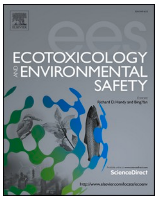
Ecotoxicology and Environmental Safety 299 (2025) 118409

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv



Unveiling the photodegradation of tralkoxydim herbicide and its formulation in natural waters: Structural elucidation of transformation products and toxicity assessment

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ARTICLE INFO

Keywords:
In silico
QTOF-MS
Pesticide
Degradation products
Vibrio fischeri

ABSTRACT

Pesticide degradation products (DPs), as emerging contaminants, are being detected in aquatic environments due to the widespread use of their active substances and pose potential risks to aquatic ecology and human health. However, their identification is challenging due to the many environmental conditions that influence their degradation processes. The photodegradation of the herbicide tralkoxydim and its formulation has been studied in ultrapure, spring and river waters and has shown rapid degradation. The photodegradation of tralkoxydim was slower in natural water and in the presence of humic acids (HA) than in ultrapure water, with half-lives of 5.1 h for river water and 1.1 h for ultrapure water. For the first time, three degradation products were identified in aquatic media using HPLC-TOF-MS/MS. These include photoisomerization, photolysis of the N-O bond of the oxime resulting in the tralkoxydim imine (major DP), and cyclization leading to tralkoxydim oxazole. Quantitative structure-activity relationship (QSAR) models were employed to approximate the potential ecotoxicological and environmental impacts of tralkoxydim and its DPs. Additionally, the toxicity of the isolated DPs was evaluated using a standard microtest bioassay with *Vibrio fischeri* bacteria. The results show that tralkoxydim imine and tralkoxydim oxazole exhibit high toxicity.

1. Introduction

Pesticides are widely used for managing pathogens and pests in sustainable agriculture to meet the needs of the growing world population (Damalas, 2009; Sharma et al., 2019). Currently, global pesticide use exceeds 4 million tonnes per year and Europe alone is responsible for using almost 400,000 tonnes (FAOSTAT, 2021). By 2050, pesticide use and related emissions are projected to intensify by 8–20 % with increasing cropland area (Nagesh et al., 2022). However, from an environmental point of view, there is increasing research regarding the behavior of pesticides and their detrimental impacts on ecosystems (Lushchak et al., 2018; Nagy et al., 2020; Shefali et al., 2021) and non-target organisms (Souza et al., 2020). Furthermore, the contamination of aquatic environments is one of the most important issues associated with pesticides. After application to crops, pesticides can enter into aquatic ecosystems through various routes such as agriculture runoff (Jing et al., 2021), leaching (Pandey et al., 2020), spray-drift (Chen et al., 2019), soil erosion, and deposition (Vagı and Petsas, 2017), These processes contribute to their presence in both surface and groundwater, and may pose potential threats to human and animal health and the environment. Therefore, more information is urgently needed to better understand the environmental fate and behavior of pesticides.

Photochemical reactions have been shown to be an important dissipation pathway in governing the fate of organic pollutants such as pesticides in surface waters (Han et al., 2024). Photolysis can occur directly, when the molecule absorbs light energy, or indirectly, mediated by reactive species generated by sunlight in the presence of natural

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https://doi.org/10.1016/j.ecoenv.2025.118409
Received 17 December 2024; Received in revised form 22 May 2025; Accepted 23 May 2025

sensitizers (Sparks and Nauen, 2015; OECD, 2023; Vione et al., 2014; Hemond and Fechner, 2015). Indirect photolysis can occur when light-absorbing molecules, commonly found in water, absorb photons and then transfer their energy to non-absorbing compounds or when transient oxidants such as hydroxyl radicals or singlet oxygen attack pesticide molecules (Sparks and Nauen, 2015). Several environmental parameters affect the photolytic transformation of pesticides, including pH, dissolved organic matter (DOM), and the presence of ions such as NO_3^-, NO_2^-, NH_4^+, and Fe(III) (Emídio et al., 2017; Chen et al., 2022; Janssen et al., 2014; Meng et al., 2022). Among these, humic acids (HA), the main component of DOM, play a particularly significant role in natural waters due to their dual ability to either sensitize or inhibit photodegradation.

Degradation products (DPs), formed through these abiotic transformations, are now recognized as emerging contaminants due to their persistence, mobility and, in some cases, higher toxicity compared to their parent compounds (Boxall, 2009; Coadou et al., 2017; Li et al., 2019; Olsson et al., 2013). Nevertheless, the detection and structural elucidation of these DPs remains a major analytical challenge, as many are not included in chemical databases and standards are not available. Recent advances in analytical instrumentation, particularly high-resolution mass spectrometry techniques such as HPLC-QTOF-MS/MS, now make it possible to identify unknown transformation products in environmental samples with greater accuracy (Brunner et al., 2019; Katagi, 2018).

Toxicity assessment of DPs is also essential for a comprehensive understanding of pesticide impacts. However, these assessments are often not included in regulatory studies (Man et al., 2021). However, regulatory studies typically do not consider all the scenarios and leave, in some cases, a large gap in the knowledge of their environmental fate and toxicity. Bioassays using indicator organisms such as *Vibrio fischeri*, along with *in silico* approaches such as QSAR models, provide valuable complementary tools to estimate the ecological risks associated with pesticide degradation products (Baird and Bridgewater, 2017; Trawinski and Skibinski, 2017; Villaverde et al., 2018a).

Despite this growing body of research, most photodegradation studies have focused on parent compounds, with limited attention paid to the photochemical behavior of commercial formulations or the identification and toxicity assessment of DPs under realistic environmental conditions. Moreover, there is a notable lack of studies that jointly assess kinetics, transformation pathways, and toxicity of degradation products for specific pesticides. In this context, this work focuses on the herbicide tralkoxydim, a representative compound of the cyclohexanedione oxime (CHD) family. Tralkoxydim, commercialized under various trade names including Splendor® (25 % w/v), is widely used for post-emergence control of annual grasses in cereal crops. It is typically applied at a dose of 150–400 g a.i. ha^{-1} and is currently registered in more than 30 countries (MacBean, 2012). This herbicide inhibits acetyl-CoA carboxylase (ACCase), an essential enzyme for fatty acid biosynthesis (Lichtenthaler, 1990). Its physicochemical properties—high solubility in water, low sorption to soil (low K_{oc}), low volatility, and high polarity—favor its transport into aquatic systems after field application, increasing its environmental relevance (MacBean, 2012; Sevilla-Morán et al., 2013). Furthermore, its molecular structure includes chromophores capable of absorbing solar radiation > 290 nm, making it particularly susceptible to photodegradation under sunlight exposure (Sandín-España et al., 2013; Sevilla-Morán et al., 2014). Photolysis has been reported as the main degradation pathway for CHD herbicides in surface water, yet little is known about the degradation kinetics and transformation pathways of tralkoxydim itself.

To date, no data are available regarding the photodegradation of tralkoxydim under environmentally relevant conditions, nor on the nature or toxicity of its potential degradation products. In addition, no studies have simultaneously examined the influence of natural water matrices and the presence of humic substances on its degradation behavior. This represents a critical gap in the understanding of the environmental fate of tralkoxydim and the potential risk posed by its transformation products.

This study presents a novel and integrated approach to assessing the environmental fate of Tralkoxydim. Specifically, (i) the photodegradation of the active ingredient and its commercial formulation (Splendor®) was evaluated under simulated sunlight in ultrapure, river, and spring waters; (ii) the influence of humic acids on photolysis kinetics was examined; (iii) transformation products (TPs) were identified and structurally characterized using high-resolution mass spectrometry; and (iv) their potential toxicity was assessed through *Vibrio fischeri* bioassays and QSAR-based modeling. These results can offer a complete assessment of the transformation pathways and potential ecological implications of tralkoxydim photodegradation, and the results are expected to support improved environmental risk assessments and pesticide regulation.

