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In situ studies of pesticides photodegradation on soils using PD-TOFMS technique: Application to norflurazon and oxyfluorfen☆

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ABSTRACT

As we have demonstrated that plasma desorption time-of-flight mass spectrometry (PD-TOFMS) is well adapted to the direct characterization of pesticides adsorbed on agricultural soils the technique has been applied for the first time to the study of their evolution under sunlight-like irradiation. Two pesticides have been selected: norflurazon which is the most documentated (both from the literature and from our previous experiments) and oxyfluorfen in order to assess the capability of the technique.

The photodegradation process has been investigated both for a deposit onto a metallic substrate and for a soil impregnated with the product.

For norflurazon degradation parameters have been extracted from the yield variation of ions representative of the molecule and breakdown products and particularly the time required for 50% dissipation of their initial concentration (DT50 values). The comparison between deposits and soils indicates clearly that the degradation is slower in the latter case with an increase of about 3.5 for the DT50 of the molecule, and about 2 for its breakdown products. These values are in agreement with the decays of other ions.

As expected, the degradation is faster when the UV of the sunlight is unfiltered, more significantly for the breakdown products.

This is also observed for the oxyfluorfen deposited onto aluminium although at a lower level (twice less). The trends are only qualitative for the impregnated soil but definitely there.

A discussion is presented for the interpretation of the photodegradation process in both cases together with suggestions of improvement in the data acquisition.

1. Introduction

Among the main dissipation pathways of pesticides in soils photolysis is not only dominant on dry, sunlight-exposed surfaces but has a determinant influence on the fate of pesticides in the environment. Direct photolysis has been estimated to be restricted to a superficial layer of 0.2–0.4 mm while the indirect photolysis depth was slightly deeper [1].

The need for an analytical tool able to probe such layer is evident considering that, in contrast to photodegradation in water, little is known about photochemical degradation of pesticides on soil surfaces. The knowledge on the photochemical behaviour of pesticides on soil is not only a key issue in terms of the formation and persistence of toxic photoproducts, but a different photolytic behaviour in soil and in water can be expected since in many cases, the electronic structures, absorption spectra, and excited state lifetimes of sorbed compound are much different from their solution properties [2]. For example Sanchez et al. [3] have shown that the absorption spectrum of methidathion adsorbed on soils was shifted to larger wavelengths than in water which allowed its photodegradation.

It has recently been demonstrated [4,5] that PD-TOFMS (plasma desorption time-of-flight mass spectrometry) analysis is a reproducible and reliable technique for the in situ analysis of pesticides deposited or adsorbed on solid materials including soils. With the great advantage to probe the pesticide where it stands, such a tool eliminates the uncertainties associated to the extraction/concentration steps inherent to the techniques widely used in the field. Since any change can be detected including the effects of the analysis procedure (under vacuum) and the storage conditions, any kind of degradation process can be safely followed. However, as for any solid surface analysis technique, the price to pay for a high spatial and in-depth resolution is the requirement of fairly high

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concentration levels of pesticide within the soil matrix (10^{-3} g g^{-1}). Then, although by no means a fast screening technique, the particular TOFMS technique we have used has the great advantage to follow the evolution of the pesticide where it stands along the analysis procedure and its initial "natural" degradation. Such a sensitivity of the method to chemical changes induced by any kind of irradiation is related to the particular mechanisms of interactions between the analyzing beam and the organic material [6].

As for any synthetic study where the couple substrate-pesticide is well characterized, the technique was first applied to the investigation of the photodegradation (sun spectrum) features of a particular pesticide (norflurazon) deposited onto an aluminium backing [5]. Degradation pathways were identified and degradation kinetics were determined both for the molecule and its breakdown products.

In the present work, we have extended the early comparison between pesticide deposited on aluminium backing and impregnated in soils [4] to their evolution under sunlight-like irradiation for two different pesticides: in addition to norflurazon which has been the most documentated (both from the literature and from our previous experiments) and in order to assess the capability of the technique results are also presented for another pesticide, namely the oxyfluorfen.

2. Experimental

2.1. Main features of the PD-TOFMS setup

The definite advantage of the PD-TOFMS technique over any static-SIMS system using low energy (keV) ions (damage-free analysis – high sensitivity to degradation – induced damages in the organic material) resides in the use of energetic heavy ions [6] available on small electrostatic accelerators (MeV energy range).

Then, our experiments have been performed using Ar^{3+} ions of 9 MeV delivered by the 4 MV Van de Graaff particle accelerator of the Institut de Physique Nucléaire de Lyon.

One beam line is devoted to the transport of such ions towards a beam chamber under 10^{-7} mbar pressure conditions where the PD-TOF mass spectrometer is installed.

Since the different parts and modes of detection of this spectrometer have been published in various articles such as in Ref. [4] we will limit our description to the most useful features.

Secondary charge species emitted under primary beam interaction are identified and counted in either positive or negative ion mode depending on the polarity of the 6 kV applied between the target sample and the grounded circular extraction aperture of 5 mm in diameter. Once extracted these ions drift at constant velocity through the 125 mm long–20 mm diameter field-free tube, at the end of which they hit the surface of a microchannel plate assembly. As the most prominent feature of such device, high detection efficiency (90% transmission) is associated to a poor mass resolution, typically 150 based on a peak width (FWH) at m/z 300. Since we are mostly dealing with thick samples, only negative ion emission is allowed using the so-called start electron technique [4].

With a primary ion beam of typically 0.25 mm in diameter and 1000 s^{-1} in intensity most of the spectra have been obtained with an integrated dose in the 10^{-8} ions cm^{-2} range, thus in non-destructive conditions.

The analysis chamber is under a 10^{-7} mbar pressure conditions.

2.2. Material, sample preparation and light irradiation setup

The norflurazon pesticide (supplied by Sigma–Aldrich, Saint-Quentin Fallavier, France) was used as-received since it was free of any surfactants or emulsifiers. A solution in ethanol (analytical grade supplied by Prolabo, Lutterworth, UK) was prepared at 5 g l^{-1}. Thin films of thickness around 100 μg cm^{-2} were obtained by spin-coating deposition (500 rpm) by spiking 100 μl of the solution onto a flat surface (ca. 5 cm^2) of polished aluminium. Then, the storage of the samples at room temperature before their analysis was kept at a minimum that did not exceed 3 h for the longest time.

The soil used in this work was shallow and formed from basaltic deposits. It was first mechanically cleaned from small rocks and roots by passing through a 200 μm ultra-pure aluminium sieve, dried at 378 K to a constant weight and then pulverized and homogenized in an agate mill. The surface area of the soil was 9 m^2 g^{-1} as measured by the Brunauer, Emmet and Teller (BET) method (nitrogen adsorption). Elemental analysis of the soil using the Particle Induced X-ray Emission (PIXE) technique indicated that it was mainly an aluminosilicate with 4% sodium, potassium, magnesium and calcium oxides. Iron oxides were found to be ∼17% [7]. The organic matter content of the soil was 1.15%, the clay and the sand fractions were ∼21.5 and ∼48% respectively [8].

The samples to be analyzed were prepared by dispersing 0.5 g of such material in a circular glass vial (ca. 10 ml in volume). Then, a complete moisturization was achieved by the addition of 4 ml of the 5 g l^{-1} norflurazon in order to obtain a pesticide concentration of 40,000 ppm. The spiked soil sample was left uncovered in order to evaporate the solvent for a minimum of a 24 h. Once dry, ca. 0.15 g of the soil was mechanically homogenized and pressed (10 tons cm^2 during 2 mn) to form a pellet of 10 mm diameter and 3 mm thick.

