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Jan Kochany^a; Ghulam Ghaus Choudhry^{ab}; G. Barrie Webster^a

^a Pesticide Research Laboratory, Department of Soil Science, University of Manitoba, Winnipeg, MB, Canada ^b The Great Lakes Institute and Department of Civil and Environmental Engineering, University of Windsor, Windsor, Ontario, Canada

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ENVIRONMENTAL PHOTOCHEMISTRY OF THE HERBICIDE BROMOXNYL IN AQUEOUS SOLUTION CONTAINING SOIL FULVIC ACIDS

JAN KOCHANY*, GHULAM GHAS CHAUDHRY†‡ and
G. R. BARRIE WEBSTER

*Pesticide Research Laboratory, Department of Soil Science, University of Manitoba,
Winnipeg, MB, Canada R3T 2N2*

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Photochemistry of the herbicide 3,5-dibromo-4-hydroxybenzotrile (1) (bromoxnyl) was investigated using a narrow band of ultraviolet radiation at 313 nm. UV absorption spectrometry of 7.8 μM 1 in water without and with soil fulvic acids (FAs) (50.0 mg L^{-1}) showed that FAs exerted several fold additive effects on the spectrum of 1.

Aqueous phase photoreactions of 7.8 μM of 1 in water in the absence (pH 6.0-7.0) and presence of 5, 10, 15, 20, 40, 45, 60 and 100 mg L^{-1} FAs (pH 5.5-6.5) were carried out at 313 nm. For instance, for 15 min photolysis time, as the amount of FAs increased, the rate of the photodestruction of 1 decreased. The first-order photolytic transformation rate constants ($k_{p,\lambda}$) for 1 in the presence of 5-100 mg L^{-1} were in the range of $(1.052 \pm 0.011) \times 10^{-3}$ to $(0.083 \pm 0.006) \times 10^{-3} \text{ sec}^{-1}$, the intensity of light (I_λ) at 313 nm ranged from 3.70 to 3.80 $\mu\text{EL}^{-1} \text{ sec}^{-1}$. The light screening factor (S_λ) at $\lambda = 313 \text{ nm}$ along with I_λ and $k_{p,\lambda}$ data were used to determine the spectral response function ($X_{s,\lambda}$) for the herbicide 1 in water containing various amounts of soil FAs. The experimentally determined $X_{s,\lambda}$ values at $\lambda = 313 \text{ nm}$ together with the solar irradiance (Z_λ) data available in tabulated form in the literature assisted the calculation of the sunlight indirect photodegradation half-lives [$t_{1/2}^{\text{ind.}}$] of bromoxnyl (1) in aquatic systems containing soil FAs. For example, in summer, the [$t_{1/2}^{\text{ind.}}$] of 7.8 μM 1 in aquatic environments containing 5, 10, 15, 20, 40, 45, 60 and 100 mg L^{-1} would be 1.99 ± 0.02 , 2.02 ± 0.02 , 2.17 ± 0.02 , 2.76 ± 0.04 , 3.48 ± 0.07 , 4.06 ± 0.06 , 5.03 ± 0.09 and $17.60 \pm 1.33 \text{ min}$, respectively.

The photoproducts of 1 were identified as 3-bromo-4-hydroxybenzotrile and 4-hydroxybenzotrile by GC-MS.

KEY WORDS: Bromoxnyl (3,5-dibromo-4-hydroxybenzotrile), soil fulvic acids, aquatic photochemistry, quantum yields, photolytic rate constants, spectral response functions, sunlight indirect photodegradation half-lives, photoproducts.

INTRODUCTION

The herbicide bromoxnyl (3,5-dibromo-4-hydroxybenzotrile (1) both as potassium salt or as the octanoate or butyrate esters is commonly used for the weed

*Visiting Professor on sabbatical leave from Institute for Environmental Protection, Warsaw, Poland.

†To whom all correspondence should be addressed at the address mentioned below.

‡Present address: The Great Lakes Institute and Department of Civil and Environmental Engineering, University of Windsor, Windsor, Ontario, Canada N9B 3P4.

control in the agricultural crops grown in the Canadian prairie provinces.¹ Owing to the widespread application of bromoxynil, there is growing concern that it may contaminate soil and aquatic environments.

Chemicals present in soil and aquatic natural systems can undergo both biological and non-biological environmental transformations. The latter processes may include chemical and/or photochemical reactions. Among these environmental pathways, sunlight photoalterations of pesticide chemicals present in natural water play an important role and may proceed through direct and/or indirect photoprocesses.^{2,3} In the case of direct photolysis, the candidate compound absorbs the incidental light itself and undergoes decomposition. Indirect phototransformation may involve the transfer of electronic excitational energy from other chemicals present in the system to the candidate pesticide, the former ones being termed "sensitizers" (Sens.). In addition, the indirect photodegradation may take place via interactions of the intermediate species (see below) generated from the photolysis of other chemicals with the pesticides under consideration.^{2,4}

The occurrence of humic substances such as fulvic acids (FAs), humic acids (HAs), and humins in aquatic environments and soils is well known;⁵⁻⁸ thus, natural waters contaminated with pesticides and other pollutants will also contain humic substances. Several authors have reported the photolytic generation of reactive species, *viz.*, singlet oxygen, hydrogen peroxide, superoxide anions and alkoxy radicals in the presence of humic substances in water.^{3,4,9-11} Moreover, the photosensitizing and photoquenching effects of humic substances in some environmental chemicals is also known.^{7,12-14}

The hydrolysis of esters of bromoxynil is known to occur in non-sterile water.¹⁵ The environmentally significant photochemistry of herbicides has recently been reviewed;¹⁶ to date, no data on the photolytic fate of bromoxynil has been published. The environmental direct phototransformation of **1** dissolved in water at various PH has however been recently reported.¹⁷ In this paper, the photochemical fate of bromoxynil (**1**) present in aqueous solution containing various amounts of soil fulvic acids (FAs) is described and the resulting photoproducts are identified.

