

### **Study of the photodegradation kinetics of fluometuron by UV absorption spectrophotometry and fluorescence**

#### **Abstract**

In order to predict the fate of fluometuron in the aquatic environment and to assess the risk that it may pose, we studied its photolysis reaction in aqueous media. This reaction was monitored by UV absorption and fluorescence spectroscopy. UV irradiation source consisting of a 254 nm mercury lamp was used. The study showed that fluometuron is unstable under the effect of light radiation when irradiated in water. The absorption band and the emission of this product were at 244 nm and 325 nm respectively. This study also shows that the photodegradation of fluometuron in water follows first order kinetics regardless of the method followed. However, a difference was noted in the half-life times ( $t_{1/2}$ ). Indeed, these times found in UV and fluorescence are respectively 18.2 min and 6.6 min. The relatively lower value obtained in fluorescence could be explained by the fact that the latter is more sensitive to UV and fluorescence. In all cases, the half-lives found were relatively short ( $t_{1/2} < 1\text{h}$ ). For more information on the photolysis of this herbicide, these two methods were combined with NMR and GC-MS to identify the different photoproducts that may be formed.

**Keywords:** fluometuron, photodegradation, UV, fluorescence, photoproducts

#### **1) Introduction**

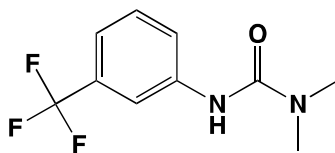
Agriculture is one of the engines of development, particularly in emerging countries. This is why many means, such as the extensive use of pesticides, are used to improve agricultural yields. Of these pesticides, herbicides such as fluometuron are generally the most widely used. Fluometuron (diagram below) is a herbicide belonging to the phenylurea family. It is commonly used in Senegalese agriculture for pre- or post-emergence weed control in various crops such as fruits, cereals and cotton. It has fairly long hydrolysis half-lives, ranging from about 110 to 144 weeks [1]. It is sparingly soluble in water at room temperature (0.0105%), but relatively highly soluble in acetone (15%) and methanol (14%) [2]. It is quite mobile in soil [3]. However, soil porosity and flow can affect this mobility [4, 5].

Due to their often high toxicity, pesticides present a major environmental risk of increasing concern. To mitigate their effects, several detoxification methods are variously used. Of these, UV degradation is the most widely used. Some studies have shown that pesticides can undergo two degradation pathways: the chemical pathway and the microbiological pathway. These two complementary routes can often be in competition. In all cases, chemical decomposition depends on parameters such as temperature and pH, but also on the content of catalysts present in the medium [6- 8]. It thus leads to the formation of new products whose structures depend on the nature of the medium [9].

Fluometuron belongs to a class of pesticides that can undergo degradation that is highly dependent on the environmental medium, especially in soils [10-12]. Studies on the fate of fluometuron in natural waters have shown slow photodegradation of fluometuron in the presence of solar radiation. In contrast, in the presence of photosensitisers, rapid photodegradation has been noted in these waters [13]. This shows that fluometuron absorbs very little sunlight. Indeed, direct photolysis of a pollutant is only possible if the pollutant absorbs sunlight [13].

Ecotoxicological studies have shown that the degree of toxicity of fluometuron is very low for mammals by oral ingestion (with an LD50 for the rat between 6416 and 8900 mg/kg) and by the dermal route (with an LD50 greater than 200 mg/kg for the rat and greater than 10 mg/kg for the rabbit) [14, 15]. For humans, we are not aware of any case of intoxication from fluometuron. However, even if some pesticides are not toxic, their degradation products can sometimes be more toxic [16]. Thus, to assess the real risk that fluometuron may pose, it will be necessary to identify the various breakdown products and test their toxicity.

In the present work, we chose to follow the photodegradation of fluometuron under UV radiation by absorption spectrophotometry and fluorescence, because of the simplicity of use and accessibility of these two methods. Then, we combined these methods with NMR and GC-MS to identify the photoproducts formed. Finally, the mechanisms of formation of these photoproducts were proposed



**Scheme 1:** Chemical structure of fluometuron

## 2) Methodology

### 2.1 Preparation of working solutions

We first prepared a  $10^{-3}$ M stock solution of fluometuron (99.8%). From this solution, we prepared daughter solutions of concentrations  $3.10^{-6}$ M.

