

Fate of Fluometuron Dissolved in Natural Waters and Exposed to Solar Light

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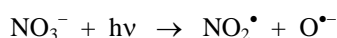
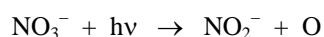
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Abstract - To predict the fate of pollutants in the aquatic environment and to assess the risk they may pose, it is necessary to improve our knowledge on their chemical reactions under environmental conditions. Photochemical reactions are a route for the attenuation of organic pollutants present in surface waters. This work was devoted to herbicide fluometuron which is used to control weeds in cotton. Phototransformation of fluometuron (1 μ M) in natural sunlight was investigated in synthetic waters containing either natural organic matter, nitrate ions or both in order to mimic reactions taking place in aquatic environments. Fluometuron underwent photolysis and its degradation was faster in the presence of fulvic acids (10 mg l⁻¹, factor 2.5) or nitrates (25 mg l⁻¹, factor 15) than in Milli-Q water showing the importance of natural waters constituents. Identification of major photoproducts was conducted under laboratory conditions. Hydroxylation of the aromatic ring with or without hydrolysis of CF₃ into CO₂H and oxidation of the urea chain leading to demethylation were observed.

Keywords: photodegradation, phenylureas herbicides, solar light, naturel waters.

Introduction

Photochemistry is one of the main abiotic degradation pathway of organic pollutants occurring in surface waters. This is a route for attenuation of organic pollutants. Several types of reactions may occur depending on the medium composition. Direct photolysis is possible if the considered pollutant absorbs solar light. In addition, photoinduced or photosensitized transformations mediated by components of the aquatic medium can also take place. In particular, dissolved natural organic matter (DOM) which absorbs a large portion of photons is a potential photosensitizer. Singlet oxygen, superoxide ion/hydroperoxyl radicals, hydroxyl radicals, excited triplet states and alkylperoxyl radicals were proved or proposed to be generated in natural waters under the influence of sunlight (Vaughan and *al.*, 1998; Canonica and *al.* 1995; Halladja and *al.* 2007). However, a part of these species are trapped by DOM itself. Nitrate ions that are present in surface waters at level varying from 0.2 to 25 mg.L⁻¹ generate the highly oxidizing hydroxyl radicals under light excitation (Boule and *al.*, 1999).



The percentage of hydroxyl radicals trapped by pollutants is thus strongly dependent on the medium composition. In the present work, we focused on the phototransformation of the phenylurea herbicide fluometuron (FM). This compound is widely used for pre- and post-emergence control of weeds in fields of conventional cotton cultivars. It is persistent (Stoeckel and *al.*, 1997) and may pose some risks to aquatic organisms (Muschal and *al.*, 2003). FM poorly absorbs solar light (*see Fig. 1*) but indeed its direct photolysis in simulated solar light ($\lambda > 290$ nm) was reported (Lam and *al.*, 2005). The CF₃ group undergoes photohydrolysis into CO₂H.

The objective of the present work was to investigate the photolysis of FM in conditions approaching real ones. FM in the micromolar range was irradiated in natural solar light. The influence of DOM or/and nitrates on the phototransformation was assessed. In parallel, laboratory experiments were conducted to identify the main photoproducts on the basis of HPLC-ESI-MS analyses.

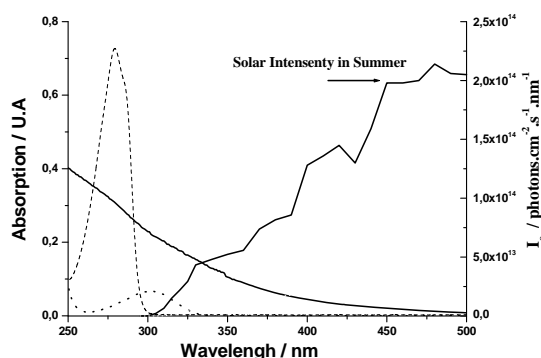


Fig. 1: Absorption spectrum of (---) FM at 3.10^{-4} M, (—) FA at 10 mg.L^{-1} , (.....) nitrates at 0.01M and solar light emission reaching the earth surface in summer (Zepp and al., 1977)

