbenzoyl) and 3,7-dimethyl-benzoatedihydrofuran. From the photoproducts above, photolysis pathway was understood that degradation primarily preceded by cleavage the N–N covalent bond.

The results obtained indicated that direct photoreaction is an important dissipation pathway of JS-118 in natural water systems while hydrolysis is negligible in these conditions.

Acknowledgment This work was supported by the financial support of National Natural Science Foundation of China (No. 20777078).

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