

Short communication

Dynamics of solar light photodegradation behavior of atrazine on soil surface

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Abstract

The photodegradation of atrazine in topsoil under solar light and the factors affecting this have been studied. A rate constant of 0.08–0.17 day⁻¹, photolytic depth of 0.5 mm and half-life of 4–8 days were determined. The results show that soil granularity, pH value, humidity, organic content, humic acid and surface-active agents could affect the photodegradation of atrazine in soil.

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1. Introduction

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) is a selective inside-absorbing herbicide which can be used in the fields of corn, sorghum, orchard and forest, controlling broad-leaf and grassy weeds. It has been employed for many years as herbicide. However, its residues have been found in the soil and the ground water, threatening human beings. The remediation technologies of atrazine in the soil were studied [1]. As we know that light radiation can degrade many pesticides under the laboratory conditions. Atrazine can be degraded either by supercritical water with UV-illuminated TiO₂-photocatalytic dispersed system or by hydrothermal water with it [2]. Kinetics of oxidative photodegradation of atrazine in aqueous Fe(ClO₄)₃ solutions and TiO₂ suspensions were investigated and compared [3]. A new kind of photochemical reaction catalyst, porphyrin and phthalocyanine, were prepared. These catalysts are able to cleave the triazine ring more efficiently than titanium dioxide [4]. If the photolysis of the herbicide still go smoothly under field's condition it will be possible to decrease the residues

of it. Soil, however, was seldom chosen to be irradiated directly. This is because solar light or ultraviolet penetrates soil poorly and photolysis only occurs on topsoil. And if the soil sample is collected too much, the degradation part of it is so small in amount that any changes of the concentration of atrazine cannot be tested. In our studies a very thin layer of soil (0.2–0.5 mm), is used for photolysis, so, the changes of the concentration can be checked easily. Under the solar light irradiation, the effects of various factors on photolysis are investigated.

2. Instrument and reagents

2.1. Apparatus for photolysis irradiation

The experiment was carried out on the roof of a building, where an iron box (60 cm × 40 cm × 20 cm) containing samples was placed. The cover of the box was opened at 7:30 a.m. and closed at 6:00 p.m. every day except windy or rainy day. It was started from 10 November 2002 to 21 January 2003. The variation of solar light UV intensity was measured by a ZDZ-1 actinometer (254 nm detector) every day. The average variation curve of solar UV intensity during the time

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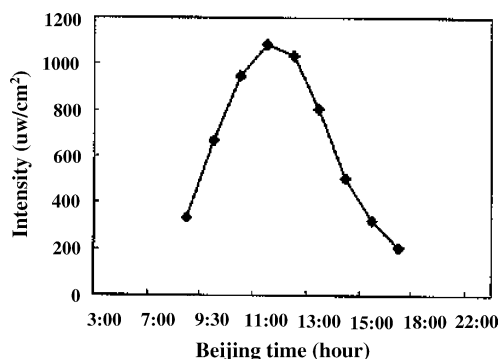


Fig. 1. Average solar UV intensity from 10 November 2002 to 21 January 2003.

when the temperature in the box was in between 1 and 13 °C (windy or rainy day not included), is showed in Fig. 1.

2.2. Materials

Humic acid (HA) and sodium dodecylbenzenesulfonate (DBS) were obtained from Beijing Chemical Reagent Corporation. A soil was obtained from an orchard located in Anxin County, Hebei Province. The orchard itself has never been treated with atrazine and was 800 m away from corn-fields where this herbicide had been applied for 4 years. Soil samples were collected from the surface (top 10 cm), freeze-dried and sieved through a 120 mesh. It did not contain any atrazine according to HPLC analysis. The composition of the soil was: clay 4.03%, silt 50.37%, sand 45.60% and organic matter 1.184%, pH 8.68, density 2.55 g cm⁻² (prior grinding), 1.50 g cm⁻² (after grinding).

3. Experimental methods

3.1. Preparation for irradiation of soil samples

In order to study the effects of the various factors, such as water, HA, surface-active agent, soil granularity and pH, on photolysis, six types of experiments were carried out (see Table 1). Methanol solutions of atrazine (1000 μg ml⁻¹) were applied uniformly to soil samples. After the solvent had been allowed to evaporate, the soil samples were ground and sieved. In some tests, HA and surface-active agent were added directly to the soil prior to grinding.

