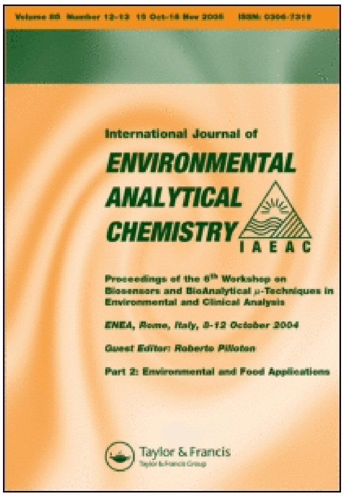

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Sunlight transformation of sethoxydim-lithium in natural waters and effect of humic acids

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To cite this Article Sevilla-Morán, Beatriz , Mateo-Miranda, Miguelina M. , Alonso-Prados, José L. , García-Baudín, José M. and Sandín-España, Pilar(2010) 'Sunlight transformation of sethoxydim-lithium in natural waters and effect of humic acids', International Journal of Environmental Analytical Chemistry, 90: 3, 487 — 496

To link to this Article: DOI: 10.1080/03067310903199500

URL: http://dx.doi.org/10.1080/03067310903199500

Intern. J. Environ. Anal. Chem.
Vol. 90, Nos. 3–6, 15 March–15 May 2010, 487–496

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(*Received 28 November 2008; final version received 6 July 2009*)

Photochemical behaviour of sethoxydim-lithium, a cyclohexanedione oxime herbicide, has been investigated in ultrapure and natural waters (mineral, well and river water). Photodegradation experiments were carried out under laboratory conditions using a solar silulator (Suntest equipment) and under natural solar irradiation in order to evaluate reaction kinetics of the active ingredient. Besides, the effect of humic acids (HA) on the degradation rate under simulated solar radiation was also studied. The photodegradation rates of sethoxydim-lithium in all the different waters and light sources studied followed first-order kinetics. Results showed that dark reactions were negligible. Experimental data showed that half-lives of the herbicide under simulated irradiation were higher in natural waters than in ultrapure, showing the lowest degradation rate in river water ($t_{1/2} = 135.5 \pm 0.3$ min). Under natural sunlight, sethoxydim-lithium photodegradation followed the same behaviour, with half-lives that range from 82 to 437 min for ultrapure and river water respectively, showing a strong dependence on the composition of water. However, rates of degradation of sethoxydim-lithium were faster under simulated radiation compared to natural sunlight (e.g. $t_{1/2\ (\text{ultrapure water})}$ 59.8 ± 0.2 min *vs.* 82.1 ± 0.7 min). The presence of different concentrations of HA (1–20 mg L^{-1}) retarded the photolytic degradation relative to ultrapure water with half-lives from 92 to 196 min.

Keywords: sethoxydim-lithium; natural waters; humic acids; Suntest equipment; sunlight

1. Introduction

The growing world population and the intensive agriculture practices make essential the use of the agrochemicals in order to assure the crops yields. The current tendency in agrochemical industry points to the development of pesticides more selective, less environmentally persistent, with less toxicity and bioaccumulation. In this regard, the family of herbicides named cyclohexanedione (CHD) has appeared in the last thirty years to fulfil these environmental requirements. These herbicides, developed for post-emergence grass weed control in broad-leaved crops, are polar, non-volatile and thermally labile [1]. The relatively high water solubility of this type of herbicides could lead to a rapid migration to aquatic compartments, where different degradation pathways could take place.

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ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310903199500
http://www.informaworld.com

Sethoxydim-lithium (Figure 1) belongs to CHD family and it is used to control annual and perennial grasses in numerous broad-leaved crops including cotton, soybean, sugar beet and tobacco. This herbicide acts disturbing lipid biosynthesis by inhibition of acetyl CoA carboxylase [2,3].

The degradation of herbicides in water is an area of research interest and, in this sense, photolysis is known to be one of the major abiotic processes affecting the fate of herbicides in aquatic media [4–6]. Information about photodegradation is necessary to estimate the persistence of these compounds and to identify the factors that influence their behaviour in the environment.

