Light-induced transformations of tribenuron-methyl in aqueous solution

A K Bhattacherjee and P Dureja*

Division of Agricultural Chemicals, Indian Agricultural Research Institute, New Delhi-110012, India

Abstract: Tribenuron-methyl a sulfonylurea herbicide, readily photodegraded in aqueous solution under sunlight and UV light. The photoproducts identified were *N*-methyl-4-methoxy-6-methyl-1,3,5-triazine-2-amine, methyl 2-(aminosulfonyl) benzoate, *o*-benzoic sulfimide, *N*-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-*N*-methyl urea and *N*-(2-carbomethoxyphenyl)-*N*-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-*N'*-methyl urea. The rate of photodegradation of tribenuron-methyl in different types of water followed first-order kinetics with significant correlation coefficient, increased with increase in pH and was also dependent upon the dissolved impurities.
© 1999 Society of Chemical Industry

1 INTRODUCTION

Tribenuron-methyl (methyl 2-[4-methoxy-6-methyl-1,3,5-triazin-2-yl(methyl) carbamoyl sulfamoyl]benzoate), a second-generation sulfonylurea herbicide, is active against broad-leaved weeds in cereals[1] at an application rate of 5–30 g ha^{-1}. Weeds such as *Polygonum convolvulus* L, *Cirsium arvense* (L) Scop, *Melilotus indica* All, *Chenopodium album* L, *Phalaris minor* Retz, *Avena fatua* L and *Echinochloa colona* (L) Link can be effectively controlled by this herbicide.[2-4] It has been shown to persist for more than four months in tap water, mineral water and lake water under three storage conditions,[5] *viz* open air, a growth chamber at 25°C and a cold room at 4°C. Like other sulfonylureas, it is also hydrolysed in aqueous media through the cleavage of the sulfonylurea linkage at a rate primarily dependent upon pH and temperature.[6,7] It can be estimated in water samples by gas chromatography after derivatising to its *N,N'*-dimethyl derivative,[8] liquid chromatography employing UV-VIS detection[9] and bioassay technique using turnip (*Brassica rapa* L) as test species.[10]

The present study was undertaken to investigate the roles of pH and dissolved inorganic substances in the photodegradation of tribenuron-methyl in aqueous solution under UV and sunlight conditions, to characterise the final photoproducts and to postulate the mechanism of the photo-transformation reaction, which could be of assistance in understanding the environmental fate and behaviour of the herbicide.

2 MATERIALS AND METHODS
2.1 Chemicals

A technical sample of tribenuron-methyl (95% purity) was supplied by DuPont Far East Inc, New Delhi, India, and was purified further by repeated crystallisation from benzene until a constant mp of 141°C was achieved. Its infra-red spectrum showed NH stretching at 3335.3 and 3243.1 cm^{-1}, presence of a carbonyl group at 1731 cm^{-1} and asymmetrical and symmetrical stretching due to SO_2 at 1348 and 1176 cm^{-1}, respectively. The [^{1}H]NMR spectrum showed one proton singlet at δ 13.98 for SO_2NH and a multiplet at δ 7.4–8.4 for four aromatic protons. In addition, it showed two singlets of three protons each at δ 4.16 and 4.01 for two methoxyl and two three-proton singlets at δ 3.5 and 2.72 for NCH_3 and CH_3 respectively. The ultra-violet spectrum of tribenuron-methyl showed absorption maxima significantly below 290 nm both in water and methanol, but had a measurable absorption tail above the base line up to 300 nm. It exhibited absorption maxima at 213.5 nm (ε 24 016) for the allowed $\pi-\pi$ transitions of the phenyl ring, 222.5 nm (ε 26 212) for forbidden $\pi-\pi*$ transitions of the phenyl ring and a shoulder band at 258 nm essentially $n-\pi*$ in character resulting from the mixed system of the sulfonylurea group. These transitions can lead to the formation of either singlet or triplet excited states which will be responsible for phototransformation. Laboratory-grade solvents and reagents were procured locally. All the solvents were dried and distilled before use.