THEORETICAL BACKGROUND

For the estimation of the sunlight first-order indirect photolysis rate constants ($k_{sp}^{Ind.}$) for pesticides in water containing sensitizers, the following expression can be used [eq. (1)]:^{2,18a}

$$k_{sp}^{Ind.} = \frac{1}{j} \sum X_{s,\lambda} Z_{\lambda} \quad (1)$$

where $j = 6.023 \times 10^{20}$ is a conversion constant that makes the units of Z and X compatible, Z_{λ} is the sunlight intensity for a specified wavelength interval (N) centred at wavelength (λ) (in photons $\text{cm}^{-2} \text{sec}^{-1} \text{N nm}^{-1}$), and $X_{s,\lambda}$ is the spectral response function at a wavelength λ , e.g., 313 nm for the photosensitized reaction.

Zepp and coworkers¹⁴ used the following relationship for the determination of the spectral response function of a photosensitized transformation of environmental contaminants:

$$X_{s,\lambda} = \frac{k_{p,\lambda}^{\text{Sens.}}}{I_{\lambda} S_{\lambda} l} \quad (2)$$

In eq. (2), $k_{p,\lambda}^{\text{Sens.}}$, I_{λ} , S_{λ} , and l are the first-order rate constant for the sensitized photodecomposition of the candidate pesticide at wavelength λ (e.g., 313 nm), the intensity of the incident light of wavelength λ , light screening factor at λ , and the cell pathlength (cm), respectively. The slope of the plot of $\ln(C_0/C_t)$ versus photolysis time (t) at a certain λ , e.g., 313 nm will provide the value of $k_{p,\lambda}^{\text{Sens.}}$ for the phototransforming reaction of the pesticide in the presence of a sensitizer, e.g., soil FAs [Eq. (3)]:

$$\ln(C_0/C_t) = k_{p,\lambda}^{\text{Sens.}} \cdot t \quad (3)$$

In Eq. (3), C_0 and C_t are the concentrations of the pesticide (expressed in mol L^{-1}) at times zero and t . The light screening factor (S_{λ}) can be computed using Eq. (4).^{2, 14}

$$S_{\lambda} = \frac{1 - 10^{-\alpha_{\lambda} l}}{2.303 \alpha_{\lambda} l} \quad (4)$$

where α_{λ} is the decadic absorption coefficient of the solution at wavelength λ . The intensity (I_{λ}) (expressed in $E L^{-1} \text{sec}^{-1}$) of the light source can be calculated from the data for a chemical actinometer (A) using the following equation:¹⁹

$$I_{\lambda} = \frac{[A]}{\phi_A X t_A} \quad (5)$$

where $[A]$ is the concentration (mol L^{-1}) of the actinometer photodecomposed after time t_A (sec); whereas, ϕ_A is the quantum yield of the actinometer reported in the literature.

Assuming the indirect photoreaction is first-order in the candidate pesticide, the half-life $[(t_{1/2})_{sp}^{\text{Ind.}}]$ for the sunlight indirect phototransformation of the pesticide in the presence of environmental photosensitizers can be determined using Eq. (6):

$$(t_{1/2})_{sp}^{\text{Ind.}} = \frac{\ln 2}{k_{sp}^{\text{Ind.}}} \quad (6)$$

In the field of solution phase environmental photochemistry, a large number of suitable chemical actinometers sensitive to wavelengths greater than 290 nm have been reported in the literature (see references cited in Choudhry and Webster²).

For instance, the quantum yield for *p*-nitroacetophenone (PNAP)/pyridine (Pyr) system is given by Eq. (7):²⁰

$$\phi_{\text{PNAP}} = 0.0169[\text{Pyr}] \quad (7)$$

where ϕ_{PNAP} is the quantum yield of the actinometer *p*-nitroacetophenone.

In addition, the first-order rate constant for the direct photolysis ($k_{p,\lambda}$) (i.e., the absence of any photosensitizer) of the pesticide at wavelength λ (e.g., 313 nm) can be calculated using an expression similar to Eq. (3) described below:

$$\ln(C_0/C_t) = k_{p,\lambda}t \quad (3a)$$

Finally, for the determination of the reaction quantum yield for the indirect photolysis ($\phi_{r,\lambda}^{\text{ind.}}$) (i.e., in the presence of a sensitizer, such as soil FAs) of a pesticide at defined λ , the following relationship can be used:¹⁹

$$\phi_{r,\lambda}^{\text{ind.}} = \frac{[C]t_A\phi_A}{[A]t_C} \quad (8)$$

In Eq. (8), $[C]$ is the concentration (mol L^{-1}) of the candidate chemical phototransformed after time t_C , while parameters ϕ_A , $[A]$, and t_A for the used actinometer have been defined above.

EXPERIMENTAL

Reagents and Chemicals

HPLC-grade solvents, *viz.*, methanol, cyclohexane and water were supplied by Caledon Laboratories Ltd., Georgetown, Ontario, Canada. Bromoxynil (**1**) (98 % purity) was obtained from Chem. Service, West Chester, PA, USA. Soil Armadale fulvic acids (FAs) (Contech Canada fulvic acids, Batch FA8) was donated by Professor Cooper H. Langford, Department of Chemistry, Concordia University, Montreal, QC, Canada. The chemistry of these FAs has been previously investigated extensively by Gamble and his coworkers^{21–25} as well as by Choudhry and Webster.²⁶

Other chemicals such as pyridine, *p*-nitroacetophenone (PNAP), phosphoric acid, sodium phosphate, sodium sulphate, potassium chromate, sodium carbonate, and 4-hydroxybenzotriazole (**B**) were purchased from Aldrich Chemical Company Inc., Milwaukee, WI, USA.

