

Research Article

Clay and Soil Photolysis of the Pesticides Mesotrione and Metsulfuron Methyl

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Photolysis may represent an important degradation process of pollutants at the surface of soil. In the present work, we report a detailed study on the degradation of two pesticides: mesotrione and metsulfuron methyl using a sunlight simulator. In a first step, we studied the photochemical behaviour at the surface of clays from the kinetic as well as from the analytical point of view. In both cases, the quantum yields were found to be higher when compared to those obtained in aqueous solutions. The effect of iron(III), water, and humic substances contents was studied. In the former cases, an increase of the degradation rate was observed while an inhibition was observed with the latter owing to a filter effect phenomenon. In a second step, we studied the photodegradation at the surface of natural soil and identified the generated byproducts. They appear to mainly arise from photohydrolysis process.

1. Introduction

Chemicals such as pesticides can be introduced into the environment as a result of their application for plant protection. Thus, the contamination of groundwater, rivers, soils, and also atmosphere is an inevitable effect of their application. The negative ecological consequences related to these contaminants are often assigned to their residence time and bioavailability. Owing to these environmental effects, there is an increase of the research activities toward the methods which could help in the study of the fate and also the elimination of such substrates. In recent years, various methods for water or air purification as well as soil decontamination have been developed including chemical, electrochemical, or photochemical processes [1–5]. In several cases, sunlight degradation may represent one of the main destructive pathways for pesticides after their application into the environment. Since several kinds of these contaminants present absorption spectra with a nonnegligible overlap with that of solar light,

an inexhaustible source, the photochemical process becomes of great interest. Under such conditions they can easily undergo photochemical transformation upon exposure to the solar light by direct absorption, namely, direct process [4, 6, 7]. This also leads to the formation of various by-products that can be more harmful than the parent compound. In the case where the contaminants do not absorb solar light, they may still undergo phototransformation through indirect reactions. In this case, other substances, added or naturally present in a specified medium, play the role of photoinducers or/and photosensitizers [8–12]. Thus, reactive species, such as excited states and reactive oxygen species (ROS), permit the degradation of the target pollutants.

Indirect photochemical processes may also occur at the surface of soils owing to the presence of organic matter originating from plant debris in various stages of decay [9, 10]. Such substance may contribute for the degradation of the pesticide through the formation of reactive species, such as

hydroxyl radicals [13] or singlet oxygen [14] or be involved as inhibitors by a screen effect phenomenon.

These processes may of course occur in aqueous solutions, in the atmosphere, on plant leaves, and at the surface of soils. The latter medium can be considered as an ultimate reservoir for pesticides whether they are applied directly or received indirectly from spray drift and residues of treated sites. It is worth noting that in sunlight exposed sites, photochemical reactions at the atmosphere-soil interface may represent important degradation pathways. They may easily dominate other degradation pathways that are normally favoured in the bulk soil [15]. Since soil support is a highly heterogeneous and unmixed medium compared with solution, it is obvious that several photophysical and/or photochemical processes as well as spectroscopic features will then be affected. Thus, pesticide fate in the soils has received much attention due to its effect (dissipation, bio- and photodegradation, transfer process, adsorption processes, etc.). Concerning the photochemical transformations, direct photolysis depends on the light penetration which cannot be precisely defined. Due to light attenuation, the direct photolysis rates are slower when compared to solution [16]. The soil texture may also be of great importance in the degradation process of pesticides. In the case of quinalphos, for example, see Gonçalves et al. [17].

In the present paper we examined the photolysis of two pesticides: mesotrione and metsulfuron methyl (Figure 7) at the surface of the clay Kaolinite, taken as a model surface, and also at the surface of soils with and without organic matter.

Mesotrione is a member of the triketone family of herbicides which is developed for use in maize culture as a substitute for atrazine [18]. It is absorbed both by roots and foliage which allows its use as preemergence or postemergence herbicide. Its photochemical behaviour was deeply studied in pure and natural waters upon simulated solar light irradiation [19]. The main generated by-products are 4-(methylsulfonyl)-2-nitrobenzoic acid, 1,3-diketo 3-(2-nitro-4-methylsulfonylphenyl)butanoic acid, and 5,7-diketo-7-(2-nitro-4-methylsulfonylphenyl)-heptanoic acid (Figures 8 and 9).

