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ORIGINAL ARTICLE

Rapid photodegradation of clethodim and sethoxydim herbicides in soil and plant surface model systems

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Abstract Photolysis is an important degradation process to consider when evaluating the persistence of a pesticide in the field. In this work, photolytic behavior of clethodim and sethoxydim herbicides under simulated solar radiation was examined in organic solvents, on glass disk and silica gel plates as leaf and soil model surfaces. The photodegradation was characterized by determination of their half-lives ($t_{1/2}$), dissipation rate constant (k) and identification of degradation products by means of HPLC-Qtof-MS. Photolytic degradation of clethodim and sethoxydim was very rapid. The photodegradation rate was enhanced in leaf model than in water with half-lives that ranged from 6.3 ± 0.5 to 10.1 ± 0.4 min for clethodim and from 8.0 ± 0.3 to 20.5 ± 0.5 min for sethoxydim. The fastest rate of degradation was obtained on silica gel plates with half-lives of 1.8 and 5.0 min for clethodim and sethoxydim respectively. Photoreduction of the oxime ether moiety was the main transformation processes giving rise to a photostable product, the corresponding dealkoxylated derivative. Isomerization of oxime ether bond and oxidation of sulfur atom to form *Z*-isomer and the corresponding sulfoxides were the others reactions involved. The different environments tested influenced the concentrations of photoproducts formed during the irradiation of both herbicides. This result suggests that photolysis will be an important pathway of dissipation of the two herbicides. On the basis of these findings, further studies could be desirable to estimate the effects of transformation products on the environment.

1. Introduction

After spray application of herbicides, they first get in contact with the plant leaves and soil surfaces. In these environmental compartments photodegradation is one of the main transformation pathways that can take place since compounds are directly exposed to sunlight. It is known that the mechanism,

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route and rate of degradation of a substance will vary according to the compartment (Boxall et al., 2004; Katagi, 2004; Tagle Martin et al., 2005). The transformation products formed present generally lower toxicity than the parent compound (Mestankova et al., 2011; Souza et al., 2013). However, in some instances degradates are more toxic (Scrano et al., 2002; Sinclair and Boxall, 2003) and consequently these compounds pose a greater risk to the environmental than the active substance. Furthermore, even if transformation products are less toxic than the parent compound, it may still have the potential to have an adverse impact on the environment.

In the European legislation, Regulation 1107/2009/EC and its associated Regulation 283/2013/EC, the environmental behavior of metabolites, degradation or reaction products which account for more than 10% of the amount of active substance in environmental conditions have to be reported. Thus, evaluating degradates in the environment is increasingly interesting to the scientific and regulatory communities.

Cyclohexanedione oxime (CHD) has emerged in the last years as a new class of herbicides highly effective at low dosages with good selectivity without side effects to non-target organism. Moreover, this class of herbicides is considered as environmentally friendly since they present relatively low persistence in most compartments and they are rapidly degraded under different environmental conditions (Sevilla-Morán et al., 2010b; Sandín-España et al., 2013; Monadjemi et al., 2014; Bridges et al., 1991; Falb et al., 1991). These herbicides are sensitive to solar radiation since they present a high absorbance over 290 nm with relatively high quantum yields (Sevilla-Morán et al., 2010a, 2014). So, the fate of these herbicides in plant and soil surfaces can be highly influenced by photochemical processes.

Clethodim and sethoxydim herbicides belong to the cyclohexanedione oxime class and they are effective against many grass weed species from post-emergence mainly in soybean, cotton, sunflower and other broad-leaved crops (Brinson Conerly, 1990; Edwards, 2005). In previous works, we studied the photolysis of clethodim (Sevilla-Morán et al., 2010a) and sethoxydim (Sevilla-Morán et al., 2014) in aqueous media. A rapid photolysis was observed for both herbicides in aqueous matrices giving rise to formation of various identified by-products. However, it is known that the nature and the distribution of degradation products depend on the environment media (Kopf and Schwack, 1995; ter Halle et al., 2006) and as a consequence, potential unknown photoproducts can be generated in environments such as leaf and soil surfaces.

Literature data concerning the photochemical behavior of clethodim and sethoxydim on leaf and soil surfaces are scarce and most of them are focused on estimating only the stability of the parent compound (Campbell and Penner, 1985; Shoaf and Carlson, 1986, 1992). Information on their transformation products is neither clear nor complete and most of the by-products remained unknown. In this sense, several authors have observed that the properties of by-products formed and their environmental behavior may be quite different from parent compounds (Brinson Conerly, 1990; Edwards, 2005). The greater persistence of photoproducts may pose a potential threat to succeeding crops or non-target organisms because of these environmental systems can be exposed to high levels of unknown photoproducts. Other studies suggested the possibility that some of transformation products together with parent compounds induce the phytotoxic effects on grasses (Campbell and Penner, 1985; Shoaf and Carlson, 1992). If photoproducts accumulate on the crops, an evaluation of their potential side effects would be desirable. Furthermore, photochemical studies have already been undertaken in water and soil for each herbicide, but their photolysis on leaves has never been considered. Information about photodegradation on leaves and soil surfaces under various environmental conditions is essential to estimate the importance of this dissipation path in the field (Schippers and Schwack, 2008; Chastain et al., 2013). Thus, we found useful to undertake a detailed study of the photochemical behavior of clethodim and sethoxydim to get a better insight of their fate in the environment.