Ultraviolet (UV) Spectrometry

UV spectra of solutions of bromoxynil in water, in the absence and presence of soil fulvic acids (FAs), were recorded on a Hewlett–Packard model 8452 A Diode Array Spectrometer.

Photochemical Experiments

Aqueous solutions of bromoxynil (7.8×10^{-6} M) as well as in soil FAs aqueous

solutions (FAs concentration: 5.0–100.0 mg/L) were irradiated around 313 nm using a Rayonet Photochemical Reactor under previously described conditions.^{17,27–29} For the isolation of the 313 nm band, an aqueous chemical filter solution consisting of a mixture of K_2CrO_4 (0.270 g L^{-1}) and Na_2CO_3 (1.000 g L^{-1}) was used.^{17,27} The light intensity was monitored with aqueous *p*-nitroacetophenone (PNAP) ($1 \times 10^{-5}\text{ M}$)/pyridine ($1.41 \times 10^{-3}\text{ M}$). For the identification of photoproducts, reaction mixtures were salinated with sodium sulphate, acidified with 1 M phosphoric acid and extracted with cyclohexane. The cyclohexane extract was dried over sodium sulphate for 30 minutes and analyzed by GC-MS.

HPLC Analytical Procedures

Quantitative analysis of bromoxynil (1) and its photoproducts were performed on a Waters Associates HPLC system (Model 6000A pump and M440 UV detector set at 254 nm) and at 0.01 absorbance unit full scale (AUFS) value. The chromatographic separation was carried out on a Waters prepacked μ Bondapak C_{18} 25 cm \times 3.2 mm (i.d.) column. Samples were injected via a Rheodyne Model 7125 injector with a 100 μ L loop. The temperature was approximately 20 °C.

In order to avoid concentration of soil fulvic acids on the column, water was injected between analyses subsequently methanol was injected. The column was also washed with 20 mL of 0.001 M NaOH solution after the analyses were completed.

The mobile phase was prepared from methanol and 0.05 M phosphate buffer of pH = 2.6 (45:55 v/v) according to the procedure described previously.³⁰ The mixed solvents were membrane filtered (FH; 0.5 μ m, Millipore Corp.) and degassed with helium (Linde-Union Carbide, USA). The solvent peak was used as the reference for dead time determination.

Gas Chromatography-Mass Spectrometry

A Hewlett-Packard 5890 gas chromatograph coupled with a VG 7070E-HF mass spectrometer was utilized for the identification of photoproducts. Chromatographic separation was performed on a 25 m capillary DB-5 column (Chromatographic Specialities Inc., Brockville, ON, Canada) at the following conditions:

injector temperature: 240 °C
column temperature T_1 : 130 °C for 2 min
rate 5 °C/min to $T_2 = 220$ °C for 5 min

Both chromatograms and mass spectra were recorded and analyzed by means of a VG-11-250T Data System.

RESULTS AND DISCUSSION

UV Light Absorption Spectral Data

Figure 1 records the UV light absorbing spectra of 7.8 μ M aqueous solution of the

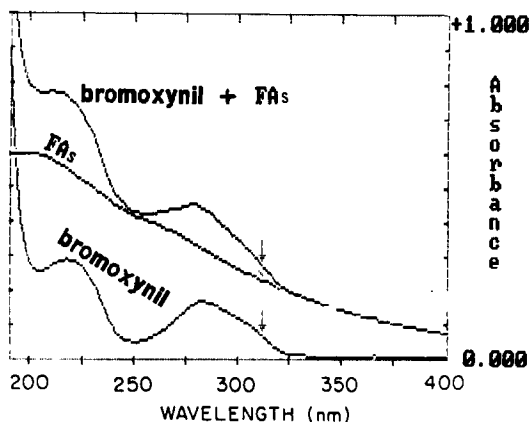


Figure 1 UV light absorption spectra of aqueous solutions of herbicide bromoxynil (**1**) (7.8×10^{-6} M), soil fulvic acids (FAs) (50 mg L^{-1}), and mixture of herbicide **1** (7.8×10^{-6} M) plus FAs (50 mg L^{-1}). The arrows indicate absorptions at 312 nm.

herbicide bromoxynil (**1**) in the absence and presence of 50.0 mg L^{-1} Armadale soil fulvic acids (FAs). This figure also includes the UV light absorption spectrum of FAs (50.0 mg L^{-1}) alone in water. It is evident from Figure 1 that the UV spectrum of soil FAs is uncharacteristic;^{5,7,10} i.e., no minima or maxima are seen. However, in the case of **1** alone, two broad absorption maxima occur at 282 and 218 nm. The spectrum of fulvic acids in the presence of **1** appears to be additive with that of **1** (Figure 1). In addition, both maxima (now occurring at 279 and 211 nm) undergo a blue shift and the intensity of these maxima decreases. Alberts³¹ noted an additive effect of 0.1, 0.5, 1.0 and 5.0 ppm Fe^{3+} ions on the UV absorption spectrum of humic acids in phosphate buffer.

Table 1 includes values of decadic light absorption coefficients (α) at 313 (α_{313}) and 320 nm (α_{320}) for aqueous solutions of bromoxynil (**1**) (7.8×10^{-6} M) in the presence of 0.0, 5.0, 10.0, 15.0, 20.0, 40.0, 45.0, 60.0, and 100.0 mg L^{-1} soil FAs, the samples codes being A, B, C, D, E, F, G, H and I, respectively. The ratios of α values for bromoxynil (**1**) solutions containing FAs to those of **1** in the absence of FAs, i.e., $\alpha_{(\text{bromoxynil} + \text{FAs})} / \alpha_{\text{bromoxynil}}$ ratios at 313 and 320 nm, are also documented in Table 1. Table 1 shows that the values of $\alpha_{(\text{bromoxynil} + \text{FAs})} / \alpha_{\text{bromoxynil}}$ ratios for 313 and 320 nm increase as the concentration of FAs rises. The trend is more pronounced at 320 nm than at 313 nm, since the contribution of bromoxynil (**1**) to α values is smaller at 320 nm than at 313 nm.

