Chapter 6

Degradation of Cyclohexanedione Oxime Herbicides

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Additional information is available at the end of the chapter

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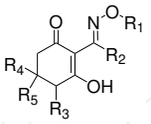
1. Introduction

The use of herbicides is the most common practice for weed control, not only in agricultural fields, but also in urban and industrial areas and communication routes. However, the growing number of detections of herbicide residues in different environmental matrices [1-5] has increased public concern about the widespread use of these compounds. In this sense, the European Union has developed a Community legal framework concerning the commercialization of plant protection products on the market (Regulation EC Nº 1107/2009) and the sustainable use of pesticides (Directive 2009/128/EC) in order to protect human and animal health and the environment from possible risks associated with the use of pesticides. Both documents emphasize that pesticides and their residues shall have no unacceptable effects on the environment, having particular regard to contamination of water bodies as well as the impact on non-target organisms.

In this sense, to meet more stringent regulations, the agrochemical industry tends to develop herbicides with low environmental persistence, effectiveness at a low application rate and minimal non-target organism toxicity. Consequently, new families of herbicides such as imidazolines, sulfonylureas or cyclohexanediones have appeared in the market in the last years.

It is important to note that Regulation EC Nº 1107/2009 describes "residues" as the substances resulting from the use of pesticides, including their metabolites, breakdown or reaction products (e.g. substances resulting from water treatment). This is particularly important for new families of pesticides, like cyclohexanedione herbicides, because the scientific literature about their environmental behaviour and persistence in the environment is quite limited. Cyclohexanedione oxime herbicides (CHD) have been developed during the last 30 years. While alloxydim-sodium was the first herbicide of this family discovered and introduced into the market in 1978 [6], profoxydim was the last CHD herbicide registered in 1998 [7]. This class

of herbicides also includes butroxydim, clethodim, cycloxydim, sethoxydim, tepraloxydim and tralkoxydim (Table 1) [8].



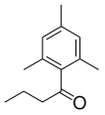
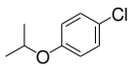
Herbicide	R_1	R_2	R_3	R_4	R_5
Alloxydim	$-CH_2-CH=CH_2$	$-CH_2-CH_2CH_3$	$-COOCH_3$	$-CH_3$	$-CH_3$
Butroxydim	$-CH_2CH_3$	$-CH_2CH_3$	H		H
Clethodim	$-CH_2CH=CH-Cl$	$-CH_2CH_3$	H		H
Cycloxydim	$-CH_2CH_3$	$-CH_2-CH_2CH_3$	H		H
Profoxydim		$-CH_2-CH_2CH_3$	H		H
Sethoxydim	$-CH_2CH_3$	$-CH_2-CH_2CH_3$	H		H
Tepraloxydim	$-CH_2CH=CH-Cl$	$-CH_2CH_3$	H		H
Tralkoxydim	$-CH_2CH_3$	$-CH_2CH_3$	H		H

Table 1. Structures of cyclohexanedione herbicides.

In general, this family of herbicides is used for post-emergence control of annual and perennial grass weeds in broad-leaved crops (including sugar beet, soybean, oilseed rape), except profoxydim which is used for the control of grass weeds in rice [9] and tralkoxydim which is used for the control of annual winter grass weeds in wheat and barley fields [7].

The site of CHD herbicides action is on acetyl-Coenzyme A carboxylase (ACCase), a key early enzyme in the lipid biosynthesis pathway. The inhibition of this enzyme prevents fatty acid formation and the lack of lipids results in loss of cell integrity of membranes and no new growth.

The chemical structure of the CHD herbicides is shown in Table 1. These compounds show a keto-enol tautomerism due to the presence of two ketone groups, as well as two isomers *E*/*Z* relating to the alkyl side chain bound to oxime ether group. The herbicidal activity of these compounds are mainly due to the cyclohexane-1,3-dione ring and the oxyimino group, although its activity can be increased depending on the different functionalization of the substituents R_1-R_5 [6,8].

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As was mentioned before, CHD herbicides have been developed to reduce the adverse effects of some herbicides and to fulfil environmental requirements set by the international legislation. However, some of their physico-chemical properties (Table 2), such as the polar and non-volatile character, and the adsorption and partition coefficients make them highly mobile. These features increase the possibility for these herbicides to reach aquatic bodies, becoming potential contaminants of this compartment.

Regarding the persistence of CHD herbicides in the environment, these xenobiotics are susceptible to rapid degradation due to the action of biotic and abiotic processes. For example, these herbicides are decomposed at a pH below 5 and above 10, and they are also photochemically and thermally unstable. Furthermore, these compounds are readily degraded through microbial and plant metabolism. In some cases the degradation is so fast that it is questioned if herbicidal activity is maybe due to some degradation products [10-12].

In this sense, to estimate the persistence of these compounds in the environment, it is of utmost importance to investigate the factors affecting the behaviour of CHD herbicides and the routes involved in their degradation, as well as to identify the degradation products formed.

Herbicide	Trade Name	Water Solubility (mg L^{-1})	V.p. (20-30 ºC)* (mPa)	Henry's Constant (Pa m^3 mol^{-1})	Log K_{ow} (pH 7)	pK_a	DT_{50} in soil (days)	K_{oc}	Soil Mobility (pH 7)
Alloxydim	Clout, Kusagard, Fervin [13]	> $2 \cdot 10^6$ (sodium salt)	< 0.133	—	0.20	3.7 [14]	2-10	60 [12]	—
Butroxydim	Falcon	6.9	$1 \cdot 10^{-3}$	$5.79 \cdot 10^{-5}$	1.90	4.36	9	6-1270	large variable
Clethodim	Select [13]	5.45 [15]	$1 \cdot 10^{-2}$	$1.4 \cdot 10^{-7}$ [15]	4.14 [15]	4.47 [15]	1-3	900 [12]	very high [15]
Cycloxydim	Focus, Laser, Stratos [16]	53	0.01	$6.1 \cdot 10^{-5}$	1.36	4.17	< 1	<10-183	high to very high [17]
Profoxydim	Aura, Tetris	5.31	$1.7 \cdot 10^{-1}$	$1.76 \cdot 10^{-2}$	3.9	5.91	3-13	81-5983 [18]	large variable [18]
Sethoxydim	Poast, Nabu	> 4700	< 0.013	$1.39 \cdot 10^{-6}$ [19]	1.65	4.1 [12]	1	100 [12]	high [20]
Tepraloxydim	Aramo	430	$2.7 \cdot 10^{-2}$	$8.74 \cdot 10^{-6}$	0.2	4.58	5.2-14	3.7 [21]	high [14]
Tralkoxydim	Achieve, Grasp, Splendor	6.7	$3.7 \cdot 10^{-4}$	$2 \cdot 10^{-5}$	2.1	4.3	2-5	30-300	very high [22]

* V.p.: Vapour pressure.

Table 2. Physico-chemical properties of CHD herbicides. Unless otherwise noted, data were compiled from Pesticide Manual [7].

2. Transformation processes affecting persistence of cyclohexanedione oxime herbicides

Following their application, the environmental fate of herbicides depends to a great extent on biotic and abiotic degradation processes. As a result of these degradation processes, different by-products, often with unknown properties, may be formed before they achieve the complete mineralization. The extent of degradation as well as the nature of by-products formed depend on the chemical structure and physico-chemical properties of the parent compound (Table 2), characteristics of the compartment in which the herbicide is present and also the environmental conditions [23].

