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Chemical Behaviour and Herbicidal Activity of Cyclohexanedione Oxime Herbicides

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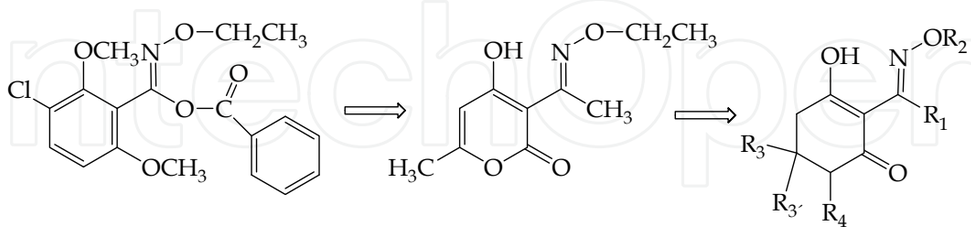
1. Introduction

Benzoximate (I; Fig. 1) is an acaricide developed by Nippon Soda in 1971 (Iwataki, 1992). However, scientifics of the company observed that some benzohydroxamates showed weak herbicidal activity. After much synthetic developments, a new lead compound, an ethoxyimino dehydroacetic acid derivative (II; Fig. 1), showed a strong pre-emergence herbicidal activity against annual grass weed without any effects towards broadleaf plants. Further developmental research was performed on the cyclohexanedione skeleton to develop a new post-emergence herbicide. It was observed that the ethoximine group between the two keto groups was essential for the herbicidal activity (III; Fig. 1). Besides, when hetero atoms were introduced in the ring, the compounds showed high pre-emergence activity. When the ring was formed by carbons, so-called cyclohexane derivatives, the compounds showed high pre- and post-emergence activities. Therefore, the synthetic research was focused towards the substituents on the cyclohexanodione skeleton. The activity was higher when side chain substituents R_1 and R_2 (Fig. 1) were alkyl groups. As for the ring substituents, mono i-Pr and germinal dimethyl at the R_3 and $R_{3'}$ position and ciano and methoxycarbonyl groups at the R_4 position provided the maximum activity. This way, alloxydim–sodium was discovered and introduced in the market in 1978.



I Benzoximate II III

Fig. 1. Pathway of lead compounds towards the discovery of cyclohexanedione oxime herbicides.

However, though alloxydim-sodium showed a potent activity against annual grass weeds, it did not against perennial grass weeds. Therefore, the synthetic research was focused towards the introduction of different substituents on the cyclohexane ring, since the structure-activity pattern of the skeletal had been already identified. It was disclosed that

substituents having a hetero atom such as chlorine, oxygen or sulfur increased the herbicidal activity. Some sulphur-containing cyclohexanodione derivatives showed very high activity against annual and perennial grass weed with post-emergence treatment. Thus, alkyl- and aryl- thioalkyl groups were introduced in position R_3 (III; Fig. 1) resulting in the discovery of other cyclohexanedione herbicides such as, sethoxydim, clethodim or cycloxydim (Fig. 2).

Thus sethoxydim, introduced in 1982, showed excellent herbicidal activity against various weed species in particular *Sorghum halepense*. Afterwards, clethodim, discovered by Chevron Chemical (Tomlin, 2006), presented almost the same herbicidal spectrum to sethoxydim but the application rates seems to be lower (Iwataki, 1992). Cycloxydim, discovered by BASF, showed a very broad spectrum with application rates similar to sethoxydim. Other herbicides like tralkoxydim have an herbicidal spectrum narrower than sethoxydim and clethodim. It has been used only for the control of annual winter grass weeds in wheat fields (Roberts, 1998). The last cyclohexanedione oxime herbicide was profoxydim (Fig. 2) developed by BASF, and first registered in 1998 for the control of grass weeds in rice.

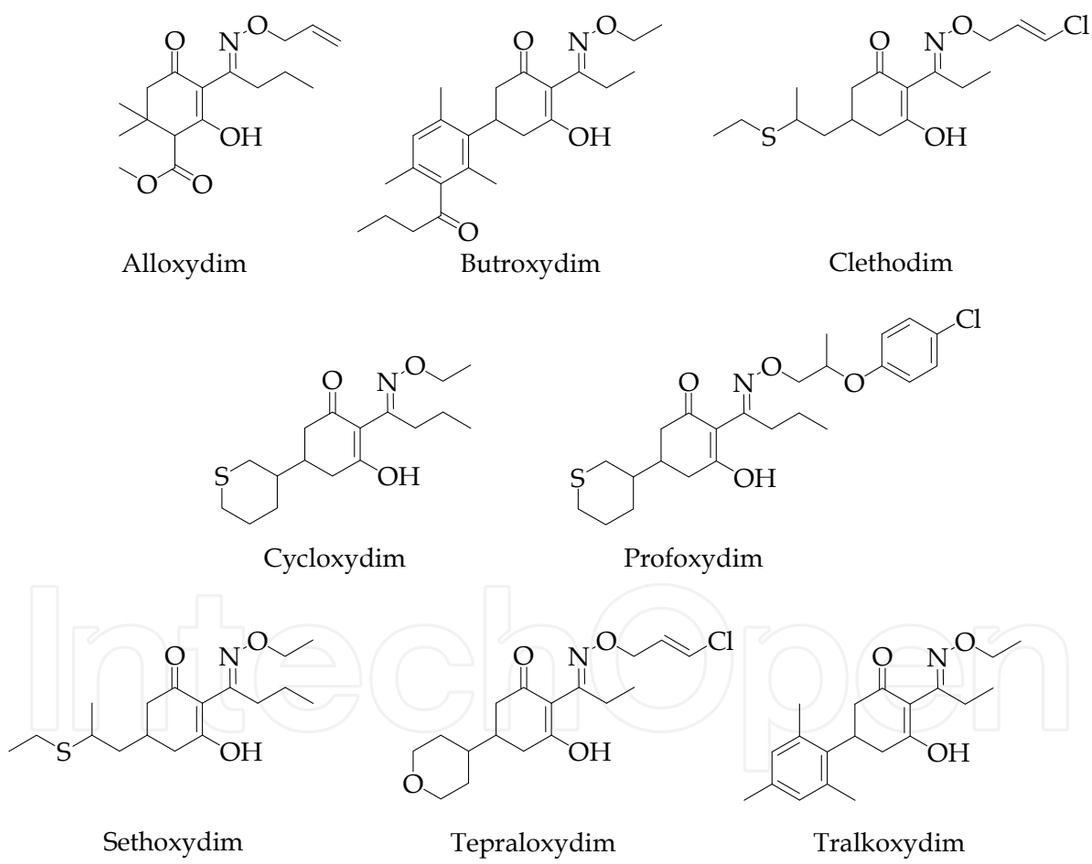


Fig. 2. Chemical structures of cyclohexanedione oxime herbicides.

The basic structure of the cyclohexanedione oxime herbicides is shown in Fig. 3. These compounds show a keto-enol tautomerism, where the enolic forms (IV and VI) is generally predominant to the keto form (V) (Iwataki, 1992; Iwataki & Hirono, 1978). Thus, general formulas for this class of compounds are expressed as the enolic form. The term "dione" is used, however, as the general term for these compounds because of its simplicity.

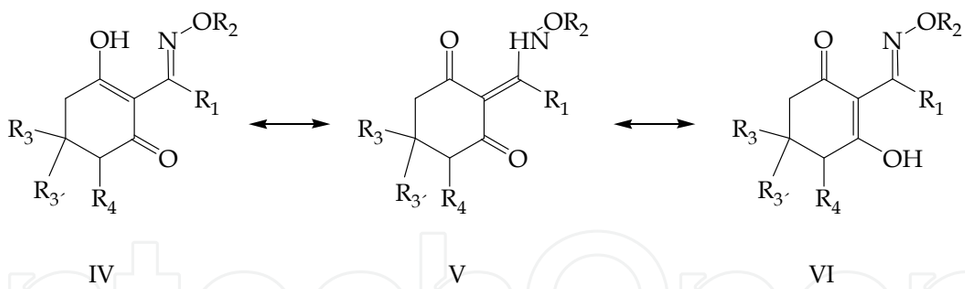


Fig. 3. Keto-enolic tautomerism of cyclohexanedione oxime herbicides.

As can be observed in Fig. 3, these herbicides present two isomers *E* and *Z* relating to the chloroallyloxy side chain, though the *E* form is more active and more stable than the Z form (McInnes et al., 1992; Sandín-España et al., 2003) and they are commercialized in this isomeric form.