Metsulfuron methyl belongs to the sulfonylurea group which presents an important role in modern agriculture because of its significant action in plant protection. It presents a high selectivity against a wide range of plants. As has been already reported for most sulfonylurea products, in aqueous solutions, hydrolysis was shown to be a significant pathway for their degradation [20–22] (Figure 10). This is obviously owing to the presence in their molecular structure of many functional groups that are subject to hydrolytic reactions. To our knowledge, their photochemical behaviour at the surface of soil is not known. However, studies have been reported on glass surface under sunlight and ultraviolet (UV) light [23] where the half-lives of metsulfuron methyl under UV light and sunlight were found to be 0.5 and 7.8 days, respectively. The major products were identified as methyl-2-sulfonylamino benzoate, 2-amino-6-methoxy-4-methyltriazine, and saccharin (O-sulfobenzoimide) (Figure 11).

2. Experimental Section

All the used reactants were of the highest grade available. They were used as received. Mesotrione and metsulfuron methyl were from Riedel de Haën. The abbreviations mentioned in Figure 7 were used throughout all the text.

Kaolinite, iron(III) perchlorate, and humic acid were purchased from Fluka, Bentonite, and Montmorillonite from Aldrich. All solutions were prepared with deionised ultrapure water which was purified with Milli-Q device (Millipore) and its purity was controlled by its resistivity. Soil sample (top 5 cm) was collected nearby Orange region (South of France). Its characteristics are pH = 7.7, natural organic matter 3.2%, Clay 31%, Limon 44.2%, and sand 24.8%. It was dried in the oven at a temperature of 80°C and sterilized by 5 autoclaving cycles for two days ($P = 2$ bar, $T = 121^\circ\text{C}$). The removal of the natural organic matter (NOM) was carried out on sterilized soil. 45 g of soil was mixed and stirred with 100 mL NaOH (12 M) at room temperature for 1 h. Then, 400 mL of pure water was added for washing and the mixture was stirred for 30 min and decanted for another 30 min. The supernatant was afterwards removed and another 400 mL of water were added for washing the solid. Such water cleaning step was repeated 4 times and then the solution was neutralized by the addition of perchloric acid solution (1.0 M) in order to reach a pH around to 6.2–6.9. After such procedure the amount of organic carbon was estimated to be about 0.5%. The soil sample was spiked with a methanol solution of the pesticide at a known concentration, mixed vigorously, and then air-dried. 200 mg of this mixture was then deposited in a Teflon mold supported by a glass slide to obtain a film of roughly 1 mm thickness with a flat surface.

The preparation of the clay layer (2.5 cm × 1.5 cm) was performed on a Pyrex glass as described in the literature [24]. In our case, the clay slurry with the desired amount of clay and defined concentration of substrate (mesotrione or metsulfuron methyl) was prepared in methanol. After deposition of a known volume on the Pyrex glass, the slurry was allowed to dry overnight at room temperature. The layer thickness of the sample was determined according to the dry amount of Kaolinite deposited on the Pyrex plate, the surface area, and the bulk density, ρ_{bulk} , of the layer ($\rho_{\text{bulk Kaolinite}} = 1.8$ [25]). With this procedure, layers of various thicknesses were obtained: from 15 μm to 200 μm . The irradiation of the dry sample was performed by using a Pyrex tube (roughly 20 cm³) as a reactor. For each irradiation time, two different sample plates were used. The layer was quantitatively collected and mixed with 2 mL of methanol. The mixture was gently agitated for 10 minutes at room temperature. After centrifugation at 3500 rpm for 10 minutes, the HPLC analysis showed that more than 95 % of product recovery was obtained.

Sunlight simulated experiments were conducted using a Suntest CPS photosimulator (Atlas) equipped with a Xenon lamp. This contains a glass filter restricting the transmission of wavelengths below 290 nm. The equipment was used with a setting of 500 W/m². In order to work at constant temperature (roughly 20°C), cold water flowed through the bottom of the Suntest photosimulator. Prior to kinetic and