Several authors have showed the importance of diverse parameters on the photolysis rates of pesticides. The composition of aquatic media also plays an important role on the phototransformation of herbicides. Various authors point out that particulate and dissolved substances present in natural waters could be responsible for the different photolysis rates of herbicides observed between natural and distilled water [7,8]. One of the primary light-absorbing species in natural waters is organic matter where humic acids (HA) are important absorbing constituents of it. Diverse studies are available from literature where HA act enhancing [9,10] or inhibiting [7,11] the degradation of herbicides.

The use of xenon arc lamps with light emissions above 290 nm is preferred in order to model the photolysis experiments under laboratory conditions since they present a wavelength distribution very close to natural sunlight [12,13]. However, it is also necessary to carry out photodegradation studies under real conditions because it is important to consider the changes of natural sunlight intensity and wavelength with time of day and season [14].

Transformation of sethoxydim-lithium by light in aquatic media has received little attention. Previous studies of Campbell and Penner suggest the rapid degradation of sethoxydim in water and organic solvents [1]. These authors exposed aqueous solutions of sethoxydim to artificial light and observed that only 2% remained after 3 h. In the same way, they also observed a rapid photodegradation on glass disks of sethoxydim dissolved in n-hexane (81% of herbicide was transformed after 1 h). Besides, sethoxydim was completely lost within seconds in aqueous media either in incandescent or UV light at pH 3.3 and 6.0 and methanolic solutions of the herbicide were transformed more than 50% after 10 min of exposition to UV light [15].

To our knowledge, there is no available information in the literature regarding the photochemical behaviour of sethoxydim-lithium under natural conditions in aqueous environment. In this context, the aim of this work was to study the photochemical

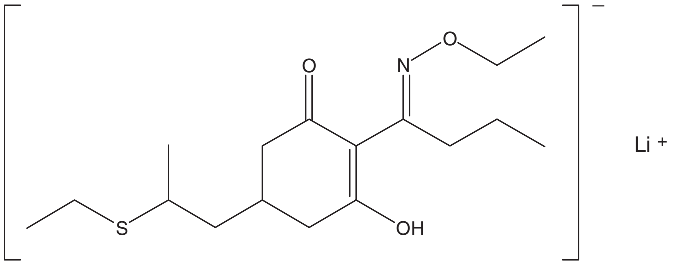

Figure 1. Chemical structure of sethoxydim-lithium.

behaviour of sethoxydim-lithium in ultrapure and natural waters using simulated solar radiation and natural sunlight to obtain results close to real field conditions. Moreover, the influence of HA on the reaction rate has been investigated.

2. Experimental

2.1 *Chemicals and water samples*

The herbicide sethoxydim [(*RS*)-(*EZ*)-2-[1-(ethoxyimino)butyl]-5-[2-(ethylthio)propyl]-3-hydroxy-cyclohex-2-enone] was supplied by BASF Ltd (Limburgerhof, Germany) as the lithium salt (99.3% purity, solubility in water $>0.5\,\mathrm{g\,L^{-1}}$) and used as received. Stock solution of sethoxydim-lithium ($50\,\mathrm{mg\,L^{-1}}$) were prepared in the proper water sample and stored at 4°C in dark. These solutions were used to prepare more dilute standard solutions for irradiation experiments.

Humic acid sodium salt (technical grade) was obtained from Aldrich (Steinhem, Germany) and formic acid (p.a.) was purchased from Merck (Damstadt, Germany).

Acetonitrile (HPLC far UV grade) was obtained from Labscan (Stillorgan, Co., Dublin, Ireland). Ultrapure water, used for LC mobile phase and aqueous solutions, was obtained from a Millipore system (Milli-Q-50 $18\,\mathrm{m\Omega}$). Well and river waters were collected from the northwestern of Spain (Valladolid) and were filtered through $0.45\,\mu\mathrm{m}$ nylon filters and stored at -18°C before use. Mineral water was a commercial trademark. The physicochemical characteristics of these waters were provided by Alcalá de Henares University and LIEC Co. (Table 1).