2. Materials and methods

2.1. Chemicals, reagents and water samples

The analytical standard of tralkoxydim (2-[1-(ethoxyimino)propyl]-3-hydroxy-5-(2,4,6- trimethylphenyl)-2-cyclohexen-1-one) (99.12 % purity) was purchased from HPC Standards GmbH (Cunnersdorf, Germany). It is marketed as the *E* isomer in all herbicides due to its higher herbicidal activity and stability compared to the *Z* form (Iwataki, 1992; Monadjemi et al., 2013). The commercial formulation of tralkoxydim, Splendor® (25 % of the active substance), was purchased from the Syngenta Group Co., Ltd. (Basel, Switzerland). Both chemicals were used without further purification. Acetonitrile (HPLC superGRAD grade) and methanol (HPLC grade) were acquired from Macron Fine Chemicals™ (Gliwice, Poland), and ultrapure water was obtained from a Millipore system (Milli-Q-50, 18 mΩ). Formic acid (p.a.) was acquired from Merck (Darmstadt, Germany), and HA (technical grade) was purchased from Aldrich (Steinhem, Germany).

Stock solutions of the tralkoxydim active substance and tralkoxydim formulation (50 mg/L) were prepared by first dissolving the appropriate amount of the analytical standard or commercial formulation Splendor® in the minimum amount of methanol (10 % methanol in the final solution) to facilitate the addition of ultrapure water to obtain the same final concentration of the active substance in both. Stock solutions were stored at 4°C in the dark and were used to prepare more dilute standard solutions (5 mg/L) by the addition of water. Under these conditions, standard solutions of the tralkoxydim active substances and tralkoxydim formulations were stable for one week.

The environmental waters used in the experiments consisted of river and spring waters, which were collected from the provinces of Valladolid and Zamora, respectively. These provinces are located in northwestern Spain. The samples were filtered through 0.45 μm nylon filters (Millipore; MA, USA) and refrigerated at –18°C until further use. The water samples were analyzed to ensure that they were free of interfering compounds. The main physicochemical properties of these natural waters are shown in supplementary information (Table S1).

2.2. Photodegradation experiments

Simulated sunlight for the photodegradation experiments was provided by a Suntest CPS+ apparatus obtained from Atlas (Linsengericht, Germany) equipped with a xenon arc lamp (1500 W) and special glass filter that restricted the transmission of wavelengths below 290 nm. A cool chiller was used to maintain a mean internal temperature of 25 ± 1ºC. This device provides a spectral distribution that is close to that of natural sunlight and a constant irradiance that allows performing experiments under reproducible irradiation conditions, avoiding variations caused by geographical, seasonal or climatic conditions.

In general, all solutions of both the tralkoxydim herbicide and the commercial formulation that were used for the irradiation experiments were prepared at concentrations of 5 mg a.s./L by dissolving the appropriate volume of the stock solution in the corresponding water sample. This concentration was chosen to ensure the detection and kinetic evolution of the tralkoxydim DPs formed during degradation. The solutions were prepared when the experiments were conducted due to their low stability.

For the photodegradation studies, aqueous solutions of the herbicide tralkoxydim and its formulation were prepared in different water samples (20 mL, 5 mg a.s./L) and exposed to an irradiation intensity of 500 W/m^2 in covered cylindrical quartz cuvettes with magnetic stirring. To simulate environmental conditions as closely as possible, a sunlight intensity of 500 W/m^2 was chosen because this intensity is similar to the solar radiation in our region (460 W/m^2).

Likewise, the photodegradation kinetics of tralkoxydim in the presence of HA were also investigated. Solutions of tralkoxydim herbicide in ultrapure water (20 mL, 5 mg a.s./L) and different HA concentrations (1, 5 and 15 mg/L) were exposed to simulated solar radiation at an irradiation intensity of 750 W/m^2 in the same quartz cuvettes described above. These working concentrations were selected because they are those found in the environment. In natural waters, the HA in organic matter range from less than 1 mg/L in alpine streams to more than 20 mg/L in some tropical or polluted rivers and rivers that drain swamps and wetlands (Barceló and Hennion, 1997; Koumaki et al., 2015). All the solutions were filtered through a 0.45 μm regenerated cellulose membrane filter (Symta, Madrid, Spain) before injection.

At selected time intervals, aliquots were taken from the cuvettes and subsequently analyzed by HPLC-DAD to quantify the amounts of tralkoxydim remaining in the solutions after exposure to irradiation based on an external calibration and following the formation of DPs. For all degradation kinetics studies, each experiment was conducted in triplicate and carried out until the disappearance of the herbicide was achieved. The results are presented as the arithmetic means of three independent analyses. In addition, parallel control experiments in the absence of irradiation were carried out under the same conditions and initial concentrations of tralkoxydim to assess whether processes other than photodegradation were occurring.

2.3. *Analytical procedure*

The kinetic evolution of tralkoxydim and the study of the DPs generated as a result of the dissipation of tralkoxydim in the aqueous samples, ultrapure, spring and river water, were carried out using an HPLC system (1100 series; Agilent Technologies, Palo Alto, CA, USA) coupled to a diode array detector (DAD). The analytical column used was a C18 Waters Atlantis® column (3 μm particle size, 4.6 mm × 150 mm) (Waters, Dublin, Ireland). The mobile phase consisted of a mixture of ultrapure water (A) and acetonitrile (B), both of which were acidified with 0.1 % formic acid. The flow rate was 1 mL/min, and the injection volume was 20 μL. Two different chromatographic methods were used. The first was an isocratic method, with a mobile phase of 90 % B, designed to follow the decay of the active substance tralkoxydim and to calculate the kinetic parameters of photolysis. The second method was a gradient method that was developed to detect and follow the evolution of the DPs formed. The percentages of B in the mobile phase were as follows: 0–16 min, 43 %; 16–17 min, 43–80 %; and 17–25 min, 80 %.

2.4. *Identification of DPs*

The next step after detecting the DPs was to identify them. As there are no commercial standards available for tralkoxydim DPs, an HPLC system (series 1100; Agilent Technologies, Palo Alto, CA, USA) coupled to a hybrid QTOF mass spectrometer (QStar Pulsar I, Applied Biosystems) was used to determine the chemical structures. Since the degradation products obtained in the three types of water were the same and the formation pattern and evolution were also very similar (Fig. 2), a sample of tralkoxydim in ultrapure water that had been irradiated for 2 hours, in which all the DPs were presented, was selected for analysis to characterise the identified DPs. To obtain an accurate response from the mass analyzer and facilitate the identification process, it was necessary to concentrate the sample prior to injection. This was achieved by evaporating the irradiated solution to dryness with a gently nitrogen stream and then reconstituting it with 50/50 CH_3CN/H_2O. The column and mobile phase used for separation were the same as those previously described. The method used a gradient with the following B percentages: 0–19 min, 43 %; 19–20 min, 43–80 %; and 20–28 min, 80 %. The flow rate was 0.8 mL/min, and the injection volume was 10 μL. The typical mass error with this instrument was < 2 mDa. The experiments were tested in both positive and negative ion modes. The instrumental parameters were a mass range of 50–1200, an ion spray voltage (IS) of 5500 V, an ion source gas pressure (GS1) of 50 psi, an ion source gas 2 (GS2) of 55 psi, a curtain gas pressure (Cur) of 20 psi, a declustering potential (DP) of 70 V, a focusing potential (FP) of 210 V, and a declustering potential 2 of 15 V. The accurate masses obtained were processed using the elemental composition calculator that was incorporated in Analyst software (Applied Biosystems). In positive ion mode, protonated molecular ions $[M+H]^+$ were observed to have the best response. Based on the proposed molecular formula, the exact masses obtained from the high resolution of the QTOF mass spectrometer and typical fragment ions, the chemical structure was confirmed.

