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Capillary electrophoretic study of atrazine photolysis

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Abstract

Capillary electrophoresis in its free solution mode (FSCE) has been used as a rapid analysis tool for the quantification of hydroxytriazines during the photodegradation of atrazine under nitrogen and oxygen atmosphers in the presence or absence of humic substances in aquatic media. Hydroxyatrazine was found to be the main photodegradation product. The presence of dissolved humic substances influenced the photodegradation pathway of atrazine by dealkylation reactions. FSCE has been found effective in the separation of the cationic hydroxytriazines from the anionic humic polyelectrolytes during the analysis without cleanup procedures.

1. Introduction

Atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine] is widely used over the world as a selective herbicide against broad weed leaves and annual grass. Many studies of atrazine and other *s*-triazine pesticides over the last two decades have provided a good understanding of their metabolic fate in different matrices under variable conditions (abiotic and biological degradation in soils or sediments and decay through the effect of UV radiation in water). *s*-Triazines have been found to degrade by dealkylation of the side chains in surface position 4 and 6 and by hydrolysis of the substituent in position 2.

One objective of photochemical studies is the understanding of the environmental relevance of this abiotic degradation pathway [1]. In more recent studies, an additional objective is the optimisation of UV degradation systems in combination with reactive oxygen precursors (O_3, H_2O_2) for decontamination/desinfection of drinking waters [2]. In both cases humic substances can have a significant effect on pesticide decay as a reaction sensitizer or inhibitor [3,4] during photochemical reactions.

The hydroxy metabolites of *s*-triazines are significant natural degradation products in soils [5] and their occurrence in streams and water reservoirs [6] may occur after slow release from soils or after photolysis of *s*-triazines in surface waters [7]. Their analysis in environmental matrices is still a challenge; they have to be derivatized for gas chromatography [8] and only a few quantitative techniques based on LC [9,10], HPLC [11–15] or enzyme-linked immunosorbent assay [16,17] are found in the literature.

High-performance capillary electrophoresis (HPCE) is a recent analytical technique that has rapidly found application in biomedical sepa-

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rations [18] as well as in environmental sciences [19]. HPCE in its free solution mode (FSCE) has proven useful in pesticide analysis [20,21] and in the separation of *s*-triazine compounds [22,23].

The present paper has two objectives: first, to examine the photochemical behavior of atrazine in the presence and absence of humic substances, under oxygen and nitrogen atmospheres in aquatic media; second, to show for the first time the application of FSCE as a rapid analysis tool for hydroxy-*s*-triazines in environmental matrices.

2. Materials and methods

Aqueous solutions of atrazine were prepared at 5 ppm and placed in a cylindrical vessel into which a Philips HPK 125 W high-pressure mercury vapor lamp, with a cooled Pyrex housing to block wavelengths shorter than 290 nm, was inserted. Humic acids were added to some of the aqueous solutions to a concentration of 5 ppm just before they were transferred to the reactor. The pH of the solution was controlled and eventually adjusted to pH 7.0 to ensure solubility of humic acids. Nitrogen or oxygen was bubbled through a sintered glass joined to the bottom of the vessel to keep the solutions saturated with gas during photodegradation experiments. The reaction temperature was kept under these conditions at 20–25°C. The same pesticide solutions were also irradiated under simulated sunlight (xenon lamp) in a Heraeus Suntest apparatus at 30–35°C, with and without fulvic acids (5 ppm). Aliquots of 1 ml were sampled during irradiation and kept in the refrigerator for future analysis. Blanks (pesticide solution with and without humic substances) were analysed to ensure that pesticide degradation was due to photochemical processes only.

The disappearance of the pesticide from reaction mixtures and the appearance of the dealkylated chloro metabolites were monitored by HPLC (Hewlett-Packard, Munich, Germany; HPLC Series 1050). Detection was with an UV filter at 220 nm. A reversed-phase column, 250 mm × 4.6 mm I.D., packed with Hypersil (RP C_{18}, 5 μm) was used for analysis. The mobile phase was acetonitrile–water (50:50) with a flow-rate of 1.0 ml/min in the isocratic mode.

