



## Photolysis of fluometuron in the presence of natural water constituents

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1                    Photolysis of fluometuron in the presence of natural water constituents

2

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16

17 **Abstract.** Phototransformation of the herbicide fluometuron (1  $\mu\text{M}$ ) in natural sunlight was  
18 investigated in neutral Milli-Q water and in synthetic waters containing either fulvic acids,  
19 nitrate ions or both in order to mimic reactions taking place in aquatic environments.  
20 Fluometuron degradation followed a pseudo-first order kinetics. The reaction was faster in  
21 synthetic than in Milli-Q water. Fulvic acids (10  $\text{mg L}^{-1}$ ) increased the rate of fluometuron  
22 photolysis by a factor 2.5 and nitrates (25  $\text{mg L}^{-1}$ ) by a factor 15. Identification of major  
23 photoproducts was conducted under laboratory conditions using LC-ESI-MS. Numerous  
24 photoproducts were detected and tentatively characterized. In the presence of nitrates,  
25 hydroxylation of the aromatic ring with or without hydrolysis of  $\text{CF}_3$  into  $\text{CO}_2\text{H}$  and oxidation  
26 of the urea chain leading to demethylation were observed. In the presence of fulvic acids,  
27 hydroxylation of the aromatic ring was the major reaction route.

28

29 Key-words: phenylurea herbicide, photosensitization, nitrate ions, fulvic acids, hydroxyl  
30 radicals

31

## 32 **Introduction.**

33 Photochemistry is one of the main route for organic pollutants attenuation in surface  
34 waters. This abiotic degradation pathway has received increasing interest in the last thirty  
35 years (Zepp and Cline, 1977; Kotzias and Korte, 1981; Durand et al, 1991; Lemaire et al,  
36 1991; Pirisi et al, 1996; Svenson and Hynning, 1997; Mansour et al, 1999). To predict the fate  
37 of pollutants in the natural environment and to assess the risk they may pose, it is necessary to  
38 improve our knowledge on their chemical reactions.

39 Several types of reactions may occur depending on the medium composition. Direct  
40 photolysis is possible if the considered pollutant absorbs solar light. In addition, photoinduced  
41 or photosensitized transformations mediated by components of the aquatic medium can also

42 take place. In particular, dissolved natural organic matter (DOM) which absorbs a large  
43 portion of photons is a potential photosensitizer. Singlet oxygen, superoxide ion/hydroperoxyl  
44 radicals, hydroxyl radicals, excited triplet states and alkylperoxyl radicals were proved or  
45 proposed to be generated in natural waters under the influence of sunlight (Zafiriou and True,  
46 1979; Zepp et al, 1981; Hoigné et al, 1989; Haag and Hoigné, 1986; Cooper et al, 1989;  
47 Vaughan and Blough, 1998; Canonica et al, 1995). However, a part of these species are  
48 trapped by DOM itself. Nitrate ions that are present in surface waters at level varying from  
49 0.2 to 25 mg L<sup>-1</sup> generate the highly oxidizing hydroxyl radicals under light excitation (Boule  
50 et al, 1999 for a review). Hydroxyl radicals that are unspecific oxidants are scavenged by a  
51 variety of aquatic components. The percentage of hydroxyl radicals trapped by pollutants is  
52 thus strongly dependent on the medium composition. Due to all these factors, studies can help  
53 to predict the fate of pollutants at the condition that they are undertaken under relevant  
54 experimental conditions.

55 In the present work, we focused on the phototransformation of the phenylurea  
56 herbicide fluometuron (FM). This compound is widely used for pre- and post-emergence  
57 control of weeds in fields of conventional cotton cultivars. It is persistent (Stoeckel et al,  
58 1997) and may pose some risks to aquatic organisms (Muschal and Warne, 2003). However,  
59 literature data are very scarce, especially concerning its photochemical reactivity. FM poorly  
60 absorbs solar light (see Figure 1) but indeed its direct photolysis in simulated solar light ( $\lambda >$   
61 290 nm) was reported (Lam et al, 2005). The CF<sub>3</sub> group undergoes photohydrolysis into  
62 CO<sub>2</sub>H. FM was also included in a recent study (Lam et al, 2003) in which the contribution of  
63 indirect processes in surface waters under sunlight simulated irradiation conditions was  
64 evaluated. Nitrate ions at a level of 8x10<sup>-4</sup> M significantly enhanced FM degradation while  
65 humic acids gave unclear results.

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

## 71 **Material and Methods**

72 **Chemicals.** FM (97.7 % purity) was purchased from Riedel de Haën (Saint Quentin Fallavier,  
73 France) and used as received. Elliott soil fulvic acids were purchased from International  
74 Humic Substances Society (IHSS). The salt used to add nitrate ions was  $\text{NaNO}_3$  (Fluka, 99  
75 %). All other reactants were of the highest grade available and used as received. Water was  
76 purified using a Milli-Q device (Millipore).