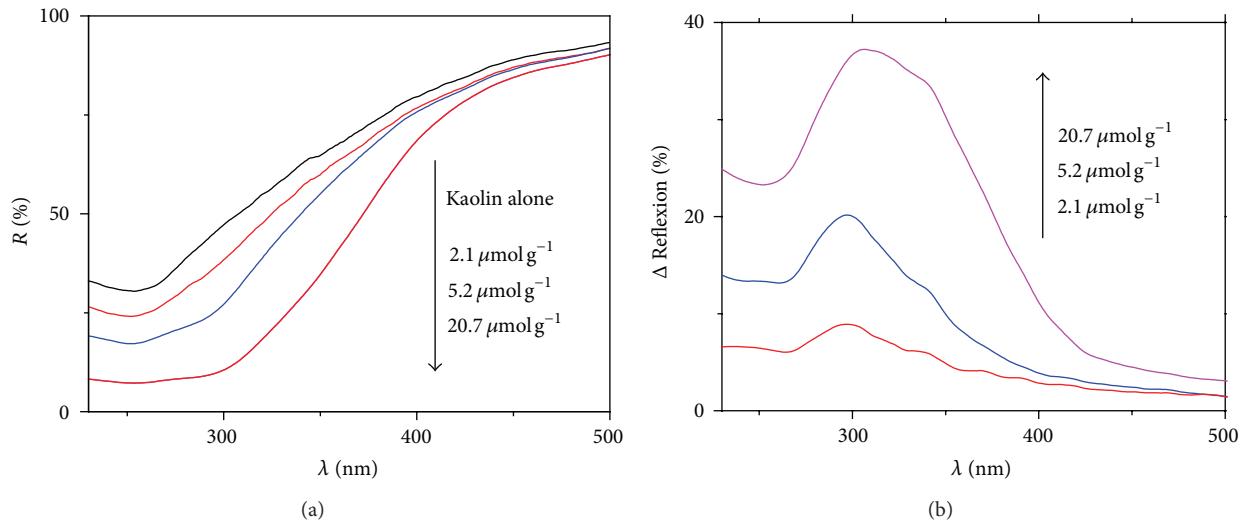


FIGURE 1: (a) Diffuse reflectance of mesotrione at the surface of Kaolinite as a function of concentration. (b) The reflection spectrum owing to the organic compound mesotrione. Film thickness: 200 μm .

analytical measurements, actinometries using p-nitroanisole as chemical actinometers [26] and also by using a radiometer (Ocean Optics QE65000) were undertaken in order to check for the uniformity of light distribution within all the surface of Suntest simulator. Within the experimental error (less than 4%), the light emitted from the Xenon lamp was found to be perfectly homogeneous.

The transformation of the substrates and the formation of the byproducts were monitored by analytical HPLC using a Waters apparatus equipped with a 996-photodiode array detector. The HPLC analyses were conducted by using a reverse phase Merck column (Spherisorb ODS-2, 250 mm \times 4.6 mm, 5 μm). The flow rate was 1.0 mL min^{-1} and the injected volume was 50 μL . The mobile phase consisted of acidified water (acetic acid 0.01%) and acetonitrile (7/3 by volume) in the case of mesotrione and water (acetic acid 0.01%) and methanol (6/4 by volume) for metsulfuron methyl.

UV-Vis diffuse reflectance and transmittance of clay layers were recorded with a Cary 300 scan (Varian) equipped with integrating sphere (DRA-CA-30I; 70 mm; Varian). The spectra were recorded within the range 230–800 nm. The recorded reflectance was corrected by using Spectralon's (Labsphere) absolute reflectance.

LC/MS studies were carried out with a Waters Q-TOF Micro, mass spectrometer equipped with a Waters Alliance HPLC system from CRMP Center (Centre Regionale de Mesures Physique) at the University Blaise Pascal. It is equipped with an electrospray ionisation source (ESI) and a Waters photodiode array detector. Each single experiment permitted the simultaneous recording of both UV chromatogram at a preselected wavelength and an ESI-MS full scan. Data acquisition and processing were performed by MassLynx NT 3.5 system. Chromatography was run using a Nucleosil column 100-5 C18 ec (250 \times 4.6 mm, 5 μm). Samples (5–10 μL) were injected either directly or after evaporation of the solvent for better detection. The following gradient program

TABLE 1: Gradient program.

| Time, minutes | Initial | 3 | 13 | 20 | 30 |
|---------------|---------|----|----|----|----|
| % A | 95 | 80 | 80 | 5 | 95 |
| % B | 5 | 20 | 20 | 95 | 5 |

was used by employing water with 0.4% acetic acid (A) and acetonitrile (B) at 1 mL min^{-1} (Table 1).