The same sample preparation protocol was applied for the other pesticide, the oxyfluorfen. However, in that case the spin-coating layer was not visually homogeneous neither the dry spiked soil even after mixing and traces of the white crystal powder of the pesticide were still visible. This may account for the reproducibility problems reported in Section 3.

Irradiations were performed using a solar simulator (Suntest CPS+, HERAEUS, Hanau, Germany), equipped with a 1.1 kW xenon arc lamp air cooled, protected with an adequate filter to simulate the solar spectrum between 290 and 800 nm. The experiments were carried out in ordinary atmosphere, the samples being placed onto a metallic plate watercooled at 20 °C. The filter can be removed to investigate the effect of the UV component. In order to ensure a uniform repartition of the light within the irradiation cell, a system of reflectors was used. Total exposure area is 560 cm^2 and a radiant flux of ca. 75 W m^{-2} for the UV fringe was measured using a radiometer (Bioblock, Illkirch, France Scientific model CX-365) which is slightly higher than the value given for the sunlight in the best conditions (65 W m^{-2}).

3. Results and discussion

3.1. Anions of interest

From all the emitted ions identified in our previous investigations [4,5] only those detected all along the photodegradation process both in deposits and impregnated soils will be selected to allow the comparison. The expected loss of sensitivity in the case of impregnated soils does not preclude the use of any relevant information from the deposits data.

3.1.1. Norflurazon

From the many peaks detected on a fresh deposit (Fig. 1a) we have selected the ones corresponding to F^-, Cl^-, OCN^-, CF_2O^- (m/z 66), the main fragment of m/z 185 (see inserted sketch), the molecular ion $[M–H]^-$ and $[M+Cl]^-$.

As a matter of fact, these peaks are still observed on the soil sample (Fig. 1b). However, it has to be noticed that Cl^- has been detected

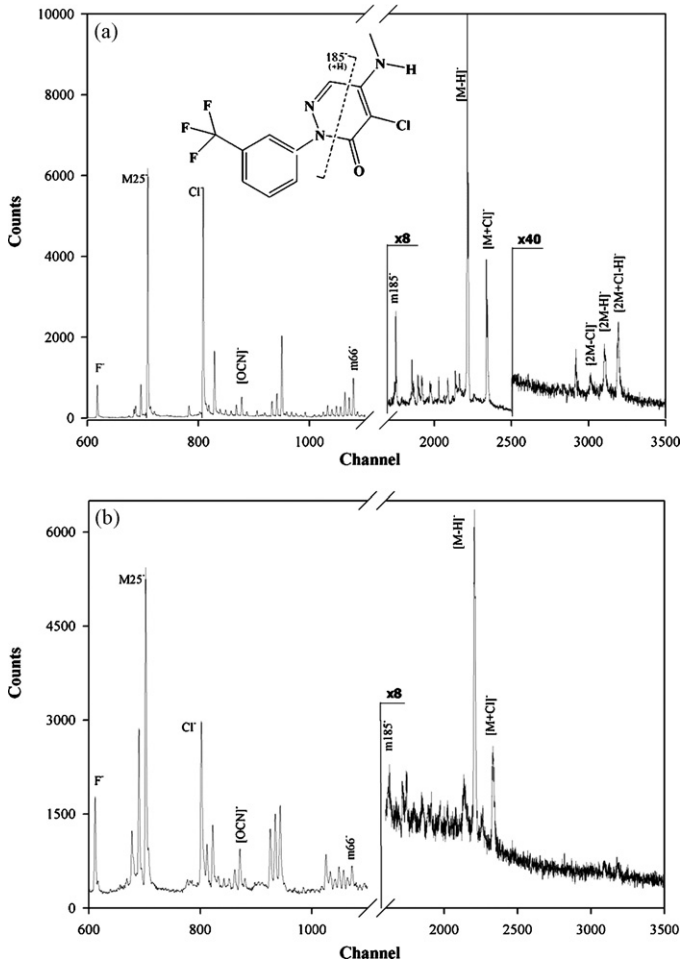

Fig. 1. Negative PD-TOF mass spectrum of a: (a) norflurazon film prepared as described in Section 2 and analyzed approximately 3 h after preparation; (b) soil impregnated with NF at a concentration of 40,000 ppm.

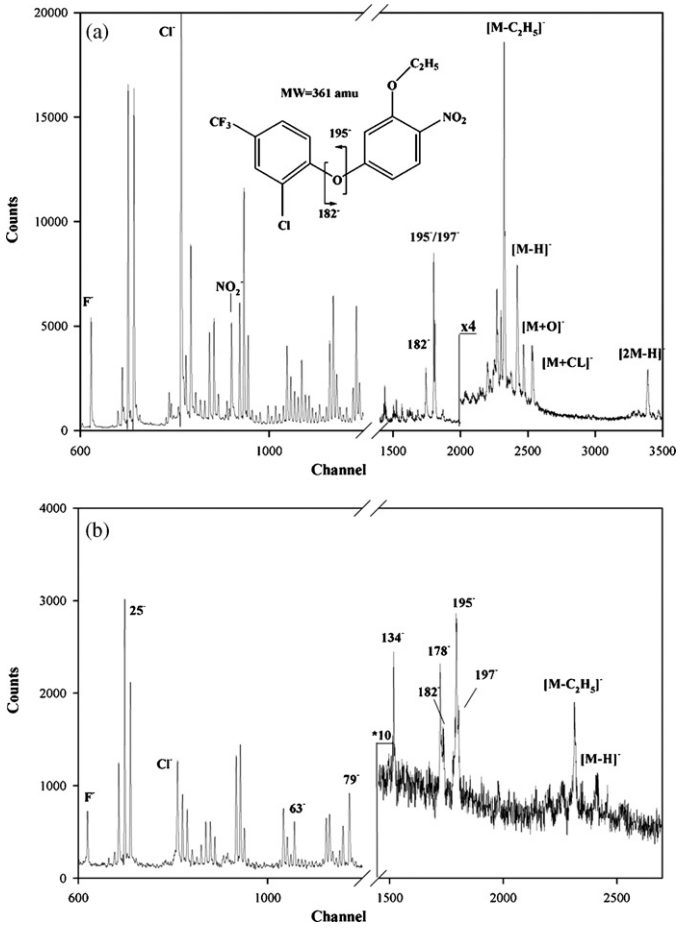

Fig. 2. Negative PD-TOF mass spectrum of a: (a) oxyfluorfen film prepared as described in Section 2 and analyzed approximately 3.5 h after preparation (inserted is a sketch of the molecule); (b) soil impregnated with of at a concentration of 40,000 ppm.

from virgin soil: then a background level must be considered for such emission.

3.1.2. Oxyfluorfen

From the spectrum shown in Fig. 2a, obtained from a deposit onto an aluminium substrate, it can be observed that, apart from the simplest ions F^-, Cl^- and $[NO_2]^-$, the main fragments of the molecule are well identified at m/z 182 and 195–197 and those associated with the molecule are $[M–C_2H_5]^-$, $[M–H]^-$, $[M+O]^-$, $[M+Cl]^-$ and also $[2M–H]^-$.

However, as shown in Fig. 2b, interferences due to soil elements [4] restrict the investigations of the photodegradation process to F^-, Cl^-, the fragment at mass 195–197 and $[M–C_2H_5]^-$.