2.5. *Data analysis*

Once the data from the photodegradation experiments were measured, the decreasing tralkoxydim concentrations versus irradiation times were adjusted to first-order kinetics (US EPA, 1998). The following equation is linearly fitted: $C_t = C_0\ e^{-kt}$, where C_0 is the initial concentration of tralkoxydim, C_t is the concentration at irradiation time t, and k is the rate constant of the photodegradation process. According to the first-order reaction law, the half-lives ($t_{1/2}$) for the photolysis process were also determined. This parameter is defined as the time taken for the tralkoxydim concentration to fall to half of its initial value and is related to the rate constant, k, by means of the equation $t_{1/2} = \ln 2/k$. The kinetic results were analyzed using the statistical software OriginPro 8.5® (OriginLab, USA).

The significant differences between the photodegradation rate constants that were obtained under the different experimental conditions at the 0.05 significance level ($p < 0.05$) were determined using one-way analysis of variance (ANOVA). The statistical software, Statgraphics 19®, was used for data analysis.

2.6. *Toxicity experiments*

The toxicity of tralkoxydim and its DPs was determined using the *Vibrio fischeri* Bioluminescence Inhibition Bioassay Microtox® according to the standard protocol, UNE-EN ISO 11348–3:2009 (ISO, 2009). The bacterium, *Vibrio fischeri* (NRRL B-11177), was purchased as a freeze-dried reagent. The samples were stored at –20°C and hydrated prior to testing. Since no standards of tralkoxydim DPs are commercially available, we obtained them in the laboratory by exposing aqueous tralkoxydim solutions to simulated sunlight irradiation. The samples were photodegraded until the maximum amount of each product was obtained. Then, the compounds of interest were isolated and collected using a fraction collector based on the elution times of the analytical column. Each collected fraction was evaporated to dryness and reconstituted with ultrapure water. The working concentrations of the three compounds under study were initially set to 50 mg/L.

Aliquots of the bacterial suspension were exposed to a series of dilutions of each compound (0, 11.36, 22.72, 45.45 and 90.91 %) previously dissolved in 2 % sodium chloride, and the pH was adjusted to 7.0 ± 0.2 by the addition of an osmotic adjuster. Bioluminescence measurements were performed after 15 minutes of exposure of the bacteria to the solutions, and the results were compared to the light output of a control sample and at an incubation temperature of 15°C. All samples were assayed in triplicate. The light emission for each sample dilution was measured in relative units of luminescence. The obtained data was used to calculate the toxicity of each compound in terms of the median concentration that causes a 50 % reduction in bacteria bioluminescence (EC_{50}). The EC_{50} values were calculated from the standard curves that were created using the serial dilutions of each compound. To examine the uncertainty around the compounds toxicity, the 95 % confidence intervals (CI) for EC_{50} values were also calculated.

The bacteria and solutions were supplied by Modern Water (New Castle, DE, USA). The emitted luminescence intensities were quantified by a BG-1 Multitox luminometer (MGM Instruments, USA).

2.7. QSAR models

The acute and chronic toxicity (chV) levels of tralkoxydim and the identified photodegradation byproducts were predicted for three aquatic organisms (fish, Daphnia and green algae) using the US EPA, OECD and EU-approved QSAR ECOSAR software (version 2.2) (Liu et al., 2019a; US EPA, 2022).

The acute toxicity parameters were demonstrated by the LC_{50} values (the concentration of the tested substance that is lethal to 50 % of Daphnia and fish after 48 h and 96 h of exposure, respectively), as well as by the EC_{50} values (the concentration of the tested substances for the growth deterrence of 50 % of green algae after 96 h of exposure) (Liu et al., 2019b; Xu et al., 2017).

Based on the criteria of the chemical classification and labelling system, the calculated parameters were classified and labelled as "very toxic", "toxic", "harmful" and "harmless".

The toxicity estimation provides beneficial information for the possible pre-emptive application of protocols to remove the desired pollutant from water and wastewater (Xu et al., 2017).

3. Results and discussion

3.1. Photodegradation kinetics of tralkoxydim and tralkoxydim formulation in natural waters

Photodegradation studies were conducted in a Suntest reactor, which provides a wavelength distribution closely resembling that of natural sunlight and a constant irradiance, thereby minimising environmental variability. The kinetic parameters obtained with this device demonstrate a high degree of correlation with those observed under natural sunlight and those obtained with a filtered xenon arc lamp (Fig. S1). While the absorption of solar radiation by herbicides is uncommon, tralkoxydim exhibits a notable overlap in its UV absorption spectrum with solar emission at wavelengths between 300 and 350 nanometers (Fig. S1). The maximum absorbance occurs at 254 nm, with significant absorption at wavelengths exceeding 290 nm. This indicates that tralkoxydim has the potential to absorb UV energy, suggesting that direct photodegradation of this herbicide in natural conditions may be feasible. In accordance with the European Commission, phototransformation must be taken into consideration when the molar extinction coefficient of a compound is equal to or exceeds 10 L/mol cm at wavelengths of 290 nm and above. The molar extinction coefficient (ε) value obtained at a wavelength of 290 nm in an aqueous solution with a natural pH for tralkoxydim was 10148 L/mol cm, indicating that photolysis can contribute significantly to its degradation in natural waters and should be considered when studying its fate in the environment.

Pesticides are usually applied as commercial formulations containing different additives to improve the performance of the active ingredient and to enhance the safety and ease of use. Certain research has highlighted that the components of formulations may either accelerate or decelerate the photodegradation process of pesticides (Filipe et al., 2013; Scrano et al., 1999). However, most photolysis studies have traditionally concentrated on the active ingredient alone, so there is a growing consensus on the importance of examining the behavior of formulated herbicides. In this work, simultaneous investigations of the photolytic kinetics of the active substance tralkoxydim and formulated Splendor® in ultrapure, spring, and river waters at a simulated solar radiation intensity of 500 W/m^2 were conducted. The purpose of this study was to evaluate and compare the photodegradation kinetics of tralkoxydim as an analytical standard and as part of a commercial formulation and to investigate the effect of water composition and the role of additives on the degradation kinetics.

The remaining concentrations of the tralkoxydim active substance and tralkoxydim in the formulation fitted well to first-order kinetics in the three types of water samples (Section 2.5). The correlation coefficients were greater than 0.99, and consequently, the rate constants and half-life times can be considered as representative values (Figs. 1a and 1b). No degradation of tralkoxydim was observed in the dark control experiments.

The statistical analysis of the rate constants for the active substance tralkoxydim and its formulation revealed significant differences among the three types of water. Additionally, the photolysis rates were lower in natural waters than in ultrapure water, with the order being river water $<$ spring water $<$ ultrapure water. Tralkoxydim photodegrades at a slower rate in river water ($\approx 0.1\ h^{-1}$) and spring water ($\approx 0.2\ h^{-1}$) than in ultrapure water ($\approx 0.6\ h^{-1}$) (Table 1). These results indicate that the photolytic behavior of tralkoxydim is influenced by the water composition. A direct correlation was also observed between the retardant effect on the photolysis rates and the total organic carbon (TOC) contents in the natural water samples (Table S1). Our research group has previously reported similar results with other herbicides from the same family. The inhibitory effect of natural water constituents may be due to an internal filtering effect, suggesting that any rate reduction in due to light attenuation by the constituents of natural water (Sandín-España et al., 2013). However, the influence of other substances present in these natural waters cannot be discarded. In relation to the effect of the commercially formulated additives on the photolysis rate of the active substance, it is important to note that the active substance tralkoxydim and the formulation exhibited similar half-lives for each of the water types (Table 1). These results indicate that the additives in the formulation do not affect the degradation rates of tralkoxydim and, therefore, do not act as photosensitizers.