3. Results

Reflection-Diffuse Spectrum. The absorption spectrum of mesotrione in aqueous solution at pH = 6.5 shows an intense band with a maximum at 255 nm and a shoulder at 285 nm more likely attributed to the $\pi-\pi^*$ and $n-\pi^*$ electronic transitions, respectively [19]. When the diffuse-reflectance spectrum is recorded at the surface of dry Kaolinite with a film thickness of 200 μm , a decrease of the percentage of reflected light was observed at $\lambda < 500$ nm when the concentration of mesotrione increased within the range 2.1–21.0 $\mu\text{mol g}^{-1}$ (Figure 1(a)). By taking into account the diffuse-reflectance owing to the Kaolinite support, a well-defined and large band was observed with a maximum at 299 nm (Figure 1(b)). A close analysis of the spectrum also indicates the presence of a shoulder at roughly 330 nm. When compared to the UV spectrum recorded in aqueous medium [19], an important bathochromic shift of about $\Delta\lambda = 44$ nm was observed for both electronic transition bands. It is worth noting that the absorption band appears to be broader when the concentration of mesotrione increased. The observed bathochromic shift when comparing spectra in aqueous solutions and at the surface of Kaolinite is more likely related to the interaction between the organic substrates inserted within the various sites of Kaolinite. However, the observed broad band is owing to the various environments

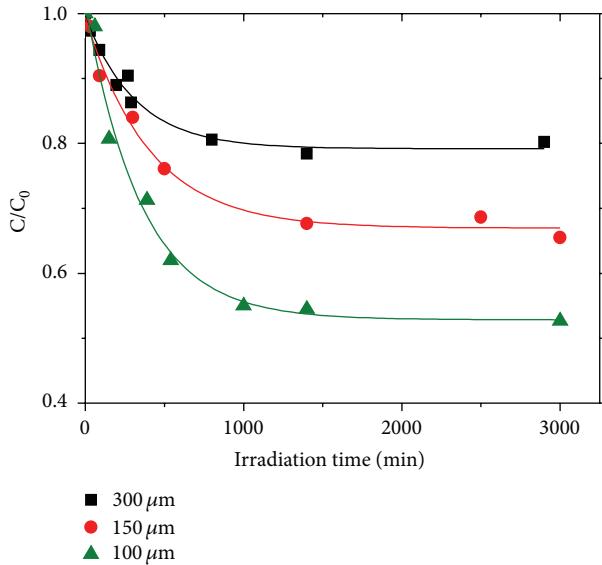


FIGURE 2: Degradation of mesotrione at the surface of various thicknesses of Kaolinite. Irradiation performed in Sunlight simulator. [Mesotrione] = 5.2 $\mu\text{mol g}^{-1}$.

of mesotrione that can be present in various sites but also in a multilayer disposition as observed with other organic substrates [24, 25]. It should be noted that similar changes were observed by using montmorillonite and bentonite as clays supports where the bathochromic shift was evaluated to be 35 and 39 nm, respectively. In the case of metsulfuron methyl, similar changes were observed within the concentration 3.5–21.0 $\mu\text{mol g}^{-1}$. The bathochromic shift was evaluated to 20 nm.

Photodegradation at the Surface of Kaolinite. Plates containing films of various and controlled thicknesses of a mixture Kaolinite/mesotrione were irradiated with sunlight simulator. The photochemical disappearance of mesotrione, extracted from Kaolinite using methanol, is shown in Figure 2. The conversion was clearly dependent on the layer thickness. It increased when the thickness decreased in complete agreement with the light attenuation within the clay layer. The degradation was fitted using a first-order kinetics and the rate constant was evaluated to be $4.0 \times 10^{-3} \pm 0.2 \times 10^{-3} \text{ min}^{-1}$, $3.0 \times 10^{-3} \pm 0.5 \times 10^{-3} \text{ min}^{-1}$, and $2.5 \times 10^{-3} \pm 0.3 \times 10^{-3} \text{ min}^{-1}$ for 100 μm , 160 μm , and 300 μm , respectively. It should be noted that by using a layer thickness of roughly 20 μm , a conversion of about 90 % was reached within 6 hours irradiation time. Under these conditions, the half-life time was estimated to be about 1.5 hour. The quantum yield of degradation was evaluated by using the method reported in the literature [25]. It was estimated under our experimental conditions to 5.0×10^{-4} which is approximately one order of magnitude higher than that obtained in aqueous solution [19]. This is more likely owing to several factors such as (i) change in the chemical environment; (ii) more efficient absorption of excitation light due to the change in the absorption spectrum, namely, the bathochromic shift. Similar

