Dynamics and mechanism of ultraviolet photolysis of atrazine on soil surface

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Abstract: The photolysis of atrazine in the soil surface under UV light and the factors affecting this has been studied. A rate constant of $0.09\text{--}0.17\text{ min}^{-1}$, photolytic depth of $0.1\text{--}0.3\text{ mm}$ and half-life of $4\text{--}8\text{ min}$ were determined. The results show that soil granularity, pH, humidity, organic content, humic acid and surface-active agents could affect the photolysis of atrazine in soil. GC-MS showed three photolytic products: 1-sec-butyl-4,4-diethyl-1-tetrazene, N^2 , N^4 -diethyl-6-methyl-1,3,5-triazine-2,4-diamine and 6-chloro- N^2 -propyl-1,3,5-triazine-2,4-diamine. The mechanism of the photolytic process is discussed.

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Keywords: atrazine; photolysis; soil; UV light

1 INTRODUCTION

Atrazine has been used extensively for the control of broad-leaf and grassy weeds in corn and other crops. Because of its persistence and wide and prolonged use, the possible contamination of surface and ground water supplies by this herbicide has become of environmental concern.^{1,2}

Ultra-violet light causes the chemical modification of many pesticides under laboratory conditions.³ If such photodecomposition were to occur under field conditions, the results could be of major importance in predicting the environmental fate of such compounds in agricultural use.^{4,5}

The photolysis of atrazine under UV light has been investigated by many workers.^{6,7} Hustert *et al*⁸ reported that atrazine is easily degraded by UV radiation in titanium dioxide suspensions or in the presence of hydrogen peroxide. Dilute aqueous solutions of atrazine in the $\mu\text{g litre}^{-1}$ range could effectively be decontaminated by photocatalysis. Pelizetti *et al*⁹ investigated the photocatalytic degradation of atrazine in the presence of semiconductor metal oxide particles (TiO_2 , ZnO) suspended in aqueous solution under simulated sunlight irradiation. They observed that the weak photocatalytic activity of the soils suspended in aqueous solution (2 g litre^{-1}) was dramatically increased by the addition of 0.5 g of a semiconductor. The half-life was $10\text{--}40\text{ min}$, depending on the nature of the soil.

Many other studies have demonstrated that small additions of semiconductor oxides, such as TiO_2 and ZnO , to soil greatly increase the photodegradation rate

of atrazine under simulated sunlight radiation. However, such semiconductors are often constituents of soil, so why did the soils themselves exhibit only a very weak catalytic activity towards atrazine? Most photolysis studies of atrazine have involved dilute aqueous suspensions of semiconductors and soil systems, which represent a considerable departure from the conditions which exist in most agricultural soils.

The present investigation deals with the fate of atrazine in the surface of agricultural soils under UV light. The influences of soil granularity, pH, humidity, organic content, humic acid and surface-active agents were examined, and the major photolytic products and mechanism of decomposition explored.

2 EXPERIMENTAL

2.1 Materials

Atrazine was purchased from Ciba-Geigy (Basel, Switzerland). Humic acid (HA) and sodium dodecylbenzenesulfonate (DBS) were obtained from Beijing Chemical Reagent Corporation. A MILLI-Q pure water device was used. All organic solvents were of analytical reagent grade and were purified by distillation.

A soil with no history of atrazine application was obtained for this study from an orchard located at the north basin of Baiyangdian Lake, North China. The orchard itself had never been treated with atrazine and was 600 m from cornfields where this herbicide had been applied for 5 years. Soil samples were collected from the surface (top 10 cm), freeze-dried and sieved

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through a 120- μm mesh. The composition of the soil was: clay 7–10%, silt 25–35%, sand 58–68% and organic matter 0.88–1.55%, pH 7.8–8.0.

2.2 Photochemical measurements

The irradiation device comprised a light-tight box containing a medium-pressure mercury lamp (1000 W) with a water-cooled quartz condenser and rotating sample shelf, so that the samples were 15 cm from the lamp. During photolysis reactions, the temperature was maintained at $28(\pm 2)^\circ\text{C}$ by air-conditioning. The UV intensity on the shelf, measured by a ZDZ-1 actinometer, was $2790\mu\text{W cm}^{-2}$.