The aim of the present work was to study the photochemical behavior of the herbicides clethodim and sethoxydim in different model matrices that mimic plant cuticle constituents and soil surfaces. The photodegradation of clethodim and sethoxydim was studied in three different organic solvents to simulate several functional groups present in plant cuticle constituents. Thus, methanol and 2-propanol were selected as the simplest models of primary and secondary alcohol groups present in cutin acids, free fatty alcohols and sterols while cyclohexane was selected to model saturated lipids. Moreover, experiments were performed on glass disks and silica gel to model soils. Photoproducts of both herbicides formed during the photolytic processes have been identified by means of LC-Qtof-MS.

2. Material and methods

2.1. Chemicals and solutions

Analytical standards of clethodim (2-{(*E*)-1-[(*E*)-3-chloroallyloxyimino]propyl}-5-[2-(ethylthio)propyl]-3-hydroxycyclohex-2-enone) (98% purity), sethoxydim [(RS)-(*EZ*)-2-[1-(ethoxyimino)butyl]-5-[2-(ethylthio)propyl]-3-hydroxycyclohex-2-enone] (99.3% purity) and deethoxylated sethoxydim [5-(2-(ethylthio)propyl)-3-hydroxy-2-(1-iminobutyl)cyclohex-2-enone] (97%) were supplied by ChemService (West Chester, PA) and BASF Ltd (Limburgerhof, Germany).

All the organic solvents (acetonitrile, methanol, 2-propanol and cyclohexane) were HPLC grade or higher quality and were purchased from Labscan (Stillorgan, Co., Dublin, Ireland). Ultrapure water, used for LC mobile phase and aqueous solutions, was obtained from a Millipore system (Milli-Q-50 18 mΩ). Formic acid (p.a.) was acquired from Merck (Darmstadt, Germany).

Organic stock solutions of clethodim (100 mg L^{-1}), as well as stock solutions of sethoxydim in methanol and 2-propanol (100 mg L^{-1}) were prepared by dissolving directly the appropriate amount of the analytical standards in the respective solvent. Because of the low solubility of sethoxydim in cyclohexane, its stock solution was prepared at a lower concentration (10 mg L^{-1}) by dissolving firstly the herbicide in the minimum amount of ethyl acetate (3%).

All stock solutions of clethodim and sethoxydim were stored at 4 °C in the dark prior to use.

2.2. Experimental setup and procedure

The photodegradation experiments were performed in a Suntest CPS + sunlight simulator from Atlas (Linsengericht, Germany) equipped with a xenon arc lamp (1500 W) and a special UV glass filter restricting the transmission of wavelength below 290 nm. Photochemical studies were performed at an irradiation intensity of 750 W m^{-2} and the temperature was kept at 25 ± 1 °C using an Atlas SunCool chiller unit. This device provides a spectral distribution close to natural sunlight and a constant irradiance that allows performing experiments under reproducible irradiation conditions avoiding variations caused by geographical situation, seasonal or climatic conditions.

The photodegradation of clethodim and sethoxydim was studied in three different organic solvents to simulate several functional groups present in plant cuticle constituents. Methanol and 2-propanol mimic primary and secondary alcohol groups of the cutin and cyclohexane model saturated lipids.

To perform the photolysis of the herbicides in organic solvents, solutions (20 mL) of clethodim and sethoxydim were prepared at 5 mg L^{-1} in the appropriate solvent and were exposed to simulated solar radiation in capped cylindrical quartz cuvettes with magnetic stirring. Aliquots were withdrawn at different irradiation times and subsequently analyzed by the chromatography system. Prior to the chromatographic analysis, the solvent of the samples in cyclohexane was removed using a vacuum centrifuge (Eppendorf AG, Hamburg, Germany) and the residue was dissolved in methanol, whereas the samples in methanol and 2-propanol were directly injected.

To mimic soils surfaces we employ glass disks and silica gel plates as model matrices. To study the photolysis of clethodim and sethoxydim as thin film on glass disks, a methanolic solution of each herbicide (50 µL, 100 mg L^{-1}) was pipetted onto glass disks (6 cm ID). The solvent was evaporated at room temperature leaving behind a thin layer of the herbicide. The disks were exposed to simulated solar light for different time intervals. After irradiation, the glass disks were rinsed with methanol (2 × 0.5 mL) to perform subsequent analysis of the resulting solution by HPLC.

The photolysis of clethodim and sethoxydim in sorbed phase was carried out using HPTLC plates (0.20 mm Silica gel C18-100) (without fluorescent indicator) which was purchased from Macherey-Nagel GmbH&Co. KG (Düren, Germany). Methanolic solutions of each herbicide (50 µL, 100 mg L^{-1}) were pipetted on the silica gel plates and the solvent was evaporated at room temperature. Spiked silica gel plates were exposed to simulated solar light for different time intervals. After irradiation, silica gel was scrapped from the plates and extracted with methanol (1 mL). The extracts were then centrifuged (Concentrator plus, Eppendorf AG, Hamburg, Germany) during 3 min and the supernatant was filtered through 0.2 µm nylon filters and injected into the chromatographic system.

The photodegradation kinetics were followed until less than 10% of initial concentration of the herbicide remained. Three replicates were carried out for each photodegradation experiment and the results presented correspond to the arithmetic mean of these three independent analyses, whereas error bars represent the standard deviation. Moreover, experiments in the absence of radiation (dark control) were performed in parallel to the photodegradation experiments under the each condition tested and initial concentrations of the herbicides to evaluate whether processes other than photolysis occurred.

2.3. Chromatographic analysis

The photodegradation kinetics of clethodim and sethoxydim were monitored using a HPLC system (series 1100; Agilent Technologies, Palo Alto, USA) coupled to a photodiode array detector (DAD). The analytical column used was a Waters Nova-Pak® C18 column (4 µm particle size, 3.9 mm × 150 mm) (Waters, Dublin, Ireland) with an ODS precolumn and was maintained at 25 °C. The mobile phase was a mixture of ultrapure water acidified (0.1% of formic acid) (A) and acetonitrile (B).