A large number of kinetic models to describe the transformation of pesticides are available. However, the simplest model that can provide a sensible and adequate description of the decline curves is preferred [24]. At relatively low concentrations of pesticides (approximately $1 \cdot 10^{-3}$ M), the model that best describes the rate of degradation of many xenobiotics is one that follows a first order kinetics

$$C = C_0 \cdot e^{-k \cdot t} \quad (1)$$

where C is the herbicide concentration at time t, C_0 is the initial concentration of herbicide and k is the rate constant of the transformation process.

Herbicide transformation is often expressed in terms of half-life ($t_{1/2}$) because it is a more intuitive parameter than the rate constant, k. This parameter is defined as the time taken for herbicide concentration to fall to half its initial value and it is related to the rate constant, k, by means of the Equation 2.

$$t_{1/2} = \ln 2 / k \quad (2)$$

Under field conditions, transformation processes occur simultaneously with other processes leading to herbicide dissipation. In these cases, the term DT_{50} value is more appropriate than $t_{1/2}$ and reflects the time for the dissipation of 50% of the initial concentration.

It should be noted that half-lives vary in a wide range depending on the nature of herbicides, the compartment characteristics as well as the environmental conditions, so caution should be taken in making comparisons between herbicides.

2.1. Abiotic processes

The main abiotic transformation processes affecting the efficiency, persistence and fate of herbicides include reactions initiated by light, temperature, reactions in aqueous media (as a reaction medium and pH variations) and reactive substances present in the compart-

ments. Below we review the most important studies about abiotic degradation of CHD herbicides to date.

2.1.1. Hydrolysis

As mentioned previously, CHD herbicides can be potential contaminants of the water compartment due to their physico-chemical properties. In this compartment, hydrolysis reactions are one of the main abiotic transformation process affecting herbicides [25]. This process can be particularly important in groundwater where other abiotic transformation processes such as thermal degradation or photolysis are not relevant. Moreover, it is well-known that the moisture content in soil also affects the persistence of herbicides [26].

Hydrolysis is a pH-dependent process and the rates of transformation can significantly vary among herbicides. For instance, some herbicides may undergo hydrolysis at pH extremes, while a slight variance of pH could give rise to a fast degradation of those herbicides that are pH-sensitive [27,28].

The penetration of herbicides in plants is also affected by the pH of the water used in the pesticide mixture and, hence, the effectiveness of the herbicide could be affected by this parameter too. Usually, the absorption by plants is higher when herbicides are in their non-ionized form. As CHD herbicides are weak acids (pKa ≈ 3.7-5.9), an increase in pH of the aqueous solution leads to an increase of ionized herbicide molecules (anionic form) and therefore, they are absorbed more slowly across the plant cuticle and its phytotoxicity would be lower.

As a first approach, Iwataki and Hirono (1979) [29] observed that alloxydim CHD herbicide was hydrolyzed in aqueous solution under acidic and basic conditions.

The influence of pH on the abiotic transformation of clethodim in aqueous solution was studied by Falb *et al.* [30]. These authors stated that clethodim is an acid labile herbicide and its degradation increased as acidity increased (Figure 1). At neutral pH, no degradation of clethodim was observed and a total recovery was obtained, while at a pH 6 and 5 the herbicide recoveries decreased by 8% and by 37%, respectively, after 20 hours.

Others CHD herbicides such as cycloxydim, profoxydim or tralkoxydim have also been reported to undergo hydrolysis. Profoxydim hydrolysis depends on the pH value with degradation rates relatively low [9]. Cycloxydim is also unstable in acidic aqueous media with half-lives of 1, 7, 104 and 102 days at pH 3, 5, 7 and 9, respectively [12].

Aqueous solutions of sethoxydim are found to be unstable at room temperature or when kept at -20° C; only 6 and 24% of the parent sethoxydim remained after 72 hours, respectively [11]. The disappearance of sethoxydim was attributed to hydrolysis reactions.

Regarding butroxydim and tralkoxydim, both herbicides are hydrolyzed in water. The hydrolysis of both CHD herbicides was faster in acidic media than under neutral or basic conditions [7]. At a pH of 5 the herbicide butroxydim is degraded by an acid hydrolysis reaction with a DT_{50} of 10.5 days, while at a neutral pH (pH = 7) the half-life exceeded 8 months and at a pH of 9 the hydrolytic degradation was negligible [7]. In the same way, the stability of

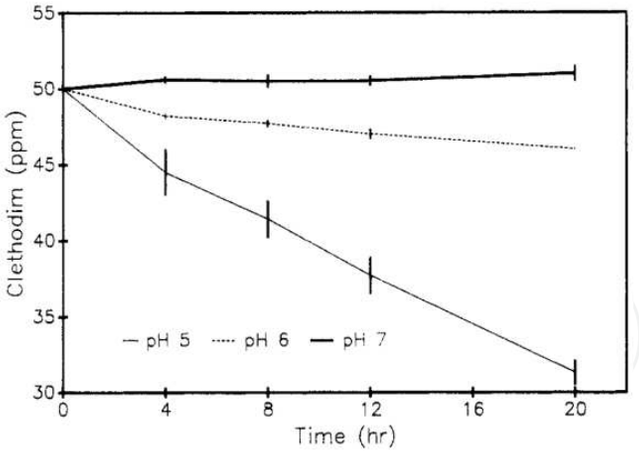

Figure 1. Degradation kinetics of technical clethodim at different pH values [30].

tralkoxydim increases with increasing pH. The value of DT_{50} for this herbicide was only 6 days at a pH of 5, whereas at a pH of 9 87% of the compound remained unchanged ($DT_{50} \approx 139$ d) [7].

2.1.2. Chlorination

Reactions with chemicals of anthropogenic origin are other important routes of abiotic degradation of pesticides in water. Residual chlorine is one of these substances commonly present in water bodies as a consequence of its use in the water and wastewater treatment plants. A residual concentration of chlorine species is maintained after disinfection processes in order to guarantee disinfected water through the distribution system or during storage. It means that residual chlorine could also react with other xenobiotic compounds present in waters such as herbicides.

Degradation of pesticides by action of residual chlorine is of great relevance if we consider that nowadays the reuse of treated wastewater for irrigation of crops, urban landscapes and other recreational areas is a common practice. Furthermore, it should be noted that some farmers also use drinking water or treated water for their pesticide preparation.

It is known that numerous pesticides are degraded during the processes of disinfection by chlorine or other forms of chlorine [31-33]. However, there is little information about the fate of CHD herbicides in the presence of residual chlorine. In this sense, our research group has carried out different studies on the chemical behaviour of CHD herbicides in the presence of hypochlorite and chloramines, two of the most common agents employed for water disinfection.

In preliminary studies to establish a method for the determination of tepraloxydim residues in drinking water, Sandín *et al.* [34] demonstrated that the presence of residual chlorine in laboratory distilled water rapidly degraded the herbicide tepraloxydim. Therefore, these authors have performed a thorough study of tepraloxydim degradation in chlorinated waters. They showed that the reaction between the herbicide and hypochlorite was very fast with a half-life below 5 seconds. Degradation of tepraloxydim was also observed when chloramines

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were added to the herbicide solution (Figure 2a), although it was slower than in the presence of hypochlorite ($t_{1/2}$ = 4.5 h) due to the lower oxidation potential of chloramines. Similar results were obtained when tepraloxydim was dissolved in tap water with a molar ratio of 1:10 (herbicide:total chlorine) and half-life of 0.86 h was calculated (Figure 2b) [34].