Herbicides of this family are weak acids with pKa below 5. Thus, they can readily ionize, and if the pH increases above the pKa value of the herbicide, the ionized form will predominate. The protonated form of a herbicide will penetrate the plant cuticle more rapidly than the ionized form (Bukovac et al., 1971).

Their solubilities and partition properties are highly dependent on pH. They are easily decomposed by pH variations and by sunlight radiation (Roberts, 1998). These properties are highly relevant to their environmental fate.

Degradation is so rapid in aqueous media that in some cases it is questioned if herbicidal activity is maybe due to some degradation product (Iwataki, 1992). Due to the rapid degradation, most degradation products are common to most systems and in some cases it is not clear if a by-product is produced by chemical or biochemical degradation.

Therefore, it is of utmost importance to study the degradation routes of these herbicides to estimate the persistence of the residues of these compounds and to identify the factors that influence their behaviour in the environment.

2. Abiotic transformations, degradation pathways and degradation products

When an herbicide is introduced into the environment, it is subjected to different biotic and abiotic processes. Abiotic transformations may include chemical (mainly hydrolysis and thermolysis) and photochemical reactions. Complete mineralization of herbicides into inorganic constituents such as carbon dioxide, ammonia, water, mineral salts, and humic substances often occurs slowly in the environment. Different compounds, however, are formed before herbicides can be completely degraded. The organic compounds formed by the different transformation processes are referred to by several names such as degradates, by-products, etc. The most widely used are "transformation product" and "degradation product". "Metabolites" is a term usually inappropriately employed as it should be use only when the transformation product is a result of biological transformation. Therefore, in this chapter mainly dedicated to abiotic processes, we will refer to these compounds as degradation products, by-products or photoproducts if they are formed by transformations induce by sunlight.

In general, one or two transformations in the molecular structure of some herbicides are enough to modify its properties. In fact, the biological activity and/or environmental contamination attributed to the parent compound can be due to the degradation products.

The understanding of the total consequences for herbicide use is limited to the fact that most studies have focused on the parent compound and generally did not consider their transformation products (Somasundaram & Coats, 1991).

Historically, some of the most serious concerns about the safety of herbicides have raised from its transformation products than can cause detrimental side effects. Different studies confirm that many degradation products are more mobile and some others are more persistent than their respective parent compound (Boxall et al., 2004; Green & Young, 2006; Kolpin et al., 2004; Tixier et al., 2000).

Information about these degradation routes is necessary to estimate the persistence of these compounds and to identify the factors that influence their behaviour in the environment.

Nowadays, some herbicide transformation products are considered as "emerging pollutants" (Richardson, 2009; Rodríguez-Mozaz et al., 2007) as most of them have been presented in the environment for a long time, but their significant and presence are only now been elucidated and, therefore, they are generally no included in the legislation. Besides, there is still a lack of knowledge about long-term risks that the presence of these emerging pollutants may pose for organisms as well as for human health. Consequently, transformation products have become a new environmental problem and have awakened great concern among scientists in the last years (Richardson, 2006; Richardson, 2007).

Besides, herbicide degradates can either be less toxic or have similar or greater toxicity than their parent compounds (Belfroid et al., 1998; Tuxhorn et al., 1986). Thus, obtaining data on parent compounds and their primary degradation products is critical for understanding the fate of herbicides in the environment.

As mentioned before, the different abiotic/biotic processes that take place in the environment modified the physicochemical properties of the parent molecule.

Most of the oxidative reactions (hydroxylation, sulfoxidation, dealkylation…) and hydrolysis impart also some degree of increase polarity and hence water solubility to the molecule. Therefore, the new xenobiotics are more mobile in soil. Reduction reactions are characterized in environments with low oxygen concentrations, low pH and anaerobic microorganism. These reactions are less commonly observed and generally give rise to products with lower polarity.

Recent studies indicate that about one-third of the degradation products derived from a range of pesticides types have an organic carbon absorption coefficient (K_{oc}) of at least one order of magnitude lower than that of the corresponding parent compound. Thus, these transformation products may be more likely to be transported to surface and groundwater.

Boxall and co-workers (Boxall et al., 2004) showed that among different classes of pesticides and its transformation products, 41% of the transformation products were less toxic than parent compound and 39% had a similar toxicity to their parents, but 20% were above 3 times more toxic and 9% were above ten times more toxic than their parent compounds.

Oxidation reactions occur frequently in some soil and are an extremely important transformation pathway. S-containing herbicides, like some cyclohexanediones, are often rapidly oxidized to sulfoxide and afterwards more slowly to sulfones (Roberts, 1998). Sulfoxidation of herbicides can occur in soil and water mediated by chemical or biological reactions. This oxidation is so rapid and complete that sulfoxides are often the compounds found in soil shortly after application of the parent sulfide compound. Furthermore, in some cases, sulfoxides and sulfones are suspected to have pesticidal activity (Ankumah et al., 1995; Campbell & Penner, 1985; Tuxhorn et al., 1986).

2.1 Chemical degradation

Chemical degradation of organic compounds includes mainly hydrolysis and thermolysis reactions. With regard to hydrolysis, pH of water is responsible for the transformation of some pesticides in solution, especially in conjunction with extreme pH (García-Repetto et al., 1994).

Furthermore, organic compounds sensitive to pH give rise to its rapid degradation even with a slight variance of pH (Dannenberg & Pehkonen, 1998; Santos et al., 1998; Sanz-Asencio et al., 1997) and hence they have a low environmental persistence.

Alloxydim-sodium is a sodium salt of an acid, alloxydim (Fig. 4), having a pKa of 3.7, which is present as the monoanion and/or the acid in aqueous solution, and the possibility of many tautomeric forms should be considered to understand the transformations in the molecule when degradative reactions occur.

Alloxydim-sodium is neutralized to the sodium free compound (alloxydim) by the action of carbon dioxide in air or components in plants or in soil.

Studies of thermal degradation of alloxydim gave two oxazole derivatives (VII and VIII; Fig. 4) at 120 ºC. The ratio was found to be 3 to 2 (VII:VIII) (Iwataki & Hirono, 1978). The mechanism of the formation of these oxazoles seems to take place when in certain tautomeric isomers, the cyclohexane ring of alloxydim is coplanar with the six membered ring which is formed by hydrogen bonding and the allyloxy group should be in the anti position against the cyclohexane group on the C=N bond. Therefore, the Beckmann rearrangement reaction occurs, which coincides with the intramolecular cyclization to form the oxazoles.

In the same way, when alloxydim is heated at 30, 40 and 50 ºC in a dark incubator for 20 days gives the mixture of VII and VIII (Fig. 4). These three degradation products also appeared when alloxydim-sodium is applied in the leaves of plants (Hashimoto et al., 1979a; Koskinen et al., 1993).

The acid hydrolysis of alloxydim gives rise mainly to the butyrylamido derivatives and the imine salt. The alkaline hydrolysis forms the demethoxycarbonylated butyrylamido derivative (Iwataki & Hirono, 1978).

Chemical degradation of herbicides can also take place when the herbicide gets in contact with water that possesses substances that promote its degradation. In this sense, it is known that the presence of substances employed for the disinfection of water such as hypochlorite and chloramines degrade the herbicide to compounds more or less toxic than the active substance (Lykins et al., 1986; Magara et al., 1994; Reckhow & Singer, 1990).