2.3 Analysis of atrazine

High-performance liquid chromatography (HPLC) measurements were carried out on a Shimadzu LC-6A instrument equipped with a Shimadzu SPD-1 detector. The stainless steel column (25 cm $\times$ 4.6 mm 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} . Mass spectra were obtained using an LK 9000 GC-MS (LKB Instruments Inc, Rockville, MD, USA). Samples were introduced by a direct probe into the ionization source, or indirectly by means of a gas chromatograph. The latter was accomplished using an SE-30 column (1% w/w on 60/80 mesh Gas-Chrom Q) with a column temperature ranging from 80 to 320°C .

2.4 Photochemical procedures

In order to study the effect of the various factors on photolysis, six types of experiment were carried out (see Table 1). Methanol solutions of atrazine (1 mg ml^{-1}) were applied uniformly to soil samples. After the solvent had been allowed to evaporate, the soil samples were ground and sieved. In the appropriate tests, HA and DBS were added directly to the soil prior to grinding.

The atrazine-treated soil samples were sieved uniformly onto the surface of plates (diameter 8.7 cm) to give an average soil thickness of 0.2–0.5 mm and then irradiated in the irradiation device. Samples were

Table 1. Variables examined for effect on atrazine photolysis

Test	Variables included in test
A	Soil granularity, organic substances, pH value: in dry natural soils
B	Soil granularity, organic substances, pH value: in wet natural soils
C	Sand, silt, clay, without organic substances
D	Humic acid
E	Surface-active agent
F	Humic acid and surface-active agent

Figure 1. Photolytic curves with soils 1 and 2.

taken out at 5-min intervals, weighed, placed in beakers, extracted three times with methanol, concentrated, cleaned up and analysed for atrazine by HPLC. Figs 1 and 2 show the variation of atrazine content with time for soils 1, 2, 3 and 4. These are typical of the curves obtained in all the tests, allow the calculation of a range of parameters, as described in Section 3.1 and 3.2.

3 RESULTS AND DISCUSSION

3.1 Photolytic depth for atrazine in soil

Atrazine was photolysed only in a very thin surface layer because of the 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, ie the maximum depth at which

Figure 2. Photolytic curves with soils 3 and 4.

Characteristic	Soil sample number							
	1	2	3	4	5	6	7	8
Sand (%)	46.1	60.7	56.4	56.5	46.1	46.1	46.1	46.1
Silt (%)	47.9	37.5	41.00	41.2	47.8	47.8	47.8	47.8
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

Table 2. Characteristics of four soils used in tests **A** and **B**

photolysis occurred, could be calculated as follows:

$$P = H \times (1 - R) = W(1 - R)/D \times A$$

where P = photolytic depth, H = total thickness of soil layer, R = percentage of atrazine remaining at equilibrium, W = total soil mass, D = soil density, and A = soil area.

3.2 Rate of photolysis of atrazine

It is difficult to calculate the photocatalytic 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:

$$\ln(C_0/C_t) = k_s t$$

Because UV light penetrates the soil surface only to a depth of less than 0.3 mm, atrazine in the lower layers is not photolysed, and this must be allowed for. The above expression thus has to be modified to:

$$\ln(C_0/C'_t) = k_s t$$

$$\begin{aligned} C'_t/C_0 &= (C_t/C_0 - C_e C_0)/(1 - C_e/C_0) \\ &= (C_t - C_e)/(C_0 - C_e) \\ C'_t &= (C_t W - C_e W)/(W \times P/H) \end{aligned}$$

where C_0 = original concentration of atrazine, C'_t = concentration of atrazine in photolysed layer at time t , C_t = measured overall concentration of atrazine at time t , C_e = measured overall concentration of atrazine at equilibrium, W = total soil mass, P = photolytic depth, H = overall soil depth and k_s = rate constant.

3.3 Test A: photolysis of atrazine in dry natural soils

Four model soil samples were used to study the effects of soil granularity and organic matter on atrazine photolysis (Table 2). The four samples were spiked with atrazine, irradiated for different times, and then analysed by HPLC.

The organic content and pH of samples **1** and **2** were similar, but they differed in granularity. The photolytic depths, rate constants and half-lives are shown in Table 3. Both the photolysis rate and photolytic depth were somewhat greater for the finer soil, **1**, than for the coarser soil, **2**, indicating that the coarser the soil, the less the UV penetration.

The granularities and pH values of **3** and **4** were

similar, but they differed in organic content. The photolysis rate in **3** was slightly greater than that in **4**, (Table 3) but the photolytic depths were similar, indicating that organic substances increase the photolysis of atrazine, but do not affect the photolytic depth.