---

* Correspondence to: P Dureja, Division of Agricultural Chemicals, Indian Agricultural Research Institute, New Delhi-110012, India

2.2 Water

The types of water used in the experiments were distilled water (double distilled from Systronic TM distilled water plant), tap water (collected from New Delhi Municipal Corporation water supply), irrigation water (collected from an irrigation well on Research Farm, Indian Agricultural Research Institute, New Delhi, India), tubewell water (collected from IARI, New Delhi) and HPLC grade water. pH of these water samples was measured before starting the experiment. The physicochemical properties of the waters are described in Table 1.

2.3 Preparation of an aqueous solution of tribenuron-methyl

An analytical sample of tribenuron-methyl (1 g) was added to 1litre of double-distilled water in a conical flask and stirred for 24h at room temperature. The stirred aqueous solution of tribenuron-methyl was filtered through Whatman No 42 filter paper. Similarly, solutions of tribenuron-methyl were prepared in HPLC grade water, irrigation water, tap water and tubewell water. The concentration of tribenuron-methyl was then adjusted to 1.3×10^{-4} M by further dilution with the appropriate type of water.

2.4 Chromatography and spectroscopy

2.4.1 High performance liquid chromatography

Tribenuron-methyl and its degradates in the rate-kinetics studies were analysed by HPLC (Thermo Separation Product model Spectra System P2000), equipped with a variable wavelength UV-150 UV-VIS detector and a Rheodyne injector (20 µl loop) and connected to a Datajet reporting integrator. The stationary phase consisted of a Lichrosorb C-18 column (250 mm × 4.6 mm ID) and the mobile phase was methanol + water (70 + 30, by volume) maintained at a flow rate of $0.8 \, \text{ml min}^{-1}$ with detector wavelength set at 230 nm.

2.4.2 UV-visible spectra

The ultraviolet-visible spectrum of tribenuron-methyl was recorded on a Hitachi Model U-2000 double beam UV-VIS spectrometer in methanol and water using a quartz cuvette (1 cm path length).

2.4.3 Infra-red spectra

The infra-red spectra of the photoproducts were recorded on a Nicolet Impact 700 FT-IR spectrophotometer using KBr disc and a nujol mull.

2.4.4 Nuclear magnetic resonance (NMR)

[¹H]NMR spectra were recorded on a Varian EM 360 L(60 MHz) instrument. Deuterochloroform ($CDCl_3$) was used as solvent and tetramethylsilane (TMS) as the internal standard.

2.4.5 Gas chromatography-mass spectroscopy

Gas chromatography-mass spectroscopy (GC-MS) was performed on a HRGC-MEGA 2 series gas chromatograph coupled to a Fisons-Trio 1000 ion-trap mass spectrometer and connected to a Panasonic KX P1150 multimode printer. The ionisation potential was 70 eV. The GC was equipped with an SE-54 capillary column (15 m × 0.25 mm ID, film thickness 0.1–0.15 µm). The column oven temperature was programmed to increase from 70 to 250°C at a rate of $10°C \, \text{min}^{-1}$. Helium was used as carrier gas with a flow rate of $2 \, \text{ml min}^{-1}$.

2.5 Irradiation and photoproducts

An aqueous solution of tribenuron-methyl was irradiated for 14h under UV light with a medium-pressure Hg lamp (125W, Philips) jacketed with a water-cooled quartz tube, and for 20 days under natural sunlight. To produce enough of the photoproducts for structural analysis, a solution of 500 mg of tribenuron-methyl in 5 litres of distilled water was irradiated in five batches (100 mg in 1litre) for 2 h through a quartz filter. The irradiated solutions were combined and extracted with methylene chloride (100 ml × 5). After drying with anhydrous sodium sulfate, the organic phase was concentrated. A brown residue was obtained which was subjected to GC-MS for identification of photoproducts. A dark control was performed by covering the flask with aluminium foil to ensure that a given product was derived by photochemical reactions.