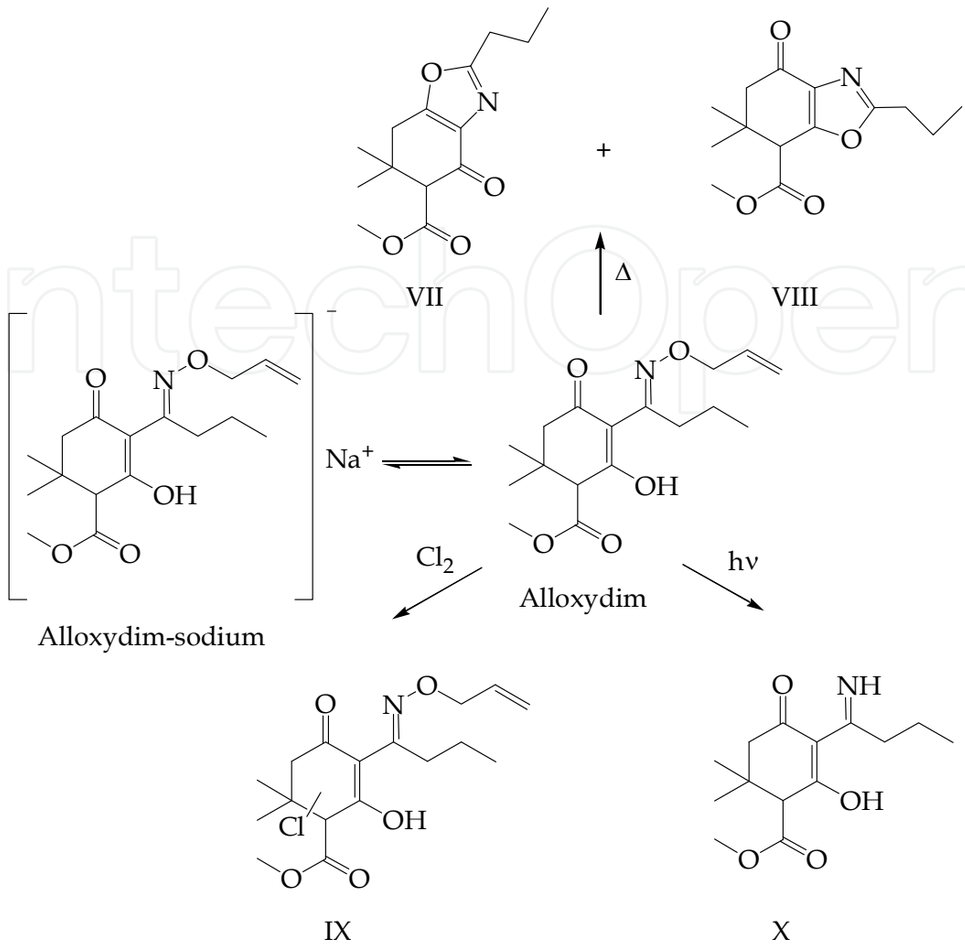


Fig. 4. Main degradation pathways of alloxydim-sodium.

Studies of alloxydim degradation in chlorinated water showed that the herbicide degrades very fast with half-lives less than one minute. As a result of the reaction one degradation product is formed that is isolated by solid phase extraction and identified by means of mass spectrometry as a chlorinated cyclohexanedione oxime compound IX (Fig. 4) (Sandín-España et al., 2005b).

Other cyclohexanedione oxime herbicide, clethodim is also an labile acid. Degradation rates significantly decreases from pH 7 to pH 5. After 20 hours, clethodim loss was 37% at pH 5 , 8% at pH 6 and 0% at pH 7 (Falb et al., 1990). Nine by-products were separated by liquid chromatography, though none of them was identified.

Falb et al., 1991 (Falb et al., 1991) also observed an increased in the degradation of clethodim when pH decreased. 19 peaks of degradation products more polar than parent clethodim molecule were separated by liquid chromatography.

As mentioned before, cyclohexanedione herbicides are marketed as the *E*-isomer at the oxime ether double bond (Fig. 5). It has been stated that some of them, like clethodim, may equilibrate with the *Z*-isomer in a polar medium such as water (Falb et al., 1990; Sandín-España et al., 2003). 4% of isomerization of clethodim to *Z*-isomer was observed when

preparation of aqueous solution and 40% after two months (Sandín-España et al., 2005a). This isomerization has been also observed in herbicide tepraloxydim where equilibrium between both isomers was slowly attained in aqueous solution. It took about 7 days to reach equilibrium with a final ratio between isomers of 2:1 (*Z:E*) (Sandín-España et al., 2003). Other studies show that isomer Z also appears in acidic water samples of *E*-tepraloxydim after 72 h of storage at 4 ºC (Sandín-España et al., 2002).

Degradation of clethodim in chlorinated water either with sodium hypochlorite or chloramines was very rapid with half-lives below 10 minutes (Sandín-España et al., 2005a). The main degradation processes was the oxidation to clethodim sulfoxide (Fig. 5). Experiments continued to follows degradation of the sulfoxide molecule. Its half-life was 4.4 seconds with hypochlorite and 9.3 hours with chloramines. Subsequent oxidative reaction of the sulfoxide generates the formation of clethodim sulfones (Fig. 5) and other minor products. The fast degradation of clethodim in chlorinated water (either with hypochlorite or chloramines) practically precludes any possible exposure of consumers to this compound when tap water is subjected to a chlorinated treatment. However, it is not possible to ensure complete destruction of the reaction product clethodim sulfoxide before the distribution point when chloramines are used for disinfection due to the slower degradation rate. Besides, whereas some minor degradation products remain unidentified, none of the major degradation products of clethodim contain more chlorine atoms than the parent compound which represents a positive aspect of this compound with respect to consumers´ safety.

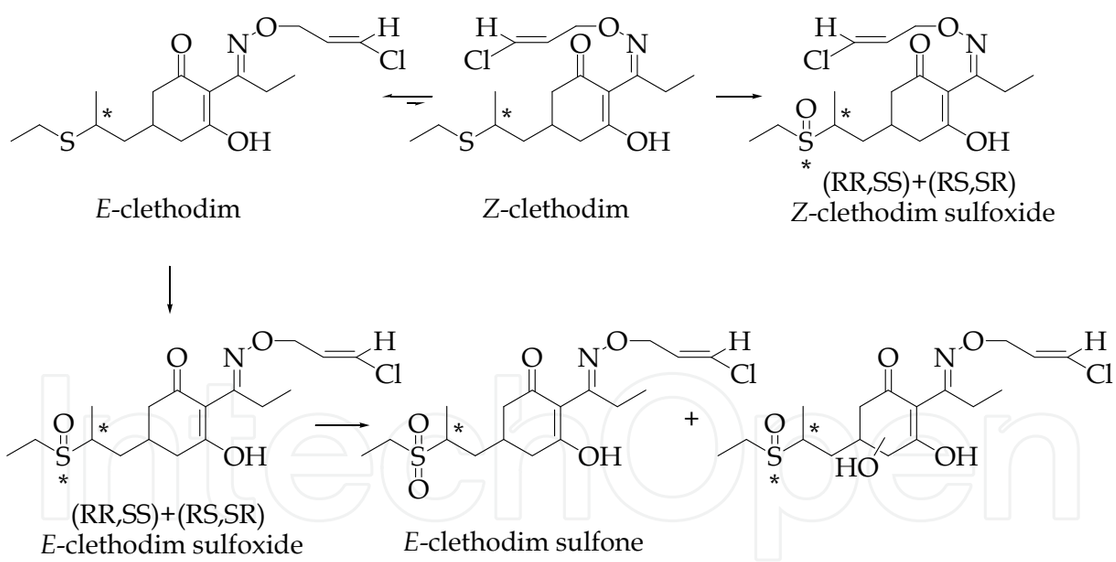


Fig. 5. Proposed degradation pathway of clethodim in chlorinated water.

Sethoxydim dissolves in water is found to be unstable at room temperature or when kept at -20º C; only 6 and 24% or the parent sethoxydim remained after 72 hours (Campbell & Penner, 1985). This herbicide also undergoes chemical decomposition at acid pH (Shoaf & Carlson, 1992; Smith & Hsiao, 1983) and in alkaline solution (Shoaf & Carlson, 1986).

Others cyclohexanedione herbicides such as profoxydim or tralkoxydim have also been reported to undergoes hydrolysis depending on the pH (Walter, 2001) of the solution and being easily degraded in aqueous solution (Sevilla-Morán et al., 2011; Srivastava & Gupta,

1994) and in chlorinated water (Sandín-España, 2004). However, scarce data exists in the open literature about degradation pathways or degradation products.

2.2 Photochemical degradation

Photochemical reactions are one of the major transformation processes affecting the fate of pesticides in the environment, especially in the aquatic compartment (Dimou et al., 2004; Neilson & Allard, 2008). Two ways of photodegradation reactions occur in sunlit natural water. In direct photolysis, organic compounds absorb light and as a consequence of that light absorption, undergo transformation. For this to occur in the water, the emission of the sun (290-800 nm) needs to fit the adsorption spectrum of the pesticide. In indirect photochemical reactions organic chemical are transformed by energy transfer from another excited species (e.g., components of natural organic matter) or by reaction with very reactive, short-lived species formed in the presence of light (e.g., hydroxyl radicals, single oxygen, ozone, peroxy radicals, etc.). Absorption of actinic radiation by nitrate and dissolved organic matter (DOM) leads to the formation of most of these species. Therefore, the composition of the aquatic media plays an important role on the phototransformation of pesticides in this compartment.

The hydroxyl radical, $OH^{\bullet}$, is one of the most reactive of the aforementioned reactive intermediates due to its non-selective and highly electrophilic nature.