3.4 Test B: photolysis of atrazine in wet natural soils

The four soil samples used in this test, **5–8**, had similar constituents and water contents, but their pH values ranged from 3.34 to 10.10 (Table 2). The characteristic parameters are given in Table 3. The rate of photolysis of atrazine was slowest in neutral soil when other conditions were constant, and increased with increase of both acidity and basicity, showing that both H^+ and OH^- ions are able to catalyse the photochemical reactions.

Soil **1** (test A) and soil **7** (test B) had similar constituents and pH values, but different moisture contents. The experimental results indicated that the rate constant, k_s for **7** (0.144 min^{-1}) was greater than that for **1** (0.0904 min^{-1}). The photolytic depth, H , was also greater for **7** (0.26 mm) than for **1** (0.16 mm).

Table 3. Photolytic data for the six tests

Test	Sample number	Soil depth H (mm)	Photolytic depth P (mm)	Rate constant k_s (min^{-1})	Half-life $t_{1/2}$ (min)
A	1	0.31	0.16	0.0904	7.7
	2	0.33	0.15	0.0873	7.9
	3	0.48	0.29	0.1291	5.4
	4	0.45	0.27	0.1049	7.1
B	5	0.46	0.28	0.2232	3.1
	6	0.47	0.27	0.1990	3.5
	7	0.45	0.26	0.1440	4.8
	8	0.46	0.27	0.1763	3.9
C	Dry sand	0.18	0.08	0.1128	6.1
	Dry silt	0.20	0.11	0.1184	5.9
	Dry clay	0.32	0.15	0.1340	5.2
	Wet sand	0.25	0.13	0.1179	5.9
	Wet silt	0.28	0.16	0.1260	5.5
D	Wet clay	0.30	0.18	0.1400	5.0
	Humic acid	0.28	0.16	0.1260	5.5
	No humic acid	0.29	0.20	0.1473	4.7
E	DBS	0.28	0.16	0.1260	5.5
	No DBS	0.30	0.18	0.1332	5.2
F	HA + DBS	0.28	0.16	0.1260	5.5
	No HA/DBS	0.29	0.22	0.1609	4.3

This suggests that water assists 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.

3.5 Test C: photolysis of atrazine in soil without organic substances

A soil sample, not containing atrazine, was placed in a beaker, moistened with a little water and mixed with hydrogen peroxide to remove organic substances. It was then washed into a 1000-ml flask and separated by Stokes' method according to particle size: sand (0.125–0.9 mm), silt (20 μ m–0.125 mm) and clay (2–20 μ m).

The parameters for these fractions under dry conditions are given in Table 3. The photolysis rate of atrazine and photolytic depth increased gradually from sand through silt to clay. This probably relates to the increase in surface area; the smaller the particle size, the greater the surface area per unit mass, and hence the greater the catalytic capability.

In the presence of 50% of water, the relationship with particle size was similar to that found under dry conditions (Table 3), but in each case the rates of photolysis were higher, again emphasising the importance of water in atrazine photolysis.

3.6 Test D: influence of humic acid on atrazine photolysis

Based on the levels used in other work,¹⁰ and taking into account possible interference with HPLC, silt samples free from organic substances were spiked with humic acid (20 mg per 1000-g sample) and 50% of water. The parameters are given in Table 3. The photolytic rate constant and photolytic depth were increased in the presence of humic acid, and the rate constant decreased, supporting the view that it can catalyse the photolysis of atrazine and accelerate the process.

3.7 Influence of dodecyl benzenesulfonate on atrazine photolysis

Based on the levels of dodecyl benzenesulfonate (DBS) used in other work and possible interference in HPLC, organic-free silt samples were spiked with DBS (20 mg per 1000-g sample) and 50% of water. The photolytic parameters are given in Table 3. In the presence of DBS the photolytic rate and photolytic depth increased slightly and the half-life decreased slightly. The influence of DBS on the photolysis of atrazine is less than that of humic acid, and is probably due to its ability to enhance the solution of atrazine and so increase its movement and that of its photolysis products.

3.8 Comparative experiments

In order to test the possible influence of biodegradation and hydrolysis, tests were carried out in comparison with the above, except that the samples were kept

Figure 3. GC-MS chromatogram of photolytic products of atrazine.

in darkness at 28 °C for 40 min. The results indicated (data not shown) that the effects of these factors were so small that they could be neglected in comparison with photolysis.