TABLE 2: The effect of moisture, iron(III), and humic substances at the surface of Kaolinite on the photodegradation rate constant of mesotrione and metsulfuron methyl; layer thickness = 100 μm ; (organic compound) = 5.2 $\mu\text{mol g}^{-1}$. Irradiation was performed with a Sunlight simulator.

| Compound | Dry layer $\times 10^{-2}$ min $^{-1}$ | Moisture $\times 10^{-2}$ min $^{-1}$ | Iron(III); 1.0 wt% $\times 10^{-2}$ min $^{-1}$ | Humic acids; 2.0 wt% $\times 10^{-2}$ min $^{-1}$ |
|--------------------|--|---|--|--|
| Mesotrione | 0.40 | 0.92 | 0.73 | 0.12 |
| Metsulfuron methyl | 2.2 | 18.0 | 4.9 | 1.3 |

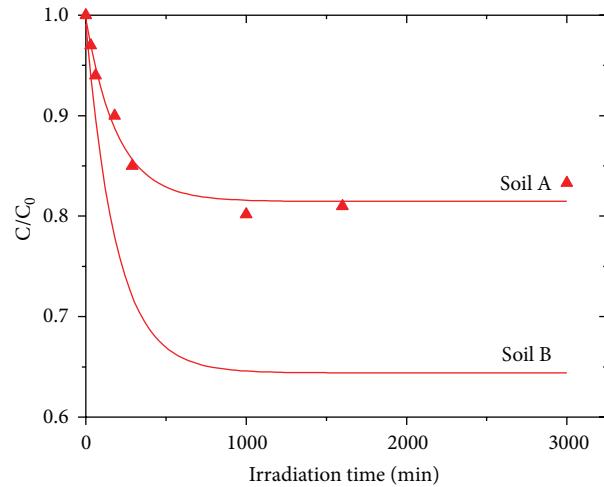


FIGURE 3: Degradation of mesotrione at the surface of soil A and soil B. Irradiation performed in Sunlight simulator. [Mesotrione] = 5.2 $\mu\text{mol g}^{-1}$. Thickness 1 mm.

behaviour was observed with metsulfuron methyl for which the quantum yield was estimated to be 8.0×10^{-3} compared to 3.0×10^{-3} in aqueous solution.

Effect of Moisture, Humic Substances, and Iron(III) Contents. The effect of the main components of soil such as moisture, humic substances, and iron(III) was studied. All the results are gathered in Table 2. The percentage of moisture was increased by adding 100 μL of pure water at the surface of the sample (layer = 100 μm). This was repeated after each 1 hour of irradiation. For mesotrione, the rate constant was estimated to be $9.2 \times 10^{-3} \text{ min}^{-1}$ which is 2.5 times higher than in relatively dry conditions, while, for metsulfuron methyl, an increase by one order of magnitude was observed. This can be explained first by a change in the chemical environment permitting the occurrence of some new reaction pathways that could be minor on dry clays and also by a change in the light penetration as well as organic compounds diffusion into humid Kaolinite [25]. It is important to note that under these conditions, no thermal degradation was observed when the sample was kept in the dark.

The addition of iron(III) species at a concentration of 1.0 wt% permitted a better degradation of both compounds