2.2 *Chromatographic method*

Photodegradation kinetics were performed in an HPLC system (series 1100; Agilent Technologies, Palo Alto, CA, USA) coupled to a photodiode array detector (DAD). The analytical column used was a Waters Nova-Pak® C18 column ($4\,\mu\mathrm{m}$ particle size, $3.9\,\mathrm{mm} \times 150\,\mathrm{mm}$) with a ODS precolumn and were maintained at 25°C. The mobile phase was a mixture of water acidified with 0.1% of formic acid (A) and acetonitrile (B). For the determination of kinetic parameters an isocratic method of 80% of B was used. The flow rate was $1\,\mathrm{mL\,min^{-1}}$ and the injection volume was $20\,\mu\mathrm{L}$.

2.3 *Irradiation procedure*

For all degradation kinetics studies, each experiment was conducted in triplicate and carried out until disappearance of the herbicide was achieved. At selected time intervals,

Table 1. Characteristics of water samples.

Water type	pH	Conductivity ($\mu\mathrm{S\,cm^{-1}}$)	TOC ($\mathrm{mg\,L^{-1}}$)	$\mathrm{Cl^-}$ ($\mathrm{mg\,L^{-1}}$)	$\mathrm{Ca^{+2}}$ ($\mathrm{mg\,L^{-1}}$)	$\mathrm{Mg^{+2}}$ ($\mathrm{mg\,L^{-1}}$)	$\mathrm{Na^+}$ ($\mathrm{mg\,L^{-1}}$)
Ultrapure	7.92	0.05	0.005	nd[a]	nd[a]	nd[a]	nd[a]
Mineral	7.94	403	0.486	10.60	83.00	24.00	4.70
Well	8.23	644	0.814	89.53	23.70	30.40	146.70
River	8.28	313	2.865	20.64	62.60	16.73	11.78

[a] nd: not determined.

aliquots of 50 μL were collected and quantitatively analysed directly by HPLC-DAD for the amount of the compound of interest remaining in solution after irradiation based on external calibration.

2.3.1 *Photodegradation experiments in natural waters*

In laboratory and outdoor irradiation experiments, 20 mL of natural water samples (mineral, well and river) as well as ultrapure water were spiked with stock solution of sethoxydim-lithium in order to achieve a final concentration of 5 mg L^{-1} of the herbicide. These solutions were exposed to simulated light and natural sunlight in capped cylindrical quartz cuvettes with magnetic stirring. For cuvettes, quartz is preferred instead of other glass materials to carried out photodegradation kinetics since it permits a greater transmission of radiation used in the experiments with the xenon lamp ($>$290 nm) [6,16].

Simulated irradiation experiments were conducted in a Suntest CPS+ apparatus from Atlas (Linsengericht, Germany) equipped with a xenon arc lamp (1500 W) and a special filter restricting the transmission of wavelength below 290 nm. The average irradiation intensity selected was 750 W m^{-2}. A Suncool chiller was used to maintain a mean internal temperature of 25 ± 1°C.

Irradiation experiments under natural sunlight were carried out on a terrace roof from our institute (40°33′ N, 3°45′ W) during July 2008. Herbicide solutions were exposed to sunlight for approximately 10 h per day. Data of incident solar radiation were obtained from Agencia Estatal de Meteorología (Madrid, Spain) (personal communication) and the mean solar radiation intensities for this period were 75 W m^{-2}, 460 W m^{-2} and 71 W m^{-2} at the beginning, middle and end of the day, respectively, with a mean temperature of 34.5°C.

Dark control experiments in different types of water under both types of irradiation were conducted concurrently with irradiation experiments for comparison without the application of light.