3.2. Evolutions under suntest exposure (UV filtered)

To get some understanding of what the ToFSIMS technique can tell about such evolutions it must be remembered that the yield of the detected ions is directly related to the ability of the analyzing beam to break the related bonds. Various models have been proposed within the frame of the electronic sputtering that prevails in our experimental conditions, such as the one reported in Ref. [9]. Then, the yield variation of the emitted anions, as a function of the exposure time under photoirradiation can be interpreted in three ways:

(1) Stable yield: The related bonds are not affected by the photoirradiation.
(2) Decreasing yield:
   - The initial or newly formed molecule is less and less available because of the photoinduced scissions or the newly formed molecule or because it is volatile as for the smallest (such as NO_2^- or Cl^- emission, for example).
   - The chemical environment has changed and the related bond is stronger.
(3) Increasing yield:
   - A new fragment is formed (breaking product) and the variation of its yield is correlated to the disappearance of the initial molecule: then first-order kinetics may apply and lead to DT50 values for both of them (see later on).
   - The bond breaking under beam impact leading to a fragment ion from the initial molecule is facilitated.

3.2.1. Comparison between deposit and impregnated soil

3.2.1.1. Norflurazon. The three categories of yield variation of the emitted anions, as a function of the exposure time, are indeed observed.

For those the emission yield increases up to a maximum, a complete identification has been published elsewhere [5]. Some are already detected on freshly prepared samples (see left part of the $[M–H]^-$ peak in the related energy window in Fig. 1a), such as

$[M–CH_3+H]^-$. Others will appear after less than 1 h irradiation in the high energy window such as $[M+185]^-$.

As already reported [5], the yield of the F^- ion as well as the one of the fragment associated with it, CF_2O^- (m/z 66), do not vary significantly over the 16 h of exposure. Data points obtained from two sets of experiments performed at quite different periods of time attest the reproducibility of the process. Commonly observed primary fragment ions of organic molecules C_2^- and C_2H^- at m/z 24 and 25, respectively, are dependent on the conditions of preparation (pollution) and analysis (vacuum conditions). If these conditions are reproducible as established in previous investigations [4], these ions can be used as "markers" of the reproducibility of experimental conditions.

A similar evolution is observed for F^- in the case of the impregnated soil with a comparable reproducibility. The possibility of a slight increase during the first hours of irradiation in the deposit case appears to be consistent for the soil. However there is a clear trend for a decrease of the CF_2O^- emission after a longer time of exposition.

As reported in Ref. [5] and shown in Fig. 3a, the yield of the ions $[M–H]^-$, $[M+Cl]^-$ and Cl^- is continuously decreasing. As for the previous results, the data values obtained for two sets of experiments distant in time are remarkably coherent. Hence such distinction will not be mentioned for the figures to come.

Should the decline of these ion yields with time obey to first-order kinetics, then a DT50 value (or time required for 50% dissipation of the initial concentration) can be obtained for the molecule of interest. We have described in details how to extract DT50 values from the molecular ion decay [5]. In the present case, the best fit is obtained using a second-order kinetics model [10] and a value of 66 ± 10 min is found for the norflurazon molecule.

Compared to the $[M–H]^-$ decay the one of Cl^- is slower: this is an indication that not all of the chlorine is released (probably in the form of Cl_2) but a significant part recombines with a neighbouring molecule: then, the yield of the $[M+Cl]^-$ ion will exhibit a faster decrease than the one of $[M–H]^-$.

A similar behaviour is observed for the soil (Fig. 3b) but at a much slower rate. This qualitative difference will be systematically observed for all the evolutions. The DT50 value from the $[M–H]^-$ decay is found to be 250 ± 15 min, which is 3.3 times longer than in the deposit case.

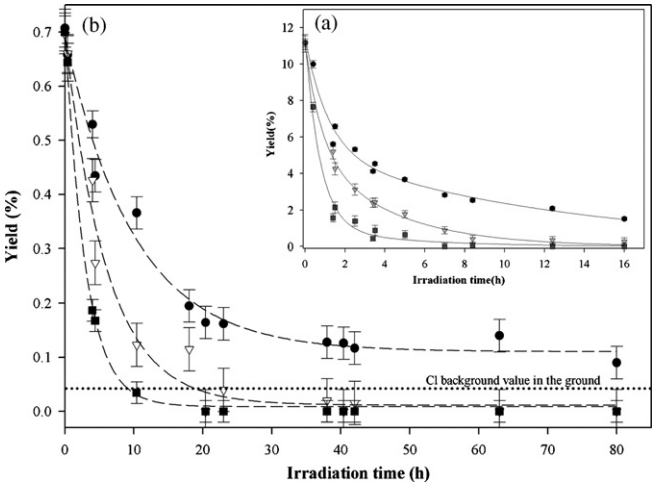

Fig. 3. Variation of the yield of the ions $[M–H]^-$ (open triangles), $[M+Cl]^-$ (black squares) and Cl^- (black circles) as a function of suntest device exposure time, for: (a) deposit; (b) soil impregnated. The curves represent the best fit from which the DT50 values are extracted.

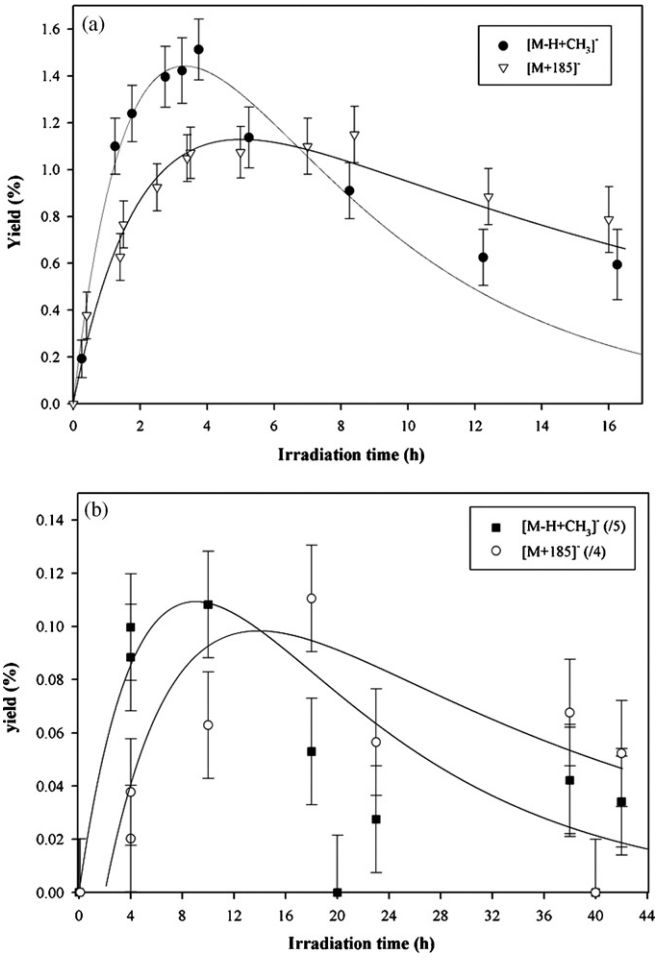

Fig. 4. Variation of the yield of the $[M+CH_3–H]^-$ and $[M+185]^-$ ions as a function of suntest device exposure time, for: (a) deposit; (b) soil impregnated. The curves represent the best fit from which DT50 values can be extracted.

Consistently, the DT50 values extracted from the decay of $[M+Cl]^-$ as well as from Cl^- are respectively 3.5 and 3.6 times longer than in the deposit case.

In Fig. 4a are represented the variations of the yield of ions corresponding to new entities formed under irradiation of the deposits. Among those associated with the demethylation and methylation of the norflurazon molecule we have selected $[M–H+CH_3]^-$, detected at m/z 317, because of its greater detection sensitivity in the soil. The yield variation of such ion under irradiation is typical of the simultaneous degradation of the parent (norflurazon molecule) and the formation and degradation of its breakdown product.