Ideally solar radiation should be used in studies of environmental photochemistry, however, meteorological conditions in most countries and a slow degradation rate do not permit reproducible experimentation. In a first approach to study the photochemical behavior of organic compounds in different matrices, it is common to conduct the degradation under controlled conditions. Generally, the use of xenon arc lamp, with light above 290 nm (provided by a filter), is preferred as its spectral emission distribution are very close to the solar radiation spectrum (Marcheterre et al., 1988). It has been demonstrated that the use of different light sources under identical aqueous conditions can produce similar degradation products, with the only difference being in their kinetic of formation (Barceló et al., 1996). As for the experimental equipment, quartz glass is preferred instead of other glass material since it permits a greater transmission of radiation (Peñuela et al., 2000).

The composition of aquatic media also plays an important role in the phototransformation of pesticides. Various authors point out that particulate matter, such as sediment particles, and dissolved substances present in natural waters could be responsible for the different photolysis rates observed between natural and distilled water (Dimou et al., 2004; Schwarzenbach Rene et al., 2002; Tchaikovskaya et al., 2007). The most important light-absorbing species that may induce indirect photolytic transformation of organic pollutants in natural waters are the chromophores present in dissolved organic matter (DOM) where humic acids are important absorbing constituents of it and in a lesser extent, fulvic acids.

Diverse studies are available from literature where humic acids act enhancing (Sakkas et al., 2002a, 2002b; Santoro et al., 2000; Vialaton & Richard, 2002) or inhibiting (Bachman & Patterson, 1999; Dimou et al., 2004; Dimou et al., 2005; Elazzouzi et al., 1999; Sevilla-Morán et al., 2010a; Sevilla-Morán et al., 2008) the degradation of pesticides. In the first case, humic acids behave as a "sensitizer" where the excited states of humic acids can participate in a charge-transfer interaction with pesticides, or generate reactive intermediates, such as

hydroxyl radicals, singlet oxygen, solvated electrons or hydrogen peroxide. In the second case, humic acids act as photon trap (optical filter effect), decreasing the photodegradation rate of pesticide.

Consequently, information about photodegradation of pesticides is necessary to estimate the persistence and to identify the factors that influence their behavior in the environment. Furthermore, it is important to investigate what these compounds degrade into, its persistence of by-products relative to the parent compounds, and whether the degradation products retain the activity of the active substance to cause a toxicological effect on non-target organisms in aqueous systems.

Studies show that alloxydim is degraded on the leaf surface by photochemical reactions. After two days, the deallyloxylated compound X (Fig. 4) is the main degradation product identified. This by-product is formed by photoreduction. Other minor degradation products identified, that accounted less than 0.5% of the applied radioactivity, were two isomeric oxazoles and a demetoxycarbonylated compound (Hashimoto et al., 1979b; Soeda et al., 1979).

When photodegradation of alloxydim was studied in sterilized soil (Ono et al., 1984), only 22% of the ^{14}C-alloxydim applied was remained. The main by-products identified by thin-layer chromatography and mass spectrometry were again the deallyoxylated compound (X) and the two oxazole isomers (VII, VIII) (Fig. 4). The demethoxycarbonylated compound was formed in a minor extent (Ono et al., 1984).

Photochemical transformation of a methanol solution of ^{14}C-alloxydim on silica gel plate, irradiated with UV light also gives by-products VII, VIII and X (Soeda et al., 1979).

Sevilla-Morán et al., studied the photodegradation of alloxydim-sodium under simulated solar irradiation using a xenon arc lamp (Sevilla-Morán et al., 2008). This light source fits the solar radiation spectrum best over the whole range of spectral emission (Marcheterre et al., 1988). Indirect photolysis under the presence of various concentrations of humic acids, nitrate and iron ions was also investigated. Results show that degradation rate in direct photolysis was higher as the radiation intensities increased. Irradiation of aqueous solutions of alloxydim containing different concentrations of humic acids (1-20 mg L^{-1}) show that increasing concentrations of humic acids, decrease photolysis rate of this herbicide, indicating that absorbed most of the photons emitted, thereby slowing down direct photochemical reaction of alloxydim. The presence of nitrate ions had no effect on the degradation rate. On the contrary, iron ions accelerate the rate of photolysis of alloxydim possibly due to the formation of a complex and later undergo a direct photolysis (Boule, 1999; Park & Choi, 2003). Simultaneously to the irradiation experiments, control experiments in absence of radiation were performed in order to discard other type of dark reactions (hydrolysis, thermolysis, ...). Quantitative recoveries of clethodim during the entire exposure period to simulated solar irradiation enable to ignore other transformation processes that are not initiated by radiation.

As for the identification of transformation products, HPLC-ESI-QTOF-MS technique was employed. QTOF provides elevated resolution and sensitivity, high mass accuracy for both parent and fragment ions in combination with the possibility of performing MS/MS acquisitions obtaining more structural information (Aguera et al., 2005; Ibáñez et al., 2004). In this way, QTOF allows the assignments of a highly probable empirical formula for

unknown compounds. Two main degradation pathways were identified. The main reaction was the photoreduction of the N-O bond dissociation of allyloxyamino moiety to give the imine (X; Fig. 4). The second reaction was the isomerization of the oxime moiety to give the *Z*-isomer (Sevilla-Morán et al., 2008).

In the same way, under UV light technical clethodim was greatly accelerated as compared to dark conditions. The degradation half-lives were 2.5, 2.6 and 3.2 hours at pH 5, 6 and 7 (Falb et al., 1990). The HPLC system separated 13 photoproducts though none of them were identified. The addition of adjuvants to clethodim increased the rate of photodegradation with UV radiation by 2 to 7 fold. The rate of degradation under sunlight was increased with the addition of adjuvant by 7 to 27 fold over the control (Falb et al., 1990).

Falb and co-workers, (Falb et al., 1991) also observed that clethodim undergoes degradation when exposed to UV light and developed a method for the separation of 31 degradation products, but none of them were characterized.

It is recommended that spraying at late evening or night may improve cyclohexanedione oxime herbicides efficacy due to a reduction in the amount of UV light present (McMullan, 1996). Applying cyclohexanedione herbicides at times when the UV light is lowest, such as late evening or at night, will maximize weed control with these herbicides.

Cyclohexanedione herbicide efficacy was affected by spray solution pH. This was probably due to the predomination of the ionized form of the cyclohexanedione molecule at high spray solution pH and the possible formation of cyclohexanedione sodium salts (Nalewaja et al., 1994).

Experiments on the efficacy of clethodim and tralkoxydim (McMullan, 1996) showed that filtering UV light 4 hours after treatment improved the efficacy between 13 and 55%. These results are in agreement with results published by McInnes et al. with sethoxydim (McInnes et al., 1992).

Indirect photodegradation of clethodim in the presence of humic acid, nitrate ions and iron ions in aqueous solution has been also studied (Sevilla-Morán et al., 2010a). The presence of humic acid increased the half-life of herbicide photolysis compared to direct photolysis [$t_{1/2([HA]=1\ mg/L])}$ = 44,2 min *vs.* $t_{1/2ultrapure\ water}$ = 28,9 min]. This retarding effect, as in alloxydim, indicates that these substances can act as an "optical filter" absorbing most of the photons emitted and thereby slowing the direct photochemical reaction of clethodim. Nitrate ions had no effect on the photodegradation of clethodim and the presence of iron ions increase the rate of photolysis up to 6 times when 20 mg L^{-1} of Fe(III) ions were present in the solution. In these experiments up to nine different by-products were observed all of them more polar than clethodim (Sevilla-Morán et al., 2010a). Identification was performed by using a QTOF mass spectrometer. A detailed study based on the exact mass measurements and fragmentation pattern makes possible for the first time to elucidate the structures of the nine photodegradation by-products. Figure 6 shows the proposed photodegradation pathway of clethodim in aqueous solution. The by-products identified were the following; *Z*-isomer of clethodim at the oxime ether double bond. The *Z*-isomer is much more polar that clethodim (26 *vs.* 41 minutes). This could be due to an internal hydrogen bond formed between the oxime oxygen and the hydroxyl group of the cyclohexane ring. Several authors stated that some *E*-isomer of cyclohexanedione oxime herbicides may equilibrate with the *Z*-isomer in polar solvents (Falb et al., 1990; Sandín-

España et al., 2002) or in chlorinated water (Sandín-España et al., 2005a). Besides, it has been reported that isomerization can be induced by light and temperature (Curtin et al., 1966; Sevilla-Morán et al., 2008).

The oxidation of the sulphur atom of the molecule generates two pairs of enantiomers (RR+SS and RS+SR) and diastereomers are chromatographically separated in two peaks, containing a pair of enantiomers each. In the same way, *Z*-isomer of clethodim gave rise to the corresponding pairs of enantiomers of *Z*-clethodim sulfoxide. As in alloxydim, photoreductive reaction of *E*- and *Z*-clethodim forms the corresponding imine. Oxidation of imine gave rise to two pair of enantiomers of clethodim imine sulfoxides. The oxidative cleavage of the C-S bond of clethodim imine gave rise to clethodim imine ketone.