The qualitative and quantitative analyses of the hydroxy metabolites employed a Beckman P/ACE 2100 Series HPCE, assisted by Beckman Gold Chromatography Software. The fused-silica non-coated CE column, 57 cm (50 cm to detector) × 375 μm 0.0 × 75 μm I.D., was obtained from Beckman Instruments (Munich, Germany). The separation runs were done at constant temperature (30°C) and voltage (20 kV) with UV detection at 230 or 214 nm.

Direct sample injection by the hydrodynamic (pressure) mode was used for all experiments; injection times were typically 10 to 20 s. Samples were systematically spiked with standards to assure identification of the hydroxy metabolites. A standard curve was prepared for each hydroxy metabolite for quantitative analysis of their degradation products.

An acetate buffer was used for qualitative and quantitative measurements since such a buffer at 50 m*M* and pH 4.65 has been shown to give good separation of different dealkylated hydroxy metabolites of atrazine [23]. Buffers were made by mixing one volume glacial acetic acid (0.1 *M*), one volume sodium acetate (0.1 *M*), and two volumes water.

Pesticide stock solutions were prepared by dissolving 5.0 mg of pesticide/metabolite in 100 ml of pesticide-grade methanol. If necessary dilutions were done in water (for standard curves) and these solutions were immediately used for CE. All buffers and stock solutions were kept under refrigeration at 4°C.

For an additional confirmation of the identity of atrazine and its metabolites thermospray liquid chromatography–mass spectrometry (LC–TSP-MS) analyses of the reaction solutions obtained after photodegradation in the presence and absence of humic and fulvic acids were carried out.

LC–TSP-MS and LC–TSP-MS-MS have been applied to the determination of polar pesticides and different metabolites of polar nature formed during photodegradation and microbial degra-

dation processes [24–28]. The use of these methods offers the advantage of the direct analysis of polar hydroxy metabolites and direct injection of photodegraded solutions into the LC–MS system.

All LC–TSP-MS experiments were performed using a Finnigan-MAT TSQ 700 triple quadrupole MS–MS system (Bremen, Germany) equipped with a Finnigan-MAT thermospray interface. Conditions were as follows for all analyses: vaporizer temperature was 100°C, source block temperature was kept at 240°C. Ionisation was done in the filament-on mode with an electron current of 600 μA and an electron energy of 600 eV. Multiplier voltage was set at 1200 V. Spectra were acquired by scanning from m/z 100 to 500 every 1 s. The instrument was used in the positive ion mode.

The HPLC pump combined with the mass spectrometer was a Waters gradient pump 600-MS (Milford, USA). The eluent consisted of methanol–water (50:50, v/v) at a flow-rate of 1 ml/min. Injection volume of the samples was 50 μl. Flow injection analysis without chromatographic separation prior to MS analysis was performed. Because similar results were obtained for all samples investigated only one mass spectrum is shown representatively in Fig. 1.

It is well known that LC–TSP-MS spectra of most pesticides are characterized by the presence of $[M + H]^+$ base peaks. Fragmentation of the molecules is hardly found. This observation was also valid for our investigations. As expected the most intense peak is observed at m/z 216 deriving from atrazine, corresponding to $[M + H]^+$. Further compound-specific ions were found for hydroxyatrazine at m/z 198 $[M + H]^+$ and desethylatrazine at m/z 188 $[M + H]^+$. Ameline [M = 127] could not be identified unequivocally because $[M + H]^+$ at m/z 128 was found only with a very small intensity.