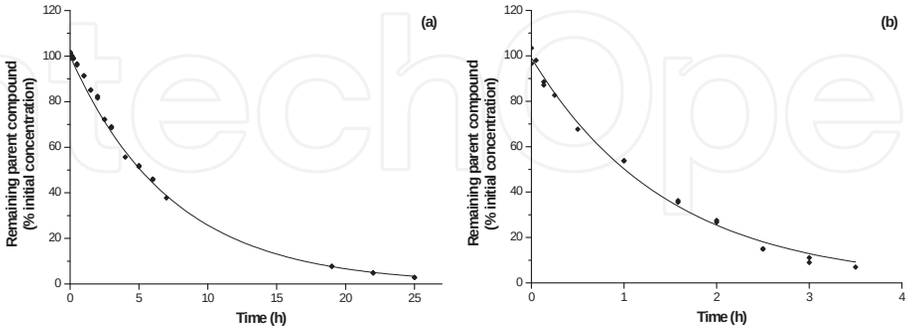

Figure 2. Degradation rate of tepraloxydim in chloramine solution (a) and in tap water (b) [34].

Our research group has also carried out other detailed studies about degradation of alloxydim and clethodim in the presence of hypochlorite and chloramines [35,36]. In the same manner as tepraloxydim, the degradation rates of both herbicides were very fast in the presence of hypochlorite with half-lives less than 1 second for alloxydim [35] and 20 seconds for clethodim [36]. The concentration of these two herbicides diminished more slowly in the presence of chloramines than in the presence of hypochlorite, showing half-lives equal to 8 min and 15.4 h for alloxydim and clethodim, respectively [35,36].

2.1.3. Photolysis

Photolysis by sunlight is one of the primary degradation routes for pesticides in different environmental compartments. Photochemical processes in the environment include all those reactions initiated by solar radiation. It should be noted that, in many cases, the thermal degradation of pesticides is associated with the absorption of the solar radiation energy.

Photodegradation of pesticides depends on various factors such as: the chemical structure and electronic absorption spectrum of the pesticides, the radiation source and its intensity, the time of exposure or the presence of other substances in environmental media. Moreover, there are two types of photochemical processes that can lead to the transformation of a pesticide: direct and indirect photolysis [37]. In the first one, the transformation of the pesticide is the result of direct absorption of solar radiation. In the second process, other compounds present in the compartment absorb firstly solar radiation to form reactive species that can subsequently react with pesticides resulting in their transformation.

Although the experimental design is not described, Iwataki and Hirono [29] observed that alloxydim was unstable and quantitatively decomposed when it was exposed to UV or sunlight. These authors also noted the thermal degradation of this herbicide at 120º C, but they did not clarify whether such degradation is related to radiation exposure [29]. Regarding the

thermal degradation of CHD herbicides, Soeda *et al.* [38] also evaluated the transformation of alloxydim when it was heated to 30, 40 and 50 ºC in a dark incubator. The thermal transformation of alloxydim was observed and 6.2% of alloxydim was degraded after 20 days of incubation at the highest temperature tested.

Falb *et al.* [30] investigated the photolytic behaviour of aqueous solutions of clethodim and the effect of adjuvants on the photolysis rates. These authors stated that photolysis reactions contributed to the degradation of clethodim to a greater extent than hydrolysis reactions. Also, the photodegradation rates of clethodim were strongly affected by the addition of adjuvants. So, the rates of degradation under UV light and sunlight were increased with addition of adjuvants up to 7 fold and up to 27 fold over the control, respectively [30]. Similar findings were also obtained by Bridges *et al.* [39]. McMullan [40] noted that clethodim efficacy was enhanced as a consequence of the presence of adjuvants in the spray solution. This effect was attributed to an increase of the adsorption rate of the herbicide and thus, a reduction of its photodegradation. These findings are in agreement with data published for sethoxydim by McInnes *et al.* [41] and Hazen and Krebs [42]. These researches suggested that spraying late at day may improve CHD herbicide efficacy due to a reduction in the amount of UV light.

The lability of cycloxydim to temperature and radiation has been also investigated. This herbicide was stable at room temperature but it becomes unstable above 30º C, decomposing at 200º C [7].

Besides the hydrolysis reactions previously mentioned, Campbell and Penner [11] identified the direct photolysis as an efficient pathway of sethoxydim degradation in aqueous solutions. 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 the herbicide was transformed after 1 h). In agreement with these results, Shoaf and Carlson [10] showed that sethoxydim was completely degraded 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 by more than 50% after 10 min of exposition to UV light.

In our research group, different experiments have been carried out to study the photodegradation of sethoxydim in natural waters (mineral, well and river) and under natural and simulated sunlight in order to obtain results close to field conditions [43]. The degradation rates in natural waters were lower than in ultrapure water. For example, 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. Results indicated that the degradation of sethoxydim-lithium has a strong dependence on the composition of the water sample. The retardant effect observed in natural waters was attributed to the presence of increasing concentrations of TOC (Total Organic Carbon) 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}) [44].

An extensive research was conducted to study the effect of different natural substances commonly present in aqueous systems on the degradation rates of alloxydim [45] and

clethodim [46]. Previous studies carried out in ultrapure water have proved that direct photolysis contributed appreciably to the degradation of both herbicides, so alloxydim and clethodim dissolved in ultrapure water were completely degraded in 4 h and 2.5 h under simulated sunlight, respectively [46]. To evaluate the effect of matrix composition, different substances that can be found in natural waters such as HA (humic acids), nitrate and ferric ions were added to aqueous solutions of alloxydim and clethodim. Figure 3 shows the photodegradation curves of clethodim in the presence of various concentrations of HA, nitrate ions and Fe(III) ions in ultrapure water under simulated solar radiation. In the case of clethodim, the presence of increasing concentrations of HA retarded the photodegradation compared to ultrapure water (Figure 3a) [46]. Analogous findings were observed for alloxydim herbicide in the presence of HA [45]. The retarding effect observed suggests that HA could be acting as an "optical filter" absorbing most of the photons emitted from the radiation source and thereby slowing the direct photochemical reaction of clethodim. In the presence of nitrate ions, the degradation rates of both herbicides, clethodim (Figure 3b) and alloxydim, were not affected at all [45,46]. On the contrary, the addition of ferric ions to ultrapure water resulted in a notable increase of the photolysis rate of clethodim (Figure 3c) and alloxydim compared to the direct photolysis. Several authors described this enhanced effect of Fe(III) ions as a result of the formation of hydroxyl radicals [47,48]. Furthermore, it has also been reported in the literature that the organic molecules can form a complex with the Fe(III) ions and later undergoes a direct photolysis [49].