2.6 Preparation of comparison compounds

2.6.1 o-Benzoic sulfimide; saccharin (11)

This was synthesized according to the literature procedure.[11]

2.6.2 Methyl 2-sulfamoyl-benzoate (3)

In a round-bottomed flask (250 ml capacity) o-benzoic sulfimide (1.5 g), concentrated hydrochloric acid (8 ml) and methanol (150 ml) were taken and refluxed for 8 h on a water bath.[12] Methanol was distilled off under nitrogen gas and the remaining liquid was extracted with methylene chloride and dried over anhydrous sodium sulfate. The organic phase was then completely evaporated off. The solid product thus obtained was recrystallised from benzene; mp 115–116°C. The IR spectrum of the product showed the presence of C=O at $1710 \, \text{cm}^{-1}$ and O=S=O at $1341 \, \text{cm}^{-1}$ (asym.) and $1166 \, \text{cm}^{-1}$

Table 1. Physicochemical properties of different waters

Property	HPLC grade	Tap	Irrigation	Tubewell
pH	6.64	7.35	8.1	8.56
EC (dS m⁻¹)ᵃ	0.0054	0.32	1.90	0.77
Salt concentration (mg litre⁻¹)	3.456	204.8	1216.0	492.8
Osmotic pressure (Atm)	1.944×10^{-3}	0.1152	0.684	0.2772

ᵃ EC = Electrical conductivity (deciSiemens m⁻¹)

(sym.). [^{1}H]NMR: δ 7.6–8.3 (m, 4H, aromatic), 5.8 (s, 2H, NH$_2$), 3.9 (s, 3H, OCH$_3$). GC-MS: m/z 215 (M$^+$), 199 (M$^+$ − 16), 184 (M$^+$ − 31), 120 (M$^+$ − 95), 105 (M$^+$ − 110).

2.6.3 N-Methyl-4-methoxy-6-methyl-1,3,5-triazin-2-amine (2)

Tribenuron-methyl (500 mg) was stirred with aqueous hydrochloric acid (pH 3.0) at 40°C for 48 h. The reaction product was extracted with chloroform. The chloroform layer was separated, dried over anhydrous sodium sulfate and distilled off. The solid thus obtained was recrystallised from methanol; mp 155°C. The IR spectrum showed the presence of NH at 3256 cm^{-1} and C=N at 1558 cm^{-1}. [^{1}H]NMR: δ 6.0 (bs, 1H, NH), 3.9 (s, 3H, OCH$_3$), 3.1 (d, 3H, NCH$_3$), 2.45 (s, 3H, CH$_3$). GC-MS: m/z 154 (M$^+$), 139 (M$^+$ − 15), 124 (M$^+$ − 30), 110 (M$^+$ − 44).

2.6.4. 2-[4-Methoxy-6-methyl-1,3,5-triazin-2-yl(methyl)carbamoylsulfamoyl]benzoic acid

In a conical flask (250 ml capacity) tribenuron-methyl (200 mg), distilled water (20 ml) and sodium hydroxide solution (0.2 M; 50 ml) were mixed and stirred for 1 h at room temperature. After stirring, the mixture was neutralised by adding hydrochloric acid (0.2 M; 52 ml) using litmus paper as indicator. The aqueous layer was extracted with methylene chloride, which was separated, dried over anhydrous sodium sulfate and completely evaporated at low temperature (25°C). Off-white solid so obtained was recrystallised from a mixture of hexane and acetone. The IR spectrum showed the presence of C=O at 1729 cm^{-1}, C=N at 1578 cm^{-1}, NH at 3250 and 3368 cm^{-1}, O=S=O at 1354 cm^{-1} (asym.) and 1170 cm^{-1} (sym.). [^{1}H]NMR: δ 7.5–8.2 (m, 4H, aromatic), 6.1 (bs, 1H, NH), 4.1 (s, 3H, OCH$_3$), 3.2 (s, 3H, NCH$_3$), 2.4 (s, 3H, CH$_3$).