77  
78 **Preparation of solutions.** A stock solution of FM was prepared by dissolving 4 mg of  
79 substrate in 100 ml of Milli-Q purified water. Solubilization was achieved after a 4-day  
80 stirring. Stock solutions of fulvic acids and sodium nitrate were prepared in Milli-Q purified  
81 water. They were at a concentration of  $40 \text{ mg L}^{-1}$  and  $50 \text{ mg L}^{-1}$ , respectively. Stock solutions  
82 were then diluted in order to obtain the desired concentrations. Solutions were buffered in  
83 order to maintain constant the pH all along irradiations. A pH of 6.5 was chosen because  
84 natural aquatic medium is generally around neutrality. Phosphate buffers were used; their  
85 final concentration was equal to  $10^{-3} \text{ M}$ . Deoxygenation of solutions was achieved by nitrogen  
86 bubbling for 20 minutes prior to irradiation and during irradiations. Solutions were  
87 oxygenated by pure oxygen bubbling.

88  
89 **Photoreaction setup.** For kinetic purpose, FM ( $1 \mu\text{M}$ ) was irradiated (i) in MilliQ water, (ii)  
90 in water containing fulvic acids ( $10 \text{ mg L}^{-1}$ ) used as a surrogate of DOM, (iii) in water

91 containing nitrate ions ( $25 \text{ mg L}^{-1}$  or  $3 \times 10^{-4} \text{ M}$ ) and (iv) in water containing both fulvic acids  
92 ( $10 \text{ mg L}^{-1}$ ) and nitrate ions ( $3 \times 10^{-4} \text{ M}$ ). Irradiation experiments in natural sunlight were  
93 performed at Clermont-Ferrand ( $46^\circ \text{ N}$ ,  $3^\circ \text{ E}$ ) in June 2006. Cylindrical quartz glass reactors  
94 (14-mm internal diameter) were filled with 14 ml of solutions. A headspace was left above  
95 solutions. Reactors were closed by a septum, attached on a rack inclined by about  $15^\circ$  from  
96 horizontal and exposed to solar light. Samples received 13 h of sunshine per day. Aliquots of  
97 0.5 mL were removed simultaneously from all the solutions at selected intervals. At each  
98 sampling, solutions were re-saturated with air. Samples were immediately analyzed by HPLC.  
99 Irradiations started at 9 am on the first day. The first samplings were made at 5 pm. Then, the  
100 next samplings were made at 9 am and 5 pm each day. Solutions were left outside overnights.  
101 Dark control experiments showed no loss of FM by adsorption on glass surfaces and no  
102 transformation, during the time required for the irradiations, irrespective of the aqueous media  
103 (variations less than 3 %).

104 Irradiations under laboratory conditions were also carried out for photoproducts  
105 identification. Irradiations were performed in a device equipped with six TLAD 15W/05  
106 fluorescent tubes emitting within the wavelength range 300-450 nm with a maximum of  
107 emission at 365 nm and in a Pyrex glass reactor (14 mm i.d). The device was cylindrical and  
108 equipped with reflecting inner walls. A ventilator was used as a cooling system. The reactor  
109 was placed in the centre of the device and was surrounded by the six fluorescent tubes. Light  
110 intensity was measured using *p*-nitroanisole/pyridine as a chemical actinometer (Dulin and  
111 Mill, 1982). PNA ( $10^{-5} \text{ M}$ ) and pyridine ( $10^{-4} \text{ M}$ ) were irradiated in the same conditions as  
112 samples in the polychromatic device and in solar light. In the polychromatic device, PNA loss  
113 was 12 % after 1 hour and 63 % after 5 h. In solar light, 56 % of PNA had disappeared after 4  
114 h of exposure between 10 am and 2 pm. It can be deduced that the average light intensity

115 delivered by the tubes of the polychromatic device was of the same magnitude order as that of  
116 solar light within the wavelength range 300-400 nm.

117

118 **Analytical procedures.** Loss of fluometuron and formation of photoproducts were monitored  
119 by HPLC-UV using a Waters apparatus equipped with two pumps (model 510), an  
120 autosampler, a photodiode array detector (model 996), a detector W2487 and a C<sub>18</sub> reverse-  
121 phase column (4.6 mm x 250 mm, Spherisorb S5 ODS2, 5  $\mu\text{m}$ , Waters). Eluent was a mixture  
122 of water acidified with 0.1% of orthophosphoric acid and methanol (50 %/50 %) delivered at  
123 a constant flow of 1 mL min<sup>-1</sup>. For the HPLC mass spectrometry analyses, samples containing  
124 fulvic acids were prepared as follows. Portions of 0.6 ml of irradiated solutions were passed  
125 over an Oasis BHL column conditioned beforehand with 1 ml of methanol and 1 ml of water  
126 acidified with formic acid 0.1 %. Fulvic macromolecules were recovered by passing 1 ml of  
127 acidified water through the column while fluometuron and its photoproducts by passing 1 ml  
128 of methanol. The HPLC-UV-MS analyses were performed using a Waters/Micromass  
129 LC/QTOF (Micromass, Manchester,UK). For the HPLC conditions, a Waters Alliance 2695  
130 HPLC equipped with a photodiode array detector (DAD) was used. A reversed-phase column  
131 (C18 Hypersil ODS, 5  $\mu\text{m}$ , 100 mm x 2.1 mm; Interchim, Montluçon, France) was used at a  
132 flow rate of 0.3 mL min<sup>-1</sup>. The mobile phase was composed of acetonitrile (solvent A) and  
133 acidified water (formic acid, 0.4% v/v; pH 2.6) (solvent B). Gradient: 0-5 min, 5% A; 5-30  
134 min, 5-95% A (linear); 30-34 min, 95% A; 34-35 min, 95-5% A; 35-40 min, 5% B  
135 (equilibrium period). The injection volume was 30  $\mu\text{L}$ . The LC-ESI-MS worked both in  
136 positive and negative mode. The optimum voltages for the probe and ion source components  
137 (to produce maximum intensity) were 3 kV for the stainless-steel capillary, 35 V for the  
138 sample cone, and 2 V for the extractor cone. In the negative mode, voltages were switched,  
139 except the capillary voltage which was -2.1 kV for better sensitivity. UV spectra were