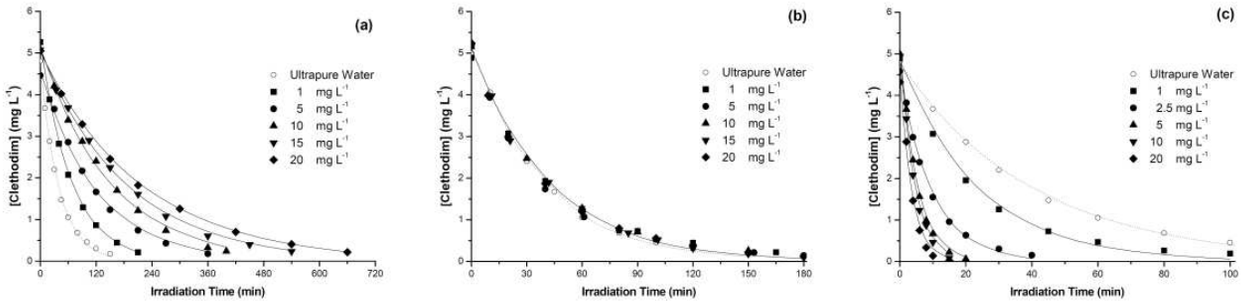

Figure 3. Photodegradation of clethodim in the presence of various concentrations of HA (a), nitrate ions (b), and Fe(III) ions (c) in ultrapure water under simulated Fe(III) ions [46].

It is noteworthy to mention that degradation of CHD herbicides occurs on soil surfaces and in plant leaves, although in many cases it is not clear if degradation is due to photolytic or biotic processes. In this sense, Hashimoto *et al.* [50] studied the fate of ^{14}C-alloxydim-sodium in soybean plants. It was observed that alloxydim was easily degraded on the leaf surface with half-life over 1-2 days [50] whereas the herbicide was detected even after 28 days in the plant. Therefore, Hashimoto *et al.* [50], like other authors [38,51], considered that the easy dissipation of the radiolabeled alloxydim from leaf surfaces was probably the result of photochemical reactions.

In order to simulate photolysis on soil surfaces, Soeda *et al.* [38] irradiated with UV light a methanol solution of ^{14}C-alloxydim spotted on TLC plates. Under these conditions, alloxydim

was photolyzed 33% (254 nm) and 9% (365 nm) after 20 minutes of irradiation. Ono *et al.* [52] also concluded that photolysis of alloxydim occurred when a soil spiked with an aqueous solution of this herbicide was exposed to sunlight.

Several authors studied the photodegradation of sethoxydim on glass slides and TLC plates as a model for soil and plant surfaces. UV irradiation (282 nm) of sethoxydim on TLC plates resulted in a large decomposition of this herbicide due to a direct photolysis process, since the absorbance spectrum of sethoxydim and the UV emission spectrum overlap at 282 nm [10]. Campbell and Penner [11] also evaluated the fate of sethoxydim on glass exposed to light and they observed a rapid photodegradation on this surface. Analogous conclusions were obtained when photodegradation experiments were carried out in the presence of different adjuvants [42]. Regarding the fate of sethoxydim on plant surfaces, it was observed that sethoxydim photodegradation on leaf surface occurred simultaneously to the uptake by corn plant leaf [42] and sugar beet [53]. In soil and under field conditions, the persistence of sethoxydim was highly affected by moisture and light [10,54].

2.2. Biotic processes

Besides abiotic pathways, biotic processes strongly affect the fate and persistence of pesticides in the environment. Biotic processes of pesticides refer to those transformations mediated by living organisms. Due to their ubiquitous nature, transformations involving microorganisms are the primary routes of biotic degradation of pesticides, although biological reactions in plants and animals can contribute significantly to their breakdown. There are a variety of factors affecting the biotic processes, including environmental conditions (temperature, moisture, pH, oxygen content), biological diversity or pesticides properties.

Biological transformations include many reactions (oxidation/reduction, hydrolysis, or conjugation/condensation) regularly catalysed by enzymes as a consequence of three major strategies [55]: (i) cometabolism where the degradation of the pesticide is coincidental to the general metabolic activity of an organism and provides no source of energy; (ii) catabolism where an organism uses the pesticide as an energy source; and (iii) processes in which extracellular enzymes secreted by an organism degrade pesticides.

Moreover, as biotic and abiotic processes usually occur simultaneously, sometimes it is complicated to determine the degree to which each contributes to degradation.

There are few scientific studies regarding the biotic processes affecting CHD herbicides; some of them refer to the difficulty of distinguishing between biotic and abiotic processes since both may occur simultaneously and may have common transformation products as a consequence of common reactions.

As mentioned before (Section 2.1.3.), photolysis was considered the main dissipation route of alloxydim from soybean plants [50]. However, some radioactivity was found as conjugates of aglycone components, which indicated that biotic transformation also occurs in the plant, reaching 5% of the total degradation of alloxydim. Similar results were obtained for alloxydim when it was sprayed on several crops such as sugar beet or wild oat [38,51]. In unsterilized soil, the half-life of alloxydim was 5 to 6 days under dark incubation [52]. In this research, the

evolution of $^{14}CO_2$ was investigated as a measure of microorganism activity in the soil. Cumulative amounts of $^{14}CO_2$ were detected over 28 days of incubation, suggesting that alloxydim can be utilized by soil microorganisms during metabolism.

After the application of sethoxydim on sugar beet leaves, the herbicide was rapidly degraded (half-life < 1 day). Moreover, up to 20% of sethoxydim was translocated to untreated leaves and to the roots in three days, where it decreased gradually as a consequence of metabolism by the plant [53]. Considering the transformation product identified, the main metabolic mechanism proposed for sethoxydim may indicate that oxidation was partially catalysed by enzymes in addition to direct oxygenation. Ishihara *et al.* [53] suggested that metabolites of sethoxydim should be regarded as target compounds when a crop residue is analyzed because these compounds remain in sugar beet as conjugates and non-conjugates 60 days after treatment. Similarly, other researches have shown a rapid degradation of sethoxydim in both grasses and dicotyledonous crops; although it is uncertain to what extent the biotic or abiotic processes are involved [56,57]. Sethoxydim is degraded in soil by microorganisms with a half-live of 25 days [58]. Despite its short half-life, the parent herbicide and/or its transformation products caused considerable root inhibition over a period of 150-280 days depending on initial concentration of sethoxydim. Therefore, Roslycky [58] pointed out that it could be expected to be a potential danger as a result of the cumulative effects of sethoxydim and/or its transformation products in soil.

The dissipation of tralkoxydim in several crops and water-soil systems has also been documented [59-62]. Under these conditions, both biotic and abiotic processes took place concurrently and a rapid degradation was observed. In maize and wheat crops, part of tralkoxydim entering the foliar tissue was probably degraded by means of non-catalysed reactions or by metabolism in plant cells [59,60]. Although abiotic processes are the major routes affecting tralkoxydim in the water-soil system, biotic processes are responsible for faster dissipation of this herbicide in the water layer as compared to plain water and soil sediment, probably due to higher microbial activity in water [62].

Several studies concerning the metabolism of CHD herbicides in animals, primarily rats, have been conducted. In general, CHD herbicides were rapidly absorbed and excreted *via* the urine and faeces [63]. The fate of ^{14}C-alloxydim orally administered to rats for 7 days has been reported [64]. After daily dosing for 7 days, radioactivity was almost quantitatively eliminated in the urine and faeces within 2 days of the last dose. Unchanged alloxydim was excreted, mainly in the urine, whereas the remaining herbicide was degraded to different transformation products. The major transformation pathway of alloxydim in rats was oxidation and subsequent hydrolysis reactions involving enzymatic catalysis, although non-enzymatic reactions such as thermal degradation also occur to a lesser extent. Analogous results were reported for various CHD herbicides such as butroxydim, sethoxydim, and cycloxydim, which were rapidly excreted within 7, 2 and 5 days, respectively [7,63].