Still following the procedure described in Ref. [10] the most precise value of DT50 appears to be 245 ± 25 min for the deposit.

As described in details in Ref. [5] the evolution of the yield of the $[M+185]^-$ ion results from the competition between the production of the M185 fragment and its degradation through the production of the $[OCN]^-$ ion: then it takes a longer time for the yield to reach its maximum and the decrease is not so pronounced. Accordingly, the extraction of the DT50 value should be not so easy in that case than it was for the previous case of breakdown product.

Surprisingly enough, such decay can be fairly well fitted from the decay of the norflurazon molecule giving rise to the production of the [M+185+H] molecule and a DT50 value of 700 ± 60 min can be extracted.

As shown in Fig. 4b the related data for the soil case exhibit larger error bars and do not allow precise determination of DT50 values.

However, a fairly good fit is found for the breakdown product $[M–H+CH_3]$ leading to a DT50 value of 600 ± 60 min.

The agreement is not so good for the [M+185+H] molecule and the fit shown in Fig. 4b is the best we can obtain from second order kinetics with a DT50 of the order of 20 h.

As for the molecule, the degradation process of the breakdown products is slower in the soil than in the deposit although the increase of the DT50 values is smaller (a factor around 2 compared to around 3.5 for the molecule).

The picture emerging from these results must take into account that we are dealing with an organic bulk into which, under light irradiation the molecules are modified and rearrange themselves with their neighbours. This proximity is likely responsible from the production of ions built up from two new entities in the mass range of the molecular dimer which disappears. An essential point is the loss of chlorine and the rearrangements on the basis of the CH_3 group and a more complex adduct with the mass 185 fragment.

3.2.1.2. Oxyfluorfen. As already reported in our previous work [4] the deposits prepared by spin-coating or simple drying may differ in terms of emission yield for an identical average thickness. In addition, neither of these techniques ensures a satisfactory homogeneity and reproducibility from sample to sample and indeed between series prepared at several months interval. More than a systematic difference in emission yields there are disparities for a particular ion. This can be observed looking at the normalisation factors between the two data series.

For those ions the intensity is slowly varying with exposure time, the discrepancies do not affect the general trend. This can be observed in Fig. 5a for the ions F^-, CF_2O^- and Cl^-.

As for the norflurazon case, the emission of ions incorporating F is weakly affected by the photoirradiation which indicates a good stability of the related φ-nucleus.

There is a more marked difference between the two series for the yield variation of the Cl^- ion especially for the first 2–3 h where the two curves cross each over. This will be discussed later on.

For the soil, in addition to the problem previously described, a poor sensitivity is due to the nature of the medium (background and interferences – see Ref. [4]). The emission of most ions is indeed lower than for the deposits and only the Cl^- and F^- ions will be considered in this comparison.

As shown in Fig. 5b, an initial increase of the yield of these ions is well observed before a stable level is reached. For both there are no significant differences between the two series of experiments although the series 2 data are limited to the shortest irradiation times.

The variation of the intensity of the molecular ion $[M–H]^-$ as well as $[M+O]^-$ is represented in Fig. 6a for the deposits, only for one of the two series because of sensitivity problems. DT50 values can be easily obtained from these decays: it is found to be 55 ± 4 min for the molecule while a value of 85 ± 10 min is deduced from $[M+O]^-$ decay.

Still for the deposit, a decrease is also observed for the ions NO_2^- and $[M–C_2H_5]^-$. As shown in Fig. 6b the data values for the two series are in good qualitative agreement although a factor of 5 in intensity is found for NO_2^- and even close to 8 for $[M–C_2H_5]^-$. It must also be noticed than an initial plateau of about 2 h is clearly observed for series 1 while a continuous decrease is found for the series 2.

Extreme values of 80 and 230 min for DT50 from the $[M–C_2H_5]^-$ decay and extreme values of 45 and 64 min from the NO_2^- decay can be extracted from the fitting curves.

As regarding the soil, and for the reasons previously developed, the emission of the molecular ions is indeed low. The emission of $[M–H]^-$ and $[M+O]^-$ being too low the only comparison between deposit and soil is for the $[M–C_2H_5]^-$ ion emission, as shown in Fig. 6c. The same discrepancy is observed between the two series of experiments for the very first hours of decay, the agreement being much better after irradiation suggesting some "homogenization" at the sample surface.

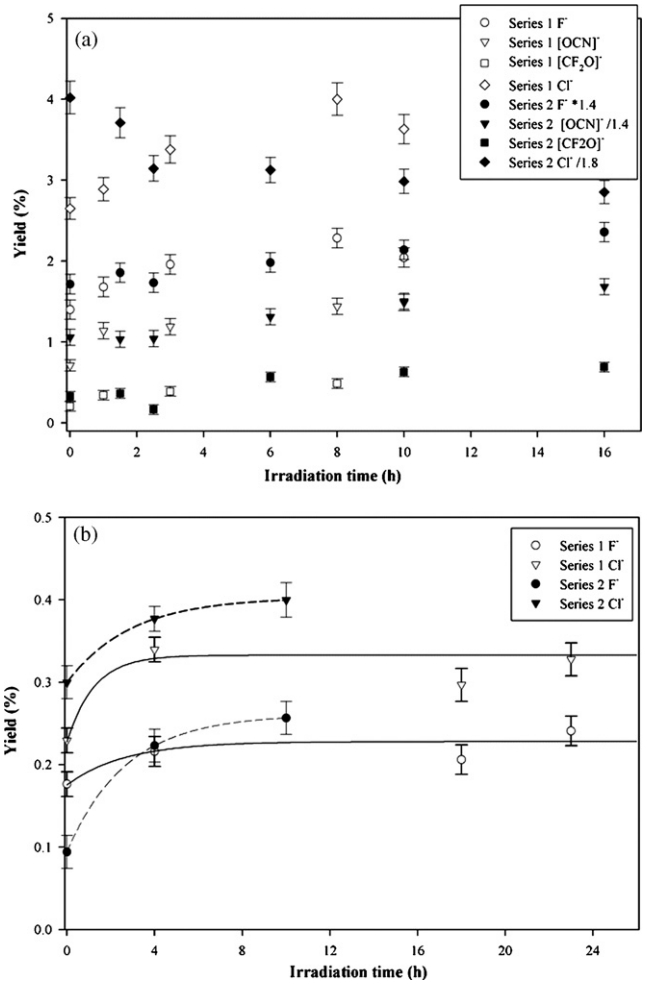

Fig. 5. Variation of the yield of the ions F^-, CF_2O^- (M66) and Cl^- as a function of suntest device exposure time, for: (a) deposit; (b) soil impregnated (only for F^- and Cl^-) (the curves between data are only to guide the eye). White symbols are for series 1 – black symbols for series 2 with normalisation factor when relevant.

A more striking difference between the series 1 and 2 appears to be the behaviour of the complementary ion fragments of the oxyfluorfen molecule under photoirradiation of the deposit (ions of *m*/*z* 182 and 195/197 – see sketch of Fig. 2a).

As shown in Fig. 7a, for the series 2 the related yields have a quasi-symmetric evolution curve: an initial plateau for the first 2–3 h, a sharp increase (decrease) leading to a crossing before a final stable level. This is not observed for the series 1, but from the variation curves of the corresponding yields (2–3 times smaller than for series 2) we may infer that their crossing happens later (after 10 h). We have also represented in this Fig. 7a the variation of the intensity of the Cl^- ion because it belongs to the fragment of *m*/*z* 195/197.