2.7 Photolysis kinetics

Aqueous solutions of tribenuron-methyl in HPLC grade water, irrigation water, tap water and tubewell water (50 mg litre^{-1}) were irradiated in quartz tubes under both UV light (24 h) with a medium-pressure Hg lamp and sunlight (35 days, 8 h day^{-1} from May to June, 1996). The sunlight intensity at 300–400 nm wavelength was 570, 1420 and 200 mW cm^{-2} at the beginning, middle and end of the day, respectively. Non-irradiated samples of the aqueous solution of tribenuron-methyl kept in the dark served as controls. At various time intervals, samples were withdrawn in triplicate and analysed by HPLC.

3 RESULTS AND DISCUSSION

3.1 Identification of photoproducts

HPLC analysis of the brown residue obtained after irradiation showed the formation of a number of degradation products. The degradation products were tentatively identified by GC-MS (Table 2, Fig 1) and by comparison with authentic standards.

Photoproduct **2**, N-methyl-4-methoxy-6-methyl-1,3,5-triazin-2-amine (M$^+$ 154) was identified by matching the mass spectrum with that of a known standard.

The mass spectrum of photoproduct **3** showed a molecular ion peak at m/z 215 (M$^+$) with a base peak at m/z 199, and fragment ion peaks at m/z 184, 120 and 104. It was identified as methyl 2-sulfamoyl benzoate (**3**) by comparison with a reference standard.

The photoproduct **4** was tentatively identified as 4-methoxy-6-methyl-1,3,5-triazin-2-amine and its mass spectrum showed a molecular ion peak at m/z 140 (M$^+$) (Table 2).

The mass spectrum of the photoproduct **5** showed a molecular ion peak at m/z 197 (M$^+$) and a base peak at m/z 181. It was tentatively identified as N-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-N-methyl urea (Fig 1).

Photoproduct **6** was tentatively identified as N-(4-methoxy-6-methyl-1,3,5-triazin-2-yl) urea and its mass spectrum showed a molecular ion peak at m/z 183 (M$^+$).

A molecular ion peak at m/z 331 (M$^+$) in the mass spectrum of photoproduct 7 helped to identify the compound as N-(2-carbomethoxyphenyl)-N-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-N′-methyl urea. The mass spectrum of photoproduct **8** showed a molecular ion peak at m/z 317 (M$^+$) with fragment ion peaks at m/z 302, 274, 194, 150, 126 and 81 (Table 2). It was tentatively identified as N-(2-carbomethoxyphenyl)-N-(4-methoxy-6-methyl-1,3,5-triazin-2-yl) urea. Photoproduct **9** was identified as N-(2-carbomethoxy phenylsulfonyl)-N′-methyl urea (Fig 1) and its mass spectrum showed a molecular ion peak at m/z 271 (M$^+$).

Photoproduct **10** was identified as 2-sulfamoylbenzoic acid (M$^+$ 201). The identification was confirmed by matching the mass spectrum of photoproduct **10** with that of a known standard.[13] Photoproduct **11** was identified as o-benzoic sulfimide (M$^+$ 183). The mass spectrum of **11** was similar to the mass spectrum of the authentic sample prepared.[14] Photoproduct **12** was tentatively identified as N-methyl-o-benzoic sulfimide by its mass spectrum which showed a molecular ion peak at m/z 197 (M$^+$) with a base peak at m/z 104 (Table 2).