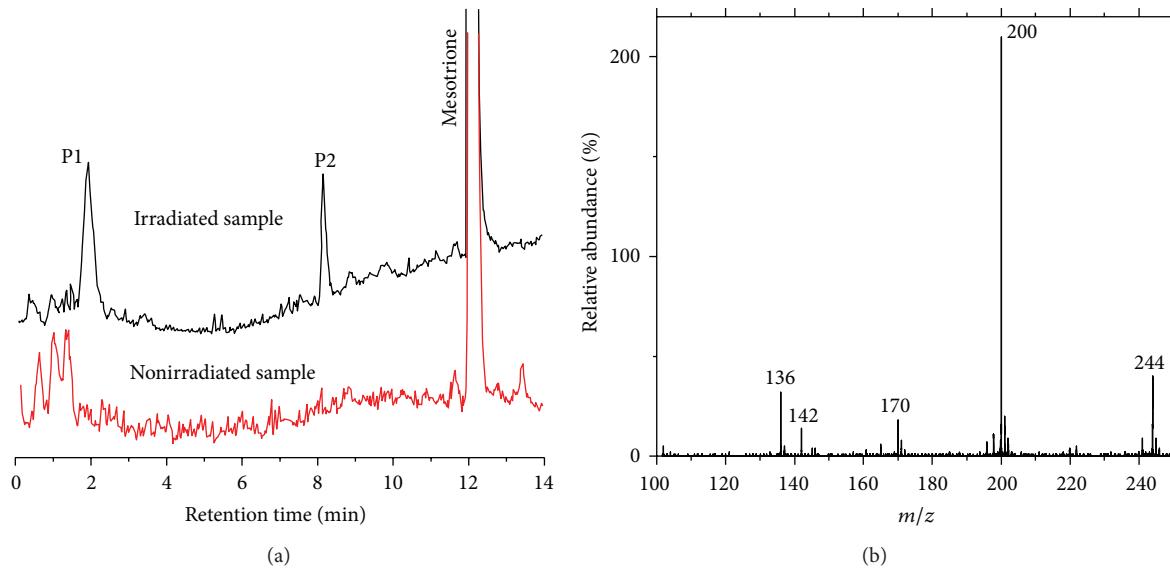


FIGURE 4: (a) HPLC chromatogram of a solution obtained by extraction with methanol of an irradiated mixture mesotrione/Kaolinite at $\lambda_{\text{max}} = 250 \text{ nm}$ using a gradient program (see Section 2). (b) Mass spectrum of product P1. [Mesotrione] = $5.2 \mu\text{mol g}^{-1}$. Irradiation was performed in a Sunlight simulator.

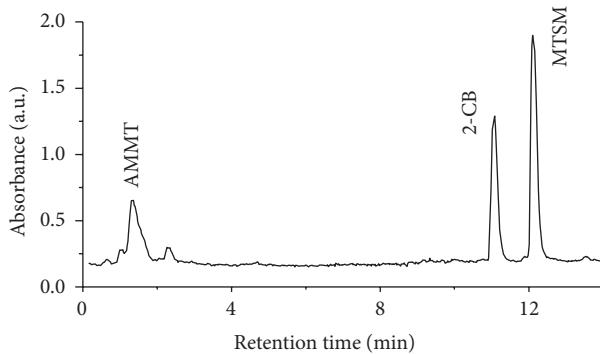
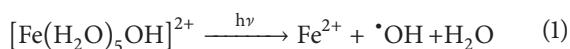


FIGURE 5: HPLC chromatogram of a solution obtained by extraction with methanol of an irradiated mixture MTSM/Kaolinite [MTSM] = $5.2 \mu\text{mol g}^{-1}$. Detection at $\lambda_{\text{max}} = 250 \text{ nm}$ using a gradient program (see Section 2). Irradiation was performed in a Sunlight simulator.

with an increase by a factor of 2 for mesotrione and 6 for metsulfuron methyl. This is more likely due to direct excitation of the substrate as observed above but also the involvement of photoinduced reactions that represent additional efficient processes as already observed with the irradiation of fenamiphos [27] as well as azinphos methyl [28] at the surface of Kaolinite. In fact iron(III), more likely as aqua complex species, absorbs the used excitation light ($>290 \text{ nm}$) and permits the generation of the hydroxyl radical species (1) [29–31]. The latter species is known for its efficient reactivity toward the majority of the organic compounds [32]:



The effect of humic substances was studied at a concentration of 2.0 wt% that corresponds to an average content

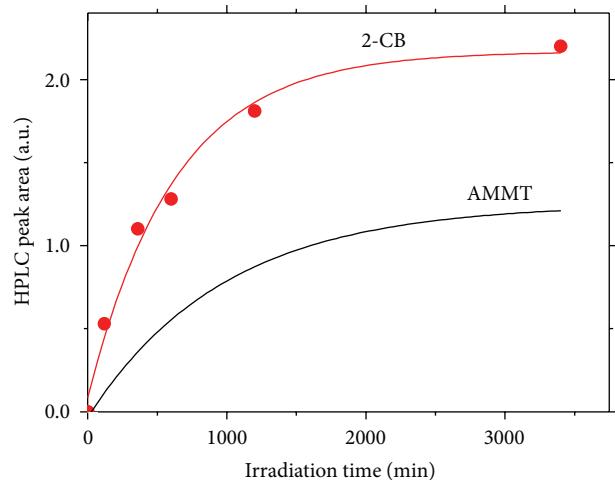


FIGURE 6: Formation of products 2-CB and AMMT upon excitation of metsulfuron methyl (MTSM) at the surface of Kaolinite. MTSM/Kaolinite [MTSM] = $5.2 \mu\text{mol g}^{-1}$. Detection at $\lambda_{\text{max}} = 250 \text{ nm}$. Irradiation was performed in a Sunlight simulator.