The fragments at m/z 174 and 146 are probably stemming from atrazine and desethylatrazine due to a loss of their isopropyl group $[M - iso\text{-}C_3H_6]^+$. In contrast to the ethyl group of these compounds the elimination of the isopropyl group is favored and can take place even under soft ionization conditions [24,29]. The presence or absence of chlorinated substances can be verified looking at the typical isotopic ratios (m/z

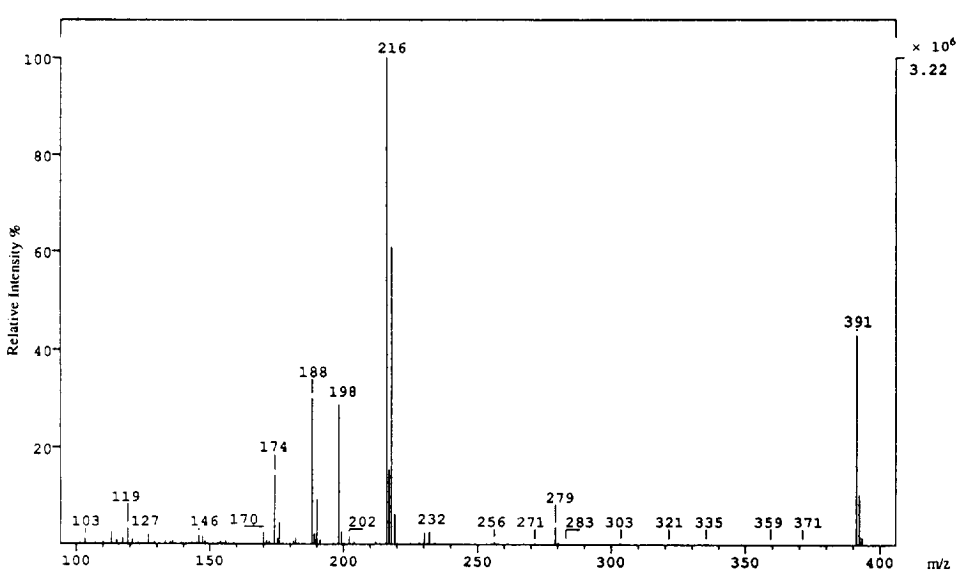

Fig. 1. TSP mass spectrum of atrazine treated with O_3 in the presence of humic acid. The spectrum was obtained after background subtraction.

Table 1
Elemental analysis and acidity data of HA and FA

	C(%)	H(%)	N(%)	O(%)	Ash(%)	C/N	$H/C_{(at.)}$	$O/C_{(at.)}$
FA	44.71	3.44	2.59	43.26	6	17.26	0.92	0.72
HA	48.3	4.04	4.44	39.52	3.7	10.88	1.01	0.61

Total acidity FA: 4, 0 meq uiv. g; HA: 2.42 meq uiv. g.

216 and 218 for atrazine, m/z 188 and 190 for desethylatrazine).

2.1. Chemical source and purity

Chloro- and hydroxy-*s*-triazines were purchased in greater than 99% purity grade from Dr. Ehrenstorfer GmbH, Augsburg, Germany or from Riedel-de Haen (Pestanal grade), Munich, Germany. All solvents, HCl, glacial acetic acid and sodium acetate (all analytical-reagent grade) were obtained from E. Merck, Darmstadt, Germany.

Humic acids (HA) and fulvic acids (FA) were extracted and isolated from the Ao horizon (0–15 cm) of a cultivated brown soil (Scheyern, Germany) according to the methods of the International Humic Substances Society (IHSS) [30,31]. Elemental analysis and functional group analysis is given in Table 1. Spectroscopic data (NMR, Fourier transform IR, pyrolysis–field ionization mass spectrometry) will be given elsewhere.

3. Results and discussion

3.1. Quantitative measurement of hydroxyatrazine

HPCE in its free zone mode has shown good potential for the analysis of *s*-triazinic herbicides [23]. This recent analytical technique allows separation of substances as cations on the basis of their relative electrophoretic mobility at a chosen buffer pH. Hydroxy-*s*-triazines are weakly basic compounds protonating at acidic pH according to Fig. 2 with dissociation constants between 4.5 and 5.2 [32].

The best buffer (signal-to-noise ratio) was found to be acetate at pH 4.5. Under those conditions, the hydroxytriazines were separated in less than 6 min with good quantitative reproducibility.

The relative standard deviations (R.S.D.s) of quantitative measurement of hydroxyatrazine in the current study were 3 and 5% at 230 nm detection wavelength and 5 and 8% at 214 nm detection wavelength for the areas and peak heights, respectively. The R.S.D. of retention times under these experimental conditions was less than 0.2% for all hydroxy metabolites studied.