Various authors have also studied the photodegradation of sethoxydim (Campbell & Penner, 1985; Sevilla-Morán, 2010; Sevilla-Morán et al., 2010b; Shoaf & Carlson, 1986; Shoaf & Carlson, 1992). The herbicide was completely lost within seconds in aqueous media either in incandescent or UV light at pH 3.3 and 6.0 and methanolic solutions of the herbicide were transformed more than 50 % after 10 min of exposition to UV light (Shoaf & Carlson, 1992) (Shoaf & Carlson, 1992). Upon 1 hour of UV irradiation sethoxydim sulfone was identified as one of the degradation products formed during the experiment. Campbell and Penner suggested the rapid degradation of sethoxydim in water and organic solvents (Campbell & Penner, 1985). These authors exposed aqueous solutions of sethoxydim to artificial light and observed that only 2 % remained after 3 h. In the same way, they also observed a rapid photodegradation on glass disks of sethoxydim dissolved in n-hexane (81 % of herbicide was transformed after 1 h). In both systems, 6 major products were detected. Five of these products were transitory and only one appeared to be the single end product. One of these compounds was isolated and identified by mass spectrometry as desethoxy-sethoxydim.

Evidence of rapid transformation of sethoxydim expose to light suggested that herbicidal activity resulted from the more stable transformation products. Five of these products were applied to barnyardgrass to determine phytotoxicity. It was found that two degradation products had significant activity as did sethoxydim and three of them showed no herbicidal activity. Though none of these isolated by-products were quantified as relative herbicidal potencies could not be determined, this is relevant information about phytotoxicity of degradation products.

Under field conditions, were sethoxydim would be applicated by spraying water-oil emulsion during daylight, it is likely that sethoxydim transformation would be rapid and levels of degradation products would be present. These findings suggest that some of the degradation products are actually the herbicidal agent (Campbell & Penner, 1985; Shoaf & Carlson, 1992).

In order to obtain results close to real field conditions different experiments have been carried out to study the photodegradation of sethoxydim in natural waters (mineral, well and river) and under natural sunlight. The degradation rates in natural waters were lower than in ultrapure water and degradation under natural sunlight also decrease the degradation rates. These results indicate that under real environmental conditions photodegradation of sethoxydim is retarded compare to laboratory studies. Besides, significant differences among types of water suggest that degradation of sethoxydim has a strong dependence on the composition of water sample. Figure 7 shows the photo-

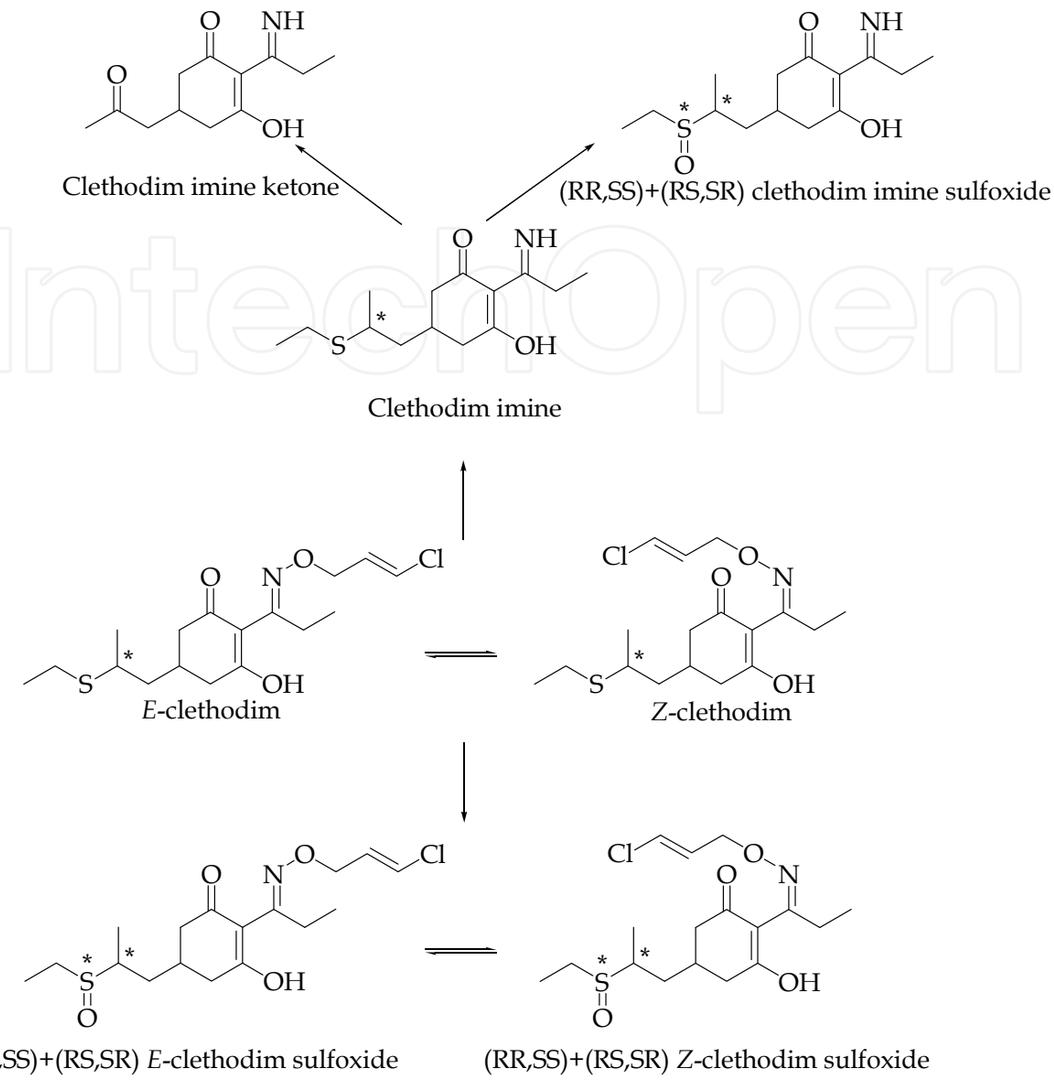


Fig. 6. Proposed photodegradation pathway of clethodim in aqueous solution.

degradation curves of sethoxydim in natural waters under solar irradiation. The photolysis rate decreases in the following order, river<well≈mineral<ultrapure water. Photodegradation of sethoxydim-lithium in natural water was approximately 5 times slower than in ultrapure water showing a half-live of 436.9 ± 0.8 min for river water and 82.1 ± 0.7 min for ultrapure water. These significant differences observed in the three water samples, under both types of irradiation, indicated that the degradation of sethoxydim-lithium depends to a large extent on the composition of aqueous matrix. Natural water contains some substance/s that induces a retardant effect of the photodegradation of sethoxydim-lithium. Thus, this difference observed (2-5 folds) could be attributed to the presence of increasing concentrations of TOC (Total Organic Carbon) in the natural waters, where river water has the highest concentration of TOC (2.865 mg L^{-1}) and ultrapure water has the lowest (0.005 mg L^{-1}).

The photodegradation of sethoxydim-lithium in all water types under simulated light was quicker than under natural sunlight (e.g. $t_{1/2(\text{river water-natural sunlight})}$=436.9 ± 0.8 min *vs.* $t_{1/2\ (\text{river}}$

$_{water)}$ 135.5 ± 0.3), which is well correlated with the lower intensity of natural sunlight (460 W m^{-2} at the middle of the day *vs.* 750 W m^{-2} of xenon lamp). These results show a great influence of the intensity radiation on the degradation of sethoxydim-lithium and they are in accordance with other authors where the degradation of active substance is dependent on the irradiation energy (Dimou et al., 2005; Sakkas et al., 2002a).