Photoproduct **13** was identified by its IR and [^{1}H]NMR spectra as 2-[4-methoxy-6-methyl-1,3,5-triazin-2-yl(methyl) carbamoyl sulfamoyl]benzoic acid (Fig 1). The IR spectrum of **13** showed the presence of N-H, C=O and O=S=O groups at 3249, 1729, 1354 and 1170 cm^{-1}, respectively. [^{1}H]NMR spectra further confirmed its structure by showing a multiplet at δ 8.2–7.5 due to aromatic protons, three proton singlets at δ 4.1, 3.2 and 2.4 for OCH$_3$, NCH$_3$ and CH$_3$ groups, respectively, and a broad singlet at δ 6.1 corresponding to NH proton.
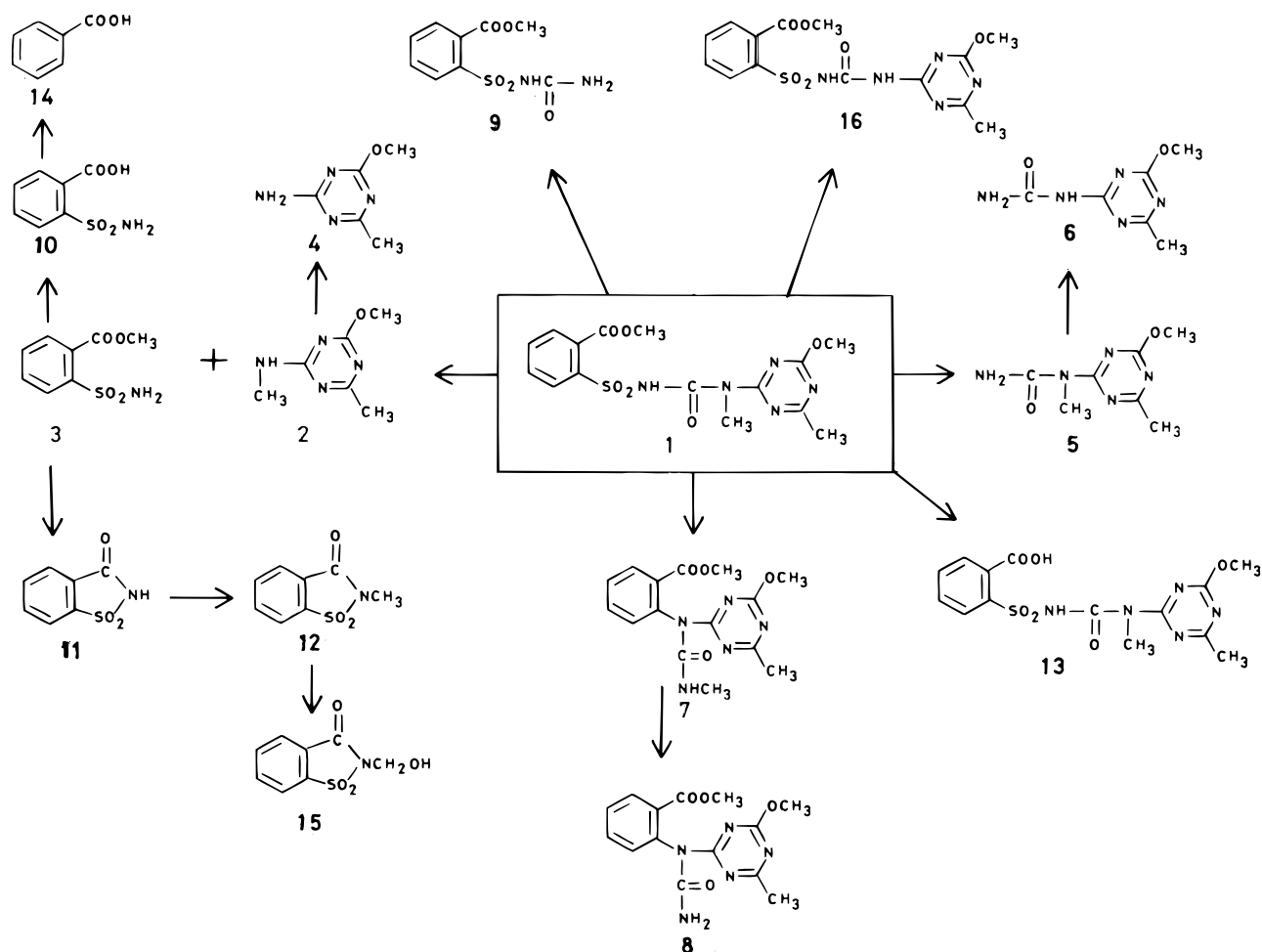
Figure 1. Phototransformation products of tribenuron-methyl (1) in aqueous solution.