Table 1
Researching contents of six types of tests

Type	Researching contents
A	Soil granularity, organic substances, pH value: in dry natural soil
B	Soil granularity, organic substances, pH value: in wet natural soil
C	Sand, silt, clay, without organic substances
D	Humic acid
E	Surface-active agent
F	Humic acid and surface-active agent

3.2. Method of irradiation

The atrazine-treated soil samples were sieved uniformly to the surface of plates (diameter 8.7 or 9.4). Then the plates were covered with a sheet of extreme thin film of polyethylene (UV penetration rate more than 85%) to avoid dust from air and put in the iron box which was placed on the roof of the building to receive solar light irradiation. The film was changed once per day and the solar light intensity and the temperature were measured every day except for rainy or windy day.

3.3. Collection and analysis of samples

Samples (15.00 g) were taken out at regular intervals, placed in 50 ml of centrifugal test tube, extracted three times with methanol ultrasonic wave, concentrated, cleaned up and analysed for atrazine by HPLC.

HPLC measurements were carried out on a Shimadzu LC-6A instrument equipped with a Shimadzu SPD-1 detector. The stainless steel column (25 cm × 4.6 cm ID) was packed with DuPont ODS chemically-bonded phase (10 μm), and was pre-tested by the manufacturer. A wavelength of 235 nm was used for all measurements. Samples were eluted with methanol + water (80 + 20 by volume) at a flow-rate of 0.8 ml min⁻¹.

3.4. Calculating method of photolytic depth and photolytic rate

3.4.1. Photolytic depth for atrazine in soil

Atrazine was photolysed only in a very thin surface layer because of low transmission of light and slow movement of atrazine in soil. On the basis of atrazine residues, soil depth, sample weight and soil density, the photolytic depth, i.e. the maximum depth at which photolysis occurred, could be calculated as follows [5]:

$$P = H(1 - R) = \frac{W(1 - R)}{DA}$$

where P is the photolytic depth, H the total thickness of soil layer, R the percentage of remaining at equilibrium, W the total soil mass, and A the soil area.

3.4.2. Rate of photolysis of atrazine

It is difficult to calculate the photolytic rate exactly because of the complexity of the soil, but provided that the photolysis of atrazine follows a first-order reaction, the rate constant k_s can be calculated approximately from [6]:

$$\ln\left(\frac{C_0}{C_t}\right) = k_s t$$

because solar light penetrates the soil surface only to depth of less than 0.3 mm, atrazine in the lower layers is not photolysed, and this must be allowed for. The above expression

Table 2
Characteristics of sample for tests A and B

	Group A				Group B			
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 1	Sample 2	Sample 3	Sample 4
Sand (%)	46.06	60.72	56.40	56.47	46.07	46.07	46.07	46.07
Silt (%)	47.87	37.48	40.99	41.19	47.87	47.87	47.87	47.87
Clay (%)	6.06	1.80	2.61	2.34	6.06	6.06	6.06	6.06
Organics (%)	1.454	1.442	1.615	0.873	1.454	1.454	1.454	1.454
pH	8.63	8.65	8.31	8.73	3.34	5.58	8.63	10.10
Water (%)	0	0	0	0	50	50	50	50

thus has to be modified to:

$$\ln \left(\frac{C_0}{C_t^1} \right) = k_s t, \quad \frac{C_t^1}{C_0} = \frac{C_t/C_0 - C_e C_0}{1 - C_e/C_0} = \frac{C_t - C_0}{C_0 - C_e},$$

$$C_t^1 = \frac{C_t W - C_e W}{W(P/H)}$$

where C_0 is the original concentration of atrazine, C_t^1 the concentration of atrazine in photolysed layer at time t , C_t the measured overall concentration of atrazine at equilibrium, W the total soil mass, P the photolytic depth, H the overall soil depth and k_s the rate constant.

4. Results and discussion

The amount of atrazine residues in the soil can be obtained from the analysed results by HPLC, and the photolytic depth as well as the photolytic rate can be calculated from the method mentioned above [7].

4.1. Test A: effects of soil granularity on photolysis of atrazine

Samples 1 and 2 were chosen from natural soil, whose organic content and pH were similar but soil granularity and composition different (soil features in Table 2). Sample 1 contained much more clay than sand while sample 2 contained more sand than clay. Two samples were treated with atrazine, irradiated by solar light at different intervals and tested to give photolytic curves (see Fig. 2), photolytic depth d , rate constant k_s and half-life $t_{1/2}$ (see Table 3).