Standard curves were measured for hydroxyatrazine in a range of 5 ppm to 50 ppb with UV detection at 230 or 214 nm. Peak area was the quantitative parameter chosen for this study with detection at 230 nm, which gave the best reproducibility and sensitivity (Fig. 3).

An example of separation with 50 mM acetate buffer at pH 4.65 is given in Fig. 4a. The five hydroxytriazines are separated in less than 5 min and are detected as cations in this buffer. The electroosmotic flow, corresponding to the speed of the neutral compounds, is indicated in this example by the negative peak at 5 min. Anions migrate after the neutral peak. Humic substances are known to be polyacids with an average pK_a around 3–4. At a buffer pH of over 4, they are partially present as anions and can be fraction-

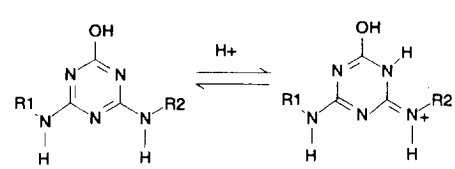

Fig. 2. Protonation of hydroxy-*s*-triazines at acidic pH [11].

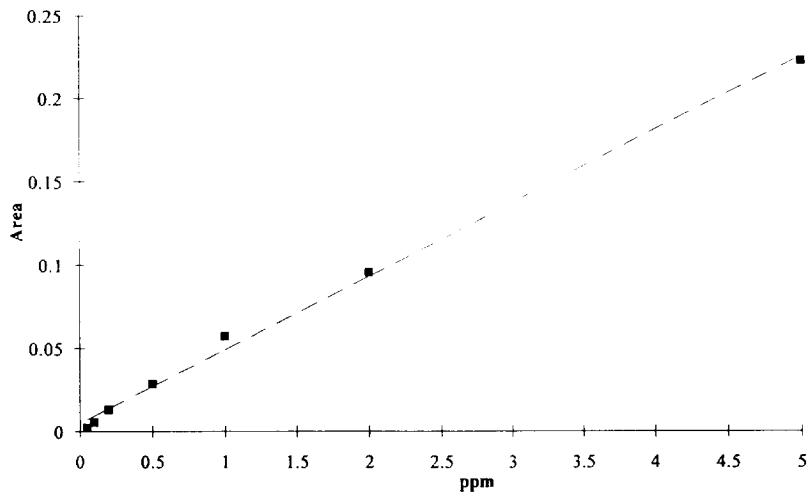

Fig. 3. Standard curve found with hydroxyatrazine. $y = 0.044021x + 0.005$; $r^2 = 99.6$

ated by FSCE on the basis of their electrophoretic mobility (relative charge-to-mass ratio). Previous studies have shown that HPCE can be a useful tool in humic substance characterizations [33] and Fig. 4b shows an electropherogram of the fulvic and the humic acids used in this study, using a 50 m*M* acetate buffer at pH 5.3 (similar experimental conditions as for the hydroxytriazines). In these conditions the electropherograms of humic substances show an average electrophoretic mobility (AEM) of negatively charged molecules.

One can see by this example that HPCE in its free zone mode is a good technique for the quantitative analysis of hydroxy-*s*-triazines, because potentially interferring humic substances in the sample matrix are separated. Sample clean-up before analysis to separate background matrix material (as in HPLC), is minimized thus avoiding loss of important information.

3.2. Photodegradation kinetics of atrazine

Under oxygen and nitrogen atmospheres, the disappearance of atrazine follows first-order kinetics with rate constants of $22.21 \cdot 10^{-3}$ and $18.32 \cdot 10^{-3}$ h^{-1}, respectively (Table 2). The oxygen atmosphere does not significantly enhance the kinetic rate. When irradiated in the Heraeus Suntest apparatus, the kinetic order is also first order; but the calculated half-lives are double those found with the high-pressure mercury lamp because of lower light intensity.