The mass spectrum of photoproduct **14** showed a molecular ion peak at m/z 121 ($M^+ - 1$) with fragment ion peak at m/z 105. It was tentatively identified as benzoic acid. Photoproduct **15** was identified as N-hydroxymethyl-o-benzoic sulfimide by its mass spectrum which showed a molecular ion peak at m/z 212 (M^+). The mass spectrum of photoproduct **16** showed a molecular ion peak at m/z 382 (MH^+) along with fragment ion peaks at m/z 213 and 140 (Table 2). It was tentatively identified as methyl 2-(4-methoxy-6-methyl-1,3,5-triazin-2-yl carbamoyl sulfamoyl)benzoate (Fig 1).

The identification of these photoproducts suggests that photoreaction of tribenuron-methyl in aqueous solution includes cleavage of the sulfonylurea bridge to give photoproducts **2** and **3** as the major products. Photoproduct **3** on de-esterification gives photoproduct **10** in minor quantity. Photoproducts **11** and **12** may be formed from intermediates such as 2-sulfamoyl benzoic acid (**10**) (formed either from **3** or by cleavage of the sulfonylurea bridge of **13**) and 2-(N-methylsulfamoyl)benzoic acid, respectively. A minor product, **13**, is likely to be formed by de-esterification of tribenuron-methyl. Photoproduct **4** may be formed from **2** by demethylation or from **16** by cleavage of the sulfonylurea bridge. Photoproduct **5** is likely to be formed by cleavage of the

NH—C=O bond of tribenuron-methyl (**I**). Photoproduct **7** may be formed by contraction of the sulfonylurea bridge. It involves concerted elimination of SO_2 with the formation of a methyl benzoate radical (A) and a 4-methoxy-6-methyl-1,3,5-triazin-2-yl urea(B) radical. The (A) radical undergoes intramolecular proton abstraction and combines with B to give photoproduct **7**, which on demethylation gives a minor quantity of **8**. Photoproduct **15** may be formed by N—CH$_3$ oxidation of **12**.

3.2 Rate of photodegradation in aqueous solution

In order to study the effects of pH and dissolved inorganic substances on the rate of photodegradation of tribenuron-methyl in aqueous solution under sunlight and UV light using a quartz filter (254–316 nm), waters from different sources with different pH were used. The pH values of the solutions studied did not change during the photodegradation process. The rate of photodegradation of tribenuron-methyl in different types of water followed first-order kinetics with significantly different rate constants and high r^2 values (Table 3). The rate constant (K) was calculated by regression analysis of recovered tribenuron-methyl concentration versus time. The half-life ($t_{\frac{1}{2}}$) was calculated with the equation $t_{\frac{1}{2}} = 0.693/K$ (Table 3). Degradation was found

Table 2. Mass spectral data of photodegradation products of tribenuron-methyl in water

Product	Mass found (m/z)	Abundance (%)	Structure
2	4	100	M+
	139	5	M+ $-CH_3$
	124	70	M+ $-CH_3NH/OCH_3$
	110	33	M+ $-(OCH_3 + CH_3)$
3	215	5	M+
	199	100	M+ $-NH_2$
	184	55	M+ $-OCH_3$
	135	18	M+ $-SO_2-NH_2$
	104	20	C_6H_5CO
4	140	6	M+
	125	6	M+ $-CH_3$
	110	5	M+ $-OCH_3$
5	197	10	M+
	181	100	M+ $-NH_2$
	153	35	M+ $-(OCH_3 + CH_3)/NH_2CO$
	126	6	4-methoxy-2-amino-1,3,5-triazine
6	183	6	M+
	169	3	M+ $-CH_3$
	155	5	M+ $-OCH_3$
	139	5	M+ $-NH_2CO$
	126	5	M+ $-NH_2CON$
7	331	28	M+
	300	45	M+ $-OCH_3$
	272	4	M+ $-CONHCH_3$
	197	10	M+ $-C_6H_5COOCH_3$
	140	73	Aminotriazinyl moiety
	104	26	C_6H_4CO
8	317	15	M+
	302	5	M+ $-CH_3$
	274	5	M+ $-CONHCH_3$
	194	75	M+ $-$triazolyl moiety
	150	8	$C_6H_4(NH)COCH_3$
	81	61	1,3,5-triazine
9	271	11	M+
	240	12	M+ $-OCH_3$
	207	100	M+ $-SO_2$
	199	40	M+ $-NHCONHCH_3$
	135	10	M+ $-SO_2NHCONH-CH_3$
	104	6	C_6H_4CO
10	201	8	M+
	200	14	M+ $-H$
	184	62	M+ $-OH$
	120	100	M+ $-SO_2NH$
11	183	62	M+
	169	3	M+ $-NH$
	140	30	M+ $-CONH$
	120	95	M+ $-SO_2$
	76	50	C_6H_4
12	197	20	M+
	169	6	M+ $-NCH_3$
	133	49	M+ $-SO_2$
	104	100	C_6H_4CO/C_6H_4CO
13	121	6	M+ -1
	105	100	C_6H_5CO
	77	36	C_6H_5
14	212	38	M+
	197	54	M+ $-CH_2$
	181	71	M+ $-CH_2OH$
	104	96	C_6H_4CO
	76	100	C_6H_4
15	382	2	MH+
	213	6	$C_6H_4(SO_2N)COO-CH_3$
	140	77	Aminotriazolyl moiety