2.3.2 *Photodegradation experiments in the presence of HA*

Concentrations of organic matter range from less than 1 mg L^{-1} in alpine streams to more than 20 mg L^{-1} in some tropical or polluted rivers and rivers draining swamps and wetlands [6]. To study the effect of HA present in natural waters, solutions of sethoxydim-lithium (5 mg L^{-1}) in ultrapure water and different concentrations of HA (1–20 mg L^{-1}) were exposed to simulated solar irradiation using the Suntest apparatus and the same quartz cuvettes previously described (Section 2.3.1). All the solutions were filtered through a 0.2 μm membrane nylon filter prior to injection.

In the presence of HA, dark control experiments were performed at the same concentrations of herbicide and HA in absence of radiation.

2.4 *Data analysis*

The photodegradation of sethoxydim-lithium in aquatic media, in case of first-order kinetics, is given by the following equation:

$$C_t = C_0 e^{-kt}$$

where C_0 is the initial concentration, C_t is the concentration at irradiation time ‘t’ of herbicide and ‘k’ is the first-order rate constant. Half-life ‘$t_{1/2}$’ of sethoxydim-lithium was calculated using the equation ‘$t_{1/2}$’ $= \ln 2/k$.

One-way analyses of variance (ANOVA) were conducted to determine differences between types of water and between concentrations of HA, at the 0.05 significance level. Results were analysed using a statistical procedure (Statgraphics Plus 4.1®).

3. Results and discussion

Spectral data indicated that sethoxydim-lithium in aqueous solution presented a maximum absorbance at 256 nm. Because absorbance spectrum of sethoxydim-lithium and the solar emission spectrum overlap in the region of 300–350 nm, direct photodegradation of herbicide in natural conditions is feasible (Figure 2).

No degradation of sethoxydim-lithium in dark experiments was observed at the end of exposure irradiation time of its solutions in natural water samples, ultrapure water as well as in the presence of HA. For this reason, other transformation processes of sethoxydim-lithium that are not initiated by radiation can be ignored during the experiment. These results agrees with those obtained by Liska *et al.* who studied the stability of sethoxydim solutions in the dark at ambient temperature [17]. However, other authors observed dark reactions at room temperature when distilled water was employed [1].

3.1 *Photodegradation in natural water under simulated and natural sunlight*

A first order kinetic was assumed for sethoxydim-lithium photodegradation in all types of water sample. The rate constants and the half-lives for the experiments carried out in different types of water under natural sunlight and simulated light (Suntest) are listed in Table 2. Correlation coefficients were higher than 0.99 in all cases and consequently rate constant and half-life times can be considered as representative values.

Figure 3(a) shows the photodegradation curves of sethoxydim-lithium in natural waters as well as in ultrapure water under simulated sunlight. Significant differences were

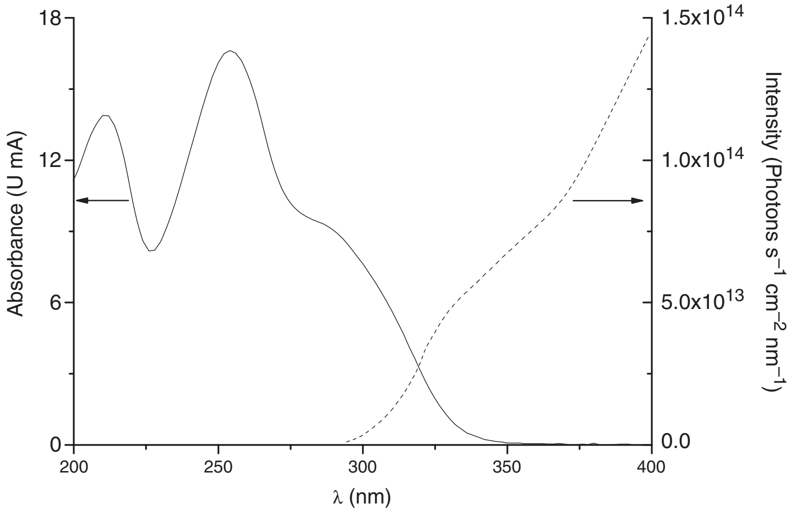

Figure 2. UV-Vis spectra of sethoxydim-lithium (—) and solar light emission (- - -).