Two different chromatographic methods were employed. The first one was an isocratic method, with a mobile phase of 80% B, for a rapid monitoring of the decay of clethodim and sethoxydim and to calculate the kinetic parameters of photolysis. The second one was a gradient method that allows separating and following the evolution of the photoproducts formed during photodegradation experiments. This was described elsewhere (Sevilla-Morán et al., 2010a, 2014) and basically the mobile phase B was as follows: 10–50% in 26 min, 50–60% in 13 min, held at 60% during 2 min. In both chromatographic methods, the flow rate was 1 mL min^{-1} and the injection volume was 20 µL.

An HPLC chromatograph (series 1100; Agilent Technologies, Palo Alto, USA) equipped with Qtof mass spectrometer (QStar Pulsar I, AB Sciex, Framingham, USA) was used to accomplish the identification of photoproducts of clethodim and sethoxydim. The high resolution and mass accuracy provided by the tof analyzer allowed for the assignment of a highly probable empirical formula for each transformation product. To determine the most probable molecular formula, various criteria were considered, such as the rule of the number of nitrogen atoms, the DBE (double bond equivalent), and the error. Additionally, the sulfur isotopic signals of the protonated molecules and the fragment ions provide additional information for the identification of the degradation products. In the same way, a detailed study of the MS/MS fragmentation pattern of each compound helps us to elucidate their structures. The column, precolumn, mobile phases and gradient employed in HPLC-Qtof analysis were the same as mentioned above except the flow rate that was 0.7 mL min^{-1}. The mass spectrometry experiments were performed in positive mode and the optimized instrumental parameters are showed in Table 1.

2.4. Data analysis

In all experiments, the disappearance of clethodim and sethoxydim from the irradiated media was postulated to follow a first-order kinetic law given by the equation:

$$C_t = C_0 e^{-k\ t}$$

where C_0 and C_t are the concentrations of the herbicides at times 0 and t, t is the irradiation time (min), and k is the rate constant (min^{-1}) of the photolytic process.

Table 1 Optimized instrumental parameters for the analysis of clethodim and sethoxydim photoproducts by Qtof mass spectrometer.

	Clethodim	Sethoxydim
Ion spray voltage (V)	5000	5500
Ion source gas pressure (psi)	65	50
Ion source gas 2 (psi)	65	55
Curtain gas pressure (psi)	20	20
Declustering potential (V)	70	70
Focusing potential (V)	250	210
Declustering potential 2 (V)	15	15
Collision energy (eV)	22	22

The rate constants of photolysis (k) are determined from the plots of herbicide concentrations/vs/irradiation time using this non-linear regression fit.

The half-lives of photolysis for clethodim and sethoxydim ($t_{1/2}$), the time required to reduce the initial herbicide concentration by 50%, are then determined from the rate constants previously calculated by means of $t_{1/2} = \ln 2/k$.

Statistically significant difference between the half-lives of clethodim and sethoxydim under the different experimental conditions studied was determined using one-way analyses of variance (ANOVA) at the 0.05 significance.

3. Results and discussion

Under the experimental conditions, it is expected that photolysis processes contribute significantly to the degradation of clethodim and sethoxydim, since both herbicides present high molar absorptivities and high quantum yields at the sunlight spectral region of 290–325 nm (Sevilla-Morán et al., 2010a, 2014).

The photolytic processes depend not only on the nature of herbicides or the incident radiation, but also on the composition of the environmental matrix. For example, different authors have studied the effect of pH and different adjuvants on the photolysis rates of clethodim and sethoxydim (McInnes et al., 1992; Hazen and Krebs, 1992; Falb et al., 1990). So it is expected that the photochemical behavior of pesticides is affected by plant cuticle constituents and composition of soils. A frequent approach that facilitates the photolysis study of pesticides on plant and soil surfaces is to use different models that simulate these complex matrices. Thus, glass and silica gel plates have been used as simple models of soil surfaces while different organic solvents have been used as surrogates of functional groups present in constituents of plant cuticles (Katagi, 2004; Schippers and Schwack, 2008; Chastain et al., 2013).

3.1. Kinetic analysis

Fig. 1 shows the kinetic evaluation of clethodim and sethoxydim under simulated sunlight in different model solvents and on model soil surfaces, respectively. Dark controls were also depicted in these figures and, in the absence of radiation, no significant changes were observed for the concentrations of clethodim and sethoxydim on the timescale of experiments. So, in all cases tested, clethodim and sethoxydim disappearance was only by radiation, allowing to discard other degradation routes such as hydrolysis and thermal reactions.

Table 2 compiles the kinetic parameters calculated from the photodegradation of clethodim and sethoxydim under the different experimental conditions evaluated. The experimental data fitted well to first-order kinetics except for the degradation results obtained on silica gel plates, which fitted to two-step processes (both first order kinetic).

Clethodim and sethoxydim were readily degraded by sunlight irradiation in the three model solvents used. They were nearly completely degraded in less than 2 h for clethodim and 3 h for sethoxydim of exposure to radiation (Fig. 1a and c). The half-lives were dependent on the solvents chosen, as shown in Fig. 1a and c. The calculated rate constants for clethodim ranged from $68.8 \cdot 10^{-3}$ min^{-1} (methanol) to $109.9 \cdot 10^{-3}$ min^{-1} (2-propanol) and for sethoxydim ranged from $33.9 \cdot 10^{-3}$ min^{-1} (2-propanol) to $86.2 \cdot 10^{-3}$ min^{-1} (cyclohexane) and the statistical analysis of photolysis rates showed significant differences between the solvents employed (Table 2). Therefore, it is expected that both herbicides suffer photolysis on plant surfaces and the rate of the process will be dependent on the functional groups present in plant cuticle. This is in accordance with previous studies on the photochemistry of different pesticides such as iprodione (Schwack et al., 1995) or sulcotrione (ter Halle et al., 2006) where different degradation rates and product distributions depend on the solvent system used. A similar photodegradation half-life of 10 min was reported previously by Shoaf and Carlson (1992) for sethoxydim in methanol under UV light.