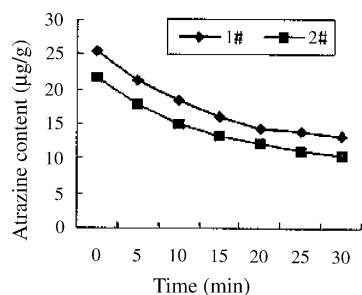


Fig. 2. Photolytic curve of samples 1 and 2 under solar light of test A.

From Fig. 2 and Table 3, it can be seen that sample 1's rate constant is somewhat larger than that of sample 2, but the half-life is a little less than that of the latter, and both photolytic depths are nearly equal. This indicates that when other conditions are same, photolytic rate in thin silt soil is larger than that in coarse sand soil, i.e. the coarser the soil is, the less the solar light penetrates.

4.2. Test B: effects of soil humidity on photolysis of atrazine

Photolysis was carried out on soil 3 from type A under dry/wet conditions for comparison. The 50% of water was added, and its photolytic curves were showed in Fig. 3, its data in Table 4.

The results indicate that the rate constant is slightly greater in wet soil than in dry one and so is the photolytic depth. This suggests that water assist the movement of atrazine from the inner layers to the surface of the soil. It may also assist the removal of the photolytic products, thus overall accelerating the photolysis of atrazine.

4.3. Test B: effects of pH value on photolysis of atrazine

In order to explore the influences of pH value on photolytic reaction, four soil samples with different pH values were chosen, whose composition was sand 46.07%, silt 47.87%, clay 6.06% and organic substance 1.454%, pH value from 3.34 to 10.10 (see Table 2). These four samples were treated with atrazine separately and then irradiated by solar light at different intervals to get photolytic data in Table 3b. It can be seen

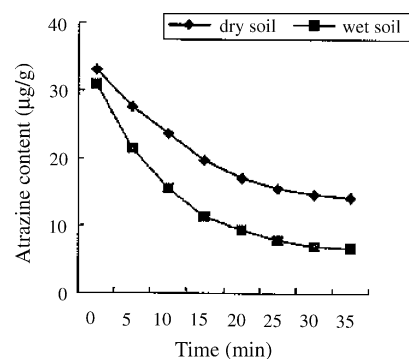


Fig. 3. Solar light photolytic curve under wet/dry condition.

Table 3
Photolysis data for types A–F test

	Soil depth, h (mm)	Photolytic depth, d (mm)	Rate constant, k_s (day^{-1})	Half-life time (day)	Standard deviation (%)
Type A test					
1	0.35	0.12	0.1399	4.9	3.02
2	0.38	0.11	0.1173	5.9	3.25
Type B test					
1	0.38	0.22	0.1864	3.7	3.12
2	0.39	0.21	0.1610	4.3	3.03
3	0.37	0.20	0.1329	5.2	3.50
4	0.40	0.21	0.1561	4.4	3.32
Type C test					
Wet sand	0.35	0.19	0.0953	7.3	3.14
Wet silt	0.36	0.20	0.1012	6.8	3.23
Wet clay	0.34	0.21	0.1316	5.3	3.01
Type D test					
No HA	0.31	0.18	0.1212	5.8	3.21
HA added	0.30	0.19	0.1527	4.5	3.08
Type E test					
No DBS	0.31	0.18	0.1212	5.8	3.54
DBS added	0.31	0.19	0.1399	5.0	3.34
Type F test					
No HA + DBS	0.31	0.18	0.1212	5.8	3.21
HA + DBS added	0.30	0.20	0.1638	4.2	3.15

from the result that when other conditions were same, both atrazine photolytic rate and photolytic depth were greater in acid soil (pH 3.34, 5.58) or base soil (pH 10.01) than in neutral soil (pH 8.63), showing that H^+ or OH^- ion is able to catalyse the photochemical reactions.

4.4. Test C: photolysis of atrazine in soil without organic substances

Soil samples were treated with the standard method to remove the organic substances and divided into three types, sand, silt and clay. The three types of soil were mixed with atrazine separately and irradiated by solar light under condition of water content 50% to get photolytic data in Table 3c. The photolysis rate of atrazine and photolytic depth increased gradually from sand through silt to clay, showing that the soil can accelerate the photochemical reaction with its smaller particle size. This probably relates to the increase of surface area; the smaller the particle size, the greater the surface area per unit mass, and hence the greater the catalytic capability.