Then, all these variations must be consistent with the general picture previously proposed to introduce the expected effects of the photoirradiation on the emission yields under beam impact.

First of all, after 3–4 h of photoirradiation the oxyfluorfen molecule is no longer emitting under beam impact (total decay of

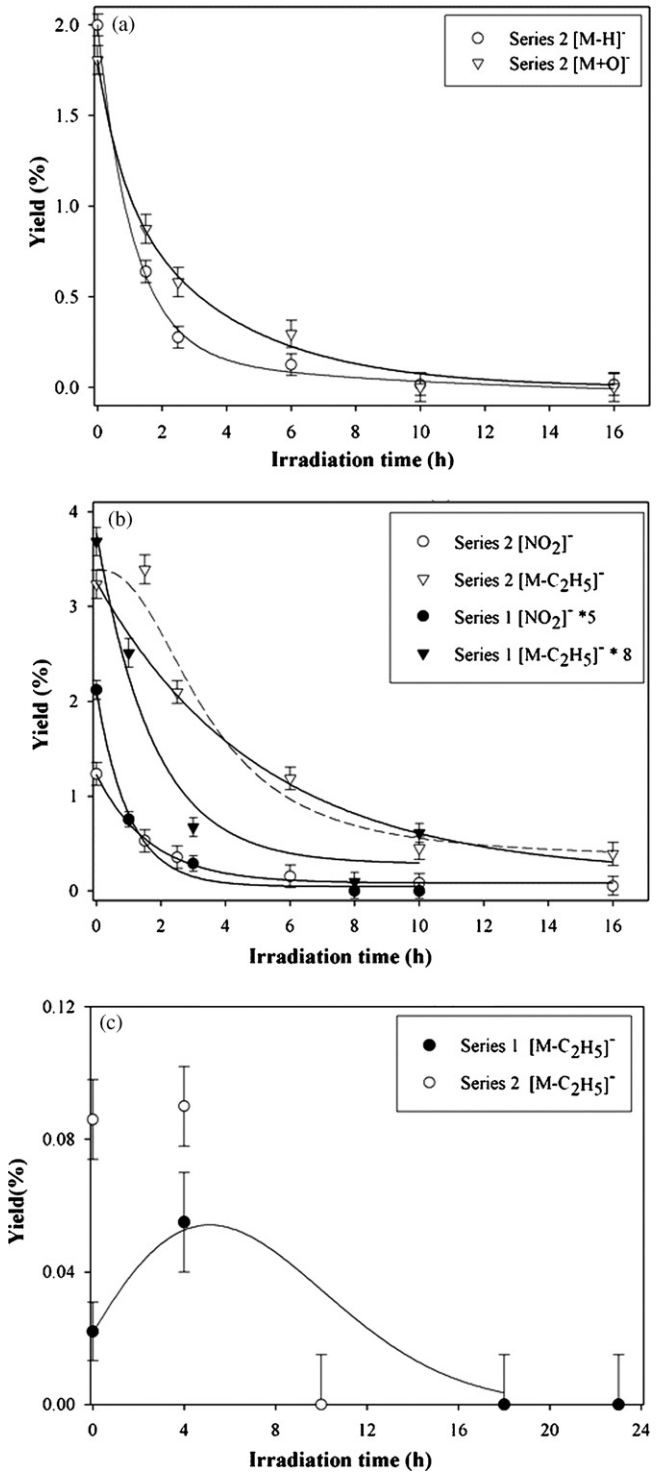

Fig. 6. Variation of the yield of the following ions as a function of suntest device exposure time: (a) $[M–H]^-$ and $[M+O]^-$, for the deposits (series 2 only). (b) NO_2^- and $[M–C_2H_5]^-$ for the deposits of the series 2 (open) and 1 (black). (c) $[M–C_2H_5]^-$ for the impregnated soil. Except for (c) the curves represent the best fit from which DT50 values can be extracted. The dotted curve of Fig. 6b has been drawn to emphasize the initial plateau of the series 2 variation of the $[M–C_2H_5]^-$ yield.

$[M–H]^-$ and $[M+O]^-$) which is in agreement with the extinction of the NO_2^- yield.

Other scissions must be considered to take into account the differences between series 1 and series 2 in the emission yields of Cl^-, $[M–C_2H_5]^-$ and of the fragments of m/z 182 and 195/197.

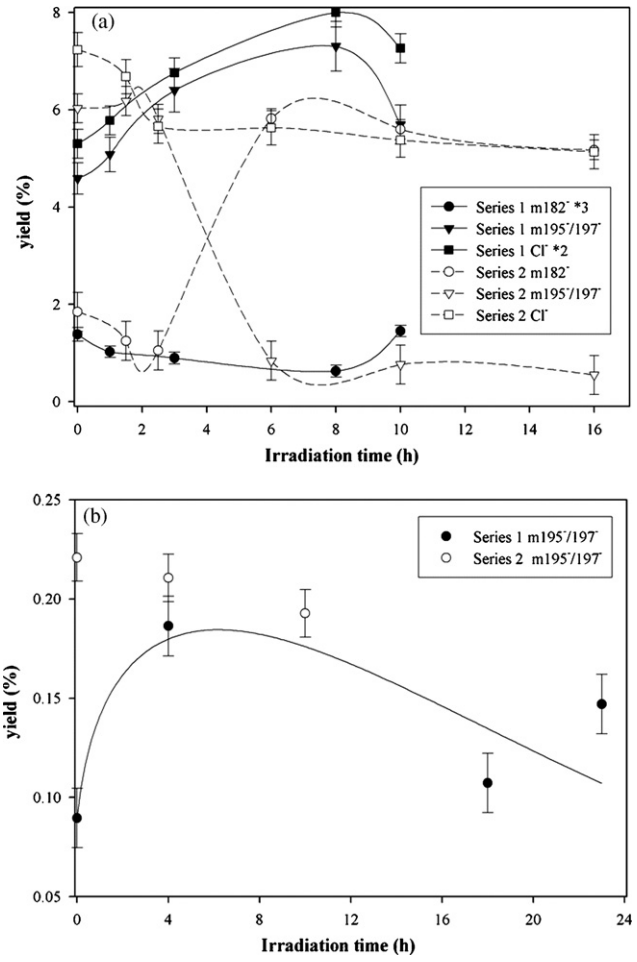

Fig. 7. Variation of the yield of the following ions as a function of suntest device exposure time: (a) Cl^- ion and the 2 main fragments of the oxyfluorfen molecule of mass 182 and 195–197 for the deposits of the series 2 and 1. (b) The main fragment of the oxyfluorfen molecule of mass 195–197 for the impregnated soil. Also indicated are the multiplicative factors used to fit the data (when applicable). The curves are only to guide the eye.

- The emission of Cl^- matches those of the fragment of m/z $195/197^-$ for both series before the steep decrease (occurring respectively at around 3 and 10 h).

When the emission of the fragment of m/z $195/197^-$ drops, those of Cl^- follows but reaches early a stabilisation level when it becomes to be emitted from the complement of the fragment of m/z 195/197 (m/z 182 – O): this gives some support to the change of the emission yield of the Cl^- related to a change in the chemical environment of Cl.

- The scissions leading to the departure of C_2H_5 and NO_2 should decrease the emission of the ion of m/z 182 except if its emission is facilitated by the photoirradiation and compensates these departures. It is interesting to note that the decay of $[M–C_2H_5]^-$ is slower than the one of NO_2^- (Fig. 6b) with a well marked rupture when the fragment yields start to evolve (series 2).