of humic substances in soil. Under these conditions, the degradation occurred but the rate significantly decreased by a factor of roughly 3 in the case of mesotrione and a factor of 2 for metsulfuron methyl. This detrimental effect may be explained by (i) an efficient interaction of humic acids with the excited states of the organic compounds leading to their efficient deactivation through electron or/and energy transfer processes and (ii) a competition in light absorption owing to the increase of the absorbance in the presence of humic substances as already observed with the irradiation of fenamiphos [27] as well as azinphos methyl [28] at the surface of kaolinite. It should be pointed out that dark control

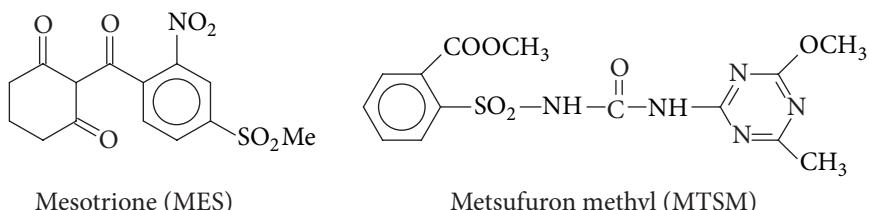
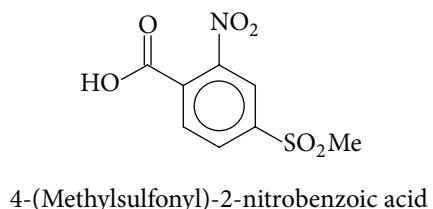


FIGURE 7



4-(Methylsulfonyl)-2-nitrobenzoic acid

FIGURE 8

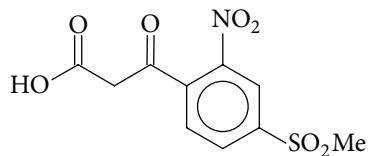
1,3-Diketo-3-(2-nitro-4-methylsulfonylphenyl)
propanoic acid

FIGURE 9

experiments showed that no degradation of both substrates was observed in the presence of iron(III) species or humic substances.

Photodegradation at the Surface of Soil. The photodegradation by excitation with a sunlight simulator of both pesticides (at $5.2 \mu\text{mol g}^{-1}$) was also explored at the surface of natural soil. It was performed using soil with (soil A) and without natural organic matter (soil B) (see Section 2). As shown in Figure 3, the degradation of the pesticides also occurred at the surface of the used soil with a rate constant that depends on the amount of NOM. This was evaluated to be $5.8 \times 10^{-4} \text{ min}^{-1}$ and $1.4 \times 10^{-3} \text{ min}^{-1}$ with soil A and soil B, respectively. This aspect is directly linked to the amount of NOM in the sample. The more organic matter we have, the lower rate constant is obtained as already observed in the presence of humic substances. It is important to note that the conversion percentage rapidly levelled off and no degradation is observed after 1000 minutes irradiation time. These conclusions suppose that the NOM removal procedure did not change soil mineral characteristics.

Photoproducts Analyses. The analysis of the mixture, extracted with methanol, was performed by using HPLC and HPLC/MS techniques. Figure 4 presents a chromatogram that was obtained for mesotrione at the surface of Kaolinite.

Besides the parent compound, it shows the presence of two main products, P1 and P2, with shorter retention times indicating the formation of more polar compounds.

Product P1 presents a retention time of about 2 minutes. By LC/ESI in negative mode, its molecular ion is $m/z = 244$. It is similar to that obtained by direct excitation of mesotrione in aqueous solution and corresponds to 4-(methylsulfonyl)-2-nitrobenzoic acid (MNBA) [19]. It leads by decarboxylation process to an intense ion at $m/z = 200$ (Figure 4(b)).