Methods and Procedures

Photoreaction setup

For kinetic purpose, FM ($1 \mu\text{M}$) was irradiated (1) in Milli-Q water, (2) in water containing fulvic acids (10 mg.L^{-1}) used as a surrogate of DOM, (3) in water containing nitrate ions (25 mg.L^{-1}) or 3.10^{-4} M) and (4) in water containing both fulvic acids (10 mg.L^{-1}) and nitrate ions (3.10^{-4} M). Irradiation experiments in natural sunlight were performed at Clermont–Ferrand (46° N , 3° E) in June 2006. Cylindrical quartz glass reactors (14 mm internal diameter) were filled with 14 ml of solutions. Reactors were closed by a septum, attached on a rack inclined by about 15° from horizontal and exposed to solar light. Samples received 13 h of sunshine per day. Aliquots of 0.5 ml were removed simultaneously from all the solutions at selected intervals. Samples were immediately analyzed by HPLC. Irradiations under laboratory conditions were also carried out for photoproducts identification. Irradiations were performed in a device equipped with six TLAD 15W/05 fluorescent tubes emitting within the wavelength range 300–450 nm with a maximum of emission at 365 nm and in a Pyrex glass reactor (14 mm i.d). The device was cylindrical and equipped with reflecting inner walls. A ventilator was used as a cooling system. The reactor was placed in the centre of the device and was surrounded by the six fluorescent tubes. Light intensity was measured using p-nitroanisole/pyridine as a chemical actinometer. PNA (10^{-5} M) and pyridine (10^{-4} M) were irradiated in the same conditions as samples in the polychromatic device and in solar light. In the polychromatic device, PNA loss was 12% after 1 h and 63% after 5 h. In solar light, 56% of PNA had disappeared after 4 h of exposure between 10 am and 2 pm. It can be deduced that the average light intensity delivered by the tubes of the polychromatic device was of the same magnitude order as that of solar light within the wavelength range 300–400 nm (limit of PNA absorption).

Analytical procedures

Loss of fluometuron and formation of photoproducts were monitored by HPLC–UV using a Waters apparatus equipped with two pumps (model 510), an autosampler, a photodiode array detector (model 996), a detector W2487 and a C18 reverse-phase column (4.6 mm, 250 mm, Spherisorb S5 ODS2, 5 μm , Waters). Eluent was a mixture of water acidified with 0.1% of orthophosphoric acid and methanol (50%/50%) delivered at a constant flow of 1 mL.min^{-1} .

The HPLC–UV–MS analyses were performed using a Waters/Micromass LC/QTOF (Micromass, Manchester, UK). For the HPLC conditions, a Waters Alliance 2695 HPLC equipped with a photodiode array detector (DAD) was used. A reversed-phase column (C18 Hypersil ODS, 5 μm , 100 mm, 2.1 mm; Interchim, Montluc, on, France) was used at a flow rate of 0.3 mL.min^{-1} . The mobile phase was composed of acetonitrile (solvent A) and acidified water (formic acid, 0.4% v/v; pH 2.6) (solvent B). Gradient: 0–5 min, 5% A; 5–30 min, 5–95% A (linear); 30–34 min, 95% A; 34–35 min, 95–5% A; 35–40 min, 5% B equilibrium period). The injection volume was 30 μl . The LC–ESI–MS worked both in positive and negative mode.

UV spectra were recorded on a Cary 3 (Varian) spectrophotometer. A 1-cm path quartz cell was used for all the experiments. The reference beam blank was always Milli-Q water.

Results

Kinetics of phototransformation in solar light

We first compared the profiles of FM loss in various conditions (Fig. 2). In the absence of fulvic acids (FA) and nitrate ions, the consumption of FM ($1 \mu\text{M}$) in solar light was very slow: less than 30% had disappeared after 6.7 d. The addition of fulvic acids (10 mg.L^{-1}) significantly increased the rate of FM consumption: about 50% of FM had disappeared after 6.7 d. A larger enhancement of the reaction rate was observed in the presence of nitrate ions (25 mg.L^{-1}): a complete FM loss was obtained after 3.3 d. In the presence of both fulvic acids (10 mg.L^{-1}) and nitrate ions (25 mg.L^{-1}), FM disappeared more slowly than in the presence of nitrates alone. To determine rate constants, we plotted $\ln C_0/C$ vs irradiation time, where

C_0 is the initial FM concentration and C the concentration at t . In all cases, FM consumption followed pseudo first order kinetics. The rate coefficients, k , and R^2 values are reported in *Table 1*.