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

142

## 143 **Results and Discussion**

### 144 **1. Kinetics of phototransformation in solar light**

145 We first compared the profiles of FM loss in various conditions. In the absence of  
146 fulvic acids (FA) and nitrate ions, the consumption of FM (1  $\mu\text{M}$ ) in solar light was very  
147 slow: less than 30 % had disappeared after 6.7 d. The addition of fulvic acids (10  $\text{mg L}^{-1}$ )  
148 significantly increased the rate of FM consumption: about 50 % of FM had disappeared after  
149 6.7 d. A larger enhancement of the reaction rate was observed in the presence of nitrate ions  
150 (25  $\text{mg L}^{-1}$ ): a complete FM loss was obtained after 3.3 d. In the presence of both fulvic acids  
151 (10  $\text{mg L}^{-1}$ ) and nitrate ions (25  $\text{mg L}^{-1}$ ), FM disappeared more slowly than in the presence of  
152 nitrates alone. To determine rate constants, we plotted  $\ln(c_0/c)$  vs irradiation time, where  $c_0$  is  
153 the initial FM concentration and  $c$  the concentration at  $t$ , taking into account that samples  
154 were irradiated for 8 h between 9 am and 5 pm and for 5 h between 5 pm and 9 am (Figure 2).  
155 In all cases, FM consumption followed pseudo-first order kinetics. The rate coefficients,  $k$ ,  
156 and  $R^2$  values are reported in Table 1.

157 These kinetic results bring insight into the photodegradability of FM in solar light. FM  
158 is hardly transformed in pure water due to the poor absorption of solar radiations. Using the  
159 rate coefficient given in Table 1 one computes a half-life of 175 h. This value is 2.6-fold  
160 higher than that of Lam et al. (2003). It shows that in the case of FM a one-day irradiation in  
161 June in our place is comparable to about 5 h of irradiation in the photosimulator used by these  
162 authors.

163 The chromophoric constituents of water (nitrate and fulvic acids) promoted FM  
164 phototransformation. The effect of fulvic acids was quite moderate. In the presence of fulvic



165 acids ( $10 \text{ mg L}^{-1}$ ), the rate coefficient was increased by a factor of 2.5 and the half-live  
166 reduced by the same factor. Nitrate ions ( $25 \text{ mg L}^{-1}$ ) had a more pronounced influence  
167 increasing the rate coefficient and reducing the half-live by a factor of 15. In the presence of  
168 fulvic acids and nitrate ions, the rate of FM photodegradation was smaller by about 40 % than  
169 in the presence of nitrate ions alone. At the considered concentrations, the absorbance of  
170 nitrates is very small (around 0.002) while that of FA bigger (around 0.22) for a 1-cm path-  
171 length (see Figure 1). The inhibiting effect of FA on nitrate photolysis through screen effect is  
172 difficult to evaluate due to the cylindrical shape of reactors. Based on a mean path-length of  
173 0.7 cm, one would compute a rate reduction between 15 and 20 %. It represents 50 % of the  
174 measured inhibition. The remaining 50 % of inhibition are likely to be due to the scavenging  
175 of hydroxyl radicals by FA (Brezonik and Fulkerson-Brekken, 1998; Schindelin and Frimmel,  
176 2000, ter Halle and Richard, 2006).

177 In an attempt to delineate the role of hydroxyl radicals in the fulvic acids mediated  
178 phototransformation of FM, we studied the influence of 2-propanol added as a hydroxyl  
179 radical scavenger on the reaction ( $k = 1.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , Buxton et al, 1988). These  
180 experiments were undertaken in laboratory conditions. In the absence of fulvic acids, the  
181 initial rate of FM phototransformation was equal to  $2 \times 10^{-8} \text{ M h}^{-1}$ . In the presence of fulvic  
182 acids ( $5 \text{ mg L}^{-1}$ ), it raised to  $5.2 \times 10^{-8} \text{ M h}^{-1}$ . The addition of 2-propanol (0.015 M) reduced the  
183 latter rate by a factor comprised between 1.5 and 2, suggesting the involvement of hydroxyl  
184 radicals in the phototransformation reaction and showing the ability of FA to produce them  
185 under irradiation. We also studied the influence of oxygen on the reaction. After 5 h of  
186 irradiation, FM consumption was twice faster in air-saturated than in oxygen-saturated  
187 medium and 3-fold faster in nitrogen-saturated medium than in air-saturated medium. Thus,  
188 oxygen clearly inhibited the reaction.