4.5. Test D: effects of humic acid on photolysis of atrazine

Humic acid can exist in the fields, so we designed test D to investigate its effects on photolysis of atrazine under

solar light condition. Based on the previous work, and taking into account possible interference with HPLC, silt samples free from organic substances were spiked with humic acid (20 mg/1000 g sample) and 50% of water. The parameters are given in Table 3d.

It can be seen that the photolytic rate constant was obviously increased in the presence of humic acid, half-life became shorter and the photolytic depth was slightly increased. This demonstrates that humic acid can catalyse the photolysis of atrazine and accelerate the process. So atrazine pollution in the fields can be decreased if proper amount of humic acid is applied in the natural soil and irradiated by solar light.

4.6. Test E: DBS influences on atrazine photolysis

In order to study the influences of surface-active agent on the photolysis of atrazine, dodecylbenzenesulfonate (DBS) was taken as a typical representative for the experiment. The organic-free soil samples (sand 46.07%, silt 47.87%, clay 6.06%) were spiked with DBS (20 mg/1000 g sample) and 50% of water and then irradiated by solar light to get the parameters in Table 3e.

The results show that the photolytic rate constant and the photolytic depth are both somewhat increased in the presence of the surface-active agent (DBS), but its influence on the photolysis of atrazine is less than that of humic acid. This

Table 4
Photolytic depth d , rate constant k_s and half-life $t_{1/2}$ under dry/wet condition

	Soil depth, h (mm)	Photolytic depth, d (mm)	Rate constant, k_s (day^{-1})	Half-time, $t_{1/2}$ (day)	Standard deviation (%)
Dry soil	0.32	0.11	0.1129	6.1	3.42
Wet soil	0.34	0.13	0.1403	4.9	3.12

indicates that DBS can play some catalyzing role in the photolysis of atrazine and assist the process.

4.7. Test F: co-effects of humic acid and DBS

The organic-free soil samples (sand 46.07%, silt 47.87%, clay 6.06%) were spiked with atrazine, humic acid and DBS (20 mg humic acid, 20 mg DBS/1000 g sample), and then 50% of water was added, irradiated by solar light to obtain the data in Table 3f.

From the results we know that the photolytic rate constant and the photolytic depth are both increased apparently in the presence of humic acid and DBS. Their influence is much more than that of humic acid or DBS singly. It suggests that humic acid and DBS cooperate with each other to promote the photolysis of atrazine.

5. Conclusion

The photolysis of atrazine only occurs very close to the soil surface (top 0.5 mm) because of the low penetration of solar radiation. It was observed that the finer the soil, the greater the photolytic rate constant; and some organic substances in the soil, such as humic acid, surface-active agent,

can promote the photolysis of atrazine. The photolytic process was approximately a first-order reaction (relative coefficient >0.920). The rate constant of photolysis ranged from 0.08 to 0.17 day^{-1} .

References

- [1] L. Di Palma, P. Ferrantelli, E. Petrucci, Experimental study of the remediation of atrazine contaminated soils through soil extraction and subsequent peroxidation, *J. Hazard. Mater. B* 99 (2003) 265–276.
- [2] S. Horikoshi, H. Hidaka, Non-degradable triazine substrates of atrazine and cyanuric acid hydrothermally and in supercritical water under the UV-illuminated photocatalytic cooperation, *Chemosphere* 51 (2003) 139–142.
- [3] H. Krysova, J. Jirkovsky, F. Krysa, et al., Comparative kinetic study of atrazine photodegradation in aqueous $\text{Fe}(\text{ClO}_4)_3$ solutions and TiO_2 suspensions, *Appl. Catal. B: Environ.* 40 (2003) 1–12.
- [4] V. Hequet, P. Le Cloirec, C. Gonzalez, et al., Photocatalytic degradation of atrazine by porphyrin and phthalocyanine complexes, *Chemosphere* 41 (2000) 379–386.
- [5] A. Gong, C. Ye, Z. Lei, et al., Dynamics and mechanism of ultraviolet photolysis of atrazine on soil surface, *Pest Manage. Sci.* 57 (2001) 358–380.
- [6] X. Fu, W. Shi, T. Yao, *Physical Chemistry* (1990).
- [7] G. Sposito, L. Martin-Neto, A. Yang, Atrazine complexation by soil humic acids, *J. Environ. Qual.* 25 (6) (1996) 1203–1209.