Moreover, it is noteworthy that clethodim and sethoxydim were photodegraded at a faster rates in organic solutions compared to their photolysis in ultrapure water (Sevilla-Morán et al., 2010a, 2014). Thus, the half-lives of photolysis for clethodim and sethoxydim in ultrapure water at 750 W m^{-2} were 28.9 and 59.8 min respectively, while in model solvents were much faster and varied from 6.3 to 20.5 min. These results suggest that constituents of plant cuticle may be decisive for the photodecomposition of these CHD herbicides. These findings also support that photolysis rates of clethodim and sethoxydim depend on the photo-reaction media. Besides, these results highlight the importance to check the relevance of the solvent experiments, not only light source or intensity of irradiation, before extrapolating studies to the processes on leaf surfaces.

In addition, in a soil environment, it is not possible to distinguish direct and indirect photolysis when a pesticide is adsorbed on soil. Without the presence of natural substances acting as a filter, photosensitizer or quencher (Katagi, 2004; Schippers and Schwack, 2008), the glass surface is a good first approach to investigate surface photodegradation of pesticides. Therefore, experiments were conducted on glass disks and silica gel plates in order to evaluate the photodegradation of clethodim and sethoxydim on the simplest models of dry soil surfaces. As in organic solvents, clethodim and sethoxydim were rapidly degraded on both model surfaces, disappearing from the media in less than 3 h in all cases (Fig. 1b and d). However, the degradation kinetic model of both pesticides on silica gel plates differs from the kinetic model on glass disks. So, while clethodim and sethoxydim fitted well to first-order reaction law on glass disk, the best fit for the degradation data on silica gel plates corresponds to a two-step process (both first-order kinetic). Both pesticides show a higher degradation

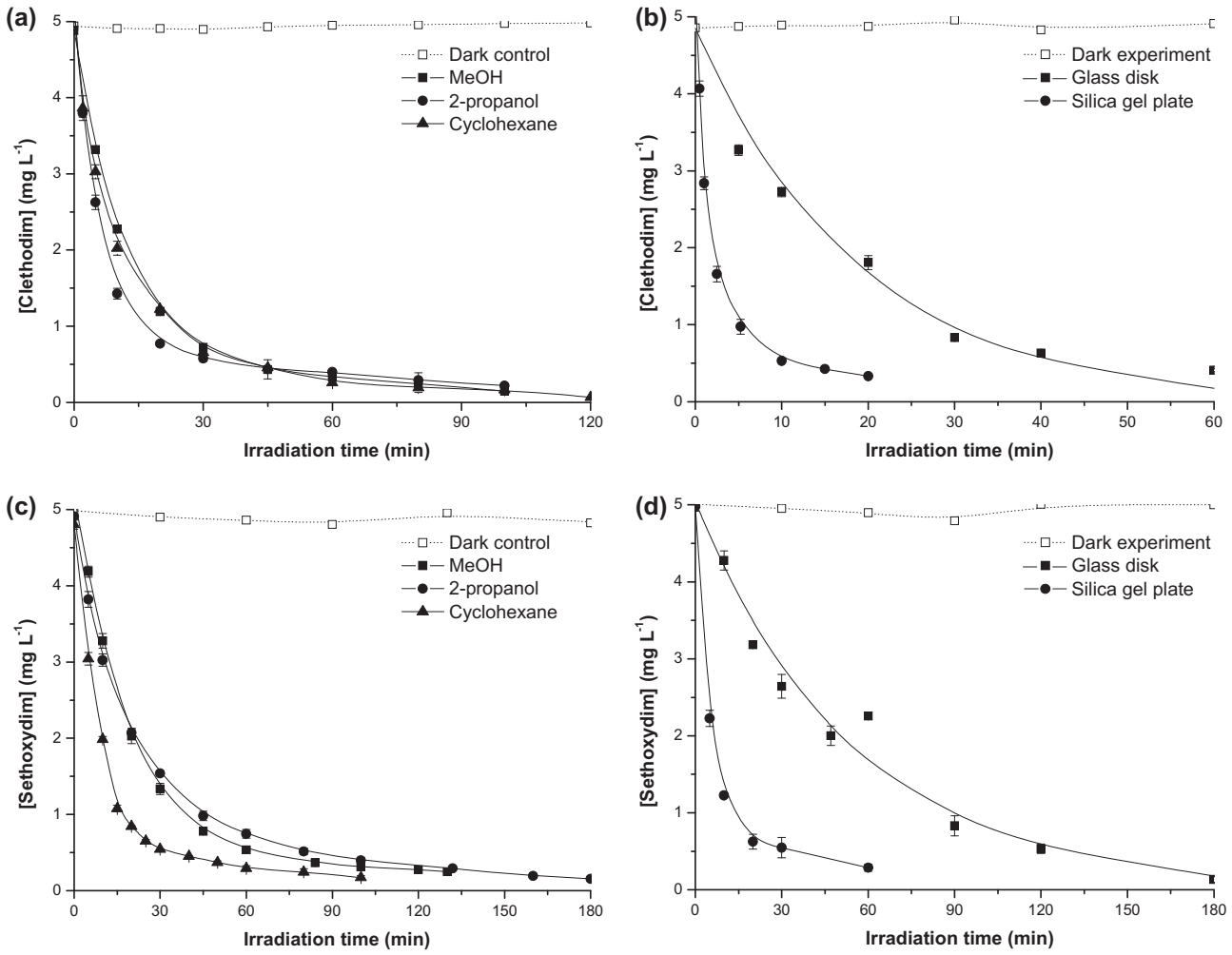

Figure 1 Kinetics of disappearance of clethodim (a, b) and sethoxydim (c, d) degradation in leaf (a, c) and soil (b, d) surface model systems under simulated solar irradiation. The results are the media of three replicates.