### 2.2 Apparatus

In this work, we used:

- A UV-visible absorption spectrophotometer (Cary 100 Scan), connected to a computer and driven by software (Win UV) for absorbance measurements;
- A multiray photoreactor (Heliosquartz) equipped with 10 UV lamps of 254 nm and 15 W power to irradiate the fluometuron solution;
- A fluorescence spectrophotometer, model Cary Eclipse, connected to a computer and controlled by Win UV software for fluorometric measurements;
- An NMR spectrometer and an HPLC equipped with a UV detector and coupled to a mass spectrum for the identification of the photoproducts formed

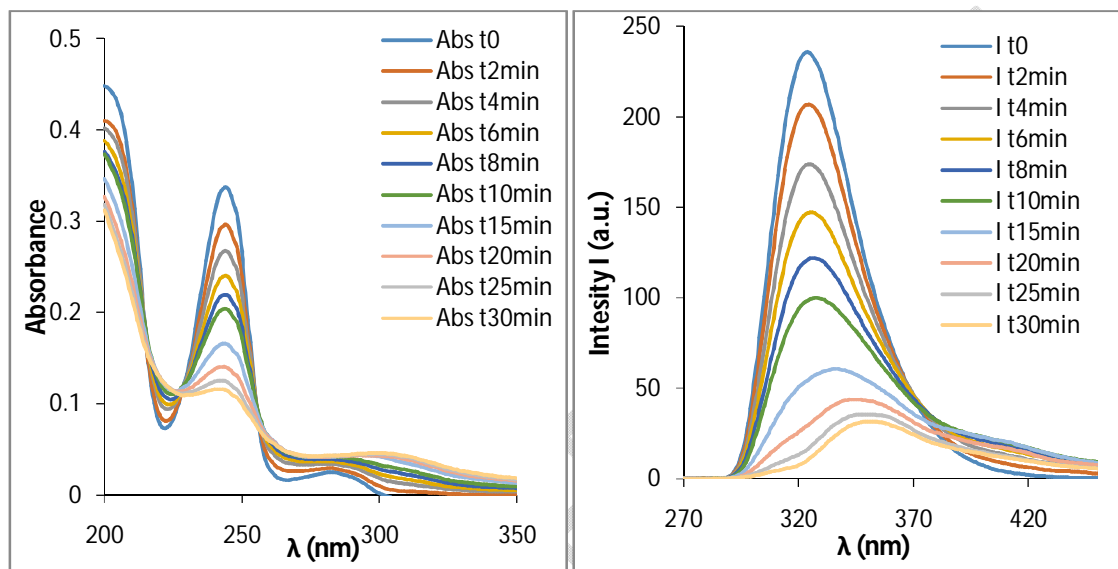
## 3) Results and discussion

### 3.1 Photodegradation and analysis of electronic absorption and emission spectra

Figure 1 shows the evolution of the electronic absorption and emission spectrum of fluometuron during irradiation. We note that the electronic absorption spectrum of fluometuron in water shows a single band located between 220 nm and 260 nm (figure 1a), with a maximum around 244 nm. This absorption wavelength is different from that obtained by Sabrina Halladja [et al](#) [13] in their study on the fate of fluometuron in natural waters when exposed to sunlight. Indeed, the results of their work indicated a maximum absorption at 275 nm. This difference in absorption wavelengths could be due to the irradiation sources, but also to the nature of the medium. In water, the absorbance of this product decreases during the irradiation time in favour of the formation of a new band. This decrease in absorbance over the course of the irradiation time shows that fluometuron is degraded by the effect of light. On the other hand, the appearance of the new band, whose intensity increases over the irradiation time, indicates the formation of a photoproduct. At around 228 nm and 256 nm, we note the existence of an isobestic point, which could indicate a dynamic equilibrium between the fluometuron and its photoproduct.