The addition of humic material to the solutions did not alter kinetic order but accelerated degradation rates by a factor of 54% under oxygen and 38% under nitrogen (Fig. 5a). Humic substances play an important role in photosensitizing processes via electronic energy transfer [34] and are precursors for the production of oxygen reactive species such as hydrated electrons [35], peroxide radicals, singlet oxygen, hydrogen perodide and OH radicals [36]. Oxygen is involved in sensitizing reactions with dissolved humics and thus the degradation rate is higher in oxygen compared to the experiment with nitrogen. With the Heraeus Suntest apparatus and dissolved fulvic acids, the atrazine degradation rate was also increased by a factor of 33% (Fig. 5b and Table 2).

3.3. Dealkylated and hydroxylated photoproducts

The analysis of hydroxylated photoproducts gave good, rapid results with HPCE without sample pretreatment. Hydroxyatrazine produced by photosubstitution of chlorinated atrazine is the major photoproduct formed without humic substance addition under simulated sunlight and

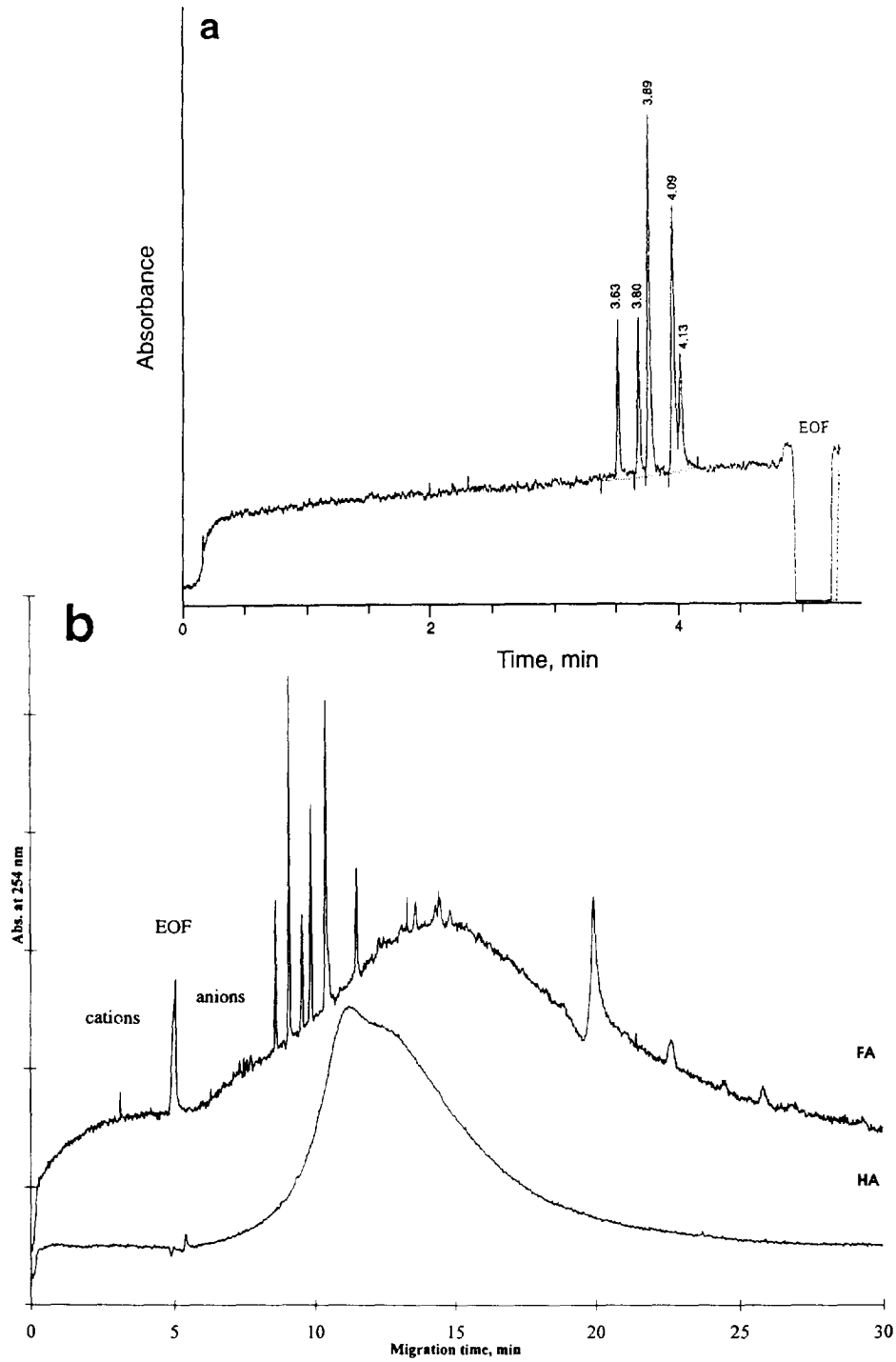