Table 2 The rate constants (k) and the half-lives ($t_{1/2}$) of clethodim and sethoxydim photolysis in leaf and soil surface model systems under simulated solar irradiation. Different letters show significant differences according to least significant differences (LSDs) test at a significance level of 95%.

		k (10^{-3} min^{-1})	$t_{1/2}$ (min)	R^2
Clethodim	Methanol	68.8 ± 4.1	10.1 ± 0.4 a	0.99
	2-Propanol	110 ± 9	6.3 ± 0.5 b	0.98
	Cyclohexane	87.3 ± 8.4	7.9 ± 0.5 c	0.98
	Glass disk	53.8 ± 2.6	12.9 ± 0.6 d	0.98
	Silica gel plate (Step-1)	1060 ± 86	0.66 ± 0.05 e	0.95
	Silica gel plate (Step-2)	217 ± 13	3.2 ± 0.2 f	0.99
Sethoxydim	Methanol	43.3 ± 2.8	16.0 ± 0.3 a′	0.99
	2-Propanol	33.9 ± 2.7	20.5 ± 0.5 b′	0.98
	Cyclohexane	86.2 ± 1.6	8.0 ± 0.3 c′	0.97
	Glass disk	17.3 ± 1.1	40.1 ± 0.8 d′	0.97
	Silica gel plate (Step-1)	160 ± 7	4.3 ± 0.2 e′	0.98
	Silica gel plate (Step-2)	30.3 ± 8.0	22.8 ± 1.0 f′	0.96

rates in the first period than in the second one, with half-lives of 0.66 ± 0.05 for clethodim and 3.2 ± 0.2 for sethoxydim (Table 2). Analogous results were obtained during the irradiation of different pesticides by Albanis et al. (2002), Gonçalves et al. (2006) and Mountacer et al. (2014), respectively.

The first period can be attributed to direct photolysis of clethodim and sethoxydim, which it was previously proved for both herbicides in ultrapure water (Sevilla-Morán et al., 2010a, 2014). In the same way, indirect processes can be also occur since the degradation rates in this first period were much higher on silica gel plates than in glass disk. In the second period, the degradation rates of clethodim and sethoxydim were reduced to 80% of initial rates. Since silica particles attenuate about 90% of the incident radiation in the top of 0.2 mm, this second period can be due to dominance of indirect photoprocesses or to the diffusion of the pesticides. In this sense, several authors have indicated that silica gel is a highly reactive surface due to the presence of many hydroxyl groups (Katagi, 2004; Rohatgi and Mukherjee, 2006). Moreover, under irradiation and in the presence of oxygen or moisture, silica particles can generate different reactive species (e.g. $^1O_2$), which can react with the pesticide adsorbed on silica gel (Katagi, 2004; Rohatgi and Mukherjee, 2006).

Therefore, it can be assumed that the molecules of the herbicides interacted with the hydroxyl functional groups of the silica or the reactive species generated, favoring the rapid photolysis of clethodim and sethoxydim.

3.2. Photoproducts analysis

During the photolysis of clethodim and sethoxydim on different leaf and soil model systems, the formation of several photoproducts was followed by HPLC-DAD. All photoproducts showed shorter retention times than their active substance as can be observed in the chromatograms showed in Fig. 2. This suggests a higher polar character and hence, a higher solubility in water, increasing the concern of groundwater contamination. Irradiation of sethoxydim and clethodim yielded a complex mixture of photoproducts. Nine transformation products for each one of the parent compounds (C1–C9 and S1–S9) were detected and all of them were identified (UV–Vis and mass spectra of clethodim and sethoxydim transformations products are showed in supplementary data). It is noteworthy that the photoproduct of clethodim C1 was detected in a small amount (8%) when a freshly prepared stock solution of clethodim was analyzed. However, this compound was considered as a photoproduct of clethodim since its concentration increased during the irradiation of the herbicide while it remained constant in dark control experiments.

Considering that clethodim and sethoxydim share similar chemical structure of a cyclohexanedione skeleton functionalized with a thioalkyl chain and an oxyimino group (Fig. 3), it should be expected that the photolysis of these herbicides led to analogous photoproducts. Due to the lack of commercially available standards, except for deethoxylated sethoxydim, the identification of photoproducts formed was accomplished using HPLC-ESI-Qtof in the positive mode. A detailed study of the exact mass measurements and the MS/MS spectra obtained for the protonated molecules of the photoproducts as well as their fragments allowed the identification of the different photoproducts formed. Thus,

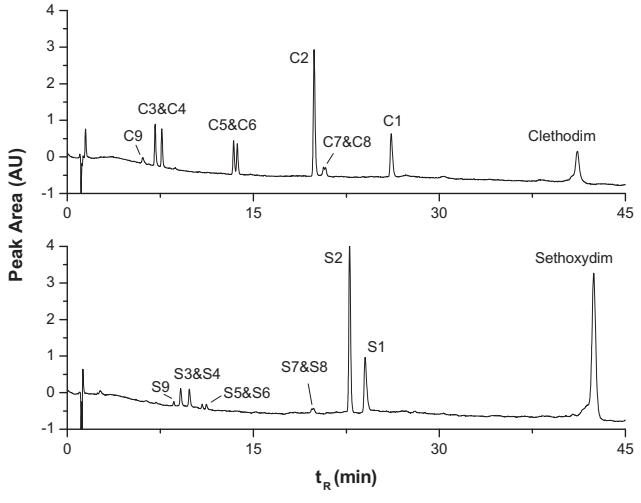

Figure 2 Representative HPLC-DAD chromatograms of clethodim and sethoxydim photodegradation in leaf and soil surface model systems under simulated solar irradiation (in 2-propanol, irradiation $time_{clethodim}$ = 60 min, irradiation $time_{sethoxydim}$ = 80 min).