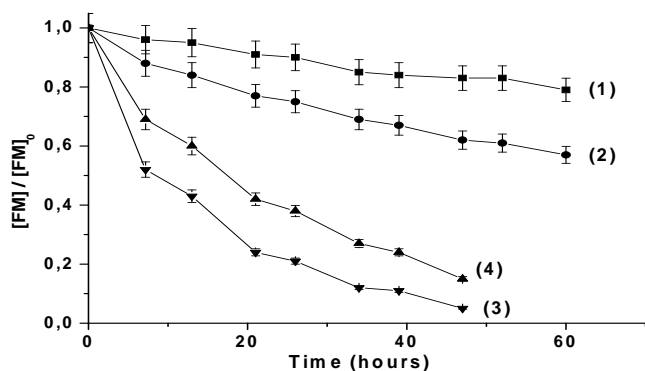


Fig. 2. Kinetics of FM (10^{-6} M) phototransformation in solar light in various aqueous media. (1): in pH 6.5 Milli-Q purified water; (2): in water containing FA (10 mg.L^{-1}); (3): in water containing FA (10 mg.L^{-1}) and nitrates (3.10^{-4} M); (4): in water containing nitrates (3.10^{-4} M).

Table 1: Phototransformation of FM (10^{-6} M) in solar light

Medium	k (s^{-1})	R^2	$t_{1/2}$ (days)
1	6.4×10^{-7}	0.974	12.5
2	1.6×10^{-6}	0.964	5.0
3	9.8×10^{-6}	0.948	0.82
4	6.2×10^{-6}	0.959	1.3

These kinetic results bring insight into the photodegradability of FM in solar light. FM is hardly transformed in pure water due to the poor absorption of solar radiations. Using the rate coefficient given in *Table 1*, one computes a half-life of 175 h. The chromophoric constituents of water (nitrate and fulvic acids) promoted FM phototransformation. The effect of fulvic acids was quite moderate. In the presence of fulvic acids (10 mg.L^{-1}), the rate coefficient was increased by a factor of 2.5 and the half-life reduced by the same factor. Nitrate ions (25 mg.L^{-1}) had a more pronounced influence increasing the rate coefficient and reducing the half-life by a factor of 15. In the presence of fulvic acids and nitrate ions, the rate of FM photodegradation was smaller by about 40% than in the presence of nitrate ions alone. At the considered concentrations, the absorbance of nitrates is very small (around 0.002) while that of FA bigger (around 0.22) (*see Fig. 1*). The inhibiting effect of FA on nitrate photolysis through screen effect is difficult to evaluate due to the cylindrical shape of reactors. Based on a mean path-length of 0.7 cm, one would compute a rate reduction between 15% and 20%. It represents 50% of the measured inhibition. The remaining 50% of inhibition are likely to be due to the scavenging of hydroxyl radicals by FA (Brezonik and al., 1998; ter Halle and al. 2006). In an attempt to delineate the role of hydroxyl radicals in the fulvic acids mediated phototransformation of FM, we studied the influence of 2-propanol added as a hydroxyl radical scavenger on the reaction ($k = 1.9.10^{10} \text{ M}^{-1} \text{ s}^{-1}$, Buxton and al., 1988). These experiments were undertaken in laboratory conditions. In the absence of fulvic acids, the initial rate of FM phototransformation was equal to $2.10^{-8} \text{ M.h}^{-1}$. In the presence of fulvic acids (5 mg.L^{-1}), it raised to $5.2. 10^{-8} \text{ M.h}^{-1}$. The addition of 2-propanol (0.015 M) reduced the latter rate by a factor comprised between 1.5 and 2, suggesting the involvement of hydroxyl radicals in the phototransformation reaction and showing the ability of FA to produce them under irradiation. We also studied the influence of oxygen on the reaction (*see Fig.3*).

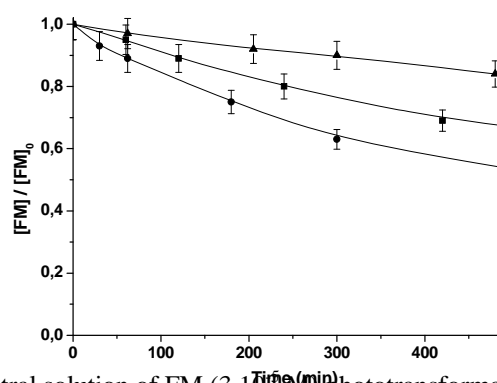


Fig. 3. Kinetics a neutral solution of FM (3.10^{-6} M) phototransformation containing fulvic acids (25 mg.L^{-1}) at 365 nm in various aqueous medias: air-saturated medium (■); oxygen-free medium (●); oxygen-saturated medium (▲)

After 5 h of irradiation, FM consumption was twice faster in air-saturated than in oxygen-saturated medium and 3-fold faster in nitrogen-saturated medium than in air-saturated medium. Thus, oxygen clearly inhibited the reaction.