189

## 190 2. Photoproducts identification

191 To achieve photoproducts characterization, we irradiated more highly concentrated  
192 FM solutions under laboratory conditions. The photolysis of FM ( $3 \times 10^{-5}$  M) in Milli-Q water  
193 yielded the acidic compound resulting from the hydrolysis of  $\text{CF}_3$  into  $\text{CO}_2\text{H}$  as previously  
194 reported (Lam et al, 2005). Its UV absorption spectrum differs from that of FM: the far UV  
195 absorption band ( $\lambda_{\text{max}} = 224$  nm) shows a shoulder and the second maximum of absorption is  
196 located at 297 nm instead of 275 nm in the case of FM.

197 The irradiation of FM ( $3 \times 10^{-5}$  M) in the presence of fulvic acids ( $25 \text{ mg l}^{-1}$ ) yielded  
198 two HPLC-UV detectable photoproducts, I and II (Figure 3A). The UV spectrum of I  
199 exhibited the same shoulder as that of the acidic product and a second maximum red-shifted  
200 by 27 nm ( $\lambda_{\text{max}} = 297$  nm). The UV spectrum of II resembled that of FM but the second  
201 maximum was red-shifted by 20 nm compared to it ( $\lambda_{\text{max}} = 295$  nm). The HPLC-mass analysis  
202 of I gave a first molecular ion at  $m/z = 223$  in  $\text{ES}^-$  mode and at  $m/z = 225$  in  $\text{ES}^+$  mode  
203 corresponding to the loss of 9 amu that may be explained by the hydrolysis of  $\text{CF}_3$  into  $\text{CO}_2\text{H}$   
204 and the addition of an oxygen atom. Fragments at  $m/z = 179$  [M-44] and at  $m/z = 134$  [M-89]  
205 were obtained in  $\text{ES}^-$  mode. These data are compatible with the structure proposed in Table 2.  
206 The first fragment would correspond to the loss of the carboxylic group and the second to the  
207 cleavage of the terminal amine group  $-\text{N}(\text{CH}_3)_2$  followed by loss of an H atom to yield an  
208 isocyanate as shown in Scheme 1.

209 Photoproduct II gave molecular ions at  $m/z = 247$  and 249 in  $\text{ES}^-$  and  $\text{ES}^+$  modes,  
210 respectively, corresponding to the addition of an oxygen atom to FM. A fragment at  $m/z =$   
211 202 corresponding to M-45 was observed in  $\text{ES}^-$  mode. The loss of 45 amu is likely to result  
212 from the departure of  $\text{N}(\text{CH}_3)_2$  by cleavage of the terminal urea C-N bond and the elimination  
213 of H to form the isocyanate. It is compatible with structure given in Table 2.

214 The irradiation of FM ( $3 \times 10^{-5}$  M) in the presence of nitrate ions ( $25 \text{ mg l}^{-1}$ ) yielded  
215 seven photoproducts detectable by HPLC-UV (see Figure 3 B). Based on HPLC retention  
216 times, UV absorption spectra and mass data, we could conclude that photoproducts I and II  
217 were present among the seven photoproducts. Two other compounds III and IV with a  
218 molecular ion at  $m/z = 223$  in  $\text{ES}^-$  mode were also detected. As they showed distinct retention  
219 times and UV maxima, but similar fragmentation at  $m/z = 179$  and  $134$  with different  
220 percentages of fragments, they are likely to be isomers of I. Photoproducts I, III and IV  
221 should differ from each other in the position of the hydroxyl group on the ring. The  
222 photoproducts V and VI that were eluted just before FM showed similar absorption spectra.  
223 One of them, V, gave a molecular ion at  $m/z = 203$  in  $\text{ES}^-$  mode corresponding to the loss of  
224 28 amu and a fragment at  $m/z = 160$ . The other one, VI, gave a molecular ion at  $m/z = 217$  in  
225  $\text{ES}^-$  mode and the same fragment at  $m/z = 160$  (see Scheme 2). These compounds could be  
226 assigned to demethylated products; VI would be the monodemethylated derivative and V the  
227 didemethylated derivative (see Table 2).

228 A molecular ion at  $m/z = 245$  in  $\text{ES}^-$  mode was also detected at a retention time longer  
229 than that of FM. This mass corresponds to the addition of 14 amu. Three fragments were  
230 observed at  $m/z = 217$  [M-28], 188 [M-28-29] and 160 [M-28-29-28]. This fragmentation  
231 indicates that the aromatic ring was not altered. It is in favour of photoproduct VII that bears a  
232 carbonyl group and for which successive losses of CO,  $\text{NCH}_3$  and CO are again possible.