Z-isomers of clethodim and sethoxydim (C1 and S1) were formed as consequence of the isomerization of the oxyimino group. In the case of clethodim, the syn-anti isomerization easily proceeds, accounting for the presence of C1 at the initiation of the study. Photoproducts C2 (m/z = 270.1520) and S2 (m/z = 284.1675) were assigned as the corresponding dechloroallyoxylated clethodim and deethoxylated sethoxydim and they were formed after the cleavage of N–O bond from oxyimino group (Fig. 3). Regarding to the photoproduct S2, it was the only one out of seven photoproducts detected by Campbell and Penner (1985) when sethoxydim was exposed to artificial light on glass disks, though conversely to our results, this compound was not a major photoproduct in their experiments. The oxidation of the sulfur atom of the *E*-isomers of clethodim and sethoxydim originates a new chiral center. As the neighboring carbon atom is also chiral, two pairs of enantiomers formed (RR + SS and RS + SR), that is C5&C6 and S5&S6, and diastereomers are chromatographically separated in two peaks, containing a pair of enantiomers each. Since the reaction took place without stereogenic control in the water achiral medium, similar amounts of each isomer are expected. In the same way, the *Z*-isomer of clethodim (C1) and sethoxydim (S1) gave rise to the corresponding pairs of enantiomers of sulfoxides, C3&C4 and S3&S4. Regarding to photoproducts C7&C8 and S7&S8, they were identified as the sulfoxides of dechloroallyoxylated clethodim and deethoxylated sethoxydim, respectively. As it occurs in the sulfoxidation of clethodim and sethoxydim, the oxidation of the sulfur atom from dechloroallyoxylated clethodim and deethoxylated sethoxydim originates a new chiral leading to the formation of two pairs of enantiomers, with each chromatographic peak corresponding to one pair of enantiomers (RR + SS and RS + SR) (Fig. 3). Finally, mass data allow identifying the photoproducts C9 and S9 as the ketone derivatives of dechloroallyoxylated clethodim and deethoxylated sethoxydim, respectively (Fig. 3).

There are very scarce references about the photoproducts of sethoxydim and clethodim formed on plant leaves, soil surfaces or model systems. Shoaf and Carlson (1992) observed that photolysis of sethoxydim on HPTLC plates and methanol yielding to various unidentified products. However, except for the main photoproduct deethoxylated sethoxydim S2 (Campbell and Penner, 1985), this is the first time that a complete identification of all photoproducts of sethoxydim and clethodim formed on model systems simulating plant constituents and soil surfaces has been achieved. Conversely with other studies where the sulfone was detected as a significant metabolite in soil (Shoaf and Carlson, 1986), plants (Ishihara et al., 1988) or chlorinated water (Sandín-España et al., 2005), we did not observe the subsequent oxidation of sulfoxides to the corresponding sulfones under the conditions studied. This could be due to the mild oxidation conditions of the experiment performed, that can oxidize the sulfur atom of the sulfide, but cannot further oxidize the sulfoxide (Hirahara et al., 2001; Smith and March, 2007). Comparative with our previous studies, the photoproducts identified in plant and soil model systems are in common with those observed in the photolysis of clethodim and sethoxydim in water (Sevilla-Morán et al., 2010a, 2014). However, it is interesting to note that some photoproducts are specifically formed in water such as the oxazole derivative and some of