Figure 1b also shows that the emission spectrum of fluometuron comprises a single band with a maximum peak intensity at 325 nm. An emission wavelength of the same order was found

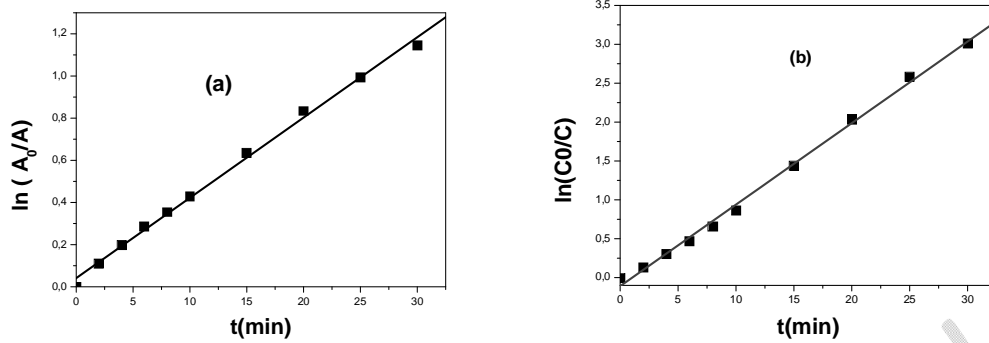
by I. Cydzik et al [ 1] when they studied the photoinduced fluorescence of fluometuron in a basic medium. Furthermore, no significant shift of the emission peak is noted during irradiation. These results therefore show that pH does not affect the fluorescence emission of fluometuron when it receives light. The decrease in the intensity of the fluorescence signal of this product as it is irradiated, thus confirms that this product is degraded by light radiation. These different results show that fluometuron is unstable in water under the effect of UV radiation.



**Figure 1:** Evolution of UV absorption and fluorescence spectra of fluometuron during photodegradation

### 3.2 Characteristics of the photodegradation kinetics of fluometuron

To determine the half-life of fluometuron in water, as well as the photodegradation rate constants for these two methods, we plotted  $\ln(A_0/A) = f(t)$  (figure 2a) and  $\ln(C_0/C) = f(t)$  (figure 2b) respectively. In both cases, we obtained lines with a positive slope and a correlation coefficient close to unity, which indicates a good precision of the measurements made.



**Figure 2:** Characteristic lines for the UV (a) and fluorescence (b) photodegradation kinetics of fluometuron

These calibration lines have the equation  $\ln\left(\frac{A_0}{A}\right) = at$  and  $\ln\left(\frac{C_0}{C}\right) = at$ . The kinetics being of order 1, the slope  $a$  is equal to the rate constant  $K$ . From the value of  $K$ , the half-life time  $t_{1/2} = \frac{\ln 2}{K}$ .

All the parameters of the photodegradation kinetics are listed in table 1

**Table 1:** Parameters of the photodegradation kinetics of fluometuron in water

Absorption	(nm)	$a$	$K(\text{min}^{-1})$	$r^2$	order	$t_{1/2}(\text{min})$
	244	0.03809	0.03809	0.9981	1	18.2
emission	325	0.10483	0.10483	0.9983	1	6.6

$a$ : slope;  $K$ : rate constant;  $r^2$ : correlation coefficient;  $t_{1/2}$ : half-life time