Table 3. Rate constant (K) and half-life ($t_{1/2}$) values for tribenuron-methyl in different types of water under sunlight and UV light[a]

Water	Light source	Rate constant (K)	Half-life ($t_{1/2}$)	r^2
HPLC grade	sunlight	$0.0228\,d^{-1}$	30.39d	0.96
Irrigation	sunlight	$0.1347\,d^{-1}$	5.14d	0.93
Tap	sunlight	$0.0723\,d^{-1}$	9.58d	0.98
Tubewell	sunlight	$0.0739\,d^{-1}$	9.37d	0.94
HPLC grade	UV-light	$0.0378\,h^{-1}$	18.33h	0.98
Irrigation	UV-light	$0.0061\,h^{-1}$	10.48	0.86
Tap	UV-light	$0.0481\,h^{-1}$	14.39h	0.93
Tubewell	UV-light	$0.0439\,h^{-1}$	15.75h	0.97

[a] Mean of three replicates.

half-lives show that the rate of photodegradation increased with increase in pH (Table 3). Results indicate that tribenuron-methyl is stable under acidic conditions, but undergoes degradation under basic conditions. Comparing the half-lives of tribenuron-methyl in irrigation water, tap water and tubewell water (5.14, 9.58 and 9.37 days under sunlight, respectively), it was observed that the rate of photodegradation was not only affected by pH but also by dissolved inorganic substances in the water. Dissolved substances have been previously shown to influence photolysis rates through light attenuation, a retarding effect, and through mediation of indirect photoprocesses, an accelerating effect.[15] In addition, humic substances are known to retain or form complexes with certain organic chemicals[16] and such interactions may alter the photochemistry of pesticides in natural water. The irrigation water, as compared to HPLC, tap or tubewell water is the most impure form of water, containing a number of dissolved impurities, natural sensitisers and sediments. These dissolved impurities, through indirect photolysis (sensitisation), are thus responsible for the increased rate of photodegradation of tribenuron-methyl in irrigation water. Moreover, the irrigation water has the maximum electrical conductivity (EC) value as compared to other waters (Table 1), which shows that it contains more dissolved salts. These dissolved salts may act as catalysts and may thus enhance the rate of degradation. The rate of degradation of tribenuron-methyl in different types of water followed the order:

HPLC grade water < tubewell water <

tap water < irrigation water

Compared with UV light, the rate of degradation under sunlight was slower but had the same pattern and was higher in irrigation water. The slower rate of photodegradation under sunlight is due to low intensity. Parallel control experiments in the dark with tribenuron-methyl in HPLC grade water, irrigation water, tap water and tubewell water showed less degradation.

to be more extensive in irrigation water than in HPLC grade water, tap water or tubewell water under both UV light and sunlight conditions. The

_

4 CONCLUSION

Irradiation of tribenuron-methyl in different types of water under both UV light and sunlight has supplied basic information about photoreactivity, photo-products and possible photochemical processes in the aqueous phase of soil. The major processes in the photolysis of tribenuron-methyl in water are cleavage of the sulfonylurea bridge, scission of the SO_2-NH bond and de-esterification, and contraction of the sulfonylurea bridge. The rate of photodegradation of tribenuron-methyl in different types of water increased with increase in pH, and with dissolved inorganic substances and impurities. Finally, it can be concluded that tribenuron-methyl can be rapidly detoxified in the aquatic environment to its different photoproducts as a result of photolysis.