Photoproducts identification

To achieve photoproducts characterization, we irradiated more highly concentrated FM solutions under laboratory conditions. The photolysis of FM (3.10^{-5} M) in Milli-Q water yielded the acidic compound resulting from the hydrolysis of CF_3 into CO_2H as previously reported (Lam and al., 2005). Its UV absorption spectrum differs from that of FM: the far UV absorption band ($k_{max} = 224$ nm) shows a shoulder and the second maximum of absorption is located at 297 nm instead of 275 nm in the case of FM.

The irradiation of FM (3.10^{-5} M) in the presence of fulvic acids (25 mg.L^{-1}) yielded two HPLC–UV detectable photoproducts, **I** and **II** (Fig. 4a).

The UV spectrum of **I** exhibited the same shoulder as that of the acidic product and a second maximum red-shifted by 27 nm ($\lambda_{max} = 297$ nm). The UV spectrum of **II** resembled that of FM but the second maximum was red-shifted by 20 nm compared to it ($k_{max} = 295$ nm).

The HPLC–mass analysis of **I** gave a first molecular ion at $m/z = 223$ in ES^- mode and at $m/z = 225$ in ES^+ mode corresponding to the loss of 9 amu that may be explained by the hydrolysis of CF_3 into CO_2H and the addition of an oxygen atom. Fragments at $m/z = 179$ [M-44] and at $m/z = 134$ [M-89] were obtained in ES^- mode. These data are compatible with the structure proposed in Table 2. The first fragment would correspond to the loss of the carboxylic group and the second to the cleavage of the terminal amine group $-N(CH_3)_2$ followed by loss of an H atom to yield an isocyanate. Photoproduct **II** gave molecular ions at $m/z = 247$ and 249 in ES^- and ES^+ modes, respectively, corresponding to the addition of an oxygen atom to FM. A fragment at $m/z = 202$ corresponding to M-45 was observed in ES^- mode. The loss of 45 amu is likely to result from the departure of $N(CH_3)_2$ by cleavage of the terminal urea C–N bond and the elimination of H to form the isocyanate. It is compatible with structure given in Table 2.

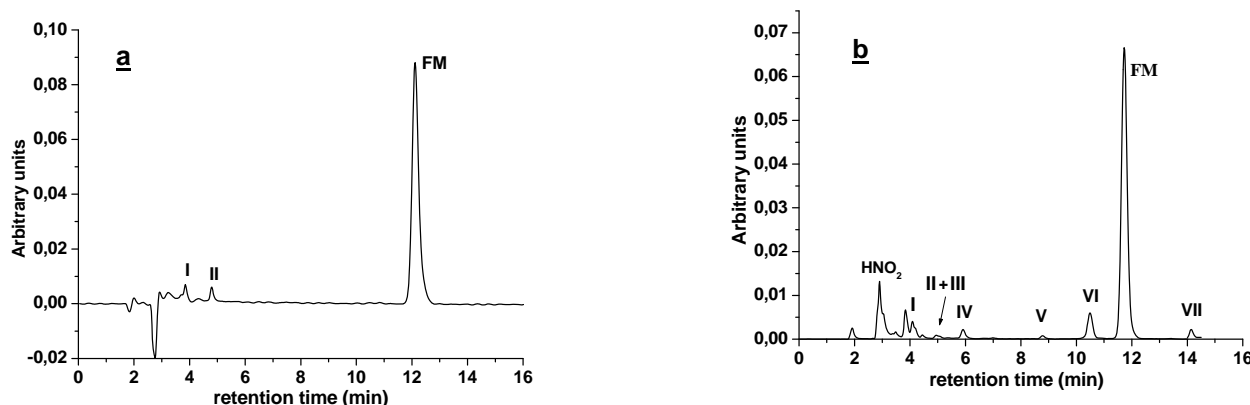


Fig. 4. HPLC chromatogram of (a) a neutral solution of FM (3.10^{-5} M) containing fulvic acids (mg.L^{-1}) at a conversion extent of 20% and (b) a neutral solution of FM (3.10^{-5}) containing nitrate ions (25 mg.L^{-1}) at a conversion extent of 46%. Both solutions were irradiated in simulated solar light. Photoproducts are numbered as indicated in Table 2.