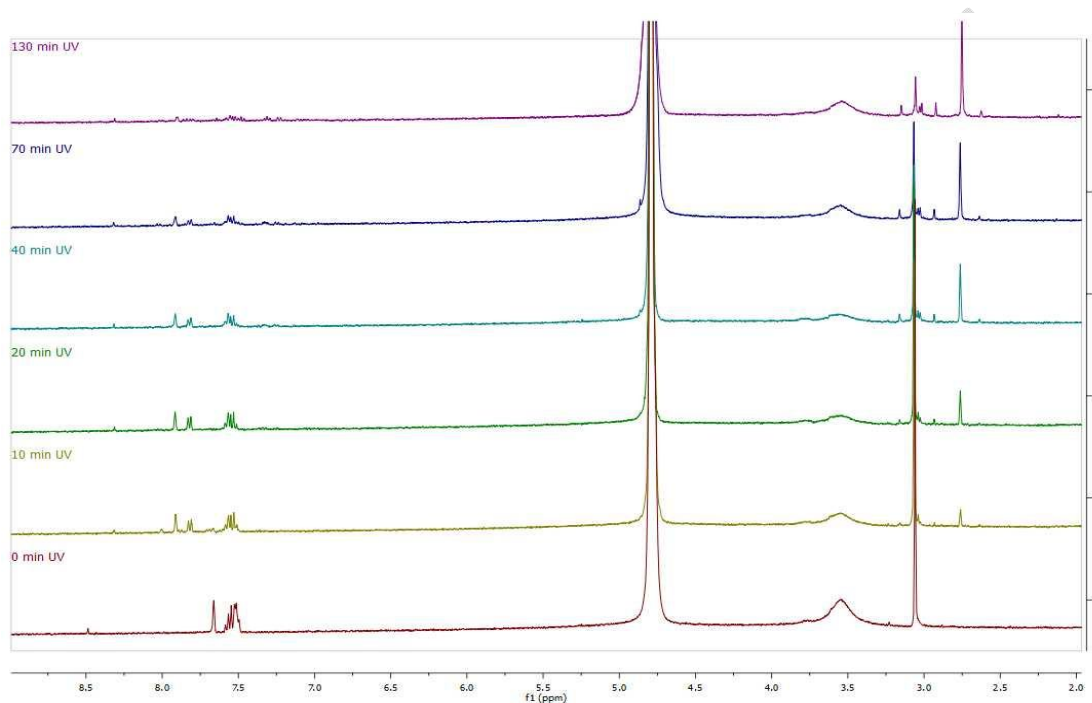
This table shows that the rate constant varies according to the method used. Indeed, it is relatively higher in fluorescence emission than in UV absorption; thus leading to a lower half-life in this state. This difference could be due to the good sensitivity of the fluorimetric method [17-21]. However, in both methods, we find that the half-life times found are relatively low ( $t_{1/2} < 1\text{h}$ ), compared to those obtained in other studies [3,17,18]. This product is therefore able to contaminate groundwater if its infiltration rate is high. This table also shows that the photodegradation of fluometuron in water obeys a kinetic of order 1 in the 2 methods used. This result found is in good agreement with that obtained for phenylurea pesticides during their chemical or photochemical degradation in water [19]. This same result is confirmed in the work of Razika Zouaghi et al [8], when they studied the photocatalytic degradation of monolinuron (MLN) and linuron (LN), which are two phenylurea pesticides of the same family as fluometuron. Other authors such as José Fenoll et al [20] and Sabrina Halladja et al [21] obtained similar kinetics by studying the photodegradation of fluometuron in water. In aqueous media, the photodegradation kinetics of phenylurea pesticides is therefore independent of the method used and the experimental conditions. However, the

nature of the degradation products may depend on these conditions. The identification of these degradation products makes it possible to determine the main degradation pathway of the pesticide when subjected to certain conditions.

In our study, the photoproducts were identified by NMR and GC-MS

### 3.3 Identification of photoproducts by NMR

In Figure 3 we show the spectrum of fluometuron before irradiation (at time  $t = 0$ ) and those of the photoproducts after irradiation ( $t \neq 0$ ).



**Figure 3:** Evolution of the proton NMR spectrum of fluometuron in acetonitrile

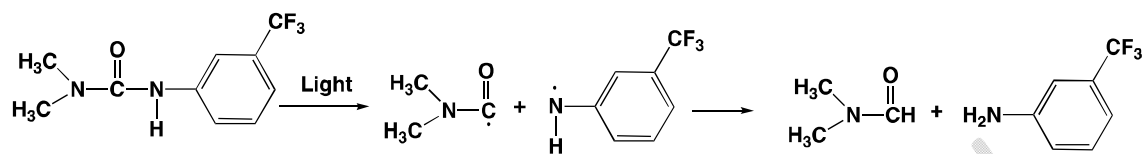
Before irradiation ( $t = 0$  min), the molecule shows:

- a signal between 7.25 -8ppm, corresponding to that of the aromatic ring;
- a second signal at 3.5 ppm corresponding to the chemical shift of the NH
- a third at 3.2 ppm corresponding to the chemical shift of the protons carried by the two methyl groups

Finally, the signal at 4.8 ppm corresponds to that of the solvent (deuterated acetonitrile).