REFERENCES

1 Ferguson DT, Schehl SE, Hageman LH, Lepone GE and Carraro GA, DPX-L5300 – A new cereal herbicide. *Proc Brighton Crop Prot Conf – Weeds* **1**:43–48 (1985).
2 Malik RS, Yadav SK and Malik RK, Evaluation of tribenuron, clopyralid and fluroxypyr for weed control in wheat. *Proc Indian Soc Weed Sci Internat Symp* **11**:174–176 (1993).
3 Mukhopadhyay SK and Mallick RB, Metsulfuron, chlorimu-ron and tribenuron – low dose, high efficiency herbicides for weed control in transplanted rice. *Proc 13th Asian-Pacific Weed Sci Soc Conf* No 1: 157–163 (1991).
4 Sangwan NK, Singh S, Pal D, Singh RP and Tamak JC, Effect of tank mixture of tralkoxydim or isoproturon with tribenuron on weed control in wheat. *Proc Indian Soc Weed Sci Internat Symp* **11**:177–178 (1993).
5 Barreda DG de, Lorenzo E, Carbonell EA and Gamon M, Sulfonylureas and quinclorac degradation in water. *Proc Brighton Crop Prot Conf – Weeds* **2**:809–814 (1993).
6 Beyer EM Jr, Duffy MJ, Hay JV and Schlueter DD, Sulfonyl-ureas, in *Herbicides: Chemistry, Degradation and Mode of Action* Vol **3**, ed by Kearney PC and Kaufman D, Marcel Dekker, Inc New York. pp 117–189 (1988).
7 Brown HM, Mode of action, crop selectivity and soil relations of the sulfonylurea herbicides. *Pestic Sci* **29**:263–281 (1990).
8 Klaffenbach P and Holland PT, Analysis of sulfonylurea her-bicides by gas-liquid chromatography III – mass spectrom-etry and multiresidue determination. *Biol Mass Spectrom* **22**:565–578 (1993).
9 Nilve G, Knutsson M and Jonsson JA, Liquid chromato-graphic determination of sulfonylurea herbicides in natural waters after automated sample pretreatment using supported liquid membranes. *J Chromatogr* **688**:75–82 (1994).
10 Gunther P, Rahman A and Pestemer W, Quantitative bio-assays for determining residues and availability to plants of sulfonylurea herbicides. *Weed Res* **29**:141–146 (1989).
11 Vogel AI, *Textbook of Practical Organic Chemistry*, 5th edn, ELBS/Longman. 649 pp (1989).
12 Shkulev VA, Abovyan LS, Dzhagatspanyan IA, Akopyan NF and Mndzhoyan OL, Saccharin derivatives. II. Synthesis and anticonvulsant activity of methyl esters of 5-substituted 2-sulfamidobenzoic acids. *Khim Farm Zh* **13**:36–40 (1979).
13 Schneiders GE, Koeppe MK, Naidu MV, Horne P, Brown AM and Mucha CF, Fate of rimsulfuron in the environ-ment. *J Agric Food Chem* **41**:2404–2410 (1993).
14 Anderson JJ and Dulka JJ, Environmental fate of sulfometuron-methyl in aerobic soils. *J Agric Food Chem* **33**:596–602 (1985).
15 Miller GC and Zeep R, Photoreactivity of aquatic pollutants sorbed on suspended sediments. *Environ Sci Technol* **13**:860 (1979).
16 Choudhry GG and Barrie Webster GR, Protocol guidelines for the investigation of photochemical fate of pesticides in water, air and soils. *Residue Rev* **96**:79–136 (1988).