The irradiation of FM (3.10^{-5} M) in the presence of nitrate ions (25 mg.L^{-1}) yielded seven photoproducts detectable by HPLC–UV (see Fig. 4b). Based on HPLC retention times, UV absorption spectra and mass data, we could conclude that photoproducts **I** and **II** were present among the seven photoproducts. Two other compounds **III** and **IV** with a molecular ion at $m/z = 223$ in ES^- mode were also detected. As they showed distinct retention times and UV maxima, but similar fragmentation at $m/z = 179$ and 134 with different percentages of fragments, they are likely to be isomers of **I**. Photoproducts **I**, **III** and **IV** should differ from each other in the position of the hydroxyl group on the ring. The photoproducts **V** and **VI** that were eluted just before FM showed similar absorption spectra. One of them, **V**, gave a molecular ion at $m/z = 203$ in ES^- mode corresponding to the loss of 28 amu and a fragment at $m/z = 160$. The other one, **VI**, gave a molecular ion at $m/z = 217$ in ES^- mode and the same fragment at $m/z = 160$. These compounds could be assigned to demethylated products; **VI** would be the monodemethylated derivative and **V** the didemethylated derivative (see Table 2).

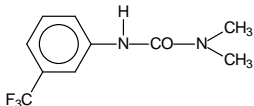
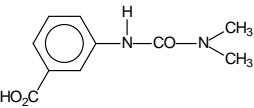
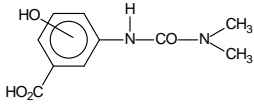
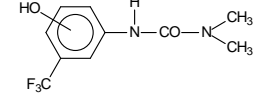
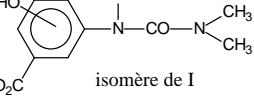
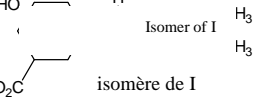
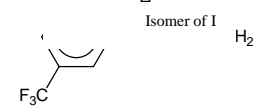
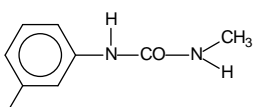
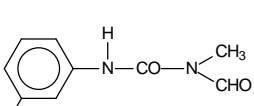
A molecular ion at $m/z = 245$ in ES^- mode was also detected at a retention time longer than that of FM. This mass corresponds to the addition of 14 amu. Three fragments were observed at $m/z = 217$ [M-28], 188 [M-28-29] and 160 [M-28-29-28]. This fragmentation indicates that the aromatic ring was not altered. It is in favour of photoproduct **VII** that bears a carbonyl group and for which successive losses of CO, NCH_3 and CO are again possible.

Finally, we used the selected peak method to detect some specific photoproducts formation of which was expected. In the case of nitrate ions, we could find nitro derivatives at $m/z = 276$ in ES^- mode corresponding to the addition of 45 amu ($+NO_2-H$). In the case of fulvic acids, careful examination of chromatograms revealed the presence of peaks at $m/z = 217$ and 245 in ES^- mode and $m/z = 219$ in ES^+ mode, showing that fulvic acids photosensitized transformation also yielded FM demethylation, but this pathway was very minor.

Conclusion

Direct photolysis of aqueous FM is slow but photosensitizing processes may promote its transformation in surface waters. In the presence of hydroxyl radicals, both the lateral chain and the ring of FM are oxidized. Photoreactants deriving from fulvic acids privilege oxidation of the aromatic ring. Photoproducts of hydrolysis or hydroxylation of the aromatic ring absorb solar light better than FM itself. They are thus susceptible to undergo photolysis faster than FM. Photoproducts resulting from oxidation of lateral urea chain are more photostable. It would be now necessary to test the toxicity of each individual compound or that of the irradiated mixtures toward reference organisms in order to access the risk that may pose FM.

Table 2: Structure of detected photoproducts, molecular weigh, maxima of absorption, molecular ions and main fragments detected by LC-ESI-MS

Formula	Number	Molecular weigh	Condition Of obtention	λ_{\max} (nm)	m/z main fragments
	FM	232		242/275	ESI ⁺ : 231
	acid	208	Pure water	224/297	ESI ⁺ : 207
	I	224	FA or nitrates	222/324	ESI ⁺ : 223 (179, 134) ESI ⁺ : 225
	II	248	FA or nitrates	242/295	ESI ⁺ : 247 (202) ESI ⁺ : 249
	III	224	Nitrates	230/311	ESI ⁺ : 223 (179, 134)
	IV	224	Nitrates	224/315	ESI ⁺ : 223 (179, 134)
	V	204	Nitrates	241/280	ESI ⁺ : 203 (160)
	VI	218	Nitrates or FA (minor)	243/279	ESI ⁺ : 217 (160)
	VII	246	Nitrates or AF (minor)	245 and shoulder at 280	ESI ⁺ : 245 (217, 188, 160)

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