After 10 min of UV irradiation, we observe a splitting of the aromatic protons and the  $\text{N}(\text{CH}_3)_2$  fragment with a shift located around 2 ppm. As the irradiation progresses, an increase in this signal is observed with a decrease in the signal corresponding to the aromatic ring (7.25-8 ppm). After 130 min of irradiation, the aromatic nucleus of fluometuron disappeared almost completely in favour of the  $\text{N}(\text{CH}_3)_2$  fragment. These different

observations indicate that fluometuron degrades under the effect of light and gives photoproducts; this confirms the results obtained in UV-visible absorption and fluorescence. We can therefore propose the following diagram of this photodegradation:



**Scheme 2:** Mechanism of the photodegradation reaction of fluometuron under UV radiation

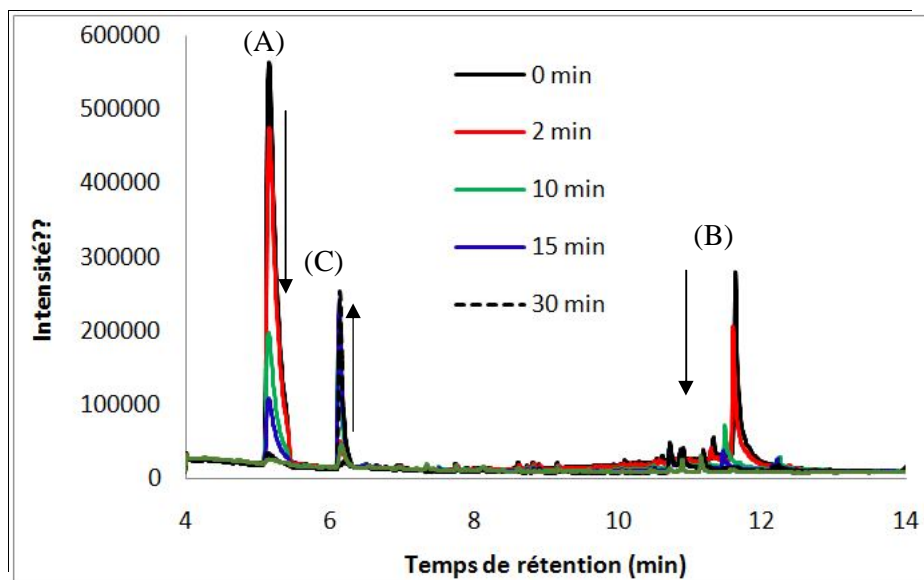
Thus, we note initially the formation of DMF (product A) and 3-trifluoromethylaniline (product B) resulting from a break between the carbonyl and the nitrogen linked to the ring. The main degradation pathway of our product is therefore the transformation of the urea chain. This result is in good agreement with that obtained by Robert M. Zablotowiz *et al* [22] when they studied the photodegradation of this product in plant residues. In this study, demethylation leading to the formation of DMF and 3-trifluoromethylaniline was noted. In another study conducted by S. Halladja *et al* [13] on the photodegradation of this product in natural waters containing nitrate ions and organic compounds (fulvic acids), hydroxylation of the aromatic ring with hydrolysis of CF<sub>3</sub> to CO<sub>2</sub>H leading to demethylation was observed. These different results show that the photodegradation mechanism of fluometuron depends considerably on the various constituents of the water or soil, thus leading to different photoproducts. In order to better identify the other degradation photoproducts formed in our study, we monitored this photodegradation by GC-MS.

### 3.4 Identification of photoproducts by GC-MS

#### 3.4.1 Chromatogram interpretation

Before irradiation, the chromatogram contained two peaks A and B (figure 4) with retention times of 5 and 12 min respectively. When irradiated, the intensity of these two peaks decreases with time, while a new peak (C) appears at about 6.5 min retention time. On the other hand, the intensity of this peak increases with the irradiation time. This shows that initially there were two compounds corresponding respectively to fluometuron and a possible complex or other product formed in the meantime. This complex could also be due to the reaction between fluometuron and the solvent. The decrease in the intensity of peaks A and B and the increase in the intensity of peak C *indicate* a link between the disappearance of

fluometuron and the formation of its main photoproduct. This result also confirms the observations noted in absorption and fluorescence. Moreover, this result is also in agreement with the NMR result. Indeed, the NMR spectrum showed the existence of a majority photoproduct.