Photolytic Kinetic Data

The first-order treatments of the photolytic data for the degradation of bromoxynil (**1**) ($7.8 \mu\text{M}$) in water in the absence and presence of 45.0 mg L^{-1} soil FAs using Eqs. (3) and (3a), respectively, are given in Figure 2. The slope of the plots in Figure 2 along with additional similar plots provide the corresponding value of

Table 1 Decadic light absorption coefficients (α) data at 313 (α_{313}) and 320 nm (α_{320}) for the 7.8×10^{-6} M bromoxynil (**1**) herbicide in water containing various amounts of dissolved soil fulvic acids (FAs).

Sample code	Amount of FAs (mg L^{-1})	α_{313}	α_{320}	Ratios of α values for bromoxynil plus FAs to those of bromoxynil alone at	
				313 nm	320 nm
A	0.0	0.065	0.024	1.00	1.00
B	5.0	0.088	0.045	1.35	1.88
C	10.0	0.113	0.068	1.74	2.83
D	15.0	0.137	0.090	2.11	3.75
E	20.0	0.160	0.113	2.46	4.71
F	40.0	0.247	0.195	3.80	8.13
G	45.0	0.256	0.210	3.94	8.75
H	60.0	0.306	0.249	4.71	10.38
I	100.0	0.460	0.389	7.08	16.21

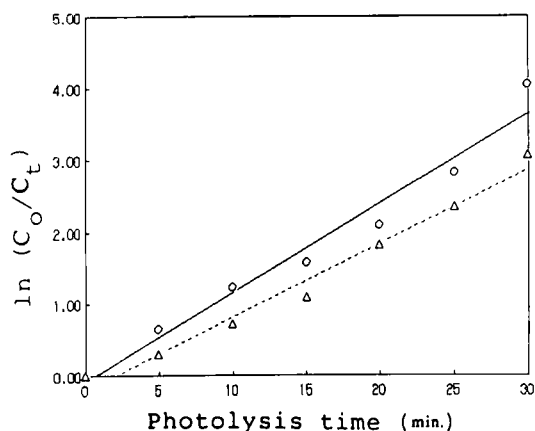


Figure 2 First-order plot of the photolysis data for 7.8×10^{-6} M herbicide bromoxynil (**1**) in the absence [Eq. 3a] (—○—○—) and presence [Eq. (3)] (---△---△---) of soil fulvic acids (FAs) (45.0 mg L^{-1}) in water.

the first-order photolysis rate constants, namely $k_{p,\lambda}$ and $k_{p,\lambda}^{\text{Sens.}}$, amounting to $(1.124 \pm 0.011) \times 10^{-3}$ and $(0.472 \pm 0.006) \times 10^{-3} \text{ sec}^{-1}$ without (Sample A) and with the presence of 45.0 mg L^{-1} FAs (Sample G), respectively (see Table 2). The values of $k_{p,\lambda}^{\text{Sens.}}$ for compound **1** in water containing various amounts of soil FAs, viz., 5.0 (Sample B), 10.0 (C), 15.0 (D), 20.0 (E), 40.0 (F), 60.0 (H) and 100.0 (I) mg L^{-1} , achieved in this fashion are also included in Table 2 (see column 5).

This table shows that with the rise of the concentration of FAs, the values of the first-order photolysis rate constants decrease.

Spectral Response Functions ($X_{s,\lambda}$)

The intensities of the light source determined using Eq. (5) and aqueous solutions of *p*-nitroacetophenone (PNAP) (0.1 μ M) plus pyridine (Pyr) (1.41 mM) as a chemical actinometer [Eq. (7)] are documented in Table 2 (column 4) during the photolysis of samples A to I of the herbicide bromoxynil (**1**) containing different amounts of soil FAs. The value of ϕ_A for the actinometer system [Eq. (7)] used for these calculations was 2.383×10^{-5} . It can be seen from Table 2 that the values of I_λ at $\lambda=313$ nm ranged from 3.70 to 3.95 μ E L $^{-1}$ sec $^{-1}$ in the case of samples A to I. Table 2 (column 3) also includes the values of the light screening factors (S_λ) at $\lambda=313$ nm determined through the utilization of Eq. (4) and α_{313} values, the cell path-length (l) being 1 cm. The corresponding values of the parameters, *viz.*, $k_p^{Sens.}$, I_λ and S_λ shown in Table 2 assisted the calculation of the spectral response functions ($X_{s,\lambda}$) using Eq. (2). The values of $X_{s,\lambda}$ for the photochemical transformation of herbicide **1** containing various amounts of FAs determined in this manner for samples B to I are given in Table 2 (column 6). It is evident from this table that a negative correlation exists between spectral response functions and concentrations of FAs.

Quantum Yields

Observed quantum yields ($\phi_{r,\lambda}^{Obs.}$) for the photodecomposition of **1** in water at $\lambda=313$ nm without (Sample A) and with varying concentrations of soil FAs (Samples B–I) are listed in Table 2 (see column 7). In the case of direct photolysis of **1**, $\phi_{r,\lambda}^{Obs.}$ data were determined following the previously cited techniques by Choudhry and Webster.²⁷ For the determination of $\phi_{r,\lambda}^{Obs.}$ values for the indirect phototransformation of **1**, Eq. (8) and relevant data were utilized. Table 2 indicates that on raising the concentration of soil FAs from 5.0 to 100.0 mg L $^{-1}$, the $\phi_{r,\lambda}^{Obs.}$ values decrease from 0.051 ± 0.008 to 0.020 ± 0.005 , while in the absence of FAs, the $\phi_{r,\lambda}^{Obs.}$ value is 0.052 ± 0.008 .