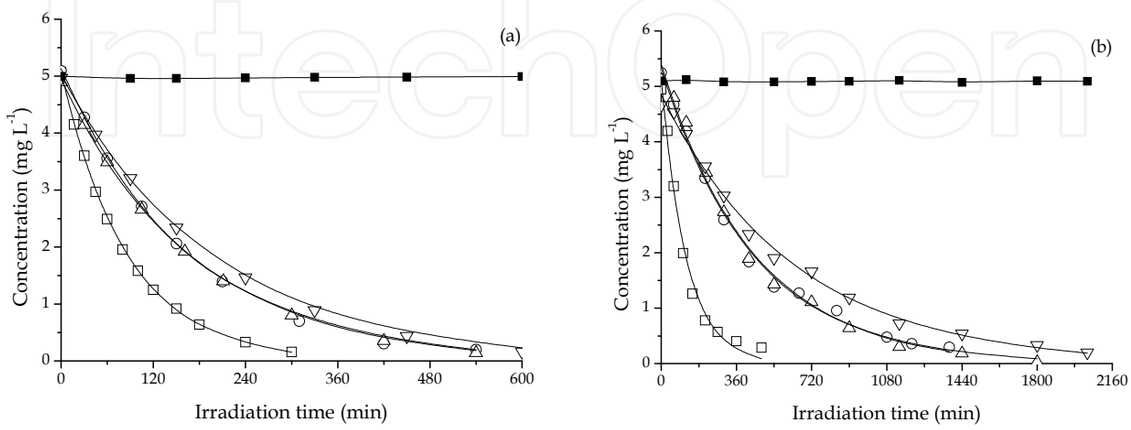


Fig. 7. Photodegradation of sethoxydim-lithium in various types of water under simulated light (a) and natural sunlight (b): (□) ultrapure water, (○) mineral water, (Δ) well water, (∇) river water, (■) dark experiment.

3. Bioassay methods to detect herbicide phytotoxicity

Weeds are a continuous problem in agriculture. The success of modern agricultural practices is due in part to the discovery and adoption of chemicals for weed control. The introduction of selective herbicides has greatly facilitated farmers' work by suppressing the need for manual weeding. Indeed, the tremendous increase in crop yields associated with the "green" revolution would not have been achieved without the contribution of these synthetic compounds. The abundance of high quality food in developed nations has eliminated concerns about access to food in these countries. However, concerns over the potential impact of pesticides on the environment have now arisen and as consequence, more pressing and more stringent pesticide registration procedures have been introduced.

The basis for much of the work done in weed control is the testing of the response to the herbicides. Bioassay methods have been developed to determine the residue level of many herbicides in soil and water (Fig. 8). There are different types of bioassays, depending on the species, the type of herbicide used, its mode of action, substrate and other environmental conditions, as well as the measured parameter. Their use offer several advantages such as the detection of very low phytotoxic residues and the detection of its bioavailability. Therefore, bioassays can be used to complement the analytical chemical methods and are useful tools to screen herbicide phytotoxicity and provide information about the phytotoxicity of herbicide residue in the soil at sowing time. The sensitivity, low cost and reproducibility of bioassays fulfill the criteria for a good technique.

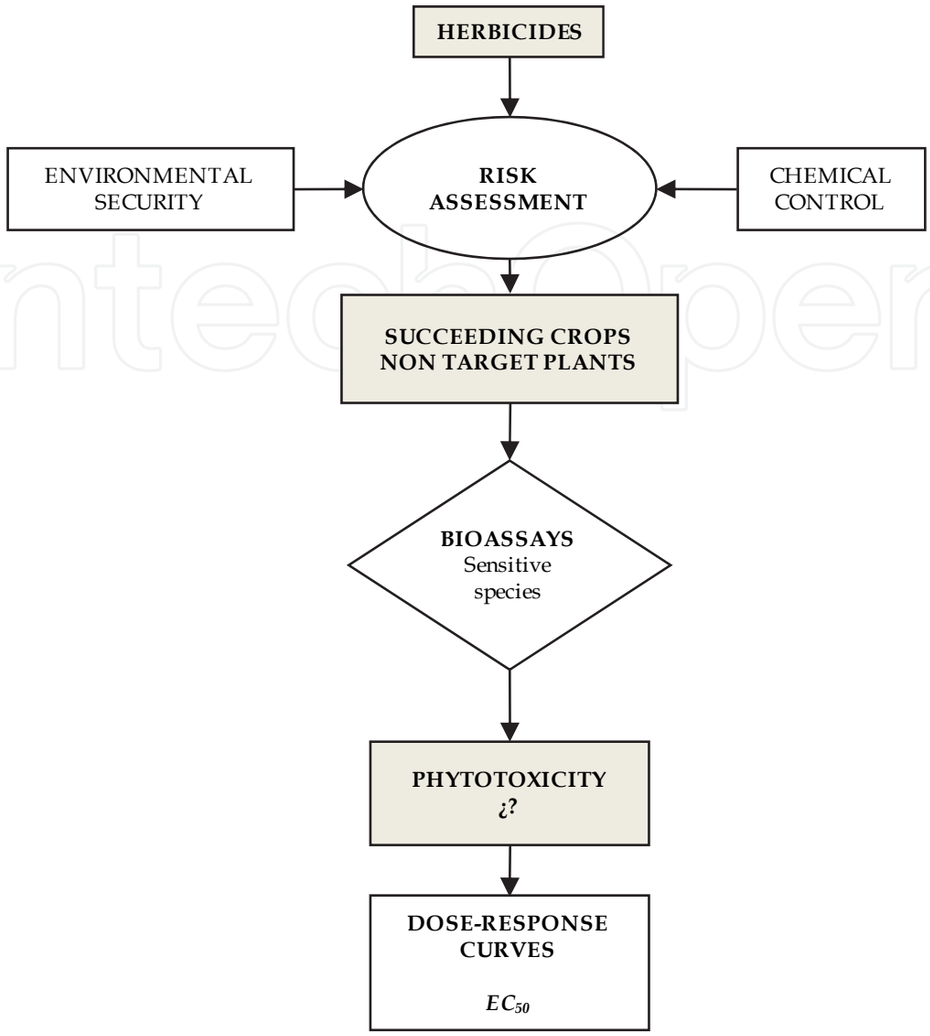


Fig. 8. Process of conducting bioassays in testing response of herbicides.

The classical bioassay, often used to quantify the amount of herbicide in soil, employs a single "standard" dose-response curve. This standard curve shows the plant response to different herbicide concentrations and report information of different concepts related to herbicide efficacy, such as selectivity, tolerance and resistance. These methods are of the utmost importance in studies of crop selectivity, herbicide resistance development and herbicide resistant weeds detection.

A typical dose-response curve is sigmoid in shape. One example of such a curve is the log-logistic curve (Seefeldt et al., 1994). The mathematical expression relating the response Y to de dose X is the following;

$$Y=C+\frac{D-C}{1+\exp\left\{b\cdot\left[\ln(X+1)-\ln(EC_{50}+1)\right]\right\}}$$

where C is the lower limit, D is the upper limit, b is the slope, and EC_{50} is the dose giving 50% response. The log-logistic is the most common model used in bioassays to describe

dose-response relations. Other relevant sigmoid curves might be the Gompertz (Ritz et al., 2006), are used sometimes, for instance, in cases where a log-logistic model did not fit well to the data. Also, the toxicity factor used in the risk assessment is usually the EC_{50} (concentration required to give 50% reduction of the plant growth with respect to the control).

The consequences of herbicide introduction into the environment could not be limited to active ingredient. It is very important to know whether any phytotoxic effects detected due to active substance applied or to some of its metabolites or degradation products. In this case, it is necessary to know the route and rate of degradation not only for the active substance but also for the products of degradation (Berenzen et al., 2005).

Besides, the herbicide formulations contain many other compounds called adjuvants. Adjuvants are defined as ''an ingredient in the pesticide prescription, which aids or modifies the action of the principal ingredient'' (Foy, 1993). These products are added to increase the effectiveness (bioavailability) of the formulation by enhancing the solubility, or the compatibility of the active ingredients. Other functions can be to improve adsorption, penetration and translocation of the active ingredients into the target, increase rain fastness, and alter selectivity of the active ingredient toward different plants (Foy, 1993; Foy & Witt, 1992; Li & Foy, 1999). Furthermore, many papers concerning effect studies of pesticides have compared effectiveness of different adjuvants (Foy, 1993). Only very few papers discuss the environmental toxicity and risk of adjuvants; Chow and co-workers have previously noted this lack of information on the effects of adjuvants on the environment (Chow & MacGregor, 1983). Especially, information on both simple toxicological properties of adjuvants and their influence in complex ecosystems is required. Actually, the ecotoxicological aspects of the use of surfactants in cleaning products mostly for household have been published (Junghans et al., 2006; Krogh et al., 2003).

The potential problems that residues of these products may present, as the effect on non-target species or in successive crops, do not provide information needed to relate these effects with the chemical nature of the residue. Therefore, it is also necessary to study the nature of this residue by conventional analytical methods to identify potential causes of environmental problems.