Table 2. Kinetic parameters of sethoxydim–lithium photolysis in different types of water under simulated light and natural sunlight. Different letters show significant differences according to least significant differences test (LSDs) at a significance level of 95%.

	Simulated light			Natural sunlight		
Water type	k (10^{-3} min^{-1})	$t_{1/2}$ (min)	R^2	k (10^{-3} min^{-1})	$t_{1/2}$ (min)	R^2
Ultrapure	11.6 ± 0.36 a	59.8 ± 0.2	0.9989	6.71 ± 0.76 a	82.1 ± 0.7	0.9927
Mineral	6.15 ± 0.15 b	112.8 ± 0.2	0.9995	2.39 ± 0.14 b	290.2 ± 0.8	0.9957
Well	5.88 ± 0.22 b	118.0 ± 0.3	0.9987	2.26 ± 0.17 b	314.1 ± 1.2	0.9932
River	5.34 ± 0.15 c	135.5 ± 0.3	0.9993	1.61 ± 0.09 c	436.9 ± 0.8	0.9951

observed in the types of water sample. The photolysis rate decreases in the following order; river < well ≈ mineral < ultrapure water. Differences were higher between ultrapure and natural waters, thus, sethoxydim-lithium photodegradates approximately twice slower in natural waters than in ultrapure water. As shown in Figure 3(a), sethoxydim-lithium was almost totally degradated after 5 h in ultrapure water versus 10 h in river water.

Solar light was used to irradiate the water samples in order to study the behaviour of sethoxydim-lithium under environmental conditions. The same retardant effect was observed when photodegradation in ultrapure water was compared to natural waters under natural sunlight following the order; river < well ≈ mineral < ultrapure water (Figure 3(b)). Photodegradation of sethoxydim-lithium in natural water was approximately 5 times slower than in ultrapure water showing a half-life of 436.9 ± 0.8 min for river water and 82.1 ± 0.7 min for ultrapure water. These significant differences observed in the three water samples, under both types of irradiation, indicated that the degradation of sethoxydim-lithium depends to a large extent on the composition of aqueous matrix.

Both irradiation experiments show the same pattern of slower degradation in natural waters than in ultrapure water. This means that natural water contains some substance/s that induces a retardant effect of the photodegradation of sethoxydim-lithium. Thus, this difference observed (2–5 fold) could be attributed to the presence of increasing concentrations of TOC in the natural waters, where river water has the highest concentration of TOC (2.865 mg L^{-1}) and ultrapure water has the lowest (0.005 mg L^{-1}) (Table 1). By contrast, degradation in mineral and well water showed no significant differences. These results are in accordance with increasing of TOC content, which follows the order; ultrapure < mineral ≈ well < river (Table 1). However, the influence of other substances present in these natural waters cannot be excluded. In these sense, several authors have studied the influence of different ions on the degradation of pesticides [18,19].

The photodegradation of sethoxydim-lithium in all water types under natural sunlight was slower than under simulated light (e.g. $t_{1/2\ (\text{river water})}$ 135.5 ± 0.3 *vs.* 436.9 ± 0.8 min) (Table 2), which is well correlated with the lower intensity of natural sunlight (460 W m^{-2} at the middle of the day *vs.* 750 W m^{-2} of xenon lamp). Increasing the irradiation energy, the degradation rate raised from 1.7 to 3.3. These results show a great influence of the intensity radiation on the degradation of sethoxydim-lithium and they are in accordance with other authors where the degradation of active substance is dependent on the irradiation energy [7,20].