Table 2 also contains the predicted reaction quantum yields ($\phi_{r,\lambda}^{Pre.I}$) calculated by method I, namely by multiplying $\phi_{r,\lambda}^{Obs.}$ in the case of direct photolysis of **1** (Sample A) by light screening factors S_λ (see Column 8). Similarly, predicted reaction quantum yields ($\phi_{r,\lambda}^{Pre.II}$) calculated by method II, *viz.*, through the multiplication of $\phi_{r,\lambda}^{Obs.}$ for the direct photoreaction of **1** (Sample A) by $\alpha_{bromoxynil}/\alpha_{bromoxynil + FAs}$ (from Table 1) are also listed (column 9).

The data in Columns 7 and 8 of Table 2 diverge as the FAs concentration increases—the values of the observed quantum yields are smaller than the corresponding $\phi_{r,\lambda}^{Pre.I}$ datas, thereby revealing that in the presence of soil FAs, the rates of photodegradation of **1** diminish not only because of the light screening effect of FAs but also partly because of the quenching of **1** in the excited state by ground state FAs molecules (see also below). On the contrary, the trends of the data given in Columns 7 and 9 are approximately parallel. The quantum yields are

Table 2 Photolysis data for the degradation of 7.80×10^{-6} M aqueous solutions of herbicide bromoxynil (I) containing soil fulvic acids (FAs) around 313 nm wavelength (λ)

Sample code	Amount of FAs (mg L^{-1})	Light screening factor ^a , S_λ	Intensity of light ^b , I_λ (10^{-6} einsteins $\text{L}^{-1} \text{sec}^{-1}$)	First-order photolysis rate constant, $k_{p,\lambda}$ (10^{-3}sec^{-1})	Spectral response function ^c , $X_{s,\lambda}$ ($\text{L mol}^{-1} \text{cm}^{-1}$)	Observed quantum yields for photo-transformation ^d , $\phi_\lambda^{\text{Obs}}$	Quantum yields for photo-transformation predicted by method I ^e , $\phi_\lambda^{\text{Pre.I}}$	Quantum yields for photo-transformation predicted by Method II ^f , $\phi_\lambda^{\text{Pre.II}}$
A	0.0	0.00	3.87	1.124 ± 0.011	—	0.052 ± 0.008	—	—
B	5.0	0.91	3.70	1.052 ± 0.011	312.44 ± 3.27	0.051 ± 0.008	0.047 ± 0.007	0.039 ± 0.006
C	10.0	0.88	3.70	1.000 ± 0.011	307.13 ± 3.38	0.049 ± 0.008	0.046 ± 0.007	0.030 ± 0.005
D	15.0	0.86	3.70	0.911 ± 0.011	286.30 ± 3.46	0.043 ± 0.008	0.045 ± 0.007	0.025 ± 0.004
E	20.0	0.84	3.95	0.748 ± 0.011	225.44 ± 3.32	0.037 ± 0.005	0.044 ± 0.007	0.021 ± 0.003
F	40.0	0.76	3.95	0.536 ± 0.011	178.55 ± 3.66	0.029 ± 0.005	0.040 ± 0.006	0.014 ± 0.002
G	45.0	0.76	3.95	0.472 ± 0.006	153.23 ± 2.00	0.025 ± 0.005	0.040 ± 0.006	0.013 ± 0.002
H	60.0	0.72	3.80	0.339 ± 0.006	12.90 ± 2.19	0.023 ± 0.005	0.037 ± 0.006	0.011 ± 0.002
I	100.0	0.62	3.80	0.083 ± 0.006	35.23 ± 2.55	0.020 ± 0.005	0.032 ± 0.005	0.007 ± 0.001

^aData were collected using Eq. (4) and values of α_{313} were utilized from Table 1.

^bData were collected using Eqs. (7) and (5).

^cEq. (2) was used.

^dIn the case of sample A, previously described procedures by Choudhry and Webster²⁷ were utilized; whereas in the case of samples B-I, Eq. (8) was used.

^eData were calculated by multiplying $\phi_\lambda^{\text{Obs}}$ for the sample A with the corresponding S_λ values.

^fData were calculated by multiplying $\phi_\lambda^{\text{Obs}}$ for the sample A with the corresponding $\alpha_{\text{Bromoxynil}}/\alpha_{\text{Bromoxynil}} \cdot \text{FAs}$ rates where α is decadic light absorption coefficients. The reciprocal of the data recorded in Table 1 (column 5) were used.

Table 3 Calculated midday, midseason sunlight indirect photolysis half-lives^a $[(t_{1/2})_{sp}^{ind.}]$ (min) of the herbicide bromoxynil (**1**) in aquatic bodies containing soil fulvic acids (FAs) during various seasons

Sample code	Amount of FAs (mg L^{-1})	Seasons			
		Spring	Summer	Fall	Winter
B	5.0	2.18 ± 0.02	1.99 ± 0.02	3.15 ± 0.04	4.48 ± 0.05
C	10.0	2.22 ± 0.03	2.02 ± 0.02	3.20 ± 0.04	4.55 ± 0.06
D	15.0	2.38 ± 0.03	2.17 ± 0.02	3.44 ± 0.04	4.90 ± 0.07
E	20.0	3.02 ± 0.05	2.76 ± 0.04	4.36 ± 0.07	6.21 ± 0.10
F	40.0	3.82 ± 0.08	3.48 ± 0.07	5.51 ± 0.11	7.86 ± 0.16
G	45.0	4.44 ± 0.05	4.06 ± 0.06	6.42 ± 0.07	9.10 ± 0.15
H	60.0	5.51 ± 0.11	5.03 ± 0.09	7.92 ± 0.17	11.33 ± 0.22
I	100.0	19.34 ± 1.29	17.60 ± 1.33	28.33 ± 2.08	40.02 ± 2.75

^aData were calculated using Eqs. (1) and (6). Z_{λ} values for $\lambda = 297.5$ to 400 nm were utilized from Roof.³²

greater than those of the corresponding $\phi_{r,\lambda}^{pre.11}$. The absorption of UV light by increasing concentrations of humic substances increases; consequently, the rate of phototransformation of (**1**) decreases, but the rate is not suppressed to the extent predicted. Thus, FAs appear to act as photosensitizers in these photoprocesses. In addition, increasing the amount of FAs from 5.0 to 100.0 mg L^{-1} , does not decrease the $\phi_{r,\lambda}^{obs.}$ value by a factor of 20 as expected; instead this parameter decreases by a factor of 2.55 (see column 7 in Table 2) providing evidence that FAs act as photosensitizers. Furthermore, the apparent retarding of the rate of phototransformation of **1** in H_2O may be attributable to the absorption of the incidental light by FAs (i.e., light screening effects of FAs).