3.1 Herbicidal activity of cyclohexanedione oxime herbicides

The graminicides are a group of commercially important selective herbicides (Harwood, 1999). One of major chemical classes of post emergence herbicides belongs to the cyclohexanedione class. This herbicides´ group is effective against a wide range of annual and perennial grasses (monocotyledonous) in a large variety of broad-leaved crop plants (dicotyledonous). Their biochemical target site is the enzyme acetyl coenzyme-A carboxylase (ACCase) (Burton et al., 1991; Rendina et al., 1990; Secor & Cseke, 1988), which catalyzes the first step in fatty acid biosynthesis. They are also known as group A herbicides or group 1 herbicides (Park & Mallory-Smith, 2004; Price et al., 2003). Since their introduction in the late 1970s, the ACCase-inhibiting herbicides have been widely used worldwide to control a number of grass weed species (Devine & Shimabukuro, 1994). Ciclohexanodione herbicides are also a family used at low-dose rate as they are biologically active at very low concentration (0.2-0.5 kg a.i. ha^{-1}). It is currently being registered in

Europe, for weed control in broad-leaved crops, mainly in sugarbeet (*Beta vulgaris* L.), soya bean (*Glycine max* L. Merr.), and pea (*Pisum sativum* L.) crops, although its use is recommended in other broad-leaved crops such as rape (*Brassica napus* L.), potato (*Solanum tuberosum* L.) and beans (*Phaseolus vulgaris* L. and *Vicia faba* L.) (Sandín-España et al., 2003).

Cyclohexanedione oxime herbicides cause a rapid cessation of growth followed by destruction of shoot meristems in susceptible species. Studies on the uptake, translocation, and metabolic fate in tolerant and susceptible plants have shown that these herbicides inhibited *de novo* fatty acid biosynthesis in isolated chloroplasts, cell cultures, or leaves of susceptible grasses such as corn, wheat, and wild oats but not in tolerant broad-leaved plants such as soybean, spinach, and sugar beet (Burgstahler & Lichtenthaler, 1984). Injury symptoms tend to develop rather slowly in sensitive plants treated with cyclohexanedione herbicides. Growth (leaf elongation) stops within 24-48 h after herbicide application. Chlorosis is first observed on the youngest tissue, usually the emerging leaves. This reflects the fact that the initial phytotoxicity occurs primarily at the apical meristem, the major site of cell division and *de novo* fatty acid synthesis in these plants. In fact, 48-72 h after treatment the youngest emerged leaf can be quite easily separated from the rest of the plant by gently pulling it upwards; again, this reflects the tissue damage at the meristem. Chlorosis then spreads slowly through the rest of the plant, although it may take 7-10 days for the entire plant to be affected. Phloem translocation of these herbicides through the plant is limited, resulting in relatively small amounts reaching the roots. For this reason, these herbicides provide excellent control of perennial grass weeds. However, uncertain conditions some control of perennials can be achieved. No injury symptoms appear on dicotyledonous crops or weeds treated at typical use rates. Physiological injury can occur in cereal crops under certain conditions (e.g., low temperature at time of application), presumably due to reduced rates of herbicides detoxification. However, most plants recover from this temporary injury within 7-10 days (Walker et al., 1988).

The cyclohexanedione oxime class has been developed at low doses to reduce the adverse effects of the use of some herbicides and fulfill environmental requirements, water and soil pollution set by international legislation. However, due to high phytotoxicity, small amounts of residual herbicide in soil may affect sensitive succeeding crops. Also their polar character makes them easily leach to groundwater and potentially contaminate at levels above 0.1 μg L^{-1} (Sandín-España et al., 2003). In this context, studies about mobility, degradation and persistence in soil and water were performed with a variety of analytical techniques like gas and liquid chromatography, mass spectroscopy, photodegradation studies, studies with ^{14}C, immunoassays, etc. Most studies have been made in water and soil; occasionally there are some bioassays in microalgae (Santín-Montanya et al., 2007). The last results obtained confirm that could be susceptible specie capable to detect the presence of some herbicides (Table 1 & Fig. 9).

Herbicides	Log-logistic curve doses-response	R^2 (%)
Alloxydim	y= 0,19+((0,63-0,19)/(1+exp(1,74*(Ln(Dose+1)-Ln(285,22+1)))))	78,03
Sethoxydim	y=-0,0022+((0,66+0,0022)/(1+exp(0,62*(Ln(Dose+1)-Ln(110,33+1)))))	83,76
Metamitron	y=0,11+((1,08-0,11)/(1+exp(0,95*(Ln(Dose+1)-Ln(0,128+1)))))	98,14
Clopyralid	Not adjusted to regression equation	

Table 1. Regression equations by Seefeldt model that describe the relationships between increased doses of herbicides and growth of *Dunaliella primolecta* (unpublished data).

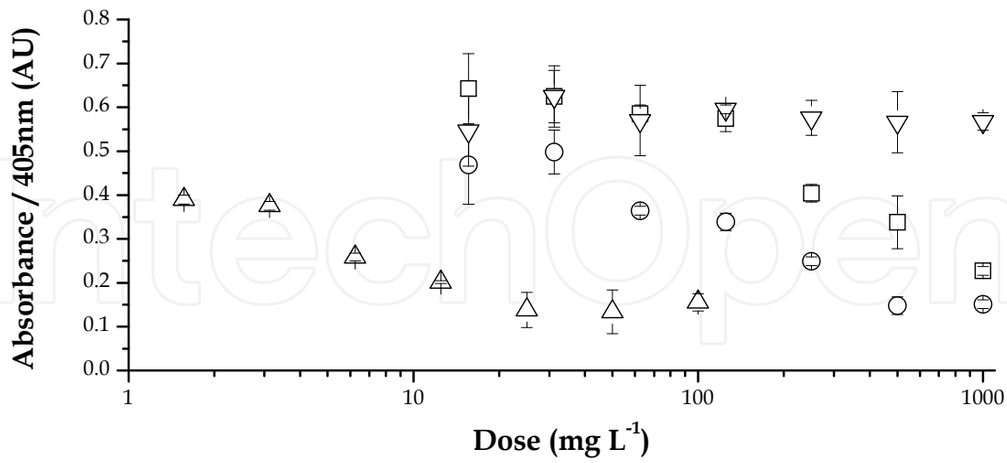


Fig. 9. Response of microalgae *Dunaliella primolecta* growth in presence of different concentrations of alloxydim (□), sethoxydim (○), metamitron (△) and clopyralid (▽) (unpublished data).

Other bioassays have been developed to detect phytotoxic residues of herbicide sethoxydim (Hsiao & Smith, 1983). In our group, initial attempts to obtain a practical hydroponic bioassay that allowed us to quantify tepraloxydim were frustrated due to the lack of repeatability and random results. Therefore, an investigation was carried out to determine the fate of tepraloxydim under bioassay conditions in order to clarify the reason for poor bioassay repeatability. The presence of residual chlorine in water was identified as the key factor on the repeatability of the bioassay.

Finally, an extensive research was conducted to develop and optimize a bioassay based on the high sensitivity of wheat (*Triticum aestivum* L.) to tepraloxydim in hydroponic culture using chlorine free mineral water (Sandín-España et al., 2003). Afterwards, similar studies were carried out with tralkoxydim (Table 2&3).

Dose (μg L^{-1})	Tepraloxydim		Tralkoxydim	
	Bioassay 1	Bioassay 2	Bioassay 1	Bioassay 2
0	11.9 a	12.1 a	9.5 a	11.9 a
2	10.2 b	10.7 b	8.2 b	11.9 a
4	6.7 c	5.8 c	7.7 b	9.3 b
8	3.5 d	3.2 d	3.9 c	3.9 c
16	1.5 e	1.6 e	1.4 d	1.2 d
32	0.7 e	0.7 e	0.8 d	0.6 d

Table 2. Mean values of root growth wheat treated with herbicides 7 days after treatment. Different letters after value, for each column, indicate differences at $p<0.05$.

	Tepraloxydim		Tralkoxydim	
	Bioassay 1	**Bioassay 2**	**Bioassay 1**	**Bioassay 2**
EC_{50} (μg L^{-1})	4,6	3,8	6,8	7,0
R^2 (%)	99,8	97,2	98,4	99,6

Table 3. EC_{50} parameter of by Seefeldt model to two ciclohexanodione oxime herbicides in hydroponic culture of wheat.

It has been demonstrated that water chlorination with disinfection purposes degrades completely any possible residue of herbicide clethodim (Sandín-España et al., 2005a). This degradation is very rapid, giving rise to different degradation products. In this sense, we have studied the phytotoxicity of alloxydim and its main metabolite with hydroponic bioassays on wheat (Sandín-España et al., 2005b).