Our findings clearly establish that photodegradation plays a critical role in the dissipation of tralkoxydim in aquatic environments. The herbicide was rapidly broken down in all three water types examined, with half-lives ranging from 5.1 hours in river water to as little as 1.1 hours in ultrapure water, as detailed in Table 1. This indicates that both direct and indirect light absorption by tralkoxydim are significant factors that contribute to its degradation pathways in water bodies.

3.2. Effect of HA on tralkoxydim photodegradation

As mentioned in the introduction, HA is an important component of organic matter and plays a crucial role in influencing the degradation efficiency of pesticides in aquatic environments. Fig. 1c illustrates that tralkoxydim photolysis in the presence of HA in ultrapure water followed first-order kinetics with correlation coefficients greater than 0.98 in all cases and with estimated half-lives ranging from 1.1 h to 5.0 h for a concentration range of 1–15 mg/L (Table 2). In the absence of this substance, the half-life was 0.7 h. This means that the presence of HA inhibited the photolysis kinetics of tralkoxydim compared to that of ultrapure water. Furthermore, the photolysis rate constants decreased by a factor of approximately 7 in solutions with HA concentrations ranging from 0 to 15 mg/L, revealing significant differences between each HA concentration. These results show a strong dependence of the photodegradation of tralkoxydim on the HA concentration present in the aqueous media. This retarding effect of HA suggested that these

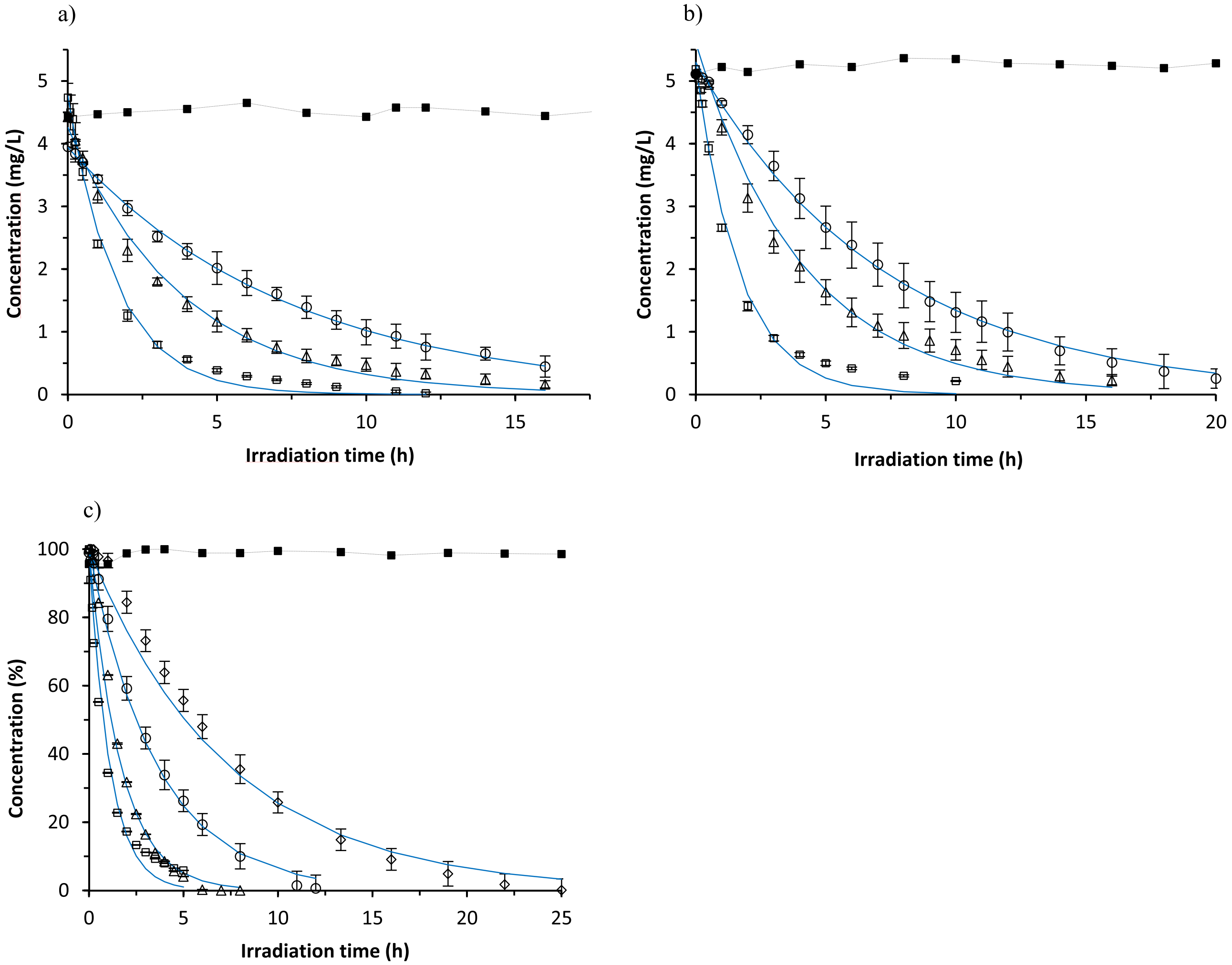

Fig. 1. Photodegradation kinetics of active substance tralkoxydim (a) and formulation Splendor® (b) in ultrapure (□), spring (△) and river water (○) under simulated sunlight (500 W/m^2). (c) Photodegradation kinetics of active substance tralkoxydim at 0 mg/L (□), 1 mg/L (△), 5 mg/L (○) and 15 mg/L (◇) of humic acids in ultrapure water under simulated sunlight (750 W/m^2). Dark control experiments (■). Error bars indicate SD (n = 3).

Table 1
Photolytic kinetic parameters of the active substance tralkoxydim and its commercial formulation (Splendor®) in different water types at an irradiation intensity of 500 W/m^2. Different letters indicate significant differences according to the least significant difference test (LSD) at a significance level of 95 %.

	Water type	k (h^{-1})	$t_{1/2}$ (h)	R^2
Tralkoxydim a.s.	ultrapure	0.610 ± 0.056 a	1.144 ± 0.107	0.994
	spring	0.258 ± 0.025 b	2.707 ± 0.271	0.991
	river	0.136 ± 0.017 c	5.151 ± 0.673	0.997
Tralkoxydim formulation (Splendor®)	ultrapure	0.601 ± 0.009 a	1.153 ± 0.018	0.991
	spring	0.245 ± 0.033 b	2.863 ± 0.385	0.991
	river	0.139 ± 0.023 c	5.084 ± 0.929	0.997

Table 2
Photolytic kinetic parameters of tralkoxydim in the presence of various concentrations of humic acids in ultrapure water at an irradiation intensity of 750 W/m^2. Different letters show significant differences according to the least significant differences test (LSDs) at a significance level of 95 %.