3. Transformation products

Taking into account human safety and environmental protection, the ideal herbicide would be the one that, after acting against the target weed, could be completely mineralized to inorganic compounds as final products such as H_2O, CO_2, NH_4^+, NO_3^-. However, the complete mineralization often occurs slowly in the environment and different intermediate compounds can be formed prior to complete mineralization. Several terms have been used for these intermediate compounds including "degradates", "breakdown products", etc. In general, "transformation products" is used as a general term for those compounds formed during biotic and abiotic processes; compounds resulting from abiotic degradations are referred to as "by-products", "degradation products" or "photoproducts" (if they are formed by photodegradation processes). "Metabolites" refer to compounds formed as a result of biological transformations and the term "residue" includes both parent compound and transformation products [55].

The understanding of overall consequences for herbicide use is limited, due to the fact that most studies have focused on the parent compound regardless of their transformation products. However, transformation products can behave very differently from the parent compound as a consequence of its different chemical structure [23]. In this sense, diverse studies have confirmed that many transformation products of pesticides are more persistent, and present a higher toxicity and/or a higher mobility compared to their parent compounds [65-67]. Furthermore, different authors have suggested that the phytotoxicity of some CHD herbicides is due not only to the parent compounds but also to their transformation products [10-12,68]. Therefore, researches involving these transformation products have become essential in order to better understand the behaviour of pesticides and to avoid underestimating the risk derived from their use.

Literature about transformation products of CHD herbicides is very limited and many studies have only reported the detection of transformation products without performing a detailed identification of them [10,11,30,69,70]. In this sense, QTof mass analyzer coupled to HPLC has been applied as a valuable tool for the identification and structural elucidation of transformation products of CHD herbicides in aqueous matrices [45,46]. Thus, QTof mass analyzer provides accurate masses for both parent and product ions in combination with the possibility of performing MS/MS acquisitions obtaining more structural information. For instance, on the basis of the exact mass measurements and fragmentation patterns provided by QTof, it was possible to elucidate the structures of nine clethodim photoproducts previously separated by a HPLC system [46].

Table 3 compiles the main biotic and abiotic transformation products of CHD herbicides in different matrices from the information available from open literature.

As mentioned before, the herbicides of the CHD family present two isomers, *E* and *Z*, due to the presence of the alkyl side chain bound to oxime ether group. These herbicides are marketed as the *E*-isomers, but the isomerization around the N-O bond seems to occur easily, making the corresponding *Z*-isomer a plausible transformation product of both biotic and abiotic

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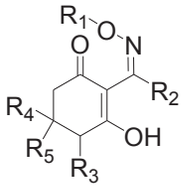
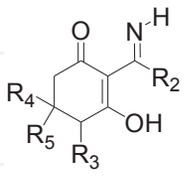
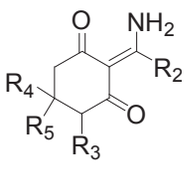
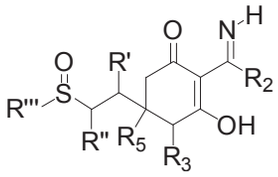
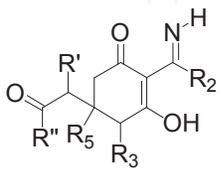
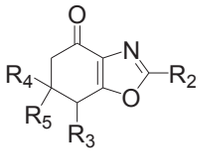
processes. Several authors have stated that some *E*-isomers of CHD herbicides may equilibrate with the *Z*-isomer in polar solvents [30,46,71] or in chlorinated water [34,36]. Moreover, it has been reported that isomerization can be induced by light [45,46] and temperature [72].

For example, equilibrium between both tepraloxydim isomers took about 7 days, with a final ratio between isomers of 2:1 (*Z:E*) [34]. Rapid isomerization has been observed for clethodim in ultrapure water reaching 4% in a freshly prepared solution and 40% after two months [36]. Clethodim *Z*-isomer was also identified as a transformation product formed resulting from the exposition to simulated solar light [46]. In the same way, the corresponding *Z*-isomer of alloxydim was detected as a photoproduct after the exposure to UV radiation ($\lambda > 290$ nm) [45].

An important feature of the oxime ether bond is its relatively low dissociation energy (ca. 53 kcal mol^{-1}). Therefore, it is expected that one of the most important reactions of CHD herbicides is the cleavage of the N-O bond to yield two possible dealkoxylated compounds, imine and/or amine (Table 3). Thus, photodegradation of alloxydim in aqueous solution was investigated under simulated and natural solar light and the main photoproduct obtained was the imine [45,73]. Both studies revealed that the amount of alloxydim imine formed can be influenced by the composition of aqueous solution and the intensity of radiation source [45]. Other authors have stated the formation of alloxydim amine in the soil and plants, although it is not clear if a biotic or abiotic mechanism is involved. In this sense, Ono *et al.* [52] identified the amine of alloxydim by thin-layer chromatography and mass spectrometry when the photodegradation of this herbicide was studied in sterilized soil. Alloxydim was also readily degraded in sugar beet [38] and soybean [50] and the main transformation product was identified as the amine compound. After 10 days of treatment with alloxydim, Soeda et al. [38] detected the corresponding amine as the main transformation product in sugar beet extracts. This transformation product persisted for 42 days and its formation seemed to occur by photoreduction on plant leaves [38]. Hashimoto et al. [50] and Veerasekaran and Catchpole [51] obtained similar results in some susceptible and resistant plants, suggesting that a large part of alloxydim transformation to amine occurred directly from the surface of the leaves as a result of abiotic degradation. The metabolism of alloxydim sodium in rats has been reported by Takano *et al.* [64]. Alloxydim amine was identified as a major metabolite of alloxydim in the rat liver, while low yields were observed in urine and faeces [64].

Transformation Product	Matrix (transformation process) *	Herbicide	Reference
Z- isomer 	Water (p,c)	Alloxydim	[45]
		Clethodim	[36,46]
		Tepraloxydim	[34]
Imine	Water (c,h,p)	Alloxydim	[45]
		Clethodim	[46]

Transformation Product	Matrix (transformation process) *	Herbicide	Reference
	Soil (p, b)	Cycloxydim	[12]
		Sethoxydim	[11]
		Tepraloxydim	[34]
		Butroxydim	[7]
		Cycloxydim	[12]
		Tralkoxydim	[59]
	Plant (p, b)	Cycloxydim	[74]
		Profoxydim	[7]
	Animal (b)	Alloxydim	[64]
		Profoxydim	[7]
Amine	Water (p)	Alloxydim	[29]
	Soil (p)	Alloxydim	[52]
	Plant (p, b)	Alloxydim	[38,50,51]
		Sethoxydim	[53]
Imine sulfoxide	Water (p)	Clethodim	[46]
	Soil (b)	Cycloxydim	[12]
		Sethoxydim	[53]
	Plant (b)	Cycloxydim	[12]
		Cycloxydim	[12]
		Sethoxydim	[53]
	Animal (b)	Cycloxydim	[12]
Imine ketone			
	Water (p)	Clethodim	[46]
Oxazole	Water (h,p)	Alloxydim	[29]
		Cycloxydim	[12]
		Tepraloxydim	[34]
	Soil (b, p, h)	Alloxydim	[29,52]
		Butroxydim	[7]
		Cycloxydim	[12]
		Tralkoxydim	[12,59]