Product P2 has a retention time of 8.8 minutes and presents an intense ion at $m/z = 242$. Such ion appears to be a daughter ion from the parent ion $m/z = 286$ via a decarboxylation process. This product was also observed when mesotrione was irradiated in aqueous solution [19]. It was identified as 1,3-diketo-3-(2-nitro-4-methylsulfonylphenyl)propanoic acid.

Both products are the result of an photohydrolysis process according to Scheme 1.

When metsulfuron methyl was used, two main products were obtained (Figure 5). They were identified as 2-(carbomethoxy) benzenesulfonamide (2-CB) and 2-amino-4-methoxy-6-methyl-1,3,5-triazine (AMMT) by comparing the retention time with authentic samples. They result from the hydrolysis of the group at the bridge moiety as observed in aqueous solutions [29]. 2-CB and AMMT appeared to be formed from the early stages of the irradiation and increased as a function of irradiation time (Figure 6).

Since these two products are commercial, we evaluated this hydrolysis process to about 40%. This percentage increased to 60% when the amount of moisture increased.

These two products were already reported to be formed by studying the photodegradation of metsulfuron methyl on glass surface [23] and were reported to be nonphytotoxic [33]. However, under our experimental conditions we were not able to detect saccharin (O-sulfonylbenzoimide) which was shown to be formed from 2-CB.

4. Conclusion

The photolysis of the pesticides mesotrione and metsulfuron methyl was studied at the surface of clays (Kaolinite) and soil. The degradation process was efficient and depends on soil components such iron(III) species, natural organic matter, and water content. In the case of iron and water, the photodegradation rate increased by increasing their amount owing to the involvement of additional reaction pathways such as hydrolysis and photoinduced reactions. The degradation rate drastically decreased when the natural

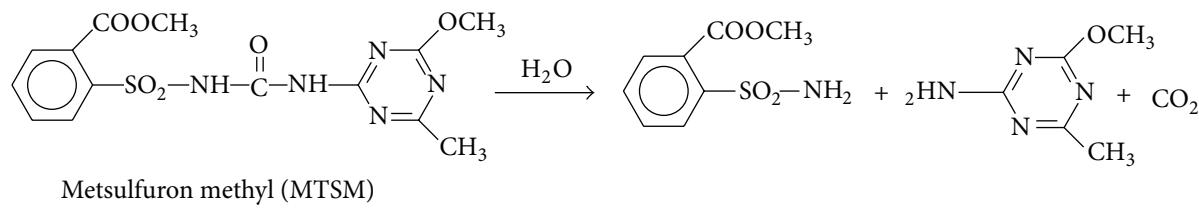
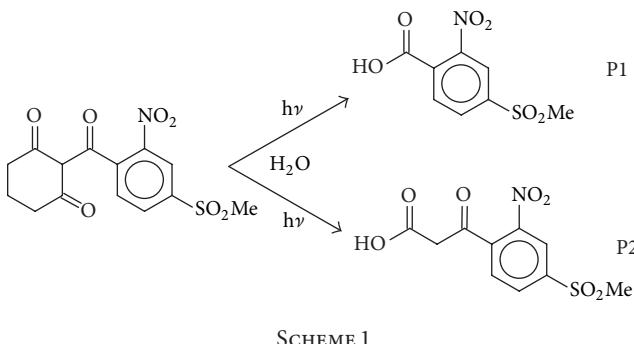


FIGURE 10



SCHEME 1

organic matter content increased due to an inner filter effect. In the case of both pesticides, the products were similar to those obtained in aqueous solutions. They mainly arise from photohydrolysis processes.

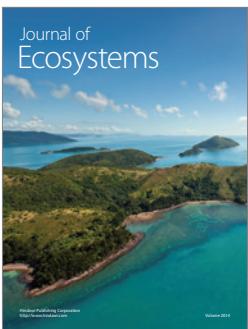
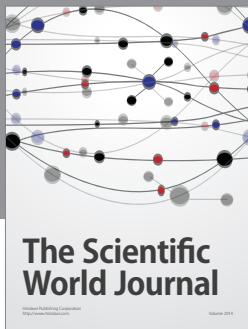
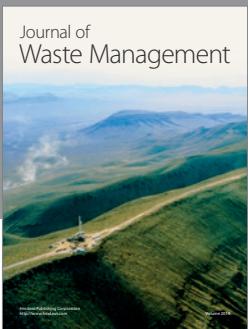
Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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