A chlorinated degradation product (IX; Fig. 4) of alloxydim was the main product obtained in its degradation with chlorine, one of the most common disinfectant agents employed in water treatment. Results showed that after seven days of treatment the most sensitive biological parameter for alloxydim was root length, causing in the root growth of plants a 40% of significative reduction at the dose of 0.3 mg L^{-1} and 94% of reduction at the highest dose. However, the effect of metabolite on root growth only occurred at the highest metabolite dose (10 mg L^{-1}), causing a 32% of reduction in root growth. Root system control presented normal growth (main tap root plus secondary roots), while those from injured plants were increasingly deformed (main tap root twisted and lack of secondary roots). Root growth was increasingly affected with doses from 0.1 mg L^{-1} to the highest dose (Table 4).

The foregoing results suggested that the use of low dose herbicides can produce damage on succeeding crops, neighbouring crops and on non-target plants. Overall, there is no one species or endpoint that is consistently the most sensitive for all species or all chemicals in all soils, and differences in bioavailability among compounds may confound comparison of test results (Clark et al., 1993). Therefore, bioassays can provide additional information, with acceptable reproducibility (Ritz et al., 2006) on herbicide uptake and translocation (Horowitz, 1980; Reineke et al., 2002).

Dose (mg L^{-1})	RG with Alloxydim (cm)		RG with Metabolite (cm)	
0	15.20 a		12.60 a	
0.1	13.67 a		13.15 a	
0.2	11.65 a		13.07 a	
0.3	9.04 b	↓ **40** %	13.59 a	
0.4	4.93 c		13.30 a	
0.5	2.64 d		13.35 a	
0.7	1.58 e		12.94 a	
1	0.90 e	↓ **94** %	12.23 a	
5			12.60 a	
10			8.55 b	↓ **32** %

Table 4. Response of root growth (RG) of wheat plants to different doses of alloxydim and its metabolite 7 days after treatment (means values of root growth). Different letters after value, for each column, indicate differences at $p<0.05$.

3.2 Occurrence of weed resistance to cyclohexanedione oxime herbicides

The reliance on herbicides for weed control has resulted in shifts in the weed flora and, more importantly, in the selection of herbicide-resistant weed populations. This is particularly true for herbicides with a single target, such as herbicides inhibiting acetyl coenzyme-A carboxylase (Devine & Shimabukuro, 1994).

Since their introduction to world agriculture in the 1980s, cyclohexanedione oxime herbicides have been widely used to control a variety of grass weeds. As a consequence, they rapidly selected, and are still selecting, resistant plants within grass weed species.

The resistance to acetyl coenzyme-A carboxylase-inhibiting herbicides was reviewed in detail (Devine & Shimabukuro, 1994), the number of grass weed species in which resistant plants have been reported increased from 9 to 34 (Delye et al., 2005) and resistance to ACCase-inhibiting herbicides has been reported in 26 countries. The estimates of cultivated land surfaces concerned by this resistance vary between 3 to 4.6 million hectares (Delye et al., 2005).

One of the best-studied weeds is black-grass (*Alopecurus myosuroides* Huds.), a major grass weed in winter crops in Europe. Similar findings were obtained in annual ryegrass (*Lolium rigidum* Gaud.) (Delye et al., 2003a), green foxtail (*Setaria viridis* L. Beauv.), wild oat (*Avena fatua* L.) and winter wild oat (*Avena sterilis* ssp. *Ludoviciana* Malzew.) (Christoffers & Kandikonda, 2006; Delye et al., 2003b; Delye et al., 2005; Shukla et al., 2004; Zagnitko et al., 2001), slender foxtail (*Eleusine indica* L. Gaertn.), barnyardgrass (*Echinochloa colona* L. Link) and little canarygrass (*Phalaris minor* Retz.).

Species	Location	Chemical class*
Avena fatua	Canada, USA, Australia, UK	AOPP, CHD
Avena sterilis	Australia, UK	AOPP
Alopecurus myosuroides	UK, Spain, Germany, France	AOPP
Digitaria ischaemum	USA	AOPP
Digitaria sanguinalis	USA	AOPP
Echinochloa colona	Costa Rica	AOPP
Eleusine indica	Malaysa	AOPP, CHD
Festuca rubra	USA	CHD
Lolium rigidum	Australia, Spain	AOPP
Lolium multiflorum	UK, USA	AOPP
Phalaris minor	Israel	AOPP
Setria faberi	USA	AOPP, CHD
Setaria viridis	Canada	CHD
Sorghum halepense	USA	AOPP

Table 5. Weed species exhibiting resistance to ACCase-inhibiting herbicides. Resistance has been conferred to one or more biotypes or accessions of the above weed species by reduced ACCase sensitivity. * AOPP: Aryloxyphenoxypropionate, CHD: Cyclohexanedione.

The occurrence of resistance in grass weeds, *Setaria faberi* Herrm. and *Digitaria sanguinalis* L.) Scop., to cyclohexanedione herbicides has been confirmed also in the United States (Stoltenberg & Wiederholt, 1995; Wiederholt & Stoltenberg, 1995). Sethoxydim had been the

only ACCase-inhibiting herbicides applied to fields in which resistant plants were identified. In whole-plant dose–response experiments, resistant *S. faberi* was 134-fold resistant to sethoxydim (Stoltenberg & Wiederholt, 1995), but showed low levels of resistance to the cyclohexanedione herbicide clethodim. Similarly, Table 5 summarizes the weed species that are known to have developed resistance to ACCase-inhibiting herbicides around the world (Delye et al., 2005; Hatzios, 2001).

The development of resistance to ACCase-inhibiting herbicides in several grass weeds is an increasing problem in several parts of the world. Resistance to these herbicides can arise easily following selection pressure with cyclohexanedione herbicides for six to ten years. The judicious use of ACCase-inhibiting herbicides in combination with herbicides from other classes and methods of non-chemical weed control will be important for prolonging the usefulness of the cyclohexanedione herbicides.

4. Conclusion

The continuous use of plant protection products has led to the contamination of different environmental compartments, such as water, soil and air, being water contamination of great concern due to the risks for human consumption.

The synthetic research of herbicides in the last decades has shifted from long-life compounds to less persistent and more polar compounds, in order to avoid their accumulation in the environment. However, the low persistence of these compounds does not imply their completely mineralization but they are going to degrade to smaller molecules with different physicochemical properties than the active substances. In fact, it has been demonstrated that some of their transformation products are more mobile, persistent and/or more toxic than the parent molecule. Therefore, the knowledge of the fate of herbicides in the environment is underestimated if we do not take into account their transformation products whose behaviour and agro-environmental fate is in many cases unknown.

Besides, the lack of data on the phytotoxic effects of herbicide residues has been highlighted. In this sense, it is necessary to study and develop simple methods for evaluating the environmental impact of these products based on hard scientific data. Furthermore, it is also important not only study the phytotoxicity of the herbicide by means of bioassays, but also of their degradation by-products. From these studies should be able to derive recommendations for agricultural practices for the use of these products are environmentally friendly in general and in particular the agricultural environment capable of guaranteeing the future productivity of farms in the context of sustainable agriculture.

Cyclohexanedione oxime herbicides have been developed for the post-emergence control of grasses in dicotyledonous agricultural crops. These herbicides are unstable in aqueous solution and are very sensitive to pH and sunlight. These properties are highly relevant to their environmental fate. Degradation is so rapid that degradation products apparently could contribute to the activity of the parent molecule. Until now, some of these degradation products and the degradation pathways have been identified. However, the fate, significance and phytotoxicity of their degradation products is not fully known and future research is still need to attain a complete understanding of the fate of cyclohexanedione herbicides in the environment.

5. Acknowledgment

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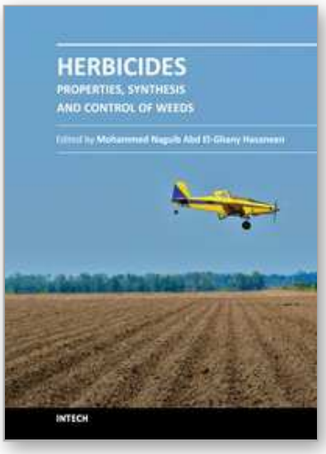

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This book is divided into two sections namely: synthesis and properties of herbicides and herbicidal control of weeds. Chapters 1 to 11 deal with the study of different synthetic pathways of certain herbicides and the physical and chemical properties of other synthesized herbicides. The other 14 chapters (12-25) discussed the different methods by which each herbicide controls specific weed population. The overall purpose of the book, is to show properties and characterization of herbicides, the physical and chemical properties of selected types of herbicides, and the influence of certain herbicides on soil physical and chemical properties on microflora. In addition, an evaluation of the degree of contamination of either soils and/or crops by herbicides is discussed alongside an investigation into the performance and photochemistry of herbicides and the fate of excess herbicides in soils and field crops.

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