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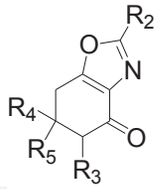
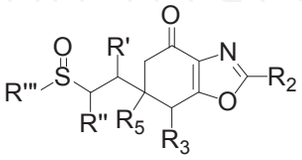
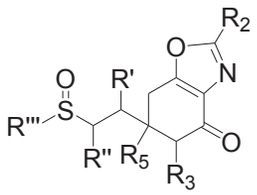
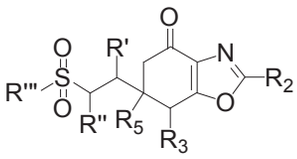
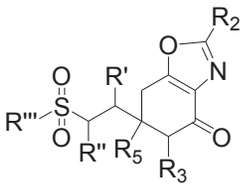
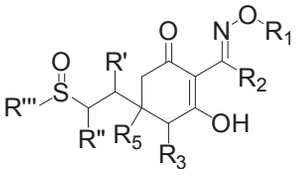
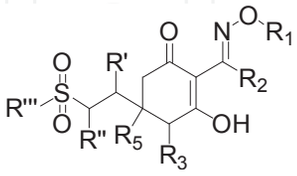
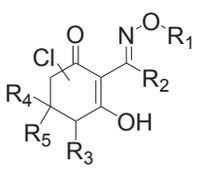
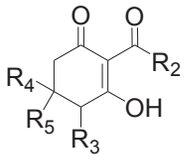
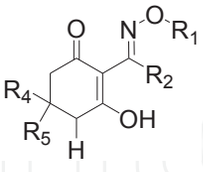
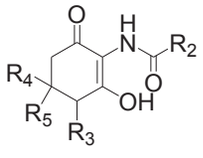
Transformation Product	Matrix (transformation process) *	Herbicide	Reference
	Plant (p, t, b)	Alloxydim	[38,50,51]
		Cycloxydim	[74]
		Tralkoxydim	[61]
	Animal (b)	Alloxydim	[64]
Oxazole sulfoxide	Water (h,p)	Cycloxydim	[12]
	Soil (p,b)	Cycloxydim	[12]
	Plant (t, b)	Cycloxydim	[12]
		Sethoxydim	[53]
	Animal (b)	Cycloxydim	[12]
Oxazole sulfone	Soil (n.d.)	Cycloxydim	[12]
	Plant (t)	Sethoxydim	[53]
			
Sulfoxide	Water (p,c)	Clethodim	[36,46]
		Cycloxydim	[12]
		Profoxydim	[75]
	Soil (p)	Cycloxydim	[12]
	Plant (b)	Clethodim	[7]
		Cycloxydim	[12]
		Profoxydim	[7]
		Sethoxydim	[53]
	Animal (b)	Clethodim	[7]
		Cycloxydim	[12]

Transformation Product	Matrix (transformation process) *	Herbicide	Reference
		Profoxydim	[7]
Sulfone 	Water (c, h, p)	Clethodim	[36]
		Sethoxydim	[70]
	Soil (n.d.)	Cycloxydim	[12]
	Plant (b)	Clethodim	[7]
		Cycloxydim	[12]
		Sethoxydim	[53]
	Animal (b)	Clethodim	[7]
		Cycloxydim	[12]
		Profoxydim	[7]
Chlorinated 	Water (c)	Alloxydim	[35]
Ketone 	Soil (b)	Alloxydim	[52]
		Butroxydim	[7]
	Animal (b)	Alloxydim	[64]
Demethoxycarbonylated 	Water (h)	Alloxydim	[29]
	Soil (b)	Alloxydim	[52]
	Plant (b)	Alloxydim	[50]
	Animal (b)	Alloxydim	[64]
Amide 	Water (h)	Alloxydim	[29]
	Animal (b)	Alloxydim	[64]
Glutaric acid derivative	Soil (b)	Alloxydim	[52]
		Butroxydim	[7]
		Tralkoxydim	[59]

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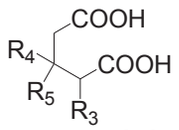
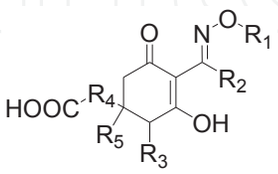
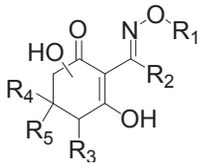
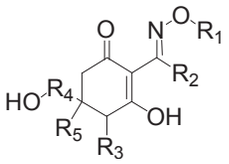
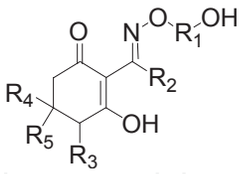
Transformation Product	Matrix (transformation process) *	Herbicide	Reference
	Plant (b)	Tralkoxydim	[61]
Carboxylic acid derivative 	Soil (n.d.)	Tralkoxydim	[59]
Hydroxylated derivative 	Water (c)	Clethodim	[36]
	Soil (b)	Cycloxydim	[12]
		Cycloxydim	[12]
		Alloxydim	[64]
		Profoxydim	[7]
	Animal (b)	Tralkoxydim	[61]
			

Table 3. Biotic and abiotic transformation products of CHD herbicides in different matrices. *(h: hydrolysis, c: chlorination, p: photodegradation, t: thermal, b: biotic, n.d.: no defined).

Sevilla *et al.* [46] performed the identification of transformation products formed during the photolysis of aqueous solutions of clethodim. By means of HPLC coupled to Qtof, the structures for nine photoproducts detected were proposed, being clethodim imine the major photoproduct identified [46]. In the same way, up to six products were detected and isolated by Campbell and Penner [11] when aqueous solutions of sethoxydim were exposed to artificial light. Five of these products were transitory and only one appeared to be the single end product, which was identified as sethoxydim imine. Imine was also detected as a by-product of cycloxydim when the herbicide was subjected to solar radiation on the soil surface and under acidic conditions [12].

As for other transformation products, the formation of oxazoles and isoxazoles was frequently observed as a consequence of both biotic and abiotic transformations and their presence has been detected in several matrices (water, soil, plant, animal) (Table 3). In this sense, studies of thermal degradation of alloxydim gave two oxazoles as transformation products at 120 ºC with a ratio between them of 3:2 [29]. The mechanism of the formation of these compounds involved the loss of alkoxy group, -OR_1 (Table 1), the Beckmann rearrangement and subsequent intramolecular cyclization. Conversion of alloxydim to oxazoles and isoxazoles also has been reported in plants treated with this herbicide [38,50,51]. In these studies, the authors suggested that the transformation occurs mainly on leaf surfaces and it was probably due to abiotic processes such as photolysis or/and thermal degradation.

Hydrolysis reactions of CHD herbicides in aqueous matrices can also lead to the formation of oxazoles and isoxazoles. The fate of tepraloxydim in aqueous solutions free of chlorine has been evaluated by Sandín *et al.* [34]. Concomitantly with the disappearance of tepraloxydim, a transformation product (identified as the corresponding oxazole) was monitored. The molar ratio of tepraloxydim oxazole detected was 7% after 7 days in solution and it increased to 12.5% after 21 days [34]. In the same way, cycloxydim is labile in aqueous media under hydrolytic conditions. After 32 days at a pH of 7, 7% of oxazole was detected, while at a pH of 3 higher yields of this transformation product were observed [12].

The biotic contribution to the formation of oxazoles in plants is not well-known. The metabolic pathway of some CHD herbicides has been reported mainly in rats. Oxazoles of alloxydim and tralkoxydim were identified as minor metabolites in both urine and faeces [12,64].