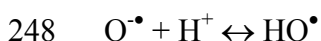
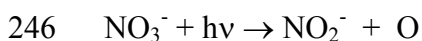
233 Finally, we used the selected peak method to detect some specific photoproducts  
234 formation of which was expected. In the case of nitrate ions, we could find nitro derivatives at  
235  $m/z = 276$  in  $\text{ES}^-$  mode corresponding to the addition of 45 amu ( $+\text{NO}_2\text{-H}$ ). In the case of  
236 fulvic acids, careful examination of chromatograms revealed the presence of peaks at  $m/z =$   
237 217 and 245 in  $\text{ES}^-$  mode and  $m/z = 219$  in  $\text{ES}^+$  mode, showing that fulvic acids

238 photosensitized transformation also yielded FM demethylation, but this pathway was very  
239 minor.

240

### 241 3. Mechanisms of reactions

242 FA and nitrates both accelerated the phototransformation of FM through different  
243 reaction mechanisms. Nitrate absorbs solar radiation in the actinic spectrum ( $\epsilon_{304} = 7.4 \text{ M}^{-1}$   
244  $\text{cm}^{-1}$ ) and produces photoreactants through the two following primary processes (Boule et al.,  
245 1999):



249 The formation of hydroxyl radicals is 9-fold more efficient than that of atomic oxygen.  
250 As hydroxyl radicals are also much stronger oxidants than atomic oxygen, they are generally  
251 considered to be the main species involved in the nitrate-photoinduced transformations of  
252 organic compounds, even though nitration reactions were also reported to occur (Machado  
253 and Boule, 1994; Vione et al., 2001). Hydroxylation of the aromatic ring and  
254 oxidation/elimination of the methyl groups of the urea aliphatic chain confirm that FM was  
255 oxidized by hydroxyl radicals (Scheme 3).

256 The aromatic ring of FM is a site of attack for hydroxyl radicals. The OH-adduct  
257 radical is expected to yield the ring hydroxylated compound (photoproduct II). Photoproducts  
258 I, III and IV are also ring hydroxylated products, but, contrary to II, they bear the  $\text{CO}_2\text{H}$   
259 substituent instead of the  $\text{CF}_3$  substituent initially present in FM. The formation of these  
260 products requires two steps. Either they are produced by photohydroxylation of the acid, or  
261 they result from the direct photolysis of photoproduct II. Photoproduct II which shows a  
262 maximum of absorption at 295 nm instead of 275 nm for FM absorbs solar light better than

263 FM, and thus could undergo faster photolysis. In both cases, several isomers corresponding to  
264 the possible sites of attack for hydroxyl radicals are expected. As three hydroxylated acids  
265 were detected, three hydroxylated derivatives of FM should be produced too. We only  
266 detected one peak at the mass  $m/z = 247$  in  $ES^-$ . Either, the three isomers show the same  
267 retention time and are eluted altogether, or we have failed to detect two of them.

268 The second site of attack of hydroxyl radicals is the urea aliphatic chain. Three  
269 photoproducts were detected: the carbonyl derivative VII, the monodemethylated product VI  
270 and the didemethylated product V. The first step should be the abstraction of a H atom from  
271  $CH_3$  to form the  $CH_2^\bullet$  radical that can add oxygen and finally give V, VI and VII. On the  
272 HPLC chromatograms and by total ion count (TIC), the area of products V, VI and VII were  
273 higher than those of products I-IV. It seems therefore that the attack of the urea terminal chain  
274 is the main reaction pathway. However, without titration of photoproduct to measure chemical  
275 yields, this argument must be taken with caution because ring hydroxylation and hydrolysis of  
276  $CF_3$  significantly shift maxima of absorption to longer wavelengths and photoproducts I-IV  
277 might not accumulate due to photoreactivity. In the chromatograms of solar-light irradiated  
278 solutions of micromolar FM, only photoproducts VI and VII were detectable.

279 Fulvic acids are known to produce several photoreactants under light excitation  
280 (oxidant excited states, singlet oxygen, radicals). The quite small photosensitizing effect of  
281 fulvic acids on FM shows that FM is not easily oxidized by these species. A part of the  
282 reaction can be attributed to hydroxyl radicals as confirmed by the detection of product VI as  
283 a minor by-product and the inhibiting effect of 2-propanol on the reaction. The two main  
284 photoproducts were I and II. Contrary to what was observed in the nitrate-mediated  
285 phototransformation, only one hydroxylated acid derivative was produced in the presence of  
286 fulvic acids. This result suggests that the FA mediated ring hydroxylation does not involve  
287 hydroxyl radicals. As an alternative, the hydroxylation reaction could involve the triplet

288 excited state of FA ( $^3\text{FA}^*$ ).  $^3\text{FA}^*$  reacts with FM either through energy transfer or through  
289 electron transfer. We found that the rate of FM phototransformation is accelerated upon  
290 deoxygenation of the medium by nitrogen bubbling as in the case of monuron (Richard et al,  
291 1997). This result confirms the involvement of  $^3\text{FA}^*$  in FM photodegradation but does not  
292 clear up the mechanism. In the case where an energy transfer reaction would occur,  $^3\text{FM}^*$   
293 would be produced. Oxidation photoproducts are formed. It implies that  $^3\text{FM}^*$  is oxidized. As  
294 direct photolysis of FM leads to acidification of  $\text{CF}_3$  substituent, one would conclude that  
295 singlet and triplet excited states of FM react differently. As an alternative, electron transfer  
296 from FM to  $^3\text{FA}^*$  could occur. It is the hypothesis proposed by Gerecke et al (2001). This  
297 hypothesis was also adopted in the case of fenuron, an analog of FM, because the FA  
298 mediated phototransformation of fenuron was found to be inhibited by removal of oxygen  
299 (Richard et al, 1997). Thus, the mechanism of reaction of FM is not clear. Further addition of  
300 dioxygen on the ring should finally produce the hydroxylated products, either photoproduct II  
301 in the case where the oxidation step involves FM or photoproduct I if it involves the acid, the  
302 photoproduct of direct photolysis. As proposed above, II might also produce I by photolysis.