Fig. 4. Separation of five hydroxytriazines with acetate buffer (pH 4.65, 20 kV, 30°C). Peaks from left to right correspond to: hydroxyterbuthylazine, hydroxydesisopropylatrazine, hydroxyatrazine, hydroxydesethylterbuthylazine and hydroxydiaminoatrazine (ameline). (b) Separation of fulvic and humic acids used in this study with acetate buffer (pH 5.3, 20 kV, 30°C). EOF = Electroosmotic flow.

Table 2
Kinetic data on photodegradation of atrazine

Lamp	Atmosphere	Atrazine (5 ppm) solution	r_2	$K \times 10^{-3}$ (h^{-1})	$t_{1/2}$ (h)
Xenon	Air	Alone	99.2	10.49	66.08
		Fulvic acid (5 ppm)	99.4	13.97	49.62
HPK	Oxygen	Alone	99.8	22.21	31.21
		Humic acid (5 ppm)	98.4	34.35	20.18
	Nitrogen	Alone	99.7	18.32	37.84
		Humic acid (5 ppm)	99.5	25.39	27.30

First-order kinetics in all cases. K = Rate constant.

with the high-pressure mercury lamp (up to 70% of total photoproducts). The proportion of hydroxyatrazine compared to total photoproducts (obtained by difference between atrazine concentration and initial concentration) reaches a maximum value in time before decreasing, probably due to further photodecomposition (dealkylation) (Fig. 6a and b).

Hydroxy metabolites have been found as photosolvolysis products of *s*-triazinic pesticides

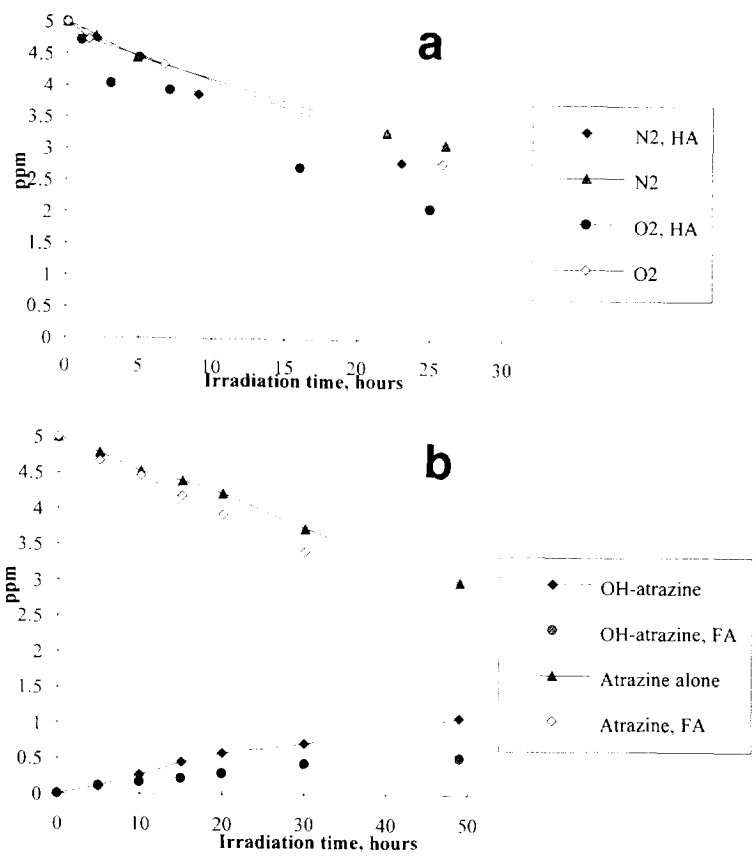

Fig. 5. (a) Atrazine photodecomposition under oxygen and nitrogen atmospheres with Philips HPK lamp; (b) atrazine photodecomposition with Heraeus Suntest apparatus.