Oxidative reactions are often involved in the transformation process of many herbicides. The mechanism of these reactions occur through (i) physico-chemical oxidations involving molecular oxygen or reactive species present in the media (acids, radicals or singlet oxygen) or (ii) biological oxidations which are mediated by enzymes. In general, the main transformation products observed as a result of these reactions include hydroxylated compounds and, in the case of S-containing herbicides like some CHD herbicides, sulfoxides, and sulfones. Sulfoxidation of herbicides may be of great importance since, in some cases, sulfoxides and sulfones are suspected to show biological/toxicological activity to target and/or non-target organisms [55,76]. Moreover, these oxidized compounds are reported to present a higher water solubility and minor soil sorption than parent pesticides, thus a higher possibility to reach and contaminate ground and surface water is expected [55].

Degradation of clethodim in chlorinated water either with sodium hypochlorite or chloramines led to a single transformation product that was identified as clethodim sulfoxide [36]. Subsequent degradation of the transformation product clethodim sulfoxide was followed and it degraded mainly to clethodim sulfone, although other minor products were detected. As a result of photolysis reactions in aqueous solutions, Sevilla *et al.* [46] have also identified oxidative transformation products such as clethodim sulfoxides, sulfoxides of clethodim imine and the ketone imine of the herbicide [46]. Roberts [12] has reported that the photolysis of cycloxydim on the soil surface led mainly to cycloxydim S-oxides whereas imine and oxazole were minor products. Shoaf and Carlson [70] observed that photolysis of sethoxydim solutions led to the formation of the corresponding sulfone, as well as the formation of five other

unidentified products. Moreover, sethoxydim sulfone was also detected during both acid and alkaline hydrolysis, although a higher conversion to this product was observed under basic conditions.

Sulfoxides and sulfones are also common transformation products during the biotic degradation of CHD herbicides in plants and animals. For example, sethoxydim was rapidly converted to its sulfoxides and sulfone in sugar beet [53]. The oxidation of the sulphur atom was partially catalysed by enzymes in addition to direct oxygenation. These authors also noted that the abundance of sulfoxide metabolites was generally higher than that of the sulfone type metabolite at the early stages after application, whereas the situation was opposite on day sixty [53]. Other studies conducted with cycloxydim on soybean have shown that its major metabolite on green foliage, stems and beans was the sulfoxide [12] while other oxidation products, such as sulfone and hydroxylated compounds, were found as minor metabolites. Roberts [12] reported the metabolism of cycloxydim in rats. This herbicide was almost completely eliminated within 5 days, with cycloxydim sulfoxide being the major metabolite in urine. Cycloxydim sulfoxide was administered to goats in order to emulate consumption of this major plant metabolite [12]. Under these conditions, cycloxydim sulfoxide remained almost unchanged in the urine, although low residues of sulfone and secondary sulfoxides were present in milk and the liver. This finding points out the higher stability of some CHD transformation products compared to the parent compound.

As mentioned previously, degradation products of some herbicides can also present an undesirable herbicidal activity against non-target plants. However, these data are still scarce for CHD herbicides. In this sense, our research group is currently studying the phytotoxicity of CHD degradation products by means of bioassays. This technique has shown to be a useful tool to screen the phytotoxicity of CHD herbicides, showing good sensitivity, low cost and reproducibility [77]. Thus, we have investigated the phytotoxicity of alloxydim and its main chlorinated transformation product on wheat with bioassays in a hydroponic culture [35,68]. Results showed that the degradation product of alloxydim caused a 32% reduction in root growth of wheat plants although this phytotoxic effect occurred at a higher dose than for the parent compound.

In a photodegration study of sethoxydim in aqueous media six degradation products were detected, where five of them were transitory [11]. A phytotoxicity experiment revealed that two of these transitory products had herbicidal activity when they were applied to *Echinochloa crus-galli*, whereas imine showed no significant injury [11]. Although quantitative analysis of these transformation products was not made and their relative herbicidal potencies could not be determined, Campbell and Penner [11] suggested the possibility that some of these transformation products actually induce the phytotoxic effects on grasses.

Table 3 shows the main transformation products of CHD herbicides, the matrix, and the processes where they are generated. Many of them are formed as a result of the combination of two or more of the reactions discussed above.

4. Analytical determination

In order to fulfil the environmental requirements of new international regulations, it is of great importance to develop reliable and sensitive methods for the determination of pesticides and their residues. In this sense, the analysis of CHD herbicides and their transformation products entails some difficulties. CHD herbicides are effective at low doses, thus trace concentrations are expected to be found in the environment. Therefore, analytical methods must provide high sensitivities. It is also important to bear in mind that CHD herbicides are polar and chemically unstable, which makes the analysis more difficult. The situation becomes more complex when transformation products are present due to the lack of analytical standards and scarce information available.

Depending on the physico-chemical properties of pesticides, the type of matrix, and the level of concentration required, analytical methods often involve preliminary steps of sample preparation. These pretreatments consist in interference removal from the matrix and concentration of the analytes of interest. Nowadays, together with classical techniques such as liquid extraction with organic solvents, more recent techniques such as solid-phase extraction (SPE), solid-phase micro-extraction (SPME), stir-bar-sorptive extraction (SBSE), or QuEChERS are commonly used prior to analytical determination [78]. Once the sample preparation is completed, the qualitative and quantitative analysis of pesticide residue are traditionally carried out using chromatography techniques since these allow separating complex mixtures. Gas chromatography (GC) and liquid chromatography (LC) are the most common techniques used for the determination of CHD residues. Although GC has been applied to the analysis of CHD herbicides, methods based on LC are more suitable for the analysis of CHD residues due to their low volatility, thermolability and the polar character. This technique is applicable not only for the parent compound but also for their transformation products.

Ono *et al.* [79] compared three different analytical methods (HPLC, GC and ultraviolet spectrophotometry) for the determination of alloxydim herbicide and the three transformation products in different crops and soils. An extraction and clean-up step was necessary before their determination. The HPLC method was found to be most suitable and the lowest limit of detection for alloxydim and all its transformation products was 0.01 ppm. Recoveries of alloxydim and three transformation products were 75-93% in various crops and 85-92% in soils. A method for the determination of the total content of alloxydim-sodium and five of its degradation products in ground water was described, using derivatization with hydrogen peroxide followed by GC-MS [80]. Derivatization of these compounds was carried out in order to obtain more stable and volatile products. An additional clean-up process was necessary to remove interferences caused by the presence of reactives used during the derivatization procedure. The detectable limit achieved was 0.1 μg L^{-1}, expressed as alloxydim-sodium equivalent, and the recoveries ranged from 53 to 85% [80].

Falb *et al.* [69] developed an LC method for the separation of clethodim and several transformation products formed during photolysis and hydrolysis of the herbicide in solution. Up to 31 and 19 photolytic and hydrolytic products were separated, although further identification was not achieved. Multi-residue methods for the analysis of clethodim and some of its

transformation products in fruits and vegetables have also been described [81,82]. For example, Klein and Alder [82] achieved the simultaneous determination of clethodim and five of its metabolites (two sulfoxides and three sulfones) by LC-MS after an extraction procedure with organic solvents and a clean-up step using SPE. These authors stated the influence of the matrix during the extraction and clean-up of clethodim, since decomposition of clethodim to the corresponding sulfoxides occurred in avocado, hindering to calculate recoveries of clethodim in this matrix. However, good recoveries (80-120%) were obtained for clethodim and its transformations products in most matrices at a concentration level 0.01 mg kg^{-1} [82].