3.9 Analysis of photolysis products

In order to minimise the effects of impurities and to increase the content of photolysis products, organic compounds were removed from the soil. The soil comprised sand 46%, silt 48% and clay 6%. Atrazine (50 mg per 1000 g of soil) was spiked onto soil samples, which were then sieved onto a tray as before, carefully wetted to a level of 50% and irradiated in the photolysis chamber. The degradation products were extracted with methanol + dichloromethane + acetone (1 + 1 + 1 by volume) and analysed by GC-MS.

The GC-MS chromatogram obtained is shown in Fig 3. Careful analysis confirmed the presence of three photolysis products: 1-*sec*-butyl-4,4-diethyl-1-tetrazene (peak 1), *N*²,*N*⁴-diethyl-6-methyl-1,3,5-triazine-2,4-diamine (peak 5) and 6-chloro-*N*⁴-propyl-1,3,5-triazine-2,4-diamine (peak 7). Their mass spectra are shown in Figs 4–6, and their structures in Fig 7.

3.10 Stages in the photolytic process

From the results of the above experiments, the photolysis of atrazine is seen as involving five steps: (1) movement of atrazine to the surface of the soil granule; (2) adsorption of atrazine on the surface of the soil granule; (3) under UV irradiation, the bonds in the atrazine molecule are distorted, forming active inter-

Figure 4. Mass spectrum of 1-*sec*-butyl-4,4-diethyl-1-tetrazene.

Figure 5. Mass spectrum of N^2,N^4 -diethyl-6-methyl-1,3,5 triazine-2,4-diamine.

Figure 6. Mass spectrum of 6-chloro- N^4 -propyl-1,3,5-triazine-2,4-diamine.

1-*sec*-Butyl-4,4-diethyl-1-tetrazene (peak 1)

N^2,N^4 -Diethyl-6-methyl-1,3,5-triazine-2,4-diamine (peak 5)

6-Chloro- N^4 -propyl-1,3,5-triazine-2,4-diamine (peak 7)

Figure 7. Molecular structures of the photolytical products.

mediate products; (4) the active intermediates undergo rearrangement, or are broken up, to form new compounds—the photo-degraded products; (5) these products leave the surface of the soil granule.

Water and surface-active agents facilitate the desorption of atrazine from organic substances in the soil and speed the movement of atrazine and its decomposition products. They thus enhance the

Figure 8. Formation of the three photolytical products.

velocities of the first and fifth steps, and so speed up the photolysis of atrazine. The main components of the soil granules are the oxides and their hydrates of Si, Ti, Fe, Al, Mn and Mg, which can adsorb atrazine molecules and rearrange or break the chemical bonds to form new compounds.

3.11 Photolysis reactions

Based on the results of GC-MS analysis of the photolysis products of atrazine, it is suggested that the following reactions occur. The chlorine substituent is lost, and the methyl substituent of the isopropyl group moves into its place, giving N^2, N^4 -diethyl-6-methyl-1,3,5-triazine-2,4-diamine. Alternatively, the N^2 ethyl is lost and the N^4 isopropyl group rearranges to n -propyl, giving 6-chloro- N^4 -propyl-1,3,5-triazine-2,4-diamine. In a more extended process, the alkylamino groups become detached, the triazine ring opens, as has been shown to occur under UV radiation, and the component parts rearrange to form 1-*sec*-butyl-4,4-diethyl-1-tetrazene. These reactions as shown in Fig 8.

4 CONCLUSION

The photolysis of atrazine only occurs very close to the soil surface because of the low penetration of UV radiation. It was observed that, the coarser the soil, the less the UV penetration and the less the photolysis of atrazine. The rates of photolysis were greater in acid and basic soil than in neutral soil. Water, humic acid and surface-active agents could accelerate the photolysis of atrazine, and when the latter two were together photolysis was even more rapid. The photolytic process was approximately a first-order reaction (relative coefficient >0.970). The rate constant of photolysis ranged from 0.09 to 0.17 min^{-1} , with a photolytic depth of 0.1 – 0.4 mm and a half-life of 4 – 8 min .

Although the photolytic half-life of atrazine is $<8 \text{ min}$, its decomposition in soil under field conditions is slow because of the weak intensity of UV radiation in solar light and the small photolytic depth

($<0.3 \text{ mm}$). The photolysis of atrazine involves five steps: movement, adsorption, distortion or breaking of chemical bonds, formation of new molecular species, and removal of photolytic products. Three main products have been identified: N^2, N^4 -diethyl-6-methyl-1,3,5-triazine-2,4-diamine, 6-chloro- N^4 -propyl-1,3,5-triazine-2,4-diamine and 1-*sec*-butyl-4,4-diethyl-1-tetrazene.

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