	HA (mg/L)	k (h^{-1})	$t_{1/2}$ (h)	R^2
Tralkoxydim a.s.	-	0.917 ± 0.101 a	0.761 ± 0.079	0.984
	1	0.597 ± 0.032 b	1.164 ± 0.065	0.994
	5	0.279 ± 0.016 c	2.489 ± 0.142	0.997
	15	0.136 ± 0.002 d	5.081 ± 0.088	0.993

substances can act as ’optical filters’ that absorb most of the emitted photons and thus slow the direct photochemical reaction of tralkoxydim (Fig. S2). Our results are in accordance with other researches where the photodegradation of many pesticides has been reported to be inhibited in the presence of humic acids (Burrows et al., 2002). For instance, compounds such as oxycarboxin, diuron and imazapyr (Moza et al., 1995; Durand et al., 1990; Elazzouzi et al., 1999), and herbicides of the CHD family (Sevilla-Morán et al., 2008) have shown a reduction of their photodegradation rates by approximately 5–25 %. It has been suggested that under solar irradiation, humic substances (HS) can attenuate light through inner filter effects, by absorbing photons or scattering incident radiation (Dimou et al., 2004; Skibiński et al., 2016). In our experiment, the transmittance of the tested solutions was determined at 290 nm and found to decrease, from 99 % for the solution without HA to 18 % for 10 mg/L, indicating absorption of light by chromophoric moieties of HA. Therefore, HA absorb most of the emitted photons compete with the herbicide for irradiation absorption due to their spectra overlap, thereby inhibiting the direct photolysis and acting as ’optical filters’.

3.3. Identification of DPs

A representative LC-DAD chromatogram for the photoinduced degradation of tralkoxydim in spring water is shown in Fig. 2a. Three different byproducts were observed during irradiation and up to the complete degradation of tralkoxydim. The same three byproducts were observed in the three types of waters studied (Fig. S3). Tralkoxydim was the least polar compound, with a retention time of 27.0 minutes. All identified DPs were found to be more polar, and they were named based on their order of appearance in the chromatogram. The major and most polar DP2 appeared at a retention time of 16.8 min. Then, at 18.2 min, DP1 appeared, which seems to be in equilibrium with tralkoxydim and was not detected at the end of the degradation process. Finally, the minority product DP3 appeared at the beginning of the degradation at a retention time of 21.7 min, and its area remained constant throughout the process.

Fig. 2b displays the progression of the tralkoxydim degradation products in spring water until full degradation at 16 hours. This process was monitored by LC-DAD, but quantification of the progression was not possible due to the lack of commercially available byproducts. The DP3 photoproduct was the minority product; it was present from the beginning of the photodegradation, and its concentration remained constant throughout the irradiation time. In contrast, DP1 and DP2 exhibited parallel evolution patterns in the initial two hours, with significant and rapid increases to 20–25 %. At this time, the DP1 photoproduct reached its maximum quantity and then decreased to trace levels. The upward DP2 trend persisted, eventually becoming the main photoproduct. The formation and evolution patter of the three photoproducts were the same for the three types of waters studied.

The identification of byproducts was performed using a QTOF mass spectrometer due to the lack of commercial standards. Tralkoxydim and its photoproducts were ionized in the positive mode of the ESI interface. The MS/MS fragmentation pattern of each compound enabled the elucidation of its structure. Plausible structures were then proposed based on the *m/z* values of their $[M+H]^+$ and MS/MS data, together with the elemental compositions obtained from accurate mass measurements. The elemental compositions of all the product ions were confirmed via accurate mass measurements.

Fig. 3a illustrates the MS/MS fragmentation and pathways of tralkoxydim, which provide detailed insights into its molecular breakdown process. The purpose of studying tralkoxydim was to aid in the interpretation of the MS/MS spectra of unknown byproducts. The tralkoxydim fragmentation pathways begin with the ionization process, resulting in the formation of the radical cation I. This intermediate may proceed to cation II by abstracting hydrogen from the medium, resulting in the peak $[M+H]^+$ at *m/z* 330.2049. Alternatively, the loss of ethene from the oxime may result in the formation of oxime III, which, through homolytic cleavage of the oxime-cyclohexanedione bond, would lead to the formation of cation IV at *m/z* 72.0443. Finally, the loss of the ethoxyl radical may result in the formation of the cation V. This cation could evolve through two pathways. First, the loss of ethene could lead to the formation of the cation VI at *m/z* 256.1320, which could further evolve to a peak at *m/z* 138.0560 (compound VII). Second, the loss of carbon monoxide could lead to the formation of cyclopentanone IX, which could evolve to the peak at *m/z* 96.0445 (compound X).

DP1 showed MS/MS fragmentation patterns that were very similar to those of commercially available tralkoxydim. This suggested that the most likely structure was the *Z*-isomer of tralkoxydim.

Fig. 3b details the fragmentation pathway of DP2, highlighting a peak at *m/z* 286.1790 (compound XII) that is likely attributed to the protonated nature of the tralkoxydim imine resulting from the cleavage of the N-O bond in the oxime group. DP2 has multiple fragmentations that have been explained in different ways. The detection of the XIV cation (*m/z* 85.0284) could be attributed to the loss of the fragment with a nitrile group followed by the loss of the styrene derivative.

Compound XVI at *m/z* 98.0601 could be formed by the loss of carbon monoxide from radical cation XI, which passed through compound XV with cyclopentanone, as shown in tralkoxydim (Fig. 3a). In another pathway, the equilibrium between XI and XII could lead to the detection of the peak at *m/z* 269.1524 of compound XVIII by loss of ammonia. The peak at *m/z* 56.0493 could correspond to compound XIX due to heterolytic fragmentation of the bond between the imine and cyclohexanodione. Finally, another peak was detected at *m/z* 140.0716, where the loss of ethene led to the formation of compound XX, which eventually led to the formation of XXI.

Fig. 3c shows the MS/MS fragmentation patterns and the pathways of DP3. A peak at *m/z* 286.1790 was detected, which could correspond to the protonated molecule of tralkoxydim oxazole (compound XXIII). Based on these data, it can be concluded that DP3 is most likely the oxazole of tralkoxydim. Unlike other herbicides in the cyclohexanedione family, such as alloxydim it can only form one type of oxazole due to the intrinsic symmetry of its molecule. This is because both possible routes lead to the same compound.

DP3 exhibits multiple fragmentations, which could be explained by

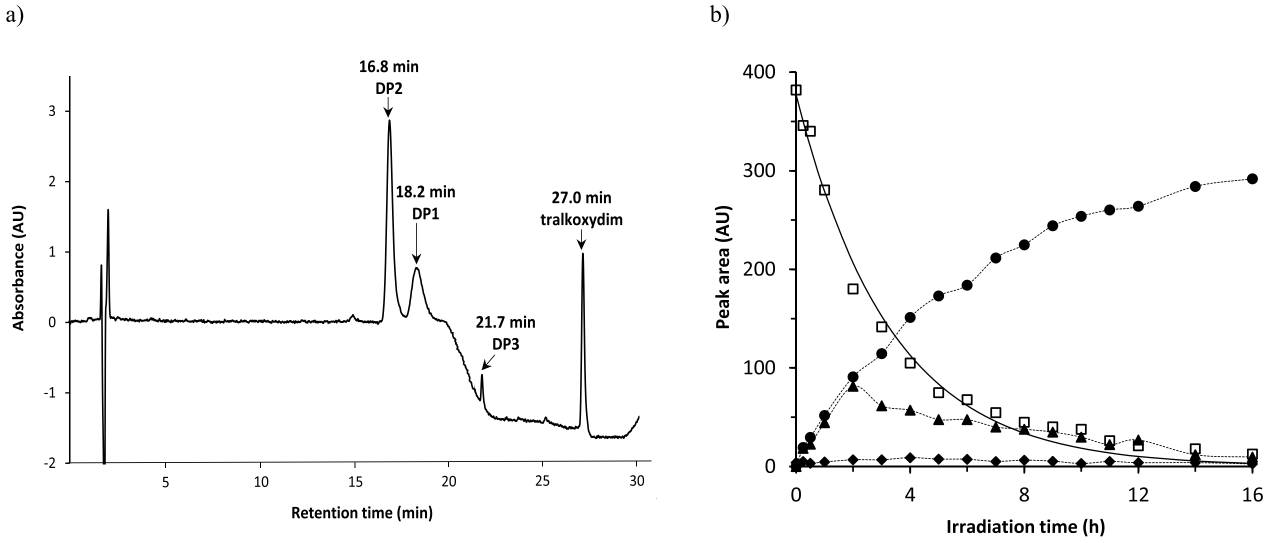

Fig. 2. a) HPLC-DAD chromatogram of tralkoxydim degradation and its DPs and b) kinetic evolution of tralkoxydim (□) and its degradation products DP1 (▲), DP2 (●) and DP3 (◆) in spring water at an irradiation intensity of 500 W/m^2.