An analytical method for sethoxydim in several crops was established using HPLC with UV detection by Gomyo and Ono [83]. The herbicide was extracted from crops with organic solvents prior to the analysis by HPLC. The lowest detection limit was 0.02 ppm and the recoveries ranged from 79 to 87%. In a later work, Gomyo *et al.* [84] reported a study showing a comparison between HPLC and GC methods for the determination of sethoxydim and ten of its transformation products in different crops. The experimental data showed that the HPLC method was more suitable for these compounds. After the extraction with methanol from crops, sethoxydim and all its transformation products were converted to sulphone derivatives by reaction with hydrogen peroxide and afterwards a clean-up step was performed using a Woelm column. This method provided a detection limit of 1.0 to 0.05 ppm for sethoxydim and its metabolites [84]. Hu *et al.* [85] established a multi-residue method based on LC-APCI/MS for the determination of sethoxydim and different pesticides in several aqueous matrices. The extraction recoveries of this herbicide in distilled water were 64%, whereas it was impossible to recover it from treated and raw water, probably due to degradation processes during the extraction step. Analogous findings were achieved by Shoaf and Carlson [70] during the optimization of a HPLC method for the determination of sethoxydim in aqueous solutions. These authors stated that recoveries of the parent compound were improved considerably at acidic pH values.

A SPME-HPLC-UV method has been reported for the determination of profoxydim herbicide in rice fields [86]. The technique of SPME was applied on-site at a flooded rice field in real time. This technique allowed extracting the target analyte under field conditions, decreasing time-consuming sample shipment and later sample preparation in the laboratory. Moreover, the stability of profoxydim during the storage of SPME fiber was increased during the storage compared to aqueous samples. The detection limit of the SPME-HPLC-UV method for the detection of profoxydim was 5 μg L^{-1} [86]. Tsochatzis *et al.* [87] developed and validated a multi-residue HPLC-DAD method for the separation and determination of nine commonly applied rice pesticides, including profoxydim, in paddy water samples. Preliminary clean-up of water samples and isolation of pesticides was performed on SPE cartridges. The limit of detection (LOD) and quantification (LOQ) for profoxydim herbicide were 0.4 μg L^{-1} and 2 μg L^{-1}, respectively. The method was subsequently employed for the determination of pesticides in paddy fields and surface water systems located in the Axios river basin (Greece). Profoxydim was detected at a relatively high concentration (6.3 μg L^{-1}) close to its dose of application [87].

In 2005, Lehotay *et al.* [1] applied QuEChERS for the determination of 229 pesticides, including cycloxydim and sethoxydim in two representative commodities (lettuce and orange). Recov-

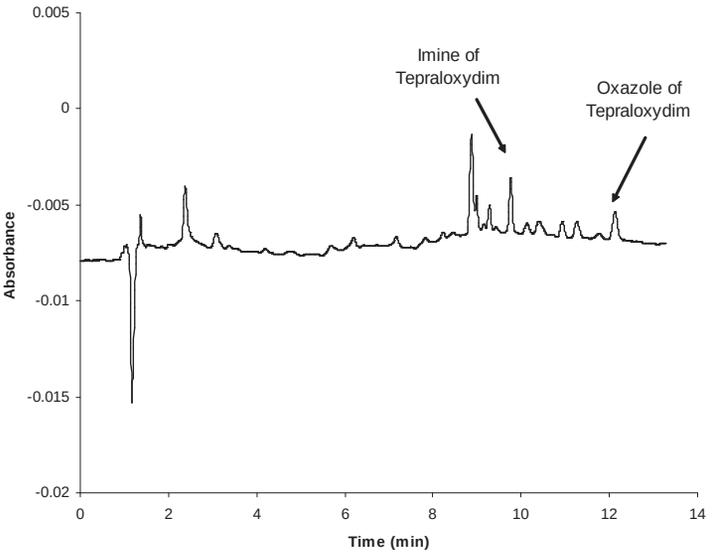


Figure 4. Chromatogram of commercial mineral water fortified with 0.1 μg. L^{-1} metabolites tepraloxydim oxazole and tepraloxydim imine (Modified from [71]).

eries of cycloxydim and sethoxydim vary from 80-89% and 50-69%, respectively. The low recoveries could be due to degradation processes, incomplete extraction and pH of the sample. Therefore, further investigations and modifications of the QuEChERS method are needed for the determination of these herbicides.

Liska *et al.* [88] developed a multi-residue method for the detection and quantification of 50 pesticides, including alloxydim-sodium and sethoxydim herbicides, in ultrapure and river Rhine water. Trace enrichment of water samples was necessary to obtain enough sensitivity for further analysis by LC-DAD. The detection limits achieved were 0.5 mg L^{-1} for sethoxydim and 1 mg L^{-1} for alloxydim-sodium in both types of waters. Sandín *et al.* [71] have established a method for direct analysis of tepraloxydim and its main metabolites in water. It has been demonstrated that chlorine content added to disinfect tap water is a critical parameter for the determination of tepraloxydim. In this work an analytical method for determination of two metabolites of tepraloxydim, oxazole and imine, has been validated to an LOQ of 0.1 μg L^{-1} in tap and commercial mineral water (Figure 4).

Different studies have shown that the methods based on the technique LC coupled with electrospray ionization (ESI) tandem mass spectrometry (MS), using previous SPE as the extraction procedure, are a powerful tool for the analysis of CHD herbicides. For example, Shen *et al.* [89] proposed a multi-residue method for the simultaneous analysis of six CHD herbicides employing LC-MS/MS. The method was successfully used to determine these herbicides in rice and corn, obtaining recoveries within 70.0-97.9% at the spiked levels of 5-20 ng g^{-1}. Marek *et al.* [90] described a multi-residue method for the determination of alloxydim, clethodim and sethoxydim in river water and distilled water after extraction/clean-up with C18/SAX. The recoveries of the herbicides from distilled water were 117% (alloxydim), 96% (clethodim) and 89% (sethoxydim).

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5. Conclusion

New herbicides, like cyclohexanedione oximes which are effective at low doses and easily decomposable, have been developed in recent years in order to reduce herbicide impact in the environment. However, degradation of these herbicides does not guarantee their detoxification and, in many cases, transformation products are more toxic, mobile and/or persistent than their active substances. Therefore, it is of utmost importance to improve our knowledge about these herbicides in order to minimize the possible adverse effects of their residues on human health, non-target organisms and the environment.

In this sense, this review provides an overview about the environmental behaviour of cyclohexanedione oxime herbicides under biotic and abiotic conditions. The most relevant studies in literature have been compiled and significant aspects such as factors affecting the behaviour of this herbicide family, as well as degradation routes and transformation products formed have been discussed. Moreover, illustrative examples about sample preparation, methods of determination and analytical techniques used for the analysis of cyclohexanedione herbicides and their transformation products have been described.

Although the availability of new scientific information on cyclohexanedione herbicides and their environmental fate and behaviour is increasing in recent years, more data are still needed. Thus, a better understanding of the degradation mechanism of cyclohexanedione herbicides is important for studying the fate and the effects of herbicides in the environment. In this sense, since most studies are conducted under laboratory conditions, more field research should also be desirable.

Moreover, to assess the overall impact of these herbicides, a major emphasis must be done on investigating their transformation products. It would also be interesting to perform monitoring programs of the parent compounds together with their transformation products in aqueous media because they could be potential contaminants of this compartment.

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