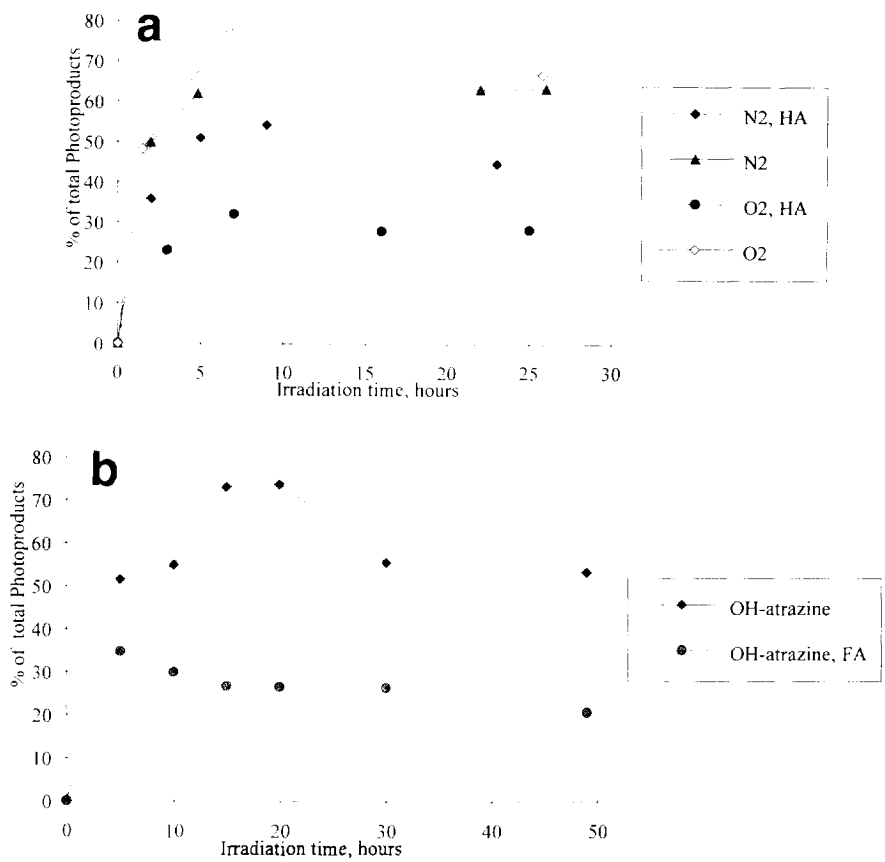

Fig. 6. (a) Variation of hydroxyatrazine produced by photodecomposition of atrazine under oxygen and nitrogen atmospheres with Philips HPK lamp; (b) variation of hydroxyatrazine produced by photodecomposition of atrazine in Heraeus Suntest apparatus.

in many other photochemical studies in aqueous media [37,38]. Low concentrations of desethylatrazine were found in the absence of humic substances. Deisopropylatrazine and ameline (2-hydroxy-4,6-diamino-*s*-triazine) were minor degradation products found in trace levels under those conditions.

The addition of dissolved humic material changed the photochemical degradation pathway of atrazine in aqueous solution. All quantitative results are given in Table 3. With humic acids and in the presence of oxygen, the absolute amount of hydroxyatrazine produced decreased 43% as shown in Fig. 6a. Under nitrogen con-

Table 3
Measured amount of products after irradiation (ppm)