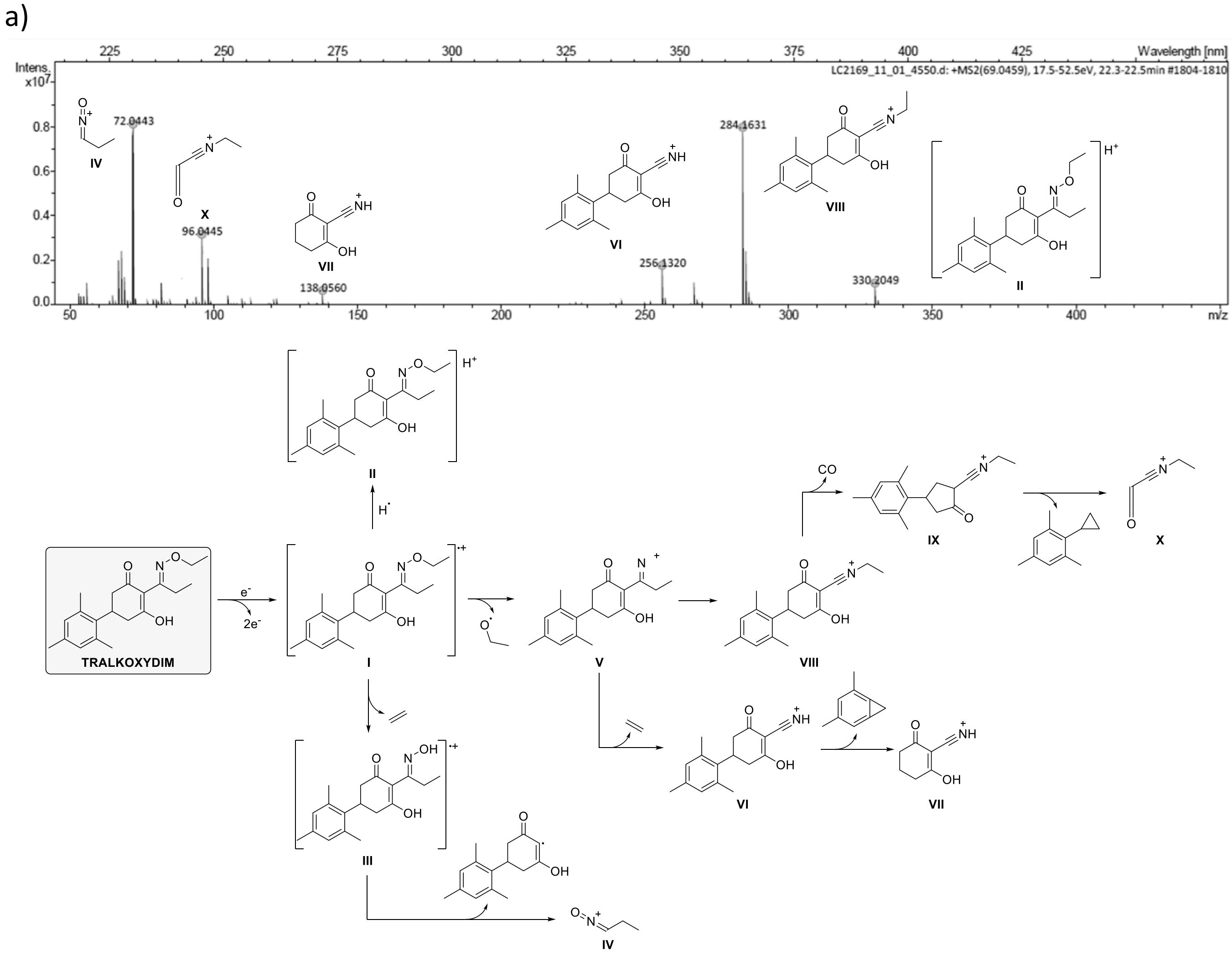

Fig. 3. LC-QTOF mass spectra and fragmentation pathways of a) tralkoxydim b) DP2 and c) DP3.

different pathways. The peak at *m/z* 98.0599 could correspond to the XXV cation and result from inductive cleavage assisted by β-hydrogen removal, providing the XXIV ketene. A similar process in the aryl group of the compound could also explain the detection of the peak at *m/z* 121.1008, which was identified as a fragment derived from mesitylene XXVI.

However, the radical cation XXII could lose carbon monoxide, resulting in the polycyclic compound XXVII. This compound could then subtract hydrogen from the medium, producing a peak at 256.1687 (XXX). Alternatively, intermediate XXVIII could be formed through elimination of the heterocycle, leading to fragment XXIX at 157.1005 by loss of a hydrogen. Another possible outcome is the detection of peak XXXI at 72.0444 from intermediate XXII, which could result from a similar elimination in the heterocycle. Following the same pathway as in the DP2 product for fragment XXI (Fig. 3b), a peak at 138.0544 was detected by two consecutive steps in which ethene and a methylene derivative were lost, giving fragment XXXIII.

Previous QSAR studies on herbicides from the same family have revealed the formation of similar fragments. For instance, the literature reports indicate that sethoxydim (Sevilla-Morán et al., 2014) and clethodim (Sevilla-Morán et al., 2010) lose carbon monoxide or the -OR group of the oxime.

3.4. Toxicity analysis

Using Microtox® bioassays, aqueous solutions of the active substance, tralkoxydim, and its DPs, DP2 and DP3, were screened for acute toxicity to the bacterium *Vibrio fischeri*. The reproducibility of the bioassay responses was evaluated by simultaneously performing three replicates of the measurements. Interestingly, the Microtox® bioassay did not show any toxicity to the bacterium, *Vibrio fischeri*, at the tested tralkoxydim concentrations. It was not possible to prepare higher starting concentrations of tralkoxydim due to its poor solubility in water. The bioassay, however, showed potential toxicity for the DPs, as revealed by the estimated toxic endpoints (in terms of the concentrations that promoted 50 % bioluminescence inhibition, EC_{50}). The mean EC_{50} values and respective 95 % confidence interval for DP2 and DP3 were 11.70 ± 1.40 (10.52–12.88) mg/L and 15.93 ± 1.57 (14.15–17.71) mg/L, respectively. These results are in line with those previously observed by our research group with the cyclohexanedione herbicides alloxydim (Sandín-España et al., 2013), sethoxydim (Sevilla-Morán et al., 2017) and clethodim (Villaverde et al., 2018b), where the photodegraded solutions showed greater toxicity to the bacterium *Vibrio fischeri* than the active substance. These findings are of great interest and provide evidence for the risk of tralkoxydim DPs to aquatic biota, and further studies are needed to assess whether there are additive, synergistic or antagonistic interactions among these DPs.