Midday, Midseason Sunlight Indirect Photolysis Half-lives $[(t_{1/2})_{sp}^{ind.}]$

Experimentally determined spectral response functions ($X_{s,\lambda}$) (described in Table 2, column 6) at 313 nm for the photodegradation of bromoxynil (**1**) in water containing various concentrations of FAs as well as solar irradiance data (Z_{λ}) from Roof³² were used to determine the sunlight first-order indirect photolysis rate constants ($k_{sp}^{ind.}$) for Samples B–I at midday, midseason, viz., spring, summer, fall and winter. The estimations of $k_{sp}^{ind.}$ values for **1** were done using Eq. (1) assuming that the $X_{s,\lambda}$ data are independent of the wavelength. Table 3 records the corresponding midday, midseason, sunlight half-lives for the indirect photolysis $[(t_{1/2})_{sp}^{ind.}]$.

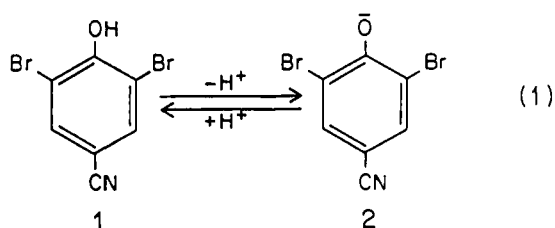
It is evident from Table 3 that as the concentration of soil FAs increases, the values of $(t_{1/2})_{sp}^{ind.}$ for **1** increase during each season. For example, during summer, the sunlight half-lives in the presence of 5.0 and 100.0 mg L^{-1} soil FAs were 1.99 ± 0.02 and 17.60 ± 1.33 min, respectively. It can be seen from Table 3 that the trend of the $(t_{1/2})_{sp}^{ind.}$ data over the four seasons is as follows:

Summer < Spring < Fall < Winter.

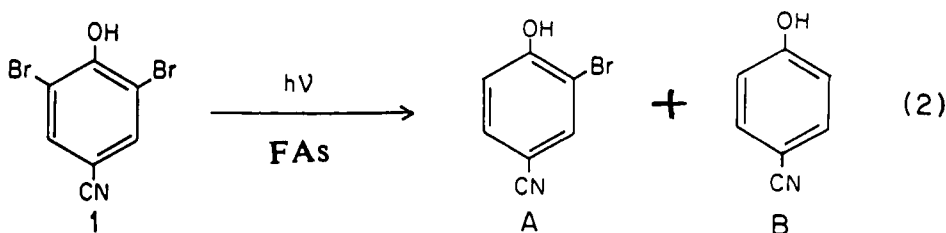
Solar intensity data (Z_λ) up to $\lambda=400\text{nm}$ was used for the calculation of k_{sp}^{ind} . The energy of visible light at 400nm is 300kJ/einstein ;³³ whereas, the required energy for the homolytic cleavage of the C-Br bond of monobromobenzene is 335kJ/mol .³⁴ The solar radiation $>400\text{nm}$ is not important in the photodecomposition of bromoxynil in the presence or absence of FAS.

Photoproducts

The $\text{p}K_a$ value of bromoxynil (**1**) is 4.06 .³⁶ Thus the following equilibrium between the unionized form (phenol **1**) and the ionized form (phenolate anion **2**) is expected to exist in water (Reaction 1):



At $\text{pH} \ll \text{p}K_a$, the phenol form of **1** is the major species in solution; whereas, in basic solution ($\text{pH} \gg \text{p}K_a$), phenolate ions **2** predominate. In these studies, Sample A and Samples B–I were at $\text{pH} 6.0\text{--}7.0$ and $5.5\text{--}6.5$, respectively; thus, bromoxynil in all samples with and without soil FAs was largely in the anion form **2** (see Reaction 1). Both in the absence and presence of soil FAs, two major photoproducts were generated; viz., 3-bromo-4-hydroxybenzonitrile (**A**) and 4-hydroxybenzonitrile (**B**) (Reaction 2):



The structure of the photoproduct **B** was confirmed with the aid of an authentic standard compound using their retention times and GC-MS spectral data. However, owing to the unavailability of an authentic standard of the product **A**, its identity was assigned by interpreting its mass spectrum (see below).

The photoproducts **A** and **B** were quantitatively monitored by HPLC. Typical plots showing the relative changes in the concentrations of **1** and its photo-

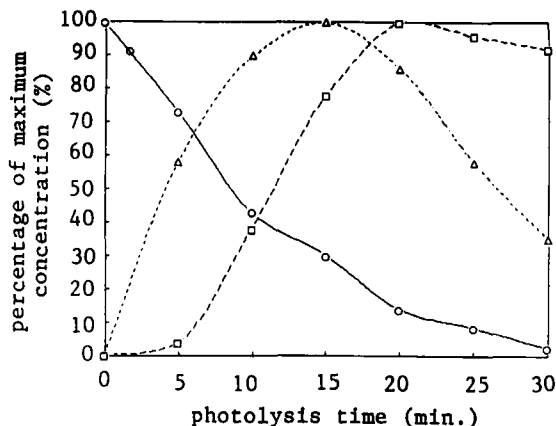


Figure 3 Plots of variations in the concentration of 7.8×10^{-6} M aqueous bromoxynil (**1**) (—○—○—) and its photoproducts 3-bromo-4-hydroxybenzoxynitrile (**A**) (---△---△---) and 4-hydroxybenzoxynitrile (**B**) (---□---□---) in the presence of soil fulvic acids (45.0 mg L^{-1}) vs. irradiation time at 313 nm.

products in water containing 45.0 mg L^{-1} soil FAs are given in Figure 3. After 5 min, ca. 27% of the starting material **1** had decomposed yielding 57% and 4% of the maximum concentration of the photoproducts **A** and **B**, respectively (Figure 3).