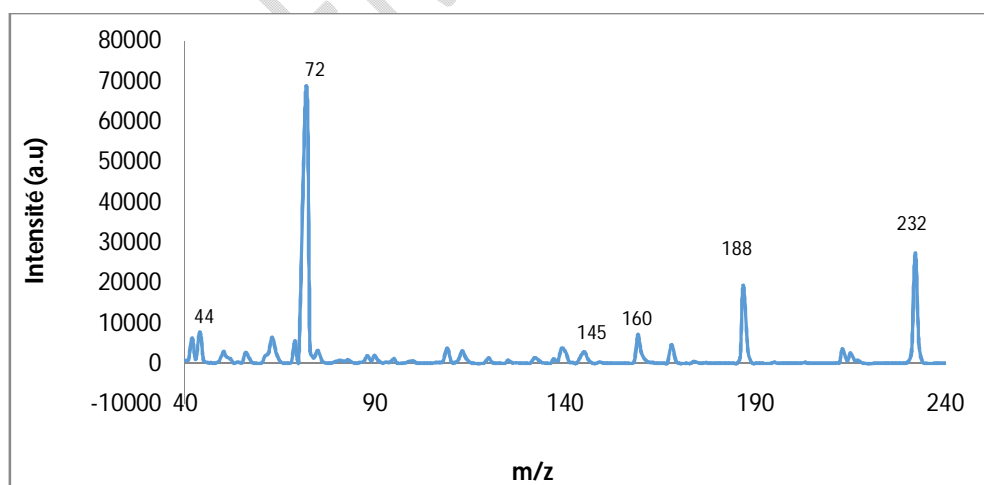


**Figure 4:** Chromatogram during photodegradation

To better identify the other photoproducts formed, we analysed the mass spectrum.

#### 4.2 Mass spectrum analysis

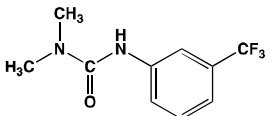
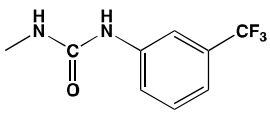
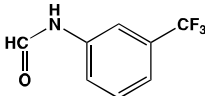
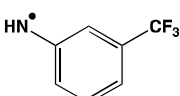
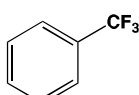
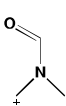

To confirm the previous results, we determined the mass spectrum of fluometuron after irradiation (figure 5)



**Figure 5:** Mass spectrum of fluometuron under UV light

The spectrum shows the molecular peak at  $m/z = 232$ , the fragments  $m/z = 217, 188, 160, 145, 72$  and  $44$ . The main peaks of this spectrum correspond respectively to the molar masses 232 (molecule I), 218 (II), 187(III), 160 (IV), 146 (V), 71(VI) and 45 (VII). All the results are shown in Table 2

**Table 2:** Photoproduct structure, molar mass and molecular peak  $m/z$

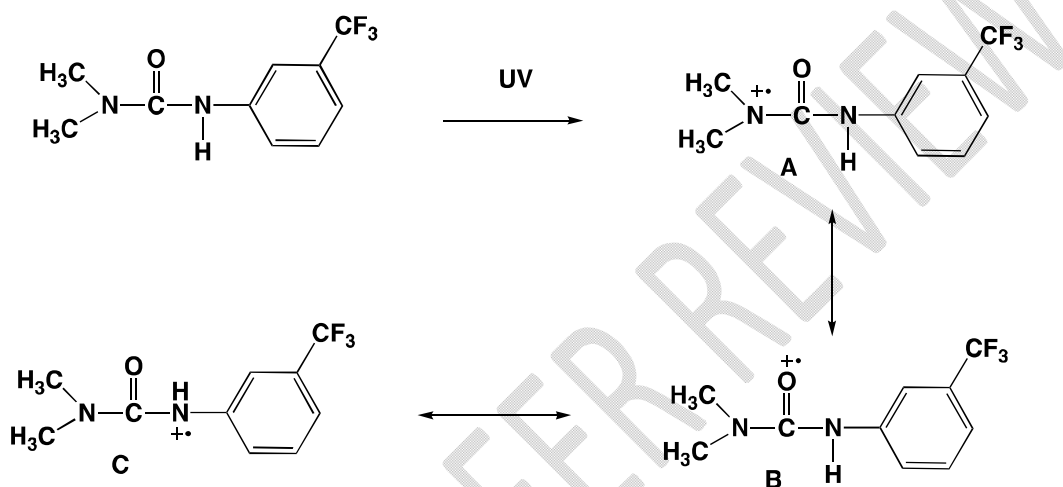
Chemical structure of photoproducts	Designation	Molar weight	$m/z$
	(I)	232	232
	(II)	218	217
	(III)	188	188
	(IV)	160	160
	(V)	146	145
	(VI)	71	72
	(VII)	45	44