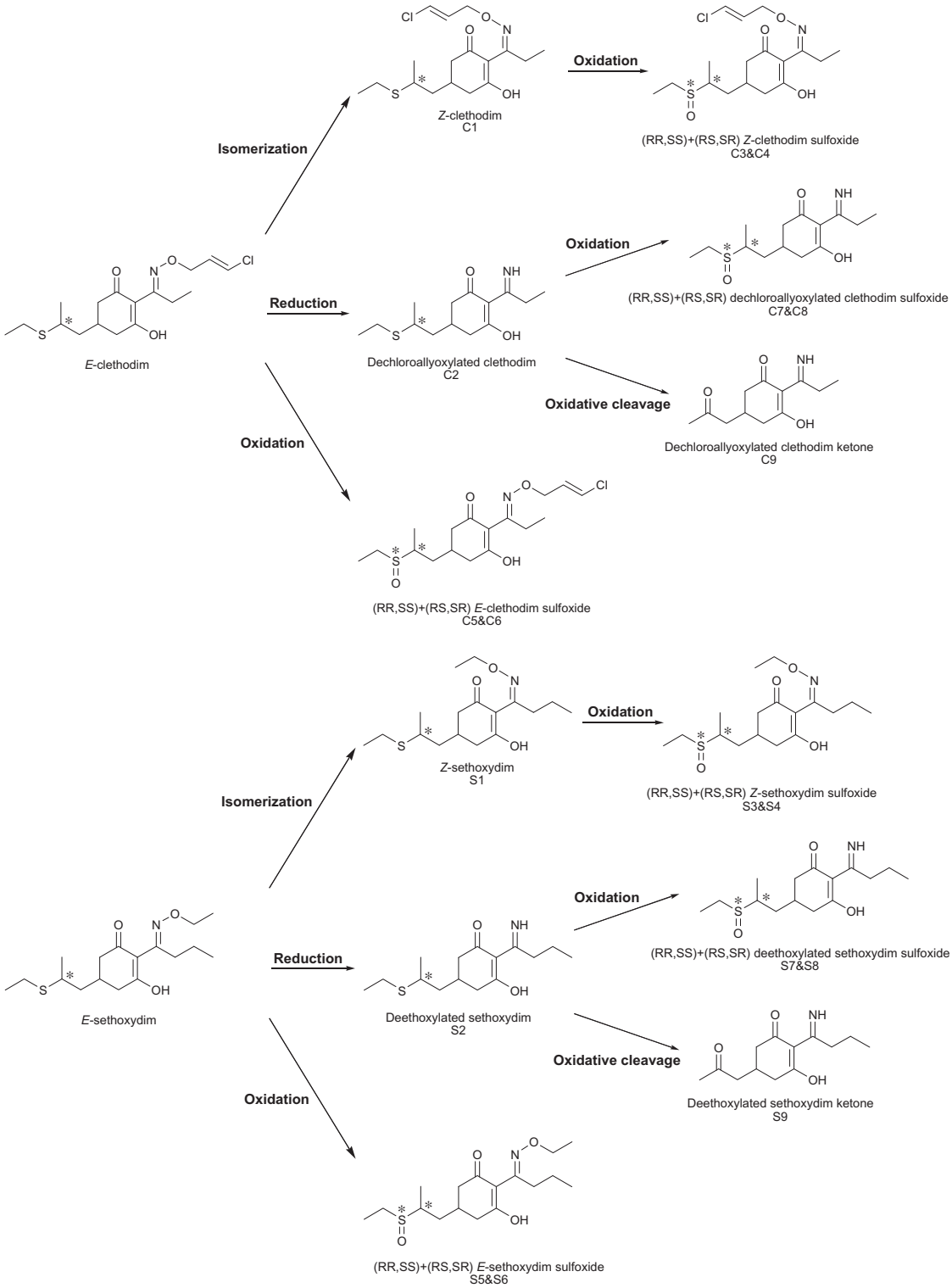

Figure 3 Transformation processes involved in the photodegradation of clethodim and sethoxydim in soil and leaf surface model systems under simulated solar irradiation.

the by-products distribution varied in a certain extent as it can be observed in Fig. 4.

With regard to the formation profiles of the different photoproducts of clethodim and sethoxydim, it was observed that their pathways were similar in both plant and soil surface models. Thus, the first photoproducts formed were the *Z* isomers (C1, S1) and the dealkyloxylated photoproducts (C2, S2). It seems that the photoisomerization (photoproducts C1

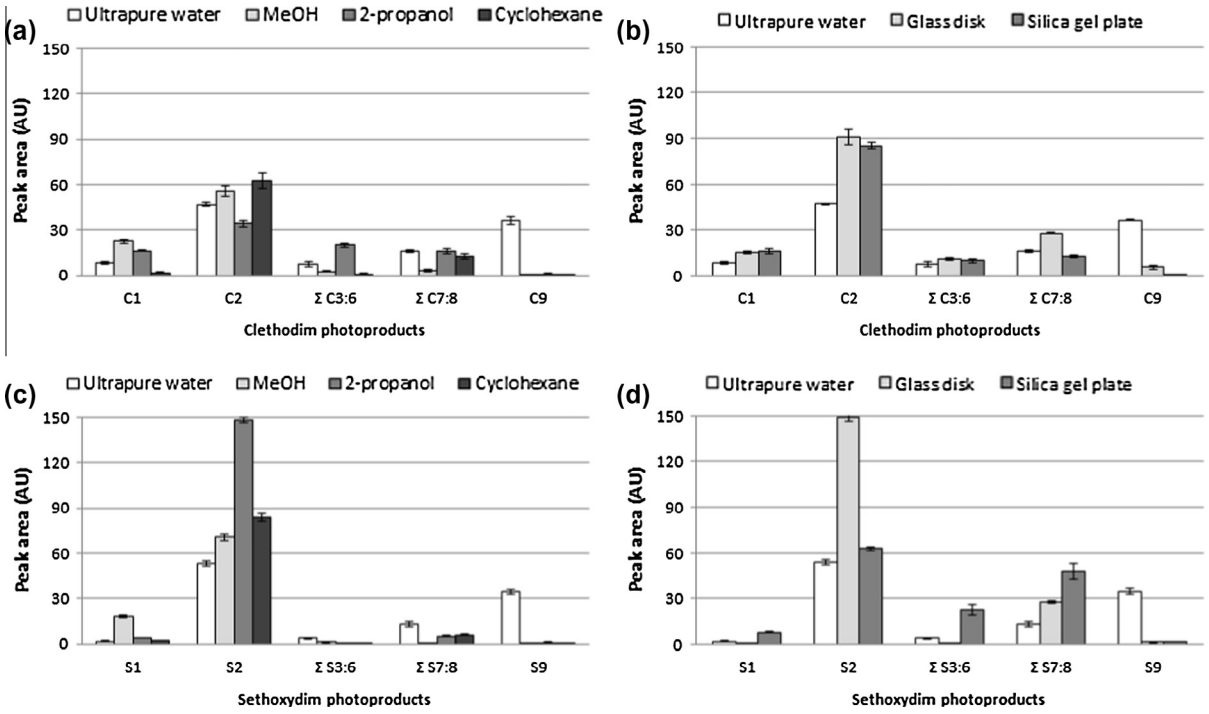

Figure 4 Photoproducts distribution of clethodim (a, b) and sethoxydim (c, d) at the end of the photolysis time in leaf (a, c) and soil (b, d) surface model systems under simulated solar irradiation. Data for the aqueous media were previously reported (Sevilla-Morán et al., 2010a, 2014). The results are the media of three replicates.