Mass Spectral Data

Mass spectra of compound **1** and its photoproducts **A** and **B** are documented in Figure 4. In Figure 4(a) and (b), pattern of the parent molecular ions (M^+) clusters provide evidence for the presence of two and one Br atom(s) in **1** and **A**, respectively.³⁷ Based on fragments containing the ^{79}Br isotope solely, these spectra can be interpreted as follows: the m/e value of the M^+ of **1** is 275, an odd number, showing that this compound may contain an odd number of N atoms. The peaks observed at 246, 195, 168, 117 and 88 m/e in the mass spectrum of **1** [see Figure 4(a)] are attributable to the loss of HCO, HBr, HCN, Br_2 , and HBr groups from species of 275, 275, 195, 275 and 168 m/e value, respectively. Likewise, the structure 3-bromo-4-hydroxybenzoxynitrile (**A**) can be ascribed to the photoproduct whose mass spectrum is recorded in Figure 4(b). In the mass spectrum of **A** shown in Figure 4(b), the possible sources of the peaks occurring at 168, 117 and 90 m/e are $M^+ - \text{HCO}$ (i.e., 197-HCO), $M^+ - \text{HBr}$, and 117-HCN, respectively. Furthermore, in the case of the mass spectrum of 4-hydroxybenzoxynitrile (**B**) [Figure 4(c)], the peak at 91 m/e can be attributed to the loss of CO from M^+ ; whereas, the species at m/e 64 is possibly formed via the ejection of an HCN group from the m/e 91 fragment.

Additional findings on the environmental photolytic fate of bromoxynil (**1**) will be reported elsewhere.³⁵

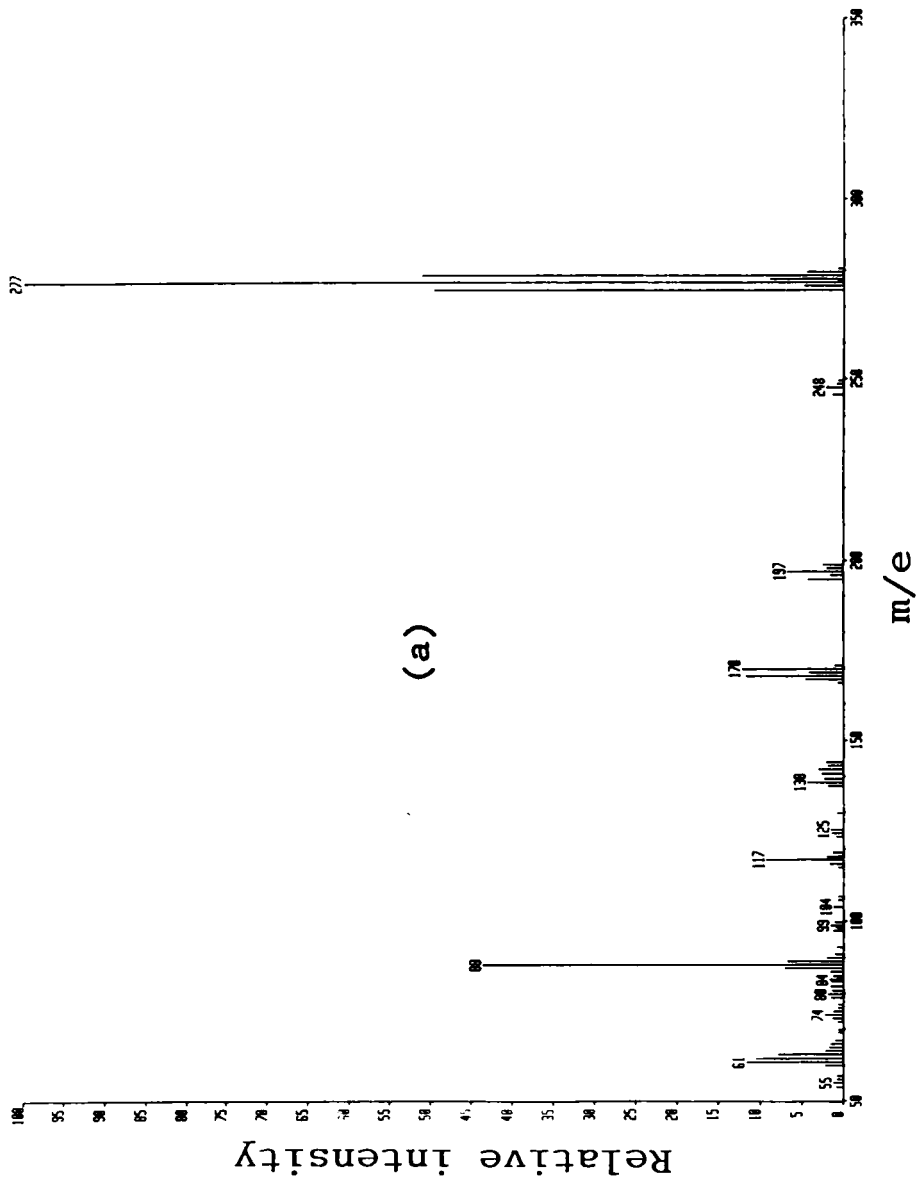


Figure 4 (a) Mass spectra of bromoxynil (1).