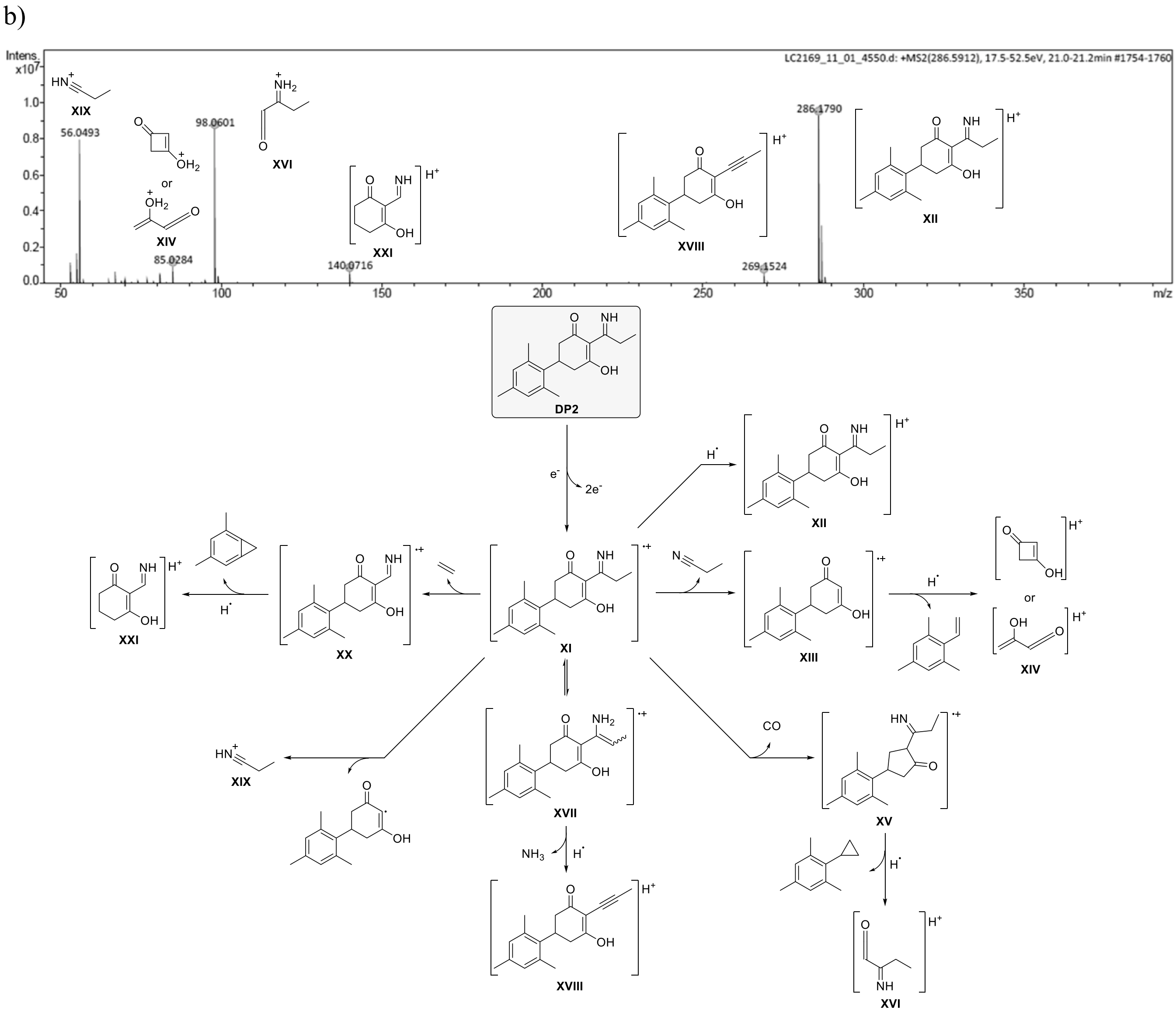

Fig. 3. (*continued*).

3.5. QSAR estimations

According to the GHS classification (Table S2), all substances in aquatic environments are classified into four levels: "not harmful", "harmful", "toxic" and "very toxic". As shown in Table 3, our compounds have different toxicity values according to the ECOSAR and Vega QSAR simulations.

The acute toxicity levels of the fish (96 h of exposure), daphnia (48 h of exposure), and algae (96 h of exposure), in addition to the chronic toxicity (ChV) values, were assessed using the median lethal concentration (LC_{50}) and the median effect concentration (EC_{50}) values (Al Rawas et al., 2023). The calculated acute toxicities for tralkoxydim (*Z* and *E* isomers) were 0.82, 0.14, and 0.06 mg/L for fish, Daphnia, and algae, respectively. These values indicate that tralkoxydim was highly toxic to all aquatic organisms.

The chronic toxicity data of tralkoxydim showed concentrations of 0.02 mg/L for fish, 0.02 mg/L for Daphnia, and 0.03 mg/L for algae. These concentrations were found to be highly toxic to all aquatic organisms. Based on the results obtained for tralkoxydim, the herbicide seems to have very negative effects on the marine species studied, presenting high levels of toxicity.

The acute toxicity levels of tralkoxydim byproducts for the studied marine species ranged from 30.30-49.70 mg/L for DP2 and 0.27-0.67 mg/L for DP3. DP2 was found to be harmful, while DP3 was very toxic, with concentrations similar to those of tralkoxydim. DP2 had not chronic toxicity, and DP3 was very toxic, with values of 3.58-9.17 mg/L and 0.05-0.33 mg/L, respectively. The acute and chronic toxicity values of these tralkoxydim DPs demonstrate how the formation of new products from an initial compound can affect aquatic organisms differently.

The molecular structures of tralkoxydim and DPs exhibit high toxicity. The loss of the oxime from tralkoxydim to give DP2 appears to reduce the ecotoxicity, which may indicate that the oxime is an active component, but it is still harmful to the different aquatic organism. Regarding DP3, the formation of an oxazole appears to maintain the high ecotoxicity of the parent compound. Even if the oxime is lost, the formation of a heterocycle could explain the compound's ecotoxicity, as heterocycles are present in many bioactive substrates (Kabir and Uzzaman, 2022).

The *n*-octanol−water partition coefficient (K_{ow}) serves as a measure of the relationship between the lipophilicity and hydrophilicity of a chemical (Hodges et al., 2019). Table 3 shows the log K_{ow} values of tralkoxydim and its DPs. Log K_{ow} values above 3 may indicate a high risk