and S1) is very minor in cyclohexane. In this regard, Monadjemi et al. (2013) attributed this different behavior in the cyclohexanedione herbicides to the inhibiting effect of the intramolecular hydrogen bond existing in aprotic solvents. The photoreduction of the oxime group giving rise to the formation of dechloroallyoxylated clethodim (C2) and deethoxylated sethoxydim (S2) was the main transformation process in all the system models studied. These degradation products (C2 and S2) have in common that they were formed as result of reactions in the N–O bond, since this covalent bond is relatively weak (bond dissociation energy of ca. 53 kcal mol^{-1}). Afterward, these compounds (*E*/*Z* isomers (C1, S1) and dealkoxylated derivatives (C2, S2)) that possess a sulfur atom in their structure, which is easily oxidized even in mild conditions, suffer a photooxidation reaction yielding the corresponding sulfoxides (C3–C4, S3–S4). It is noteworthy that all the photoproducts that have lost the oxyimino group (C2, C7–C9 and S2, S7–S9) and the sulfoxides appear to be more photostable than the active substance and as a consequence there is a risk for them to accumulate in the plant, soil or water environment. On the other hand, the *Z* isomers (C1, S1) are the only photoproducts that are not expected to be found in the field since they are short-lived compounds as their maximum concentration is reached at the first stages of photolysis and then go down to trace levels. These photoproducts are suspected to degrade to the corresponding sulfoxides and imine derivatives.

Thus, though the nature of the photoproducts did not differ between the different environments tested, the distribution of the photoproducts formed is partly influenced by the photoreaction media (Fig. 4). In this sense, it is significant that the photoproducts most affected by the reaction media were the main photoproducts C2 and S2. These photoproducts were found to be the only main products in all the model systems studied, whereas the ketone derivatives (S9 and C9) were determined to be also the major products in aqueous degradations (Fig. 4). So, C2 was found in higher concentrations in models that simulates soil than leaf surfaces. In the case of S2, the analytical standard allows us to quantify its concentration. Thus, more than 90% of the initial sethoxydim was degraded into S2 on glass disks and isopropanol, whereas the rest of the environments tested the percentage of conversion of sethoxydim to S2 ranged from 42% to 58%, so this photoproduct could be accumulated in plants with a high content in secondary alcohol groups or on surfaces where the solvent was evaporated. The reason for this result could not be clarified and further studies would be desirable in order to understand the mechanism of the reactions. Contrarily, sulfoxide derivatives S3–S8 were detected in a greater extent on silica gel plates to the detriment of deethoxylated sethoxydim (S2). These findings suggest that sulfoxidation of sethoxydim and deethoxylated sethoxydim (S2) to sulfoxide derivatives (S3–S8) was favoured on silica gel plates compared to on glass disks, probably due to reactive oxygen species photolytically formed on the silica surface may be involved (Katagi, 2004; Rohatgi and Mukherjee, 2006). Therefore, it could be expected that sulfoxides (S3–S8) were present on soil matrices. This result is in accordance with previous studies where the photolysis rates of different organic compounds were accelerated when they were sorbed on silica (Larson and Weber, 1994). These results are highly important since sulfoxides of some pesticides are suspected to show biological and/or toxicological activity

to target and non-target organisms (Dzyadevych et al., 2002; Sinclair and Boxall, 2003; Sandín-España and Sevilla-Morán, 2012). Moreover, these oxidized compounds are reported to present a higher water solubility and minor soil sorption than parent pesticides, thus showing a higher possibility to reach and contaminate ground and surface water (Somasundaram and Coats, 1991).

Therefore, due to the fast photolysis of clethodim and sethoxydim on leaf and soil model systems, it can be expected that a large number of photoproducts of both herbicides are formed on plant leaves and on soil surfaces after their application. Additionally, these photoproducts can be potential contaminants of aqueous media because they can reach water compartments as result of foliar wash-off, leaching or runoff processes by rain or irrigation water.

4. Conclusions

On the basis of the present results we can conclude that photochemical processes can play an important role in the fate of clethodim and sethoxydim herbicides after their application in the field. However, it is important to consider that besides photolysis, a wide variety of abiotic and biotic reactions can contribute to its transformation in the environment. Our investigations on the phototransformation in leaf and soil model systems increase our knowledge on the environmental fate of these compounds once they are applied in the field on different aspects. Firstly, we acquired kinetic data on the photodegradation of compounds that little had been studied under these environments. Thus, the kinetic data showed higher photodegradation rates on leaves and soil model systems than in aquatic environments previously studied, showing that is not possible to extrapolate the photoreactivity between these matrices.

The different environments tested influence on the distribution of the photoproducts. Secondly, we identified the degradation products generated, some of them had never been identified in leaf or surface soil before. Some photoproducts such as the alkoxy and the sulfoxide derivatives are photostable compounds and they possess unknown properties from a physicochemical and ecotoxicological point of view. These photoproducts should be taken under consideration in the analysis and assessment of clethodim and sethoxydim residues. Our findings highlight the importance of obtaining data on transformation products to finally understand not only the fate of a compound but also its overall effects on the environment. With the understanding of primary photodegradation principles, it would be highly interesting to perform experiments on real plant and soil surfaces.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.arabjc.2015.04.007.

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