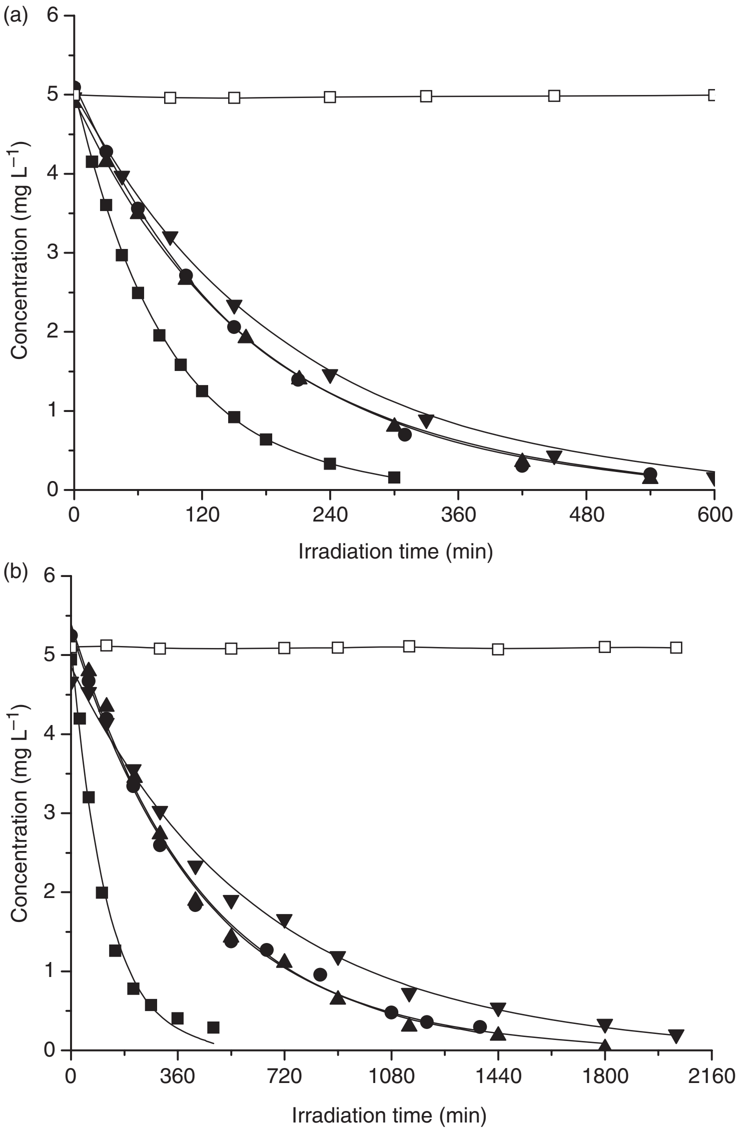

Figure 3. Photodegradation of sethoxydim-lithium in various types of water under simulated light (a) and natural sunlight (b): (■) ultrapure water, (•) mineral water, (▲) well water, (▼) river water, (□) dark experiment.

3.2 *Photodegradation in the presence of HA under simulated light*

As has been mentioned previously, HA are an important constituent of organic matter. Major functional groups of HA include phenolic, carbonylic and carboxylic acids and they absorb radiation in the range 300–600 nm [6]. HA present two different effects on the photodegradation rates of herbicides, a 'sensitiser' or an 'optical filter' effect. In the first case, the excited states of HA can participate in a charge-transfer interaction with herbicides, or generate reactive intermediates, such as hydroxyl radicals, singlet oxygen,