303

## 304 **Conclusion**

305 In conclusion, direct photolysis of aqueous FM is slow but photosensitizing processes  
306 may promote its transformation in surface waters. In the presence of hydroxyl radicals, both  
307 the lateral chain and the ring of FM are oxidized. Photoreactants deriving from fulvic acids  
308 privilege oxidation of the aromatic ring. Photoproducts of hydrolysis or hydroxylation of the  
309 aromatic ring absorb solar light better than FM itself. They are thus susceptible to undergo  
310 photolysis faster than FM. Photoproducts resulting from oxidation of lateral urea chain are  
311 more photostable. It would be now necessary to test the toxicity of each individual compound

312 or that of the irradiated mixtures toward reference organisms in order to access the risk that  
313 may pose FM.

314

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316

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**Captions for figures**

420

421 Figure 1 : Absorption spectrum of (----) FM at  $3 \times 10^{-4}$  M, (—) FA at  $10 \text{ mg L}^{-1}$ , (····) nitrates at  
422  $0.01 \text{ M}$  and solar light emission reaching the earth surface in summer from Zepp and Cline,  
423 1977.

424

425 Figure 2 : Kinetics of FM ( $10^{-6}$  M) phototransformation in solar light in various aqueous  
426 media. Plot of  $\ln c_0/c$  vs the irradiation time, where  $c$  and  $c_0$  were the concentrations at  $t$  and  
427  $t=0$ , respectively.

428 ■ : in pH 6.5 MilliQ purified water

429 ● : in water containing FA ( $10 \text{ mg L}^{-1}$ )

430 ▲ : in water containing FA ( $10 \text{ mg L}^{-1}$ ) and nitrates ( $3 \cdot 10^{-4}$  M)

431 ▽ : in water containing nitrates ( $3 \cdot 10^{-4}$  M)

432

433 Figure 3 : HPLC chromatogram of (A) a neutral solution of FM ( $3 \times 10^{-5}$  M) containing fulvic  
434 acids ( $25 \text{ mg L}^{-1}$ ) at a conversion extent of 20 % and (B) a neutral solution of FM ( $3 \times 10^{-5}$  M)  
435 containing nitrate ions ( $25 \text{ mg L}^{-1}$ ) at a conversion extent of 46 %. Both solutions were  
436 irradiated in simulated solar light. Photoproducts are numbered as indicated in Table 2.

437

438

439 Table 1 : Phototransformation of FM ( $10^{-6}$  M) in solar light. Rate coefficients deduced from  
 440 logarithmic decay, correlation values and half-lives considering that samples were irradiated  
 441 for 13 h per day.

442

Conditions	k (s <sup>-1</sup> )	R <sup>2</sup>	t <sub>1/2</sub> (h)
FM in MilliQ water, buffered at pH 6.5	$1.1 \times 10^{-6}$	0.972	175
FM in presence of FA (10 mg L <sup>-1</sup> )	$2.7 \times 10^{-6}$	0.983	71
FM in presence of nitrate ions (25 mg L <sup>-1</sup> )	$1.7 \times 10^{-5}$	0.991	11
FM in presence of FA (10 mg L <sup>-1</sup> ) and nitrate ions (25 mg L <sup>-1</sup> )	$1.1 \times 10^{-5}$	0.986	18

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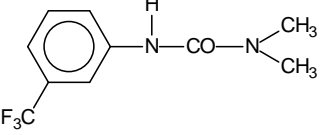
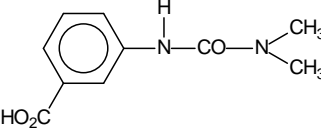
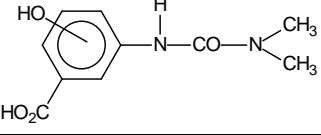
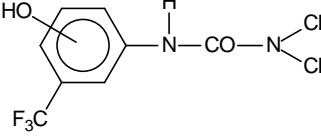
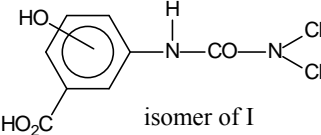
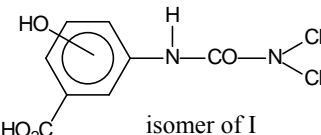
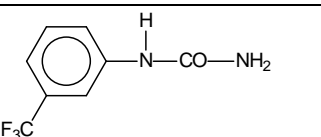
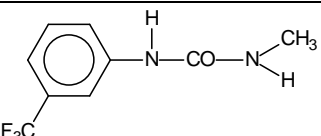
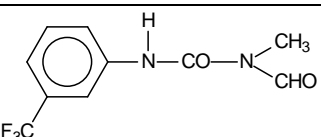
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451 Table 2 : Proposed structure of detected photoproducts, retention time in HPLC-UV,  
 452 maxima of absorption, molecular ions and main fragments detected by **LC-ESI-MS**.