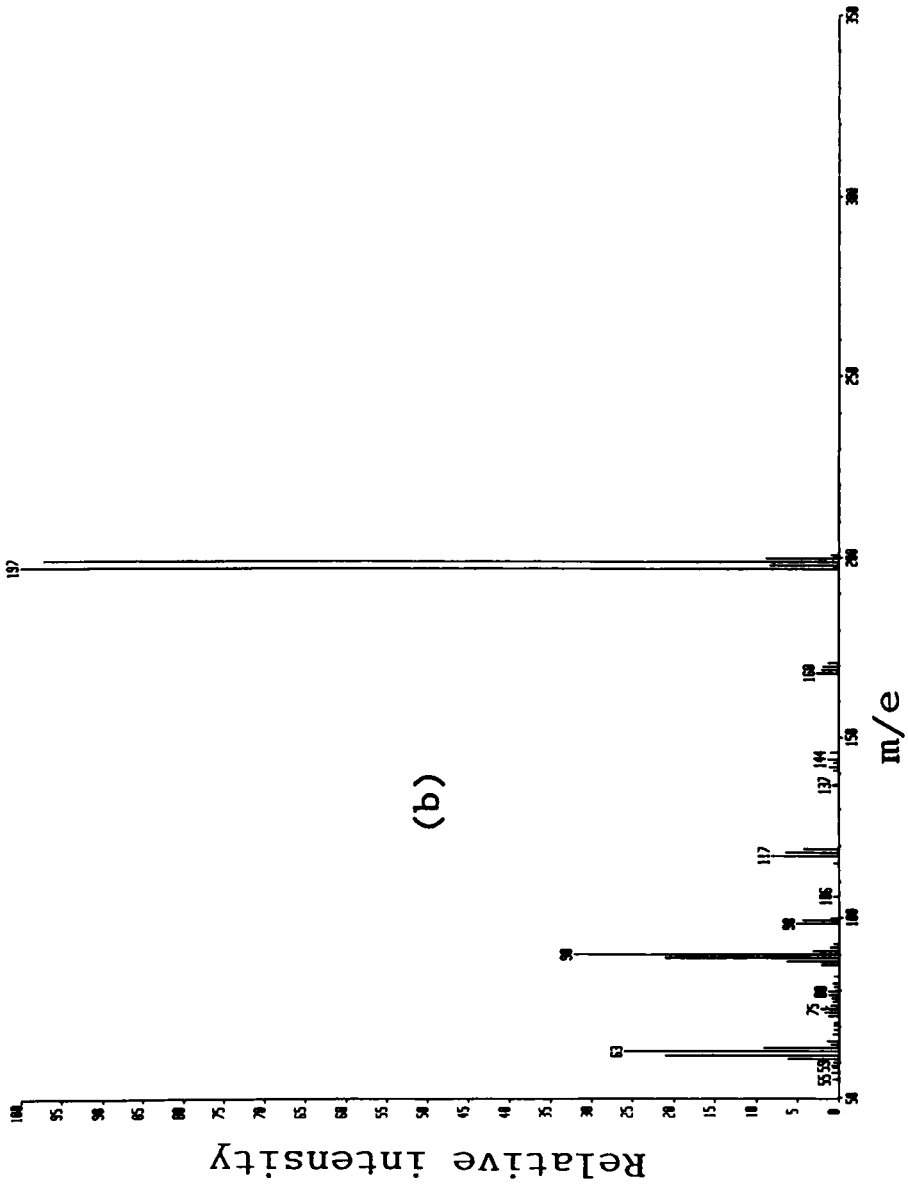


Figure 4 (b) Its photoproducts 3-bromo-4-hydroxybenzonitrile (A).

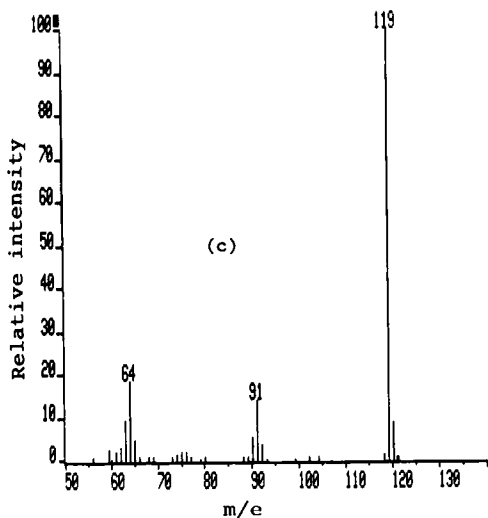


Figure 4 (c) 4-hydroxybenzoxynil (B).

CONCLUSIONS

The present laboratory investigations on the environmental aquatic photochemistry of bromoxynil in the absence and presence of dissolved Armadale soil fulvic acids (FAs) have led to several environmentally significant conclusions. For example, depending upon the concentrations of FAs, these macromolecules may exert several-fold additive effects on the UV absorption spectrum of bromoxynil (**1**) present in natural waters. First-order sunlight photolytic kinetics are expected to be followed. The sunlight indirect photodegradation half-lives $[(t_{1/2})_{sp}^{ind}]$ amount to 1.99 ± 0.02 to 17.60 ± 1.33 min during midday, midsummer, indicating that as the concentration of FAs increases, the $[(t_{1/2})_{sp}^{ind}]$ values for bromoxynil will also increase. Similarly, the observed reaction quantum yields $(\phi_{r,\lambda}^{obs})$ for the photo-transformation of bromoxynil in water are 0.052 ± 0.08 to 0.020 ± 0.005 in the presence of 0.0 to 100.0 mg L^{-1} soil FAs. The increase of FAs concentration results in a diminishing of the photolysis rates.

Sunlight can be expected to photodecompose bromoxynil (**1**) in natural waters to 3-bromo-4-hydroxybenzoxynil (**A**) and 4-hydroxybenzoxynil (**B**) whether these bodies contain soil FAs or not.

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