This behaviour as well as the fact that these yields still decrease while the $M182^-$ fragment yield increases is an indication that the corresponding scissions are less efficient when occurring on the fragment compared to the whole molecule.

In the case of series 1, the decrease is faster because the fragment of m/z 182 has a much lower yield and hence has a low compensation effect.

We still do not know what is responsible for the major difference between series 1 and 2: why the intensities of the emission yields are so different prior to the photoirradiation (although in the same proportion) and why their evolution as a function of exposure time seems shorter for series 2 before the sudden change in the photoirradiation induced bond breaking of the oxygen linking the two phi nuclei occurs: from the left side (on the sketch Fig. 2a) of the linking O atom to its right side.

The only comparison that can be made for the soil is for the fragment of m/z 195–197 as shown in Fig. 7b. As reported in Ref. [4], the complementary fragment of m/z 182 has not been considered due to interferences from the matrix itself.

As for the $[M–C_2H_5]^-$ ion, the two series data point disagree only for the initial values and after 4 h the general behaviour is closed to what was observed for the corresponding deposits of the series 1.

It remains from these results that the photodegradation process is strongly affected by the "quality" of the layer. It is not entirely clear that inhomogeneity is the only factor to invoke looking more closely to numbers. As a matter of fact, the yield of single characteristic ions or small fragments can be quite comparable to one series to another while the emission of the molecular ions may reach one order of magnitude difference. What is suspected is the morphology of the layer resulting from a crystallisation process already reported [4].

This feature has to be taken in consideration in the case of the soil that is a highly divided material and for which there is a poor sensitivity due to the nature of the medium.

It is however perfectly clear that as for the norflurazon case all the processes are significantly delayed when the pesticide is impregnating the soil instead of being deposited as a uniform layer.

3.2.2. Influence of UV component

3.2.2.1. Norflurazon. The main feature of the experiments performed without filtering the UV component is essentially a faster kinetics of degradation observed for the representative ions. This is evidenced in Fig. 8a where a comparison is made between the results with and without the UV component for the $[M–H]^-$ molecular ion and the breakdown product ion $[M–H+CH_3]^-$ in the case of a deposit.

The DT50 value of the molecular ion is indeed smaller (20 min), which corresponds to a reduction of a factor close to 4, even greater for the $[M+CH_3]$ breakdown product (38 min – reduction of 6).

From the $[M+185]^-$ ion (not represented) the reduction is found to be around 1.6.

The same trend is observed for the impregnated soil, as illustrated in Fig. 8b.

As for the deposit the decrease of $[M–H]^-$ (and of Cl^- not represented) is faster without UV filtering. However the decrease is not as important, the DT50 value of the molecular ion evolving from 250 to 100 min (factor of 2.5).

The effect is not so pronounced for the yield of the $[M–H+CH_3]^-$ ion, although it seems that a maximum is reached earlier and a faster decay is observed: any attempt to extract a DT50 value seems meaningless in that particular case.

Both the F^- and CF_2O^- ion intensities remain quasi stable.

3.2.2.2. Oxyfluorfen. The contribution of the UV component to the photodegradation of the oxyfluorfen has only been possible for a single series of experiments and for a limited number of samples (3).

As already mentioned the deposits may suffer from lack of reproducibility as attested by the differences of the yield values at T_0 (prior to exposure) for samples prepared in supposedly identical conditions. This is apparent from Figs. 9–11.

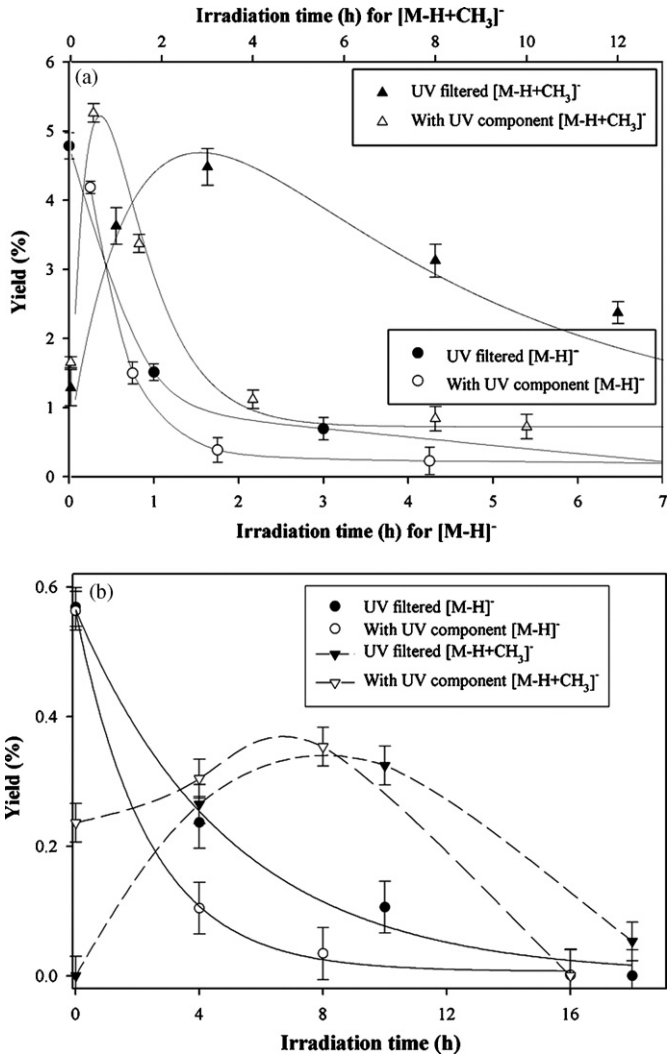

Fig. 8. Comparison of the yield variation of the ions $[M–H]^-$ and $[M–H+CH_3]^-$ as a function of the exposure time of the suntest device UV unfiltered (open symbols) and UV filtered (black symbols). (a) For the deposit. (b) For the soil. DT50 values are deduced from the fitting curves represented as solid lines. Other curves are just to guide the eye.

However, these differences do not affect the general trend of the variation of the yield of ions like CF_2O^-, CNO^-, Cl^- and F^- which was found slowly increasing as a function of the exposure time for the light spectrum UV filtered.

As shown in Fig. 9a, the most important departure from this behaviour is observed for Cl^- and F^- where a maximum of the emission seems to occur earlier.

For the impregnated soils, in addition to a reduced sensitivity for the ion emission compared to deposits, the bad reproducibility of the samples makes the study of the effect of the UV component in the photodegradation process more difficult.

However, for the limited number of ions presented, there is a definite similarity with what was observed for the deposits.

As a matter of fact, when the UV component is not filtered the F^- and Cl^- ion emission that was very slowly increasing as a function of the exposure time then seems to reach a maximum (Fig. 9b). As another trend also systematically observed, this maximum occurs later for the soil than for the deposit (a 3–4 times difference).