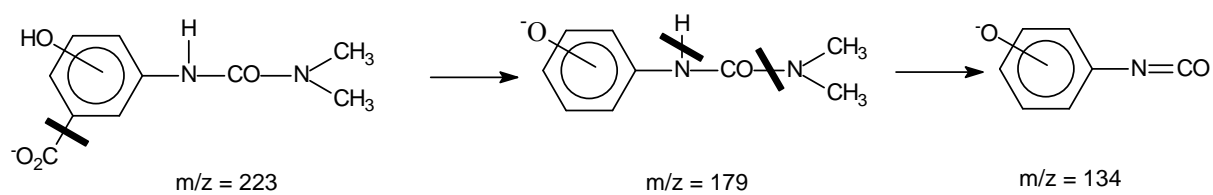
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formula	number	Molecular weight	Condition of obtention	$\lambda_{\max}$ (nm)	m/z and main fragments (%)
	FM	232		242/275	ES <sup>-</sup> : 231
	acid	208	Pure water	224/297	ES <sup>-</sup> : 207
	I	224	FA or nitrates	222/324	ES <sup>-</sup> : 223 (179, 134) ES <sup>+</sup> : 225
	II	248	FA or nitrates	242/295	ES <sup>-</sup> : 247 (202) ES <sup>+</sup> : 249
	III	224	Nitrates	230/311	ES <sup>-</sup> : 223 (179, 134)
	IV	224	Nitrates	224/315	ES <sup>-</sup> : 223 (179, 134)
	V	204	Nitrates	241/280	ES <sup>-</sup> : 203 (160)
	VI	218	Nitrates or FA (minor)	243/279	ES <sup>-</sup> : 217 (160)
	VII	246	Nitrates	245 and shoulder at 280	ES <sup>-</sup> : 245 (217, 188, 160)

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458 Scheme 1: Fragmentation of photoproduct I

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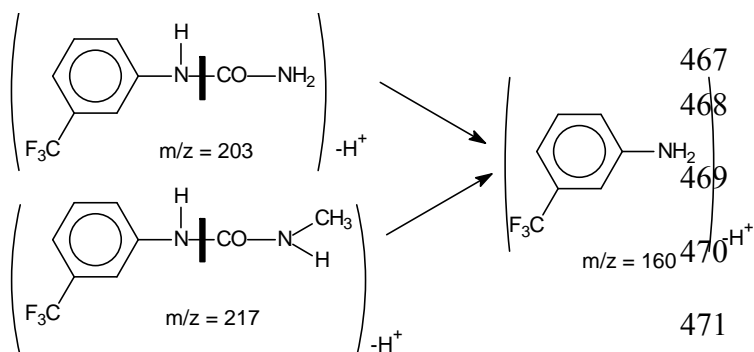
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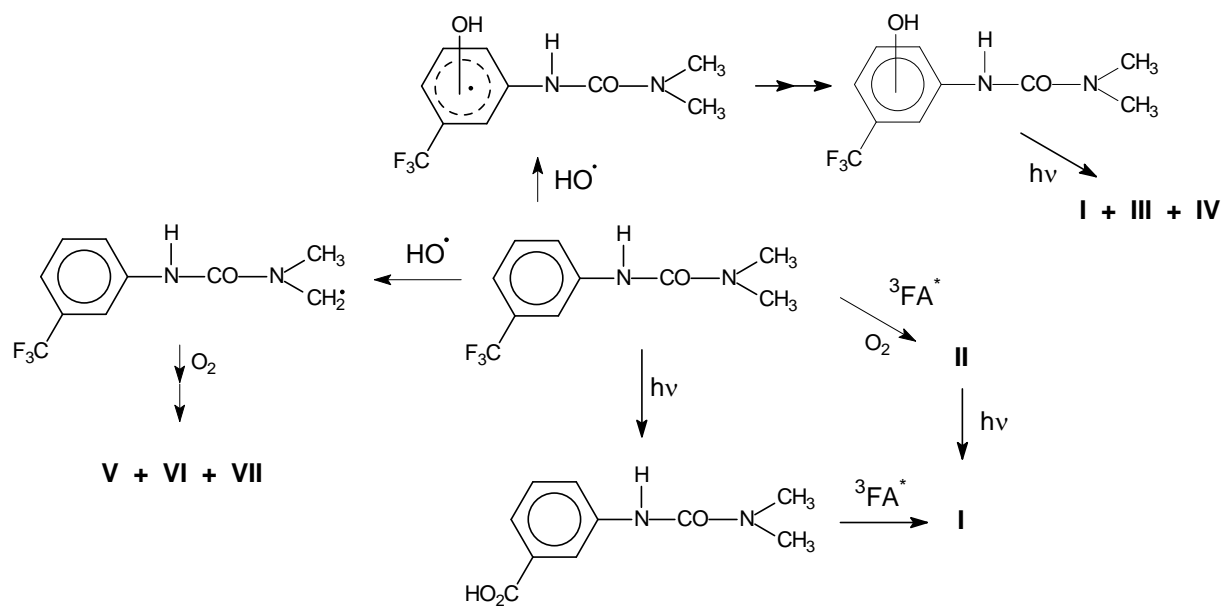
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473 Scheme 2: Fragmentation of photoproducts V and VI