In total, we noted the formation of seven main degradation photoproducts. Contrary to the results obtained by some authors, we did not note an elimination of fluorine. On the other hand, we noted modifications of the urea chain. This modification is marked by a demethylation, followed by a rupture of  $-N(CH_3)_2$  and  $-NH$ -cycle bonds. The difference obtained on the fluometuron degradation pathway could be due to the experimental conditions used. Indeed, the intensity of the irradiation source, the nature of the organic compounds in the medium or the presence of photosensitizers can affect the degradation of this product to a greater or lesser extent.

From the structure of these different photoproducts obtained, we proposed the reaction mechanism of the photodegradation of fluometuron in water.

### 3.5 Reaction mechanism of photodegradation of fluometuron

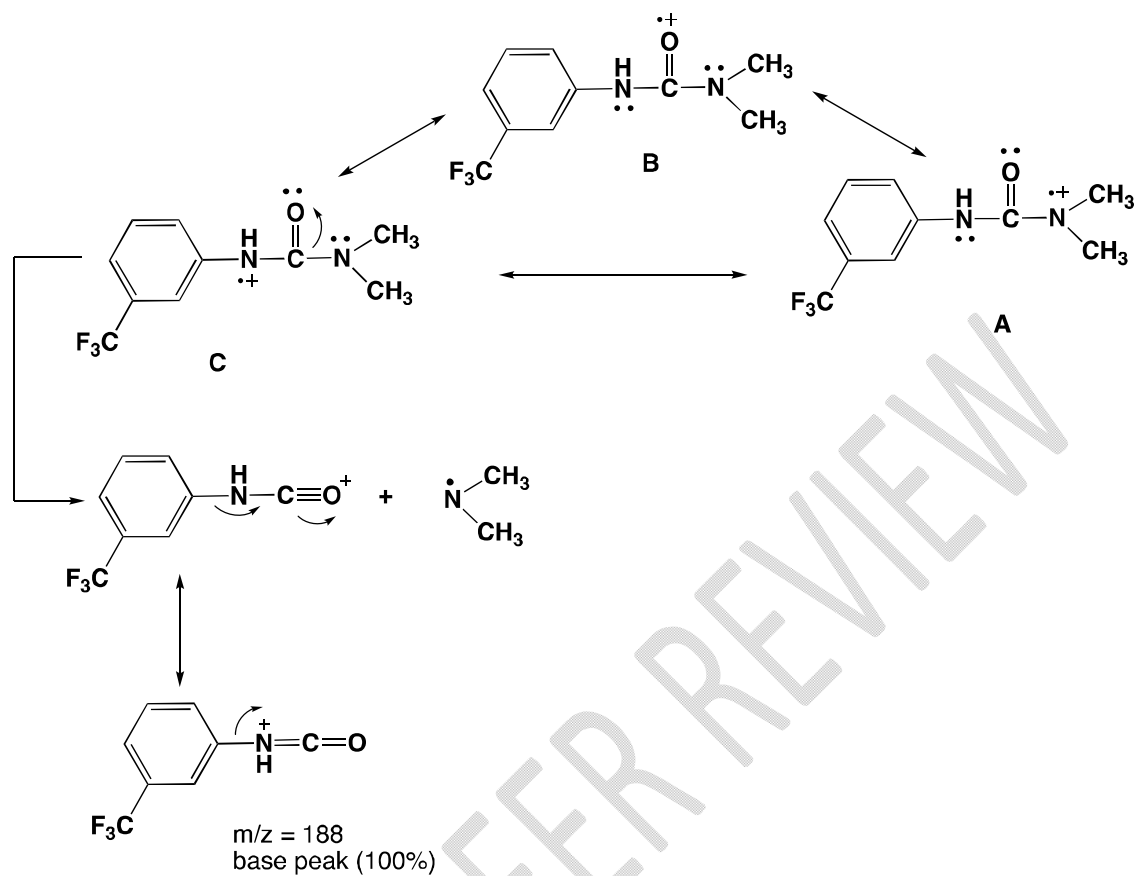
Under the effect of UV-visible radiation, the fluometuron ionizes to give three possible molecular ions according to the reaction diagram below. It can be seen that there are three possible molecular ions and all three will fragment depending on the position of the atom that underwent the ionization