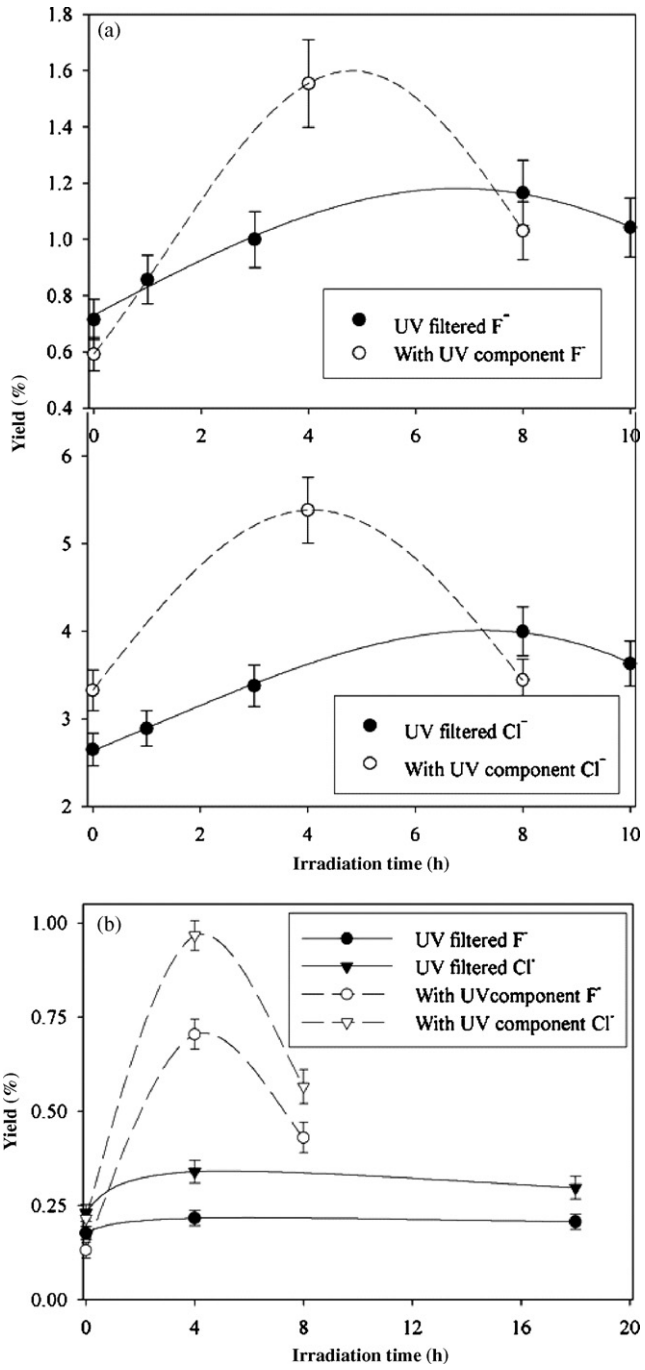

Fig. 9. Variation of the yield of the ions Cl^- and F^- as a function of the exposure time of the suntest device, UV filtered (black symbols) and unfiltered (open). (a) For the deposits. (b) For the soil. The curves are only to guide the eye.

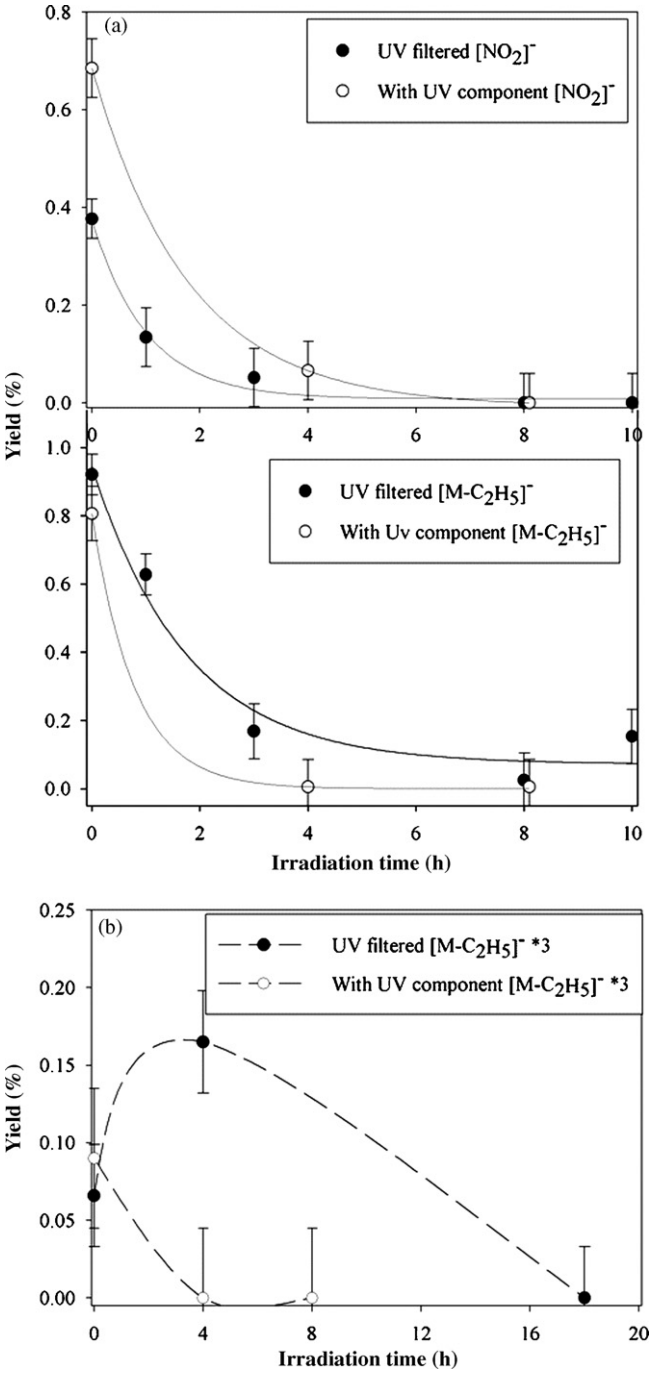

Fig. 10. Variation of the yield of the ions NO_2^- and $[M–C_2H_5]^-$ as a function of suntest device exposure time, UV filtered (black circles) and with UV component (open circles). (a) For the deposits. (b) For the soil (only for the $[M–C_2H_5]^-$ ion). DT50 values are deduced from the fitting curves represented as solid lines. Other curves are just to guide the eye.

For the ions with a yield strongly decreasing the comparison between samples with and without UV filtering has only been possible for the series where the $[M–H]^-$ and $[M+O]^-$ yields were initially low and accordingly undetectable after 1 H irradiation with UV component. Fortunately this trend towards the same accelerated decrease can be observed from the variation of NO_2^- and $[M–C_2H_5]^-$ as represented in Fig. 10a.

Although the number of data is limited for the samples irradiated with the UV component the related variations can be fitted by an exponential decay from which the following DT50 values can be extracted:

- For $[M–C_2H_5+H]$: 33 min compared to 80 min without the UV component, i.e., a decrease of a factor 2.4.
- From the NO_2^- yield variation, from 45 min to 75 min, i.e., an increase of a factor 1.6.

For the soil and despite the bad statistics, the UV effect is spectacular for the $[M–C_2H_5]^-$ ion emission that is undetectable after 4 h of exposure to the suntest device UV unfiltered, as shown in Fig. 10b.