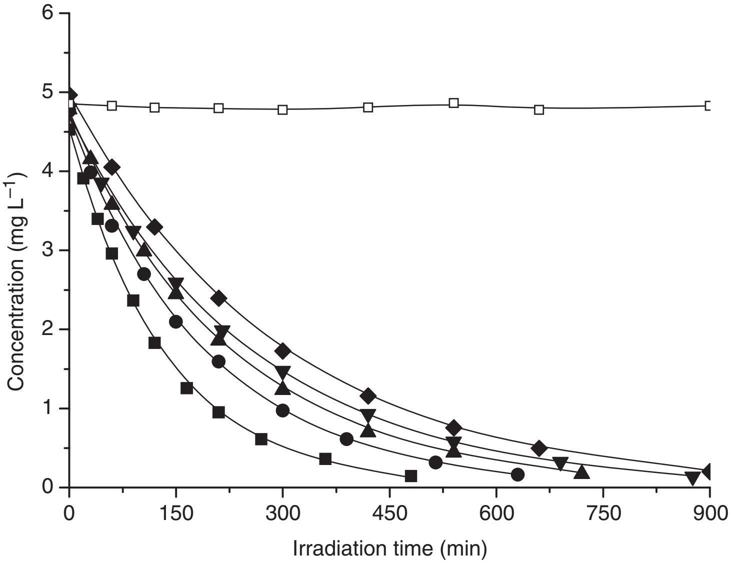

Figure 4. Photodegradation of sethoxydim-lithium in various concentrations of HA in ultrapure water under simulated light: (■) [HA] = 1 mg L^{-1}, (●) [HA] = 5 mg L^{-1}, (▲) [HA] = 10 mg L^{-1}, (▼) [HA] = 15 mg L^{-1}, (◆) [HA] = 20 mg L^{-1}, (□) dark experiment.

Table 3. Kinetics parameters of sethoxydim-lithium photolysis in the presence of various concentrations of humic acids under simulated light. Different letters show significant differences according to least significant differences test (LSDs) at a significance level of 95%.

Concentration (mg L^{-1})	k (10^{-3} min^{-1})	$t_{1/2}$ (min)	R^2
1	7.49 ± 0.20 a	92.7 ± 0.2	0.9992
5	5.27 ± 0.11 b	131.6 ± 0.2	0.9995
10	4.49 ± 0.09 c	154.5 ± 0.2	0.9996
15	3.90 ± 0.11 d	177.7 ± 0.3	0.9993
20	3.54 ± 0.09 e	196.0 ± 0.3	0.9993

solvated electrons or hydrogen peroxide [21,22]. In the last case, HA act as photon trap or scattering the incident radiation [23,24].

All measured reaction rates in the presence of HA followed first-order degradation curves. Figure 4 shows that the presence of HA slowed down the degradation rate compared to ultrapure water. Half-life of sethoxydim-lithium in the presence of 1 mg L^{-1} of HA in ultrapure water was 92.7 ± 0.2 min, while the lack of this substance gave a half-life of 59.8 ± 0.2 min. Furthermore, as the concentration of HA in solution increases the photodegradation rate decreases with rate constants from $(7.49 \pm 0.20)10^{-3}$ to $(3.54 \pm 0.09)10^{-3}$ min^{-1} for a concentration range from 1 to 20 mg L^{-1}, showing significant differences among each HA concentration (Table 3). This observation could be due to 'optical filter' effect, where HA absorbed most of the photons emitted thereby slowing down direct photochemical reaction of sethoxydim-lithium.

These results are in accordance with those obtained in natural waters, where an increased of TOC retarded the photodegradation of the herbicide and consequently show a strong dependence of sethoxydim-lithium photodegradation on the concentration of HA presents in the aqueous media. This effect has been also observed in other herbicides of this family as alloxydim-sodium [25].

4. Conclusions

In all cases studied, photodegradation of sethoxydim-lithium followed the first-order rate equation and no degradation of the herbicide was observed in dark experiments.

The degradation rates in natural waters were lower than in ultrapure water, which indicates that under real environmental conditions photodegradation of sethoxydim-lithium is retarded. Besides, significant differences among types of water suggest that degradation of sethoxydim-lithium has a strong dependence on the composition of water sample. These findings suggest that direct absorption of light by sethoxydim-lithium is important for the loss of this compound, and indirect photolysis reactions probably do not play a significant role in elimination pathways in field waters.

Simulated solar irradiation enhanced the degradation of this cyclohexanedione oxime herbicide in comparison with the use of natural sunlight, confirming the importance of the light intensity in photodegradation studies.

In addition, irradiation of aqueous sethoxydim-lithium solutions containing HA slowed down the rate of the photodegradation, suggesting a strong filter effect.

Future work will be done in order to identify the degradation products in water and its toxicity.

The results obtained in this study facilitate a better understanding of the behaviour of sethoxydim-lithium in water when different light sources and water types are used.

Acknowledgements

This work was supported by the CICYT (Project RTA2008-00027-00-00). Beatriz Sevilla-Morán is very grateful to INIA for her predoctoral fellowship.

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