**Scheme 3:** Ionization of fluometuron and formation of the molecular ion

We therefore propose the different possible significant fragmentations:

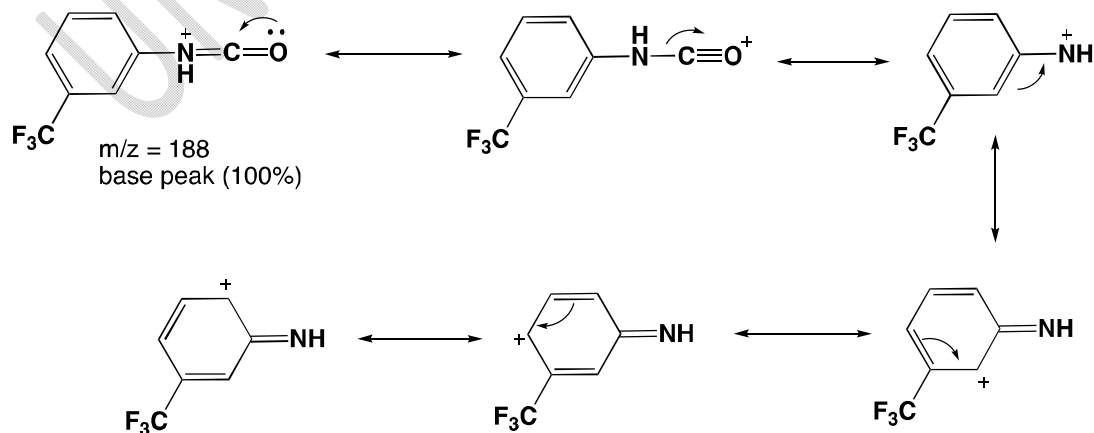
- the molar mass obtained corresponds well to that of the presumed fluometuron molecule.  $M = 232 \text{ g.mol}^{-1}$ .
- The base peak; the one corresponding to the most stable fragment is of mass 187-188. The molecular ion would therefore have lost the fragment of mass 45 UMA (or DA): This is possible from one of the first two molecular ions. Therefore, the breakage can occur on either side of the carbonyl. Thus, the basic peak comes from the fragment with many mesomeric forms that stabilize this fragment (see diagram below).



**Scheme 4:** Reaction mechanism for the formation of the base peak molecular ion

As breakage can occur on either side of the carbonyl, the base peak comes from the fragment which has many mesomeric forms; this stabilizes the formation of this fragment according to the different reaction mechanisms below (a,b,d).

a) Starting with the molecular ion corresponding to the base peak





Thus, from Scheme 4, we find all the most significant fragments of the fluometuron spectrum after irradiation

### **Conclusion**

This study has shown that fluometuron is notoriously unstable when exposed to light. In water, its photodegradation undergoes kinetics of order 1, whatever the method used. This photodegradation of fluometuron in this solvent is relatively fast ( $t_{1/2} < 1\text{h}$ ), compared to the results obtained in other matrices by various authors using different methods. This product is therefore able to contaminate groundwater more than surface water if its infiltration rate is rapid. NMR and GC-MS analysis showed in our study that the main photodegradation pathway of fluometuron in water is the progressive breaking of the urea chain; thus leading to the formation of several photoproducts.

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