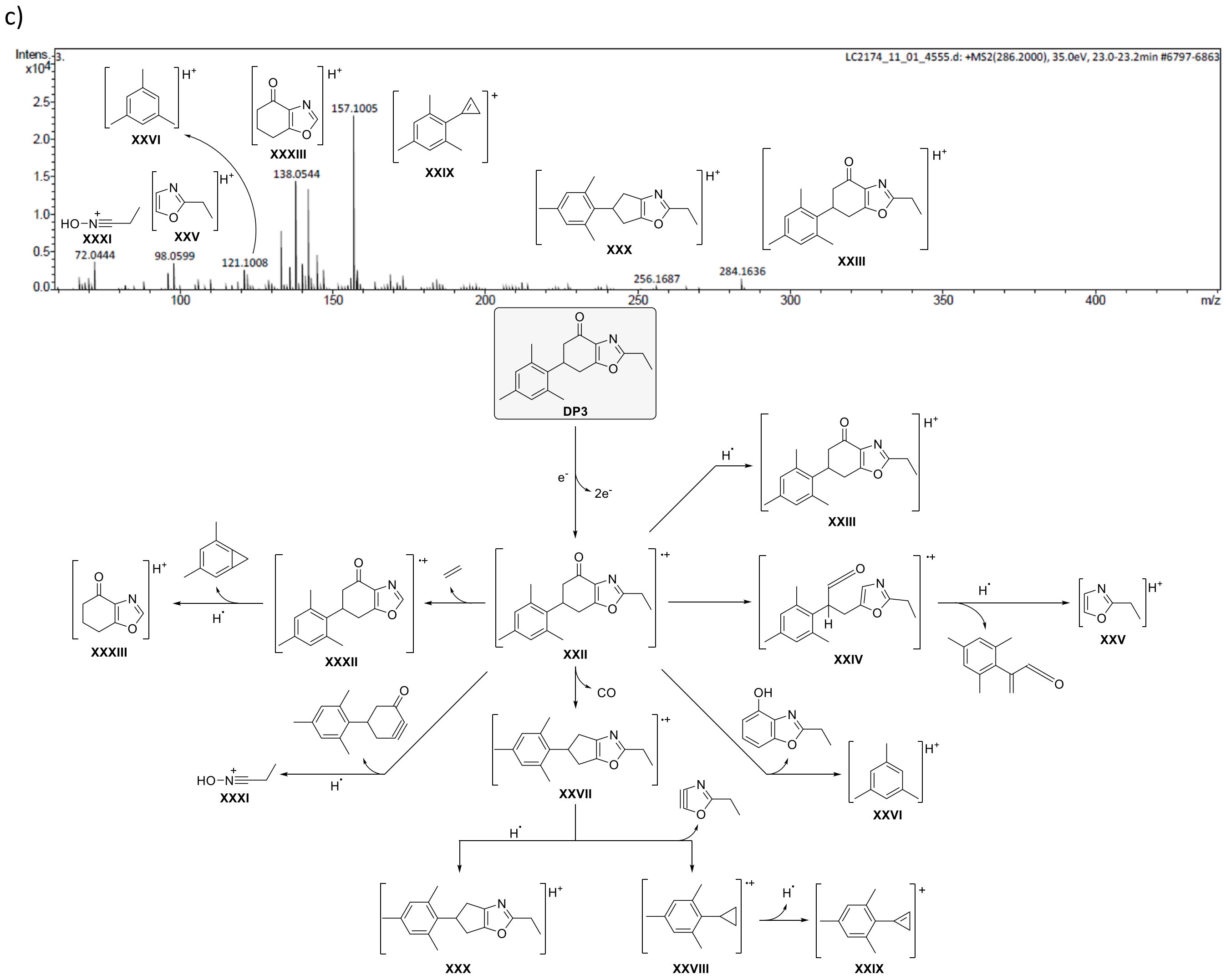

Fig. 3. (*continued*).

Table 3
Ecotoxicity results for tralkoxydim and its DPs.

Proposed compound	Acute toxicity[1,2] [mg/L]			Chronic toxicity[1,2] (ChV) [mg/L]			Log K_{ow}[2]	Log BCF[3] [L/kg]
	Fish (LC_{50})	Daphnia (LC_{50})	Algae (EC_{50})	Fish	Daphnia	Algae		
E-Tralkoxydim *Z*-Tralkoxydim (DP1)	0.82	0.14	0.06	0.02	0.02	0.03	4.90	2.61
Tralkoxydim imine (DP2)	49.70	30.30	30.30	5.27	3.58	9.17	2.75	3.17
Tralkoxydim oxazole (DP3)	0.36	0.27	0.67	0.05	0.06	0.33	5.14	2.69

[1] Predicted toxicity values classified according to the Global Harmonized System of Classification and Labelling of Chemicals (GHS). Highlighted in light gray – harmful; highlighted in medium gray – toxic; and highlighted in dark gray – very toxic.

[2] The acute toxicity, chronic toxicity and log K_{ow} levels were calculated using the ECOSAR Program.

[3] The bioconcentration factor (BCF) values were calculated using the Vega QSAR Program (model KNN/Read Across).

of bioaccumulation in organisms according to the European Chemicals Agency (ECHA) (ECHA, 2023). The log K_{ow} values for tralkoxydim and DP3 were 4.90 and 5.14, respectively, so the risk of bioaccumulation was high. DP2 also has a value close to 3 (2.75), suggesting that the three compounds are lipophilic.

The bioconcentration factor (BCF) is used in toxicology to evaluate the potential accumulation of a compound in living organisms (Arnot and Gobas, 2006). The BCF is the ratio of the concentration of a chemical in an organism to its concentration in the surrounding environment. Chemicals can be classified as non-bioaccumulative if their BCF values are less than 570 L/kg wet weight, bioaccumulative if they are greater than 2000 L/kg wet weight, and very bioaccumulative if they are greater than 5000 L/kg wet weight according to the European Commission (European Commission, 2009). Tralkoxydim and DP3 have BCF values below 570 L/kg, indicating that they are nonbioaccumulative chemicals. In contrast, DP2 had a BCF of 1479.11 L/kg, indicating slight bioaccumulation potential.

These findings indicate that both tralkoxydim and its photolysis byproducts could exhibit significant toxicity to aquatic organisms. In this sense, to reduce their environmental impact, several mitigation strategies can be considered. These include application restrictions based on crop stage and soil type, which are widely used in European regulatory frameworks. Bioremediation and the use of biochar as a soil amendment have also shown promise in enhancing pesticide degradation and reducing mobility. Additionally, agronomic practices such as no-till farming and structural measures like vegetative buffer strips and micro-dams can significantly limit pesticide runoff into surface waters. Implementing these strategies collectively can enhance environmental safety and support the sustainable use of pesticides.

4. Conclusions

This study provides new insights into the environmental fate of tralkoxydim and its commercial formulation in aquatic systems. Photolysis was confirmed as a major dissipation route, with degradation rates strongly influenced by water composition and the presence of humic acids, while formulation additives had no significant effect. Under simulated sunlight, three photodegradation products were identified for the first time in natural waters. Their structural elucidation revealed distinct transformation pathways, and toxicity evaluation demonstrated that some of these products, particularly tralkoxydim oxazole, may pose greater ecotoxicological risks than the parent compound. These findings highlight the importance of considering transformation products when assessing the environmental risk of pesticides. The practical significance of this research lies in its integrative approach—combining degradation kinetics, advanced analytical identification techniques, and toxicity assessments—to better understand pesticide behavior in surface waters. Building on these findings, future research should aim to further clarify tralkoxydim's transformation pathways and environmental implications by theoretical modelling approaches. In addition, the role of other environmentally relevant species, such as iron complexes, should be explored to better understand their influence on the phototransformation processes. Such efforts will support the development of more accurate environmental risk assessments and promote the responsible use of herbicides in agricultural systems.

CRediT authorship contribution statement

Manuel Alcamí: Writing – review & editing, Supervision, Resources, Project administration, Conceptualization. **Al Mokhtar Lamsabhi:** Writing – review & editing, Supervision, Software, Investigation, Data curation. **Pilar Sandín-España:** Writing – review & editing, Supervision, Resources, Project administration, Conceptualization. **José Luis Alonso-Prados:** Writing – review & editing, Resources, Project administration, Funding acquisition, Conceptualization. **María Cobos-Escudero:** Writing – original draft, Methodology, Formal analysis, Data curation. **Juan Carlos Nieto-Carmona:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **María José Patiño-Ropero:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work has been supported by the project PRIES-CM-Y2020/EMT-6290: "Expert system for risk identification of emerging pollutants from pesticides" financed by the Comunidad de Madrid and project PID2022–139874OR-C21 of the Ministerio de Ciencia e Innovación, Spain.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ecoenv.2025.118409.

Data availability

Data will be made available on request.

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