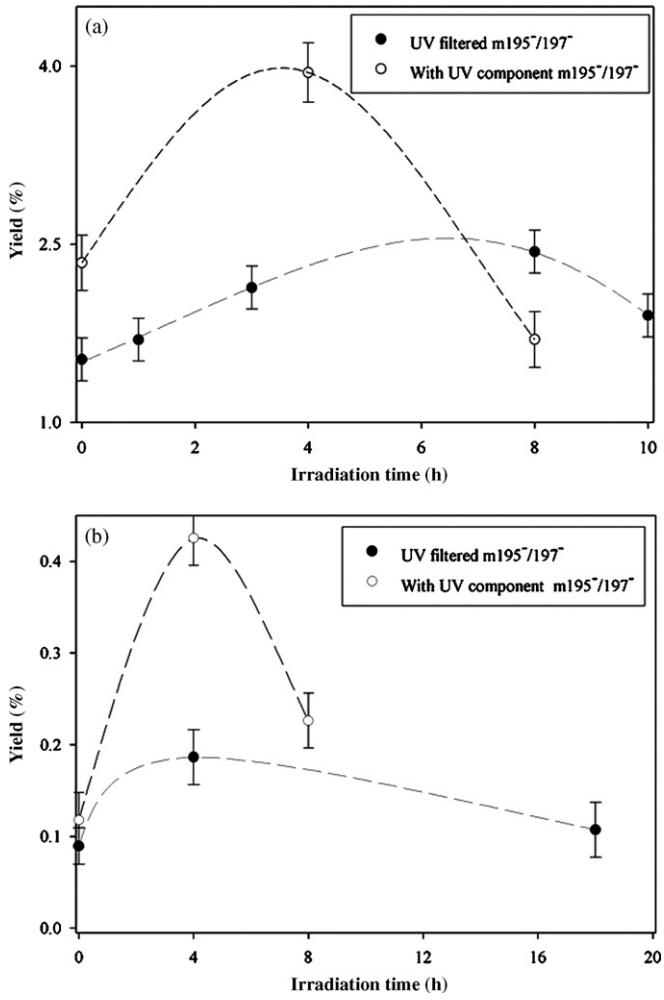

Fig. 11. Variation of the yield of the main fragment of the oxyfluorfen molecule of mass 195–197 as a function of suntest device exposure time – UV filtered (black circles) – with UV component (open circles). (a) For the deposit. (b) For the soil. The curves are just to guide the eye.

For the fragments of *m*/*z* 182 and 195–197, we have already reported in Section 3.2.1.2 that their behaviour depends in some way on the conditions of preparation as well as on "natural" degradation effects, not yet understood. As we can see from Fig. 11a, for mass 195/197, the deposits of this particular series have been probably prepared in comparable – yet uncontrolled – conditions, since the effect of the UV component is qualitatively comparable to what has been previously observed. The same qualitative difference can be observed for the soil as shown in Fig. 11b.

4. Discussion of degradation parameters

The most important results concerning the photodegradation of the two pesticides of interest are summarized in Table 1 in terms of half-lives from the yield decay of the most representative ions. These half-lives correspond to DT50 values when the ion is characteristic of the pesticide molecule or its identified degradation product.

The comparisons are particularly interesting between substrates (Soil/Al effect) with or without UV filtering (w. or wo.) or in terms of UV effect for soil or Al substrate.

For norflurazon it can be seen that the Soil/Al effect is about 3.5 for the molecule (the same for the decay of Cl^- and $[M+Cl]^-$ ions) and about 2 for the breakdown product (BP) $[M+CH_3]$ (same for $[M+185]^-$ ion), this with UV filtering (around 5 for the molecule with UV component).

The UV component effect is about 3.8 for the molecule and more intense (around 5) for the breakdown product, less on soil (around 2.5) for the molecule.

For oxyfluorfen there is a lack of data for the soil samples and the Soil/Al effect is only qualitatively observed. On the other hand, the UV component effect is also observed but less pronounced than for the other pesticide (around 1.8 for the molecule on Al substrate).

Of course the degradation mechanism appears to be quite different for norflurazon and oxyfluorfen. No new ions are observed in the later case, the molecule being essentially dissociated in its two main fragments of *m*/*z* 182 and 195/197. For norflurazon new ions are produced due to rearrangements between the molecule and the CH_3 group and the main fragment of mass 185. Such a behaviour as well as the Cl disappearance (not observed in the oxyfluorfen case) raise the question of a proximity effect between molecules and the bulk nature of the norflurazon deposit disregarding the substrate (metal plate or heterogeneous soil substrate). Then, it would be interesting to consider future experiments, on the one hand, with monolayer or sub-monolayer samples deposited on a passive substrate to analyze the degradation of the molecule, and, on the other hand, in matrices allowing to separate the effect of the environment. In particular, the role of water could be investigated from a solution irradiated before deposition and drying.

Table 1
Summary of degradation parameters (DT50 values and half-lives decay) for norflurazon and oxyfluorfen obtained from deposits on Al substrates and soil impregnated samples, irradiated with (w.) and without (wo.) UV component.

	Alu wo. UV	Alu w. UV	Alu wo./w. UV	Soil wo. UV	Soil w. UV	Soil/Al wo. UV	Soil/Al w. UV
Norflurazon							
$[M-H]^-$	66 min	20 min	3.3	250 min	100 min	3.3	5
$[M+Cl]^-$	36 min	12 min	3.0	126 min	64 min	3.5	5.3
Cl^-	151 min	70 min	2.2	545 min	171 min	3.6	2.4
$[M-H+CH_3]^-$	245 min	38 min	6.4	600 min	Unable	2.4	
$[M+185]^-$	720 min	450 min	1.6	1200 min	Unable	1.7	
Soil/Al effect	wo. UV: 3.5 for molecule, 2 for BP w. UV: 5 for molecule			UV effect	On Al: 3.8 for molecule, around 5 for BP On soil: 2.5 for molecule		
Oxyfluorfen							
$[M-H]^-$	55 min	30 min	1.8	Not detected	Not detected	Unable	Unable
$[M+O]^-$	85 min	48 min	1.8	Not detected	Not detected	Unable	Unable
$[M-C_2H_5]^-$	80–230 min	33 min	2.4–6.96	Unable	Unable	Unable	Unable
NO_2^-	45–64 min	74 min	0.6–0.86	Not detected	Not detected	Unable	Unable
UV effect	On Al: 1.8 for molecule, "Observed reduction" for other ions On soil: molecule not detected, "Observed increase" for other ions						

5. Conclusion

A coherent description of the photodegradation process of the two pesticides norflurazon and oxyfluorfen has been presented both for a deposit onto a metallic substrate and for a soil impregnated with the product.

Degradation parameters have been extracted from the yield variation of ions representative of the molecules or breakdown products. Such data are of paramount importance to extend such studies to the role of usual parameters such as biological activity, water interaction, etc.

For both pesticides the comparison between deposits and soils indicates clearly that the degradation is slower in the latter case. Numbers can only be obtained from the former: DT50 values are increase by a factor of 3.5 for the norflurazon molecule, of about 2 for its breakdown products. These values are in agreement with the decays of other ions.

As expected, the degradation is faster when the UV of the sunlight is unfiltered. This is also observed for the oxyfluorfen although at a lower level (twice less).

Of course, it is easier to assign a ion to a breakdown product when it has been separately identified such the demethylnorflurazon [11]. Extraction techniques will be extremely useful for their obtention as deposits for example, in order to confirm the present data. In any case this step seems essential to get new data on more complex degradation conditions.

From the comparison between deposit and impregnated soil it is clear that the differences do not only rely to the nature of the substrate. The soil is a medium where the photodegradation process is restricted to the surface with a large reservoir inside of more or less intact pesticide material. Such a strong gradient plays a major role for the future of the pesticide, especially considering the role of the water runoff. For the type of samples processed in this study (pellets) it is feasible to have a kind of in-depth analysis by probing the cross-section (beam spots of the order of one tenth of a millimeter).

The picture is not so clear for the oxyfluorfen case where experimental problems have to find solutions. A better homogeneity of the deposits could be achieved from a technique such as electrospray. For the soil impregnation we suspect segregation effects arising from the high concentration levels required for the detectability. Then, in order to go behind qualitative informations there is a strong need for a better sensitivity. This has to do with the use of more efficient projectiles such as cluster ions [12] or more efficient detection techniques such as O-TOF [13].

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