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481 Scheme 3: Proposed reaction scheme

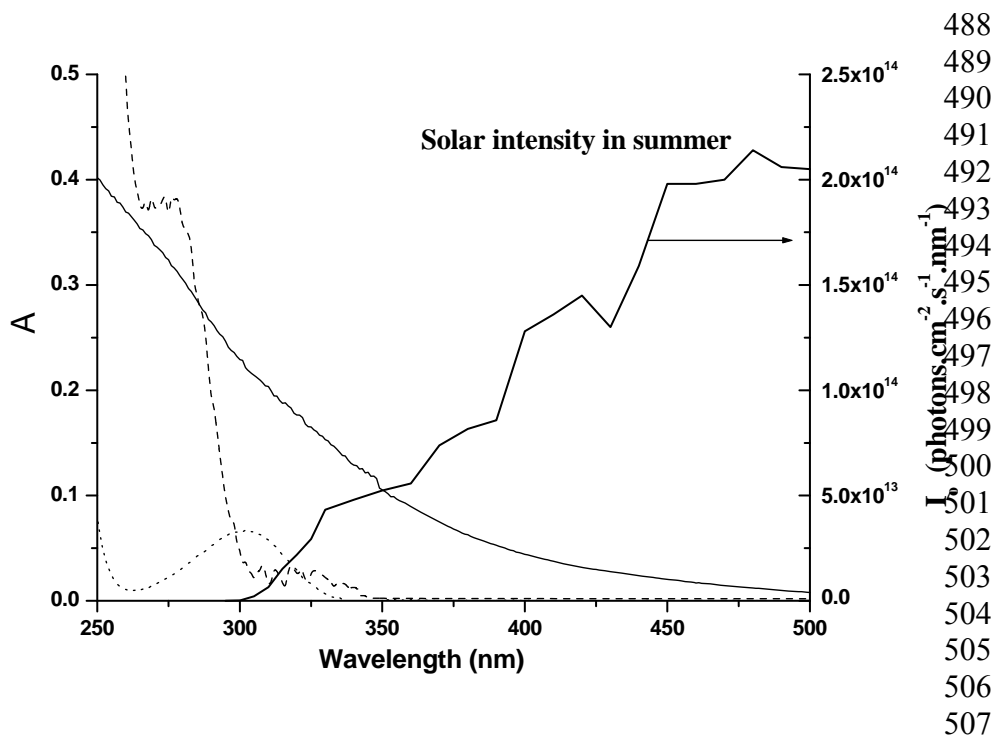
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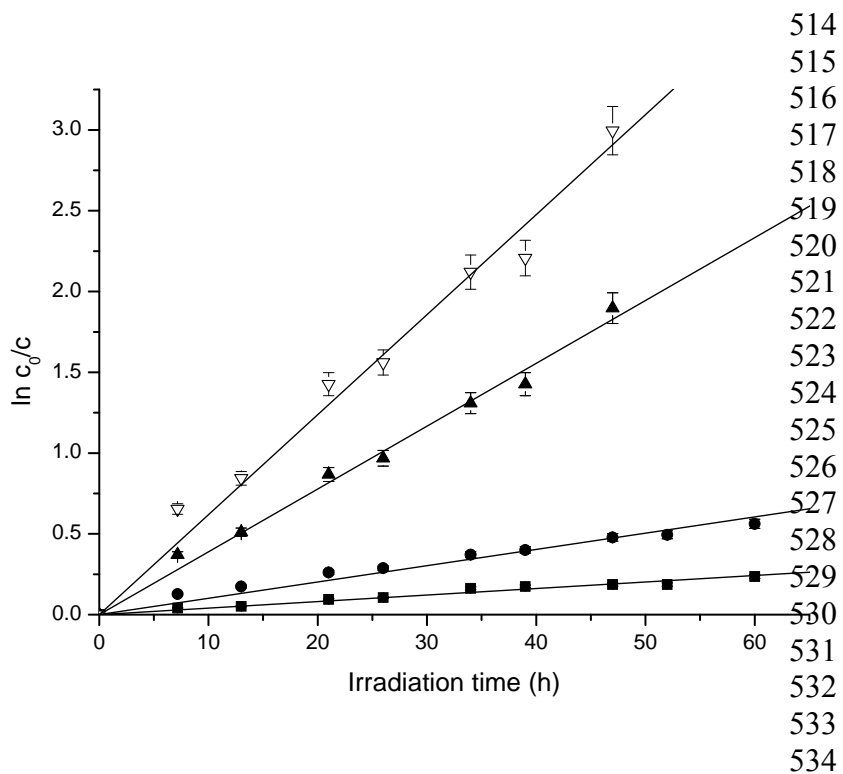


484 **Figure 1**

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512 **Figure 2**  
513



535 Figure 3  
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