	O_2	O_2, HA	N_2	N_2, HA
Atrazine	2.8	2.1	3.1	2.8
Hydroxyatrazine	1.47	0.83	1.21	0.98
Desethylatrazine	<0.08	0.37	<0.05	0.16
Ameline	Traces	0.2	Traces	0.15
Irradiation time (h)	26	25	26	23

ditions this decrease was only 20%. Rejto et al. [39] showed in a dye-sensitized photodegradation study, that riboflavine sensitizes *s*-triazine photodecomposition under sunlight and oxygen conditions by dealkylation without production of hydroxymetabolites. In this study desehylatrazine is the only dealkylated metabolite; its amount increases in the presence of humics and may occur by a sensitizing effect. Ameline is only quantified in the presence of humic substances; it is produced by the complete dealkylation of hydroxyatrazine. Khan and Schnitzer [4] also showed that the presence of fulvic acids enhances the dealkylation of photochemically formed hydroxyatrazine to ameline. The hydroxy intermediates (hydroxydesethylatrazine and hydroxydesisopropylatrazine) were not found in our experiments. Similar results were found by Khan and Gamble [40] with prometryn. Under the Heraeus Suntest apparatus, with milder simulated light conditions as shown by kinetics, only hydroxyatrazine (80%) is detected by HPCE. The amount of hydroxyatrazine is also lower in the presence of fulvic acids (30%), because as in previously described experiments, fulvic acids change the photochemical pathway of atrazine. Desethylatrazine was found under traces in those photochemical conditions.

At the end of irradiation experiments all humic solutions were decolorized because of photooxidation affecting humic substances. The structural changes of the same humic acids as under these photochemical conditions have been studied by means of modern spectroscopic instrumentation (NMR, Fourier transform IR, FI–pyrolysis–MS) and will be reported elsewhere.

4. Conclusion: effect of humic substances on photodegradation of atrazine

We have shown that the presence of dissolved humic material alters the photochemical behavior of atrazine by accelerating its degradation. Changes in the degradation pathway of atrazine by addition of humic material are shown in Fig. 7. Dehalogenation was found to be the main degradation process to yield hydroxyatrazine (up to 70% of total photoproducts). Under oxygen-saturated conditions the relative amount of hydroxyatrazine is lower in the presence of dissolved humic material because

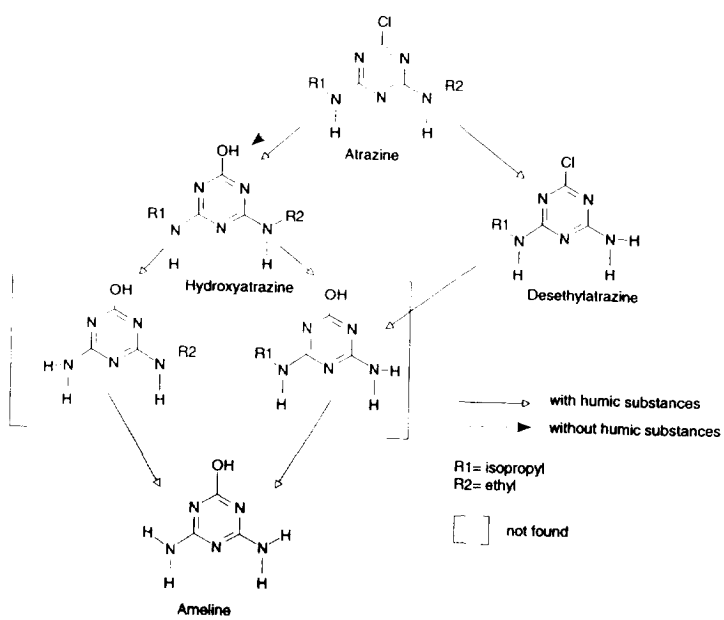

Fig. 7. Photochemical degradation pathways of atrazine with and without humic substances.

dealkylation of the side chain to produce desethylatrazine occurs (by sensitization). Under nitrogen the same photochemical pathway is observed. The production by the humics of reactive oxygen species (H_2O, OH, $^1O_2$, hydrated electrons) not only accelerates degradation of atrazine, but also effects photostability of the photoproducts.

HPCE in its free zone mode is a good tool for analysis of hydroxy-*s*-triazines in the presence of humic material. This analytical technique allows separation of the pesticides from the matrix without pretreatment of the samples.

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