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Photodegradation behaviour of sethoxydim and its comercial formulation Poast® under environmentally-relevant conditions in aqueous media. Study of photoproducts and their toxicity

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HIGHLIGHTS

- Poast® formulation increased the photodegradation of sethoxydim.
- Natural water substances influenced on kinetic rates and photoproducts distribution.
- Toxicity of photoproducts was higher than parent sethoxydim to bacteria *Vibrio f.*

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ABSTRACT

Photolysis is an important route for the abiotic degradation of many pesticides. However, the knowledge of the photolytic behaviour of these compounds and their commercial formulations under environmentally-relevant conditions are limited. The present study investigated the importance of photochemical processes on the persistence and fate of the herbicide sethoxydim and its commercial formulation Poast® in aqueous media. Moreover, the effect of important natural water substances (nitrate, calcium, and ferric ions) on the photolysis of the herbicide was also studied. The results showed that additives existing in the commercial formulation Poast® accelerated the rate of photolysis of sethoxydim by a factor of 3. On the contrary, the presence of nitrate and calcium ions had no effect on the photodegradation rate while ferric ions resulted in an important decrease in the half-life of sethoxydim possibly due to the formation of a complex. Different transformation products were identified in the course of sethoxydim irradiation and the effect of experimental conditions on their concentrations was investigated. Finally, Microtox® test revealed that aqueous solutions of sethoxydim photoproducts increased the toxicity to the bacteria *Vibrio fischeri*.

1. Introduction

The use of herbicides is a common agricultural practice to reduce crop losses caused by weeds with a relatively good cost-effectiveness ratio. As a consequence of their widespread usage, a large variety of herbicides have been detected throughout the world in different environmental matrices including surface and ground waters (Herrera-López et al., 2014; Jabot et al., 2016; Villaverde et al., 2016). Herbicides are usually applied as commercial formulations which contain different additives such as carriers, wetting agents or spreaders. In general, these additives enable to improve the performance of the active ingredient, facilitate handling and application by users and minimize or avoid adverse effects on non-target organisms and on the environment. In this sense, the reactivity of the herbicide in a commercial formulation might be affected by the presence of formulation ingredients in comparison with the pure active ingredient, leading to a different environmental fate and behaviour (Filipe et al., 2013; Mattiazzi Ušaj et al., 2014; Scrano et al., 1999).

Once released into the environment, herbicides are susceptible to suffer both biotic and abiotic transformation processes that may lead to the formation of different metabolites and degradation

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products (Chen et al., 2016; Lavtižar et al., 2014). In some cases, these resulting transformation products have not been identified and their physicochemical and toxicological properties remain unknown (Fabbri et al., 2015; Jabot et al., 2016; Lavtižar et al., 2015). Thus, it is of utmost importance to study the possible toxicological impact of these degradation products since many authors pointed out that degradation products can display very different toxicity compared with the parent pesticide (Nelieu et al., 2010; Scrano et al., 2002; Sinclair and Boxall, 2003). In this regard, there are no data in the scientific literature about the toxicological properties of the photodegradation products of sethoxydim. However, we recently demonstrated that photoproducts of alloxydim (a cyclohexene oxime herbicide like sethoxydim) are toxic to non-target species such as the bacteria *Vibrio fischeri* (Sandín-España et al., 2013) and the plant *Lycopersicon esculentum* L. (data not shown).

Sethoxydim, commercialized as Poast® (18% w/w) and Poast® Plus (13% w/w), is a post-emergence herbicide belonging to the cyclohexene oxime herbicides family, used for the control of annual and perennial weeds in broadleaf crops. After its application, this herbicide could reach water bodies via runoff, spray drift or/and leaching. As other cyclohexene oxime herbicides, the toxicity of sethoxydim to aquatic organisms is low (e.g. LC_{50} (Daphnia and algae) > 100 mg L^{-1}) (MacBean, 2012). Regarding to the environmental fate of sethoxydim, it is readily degraded under different conditions, being reactions initiated by light an important route for its abiotic degradation in waters (Sandín-España et al., 2015; Sevilla-Morán et al., 2014; Sandín-España et al., 2016). However, studies about the behaviour of sethoxydim are mainly focused on the active ingredients without including commercial formulations (Campbell and Penner, 1985; Matysiak and Nalewaja, 1999).

In a previous work, we characterize in detail the degradation products formed during the direct photolysis of sethoxydim in ultrapure water. The photodegradation process involved the isomerization of oxime ether bond of sethoxydim, the oxidation of sulfur atom and the cleavage of oxime ether bond (Fig. 1) (Sevilla-Morán et al., 2014). It is well known that the composition of natural waters can influence the photolytical behaviour of pesticides, as far as we know there are no other studies about the effect exerted by inorganic or organic substances commonly present in natural waters on the photolysis rates of sethoxydim and the nature and extent of the degradation products formed (Sandín-España et al., 2015; Sevilla-Morán et al., 2010a). Likewise, there is lack of data about the photodegradation of the commercial formulation of sethoxydim in aqueous solutions. In this regard, some studies about other pesticides stated that formulation ingredients can enhance or inhibit the photolysis (Filipe et al., 2013; Scrano et al., 1999), so the formulation ingredients could have unexpected effects on sethoxydim photolysis and its photoproducts.

In this context, the purpose of this work is to study the effect of additives present in the commercial formulation Poast® on the photolysis of its active ingredient (a.i.) sethoxydim in aqueous media. Moreover, the influence of different substances commonly present in natural waters (humic acids and nitrate, calcium and ferric ions) on sethoxydim photolysis rate was also analyzed. The photoproducts formed were identified and the effect of experimental conditions on their concentrations was studied. Microtox® test was used to evaluate the toxicity of irradiated solutions of sethoxydim on the bacteria *Vibrio ficheri*.

2. Material and methods

2.1. Reagents and solutions

Analytical standard of sethoxydim [(RS)-(*EZ*)-2-[1-(ethoxyimino)butyl]-5-[2-(ethylthio)propyl]-3-hydroxycyclohex-2-enone] was supplied by BASF Ltd (Limburgerhof, Germany) as the lithium salt (99.3% purity) and a commercial sethoxydim formulation, Poast® (18% w/w), was obtained from BASF Corporation (Florham Park, USA). Both chemicals were used without further purification.

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

Potassium nitrate (suprapur), calcium nitrate tetrahydrate (p.a.) and formic acid (p.a.) was acquired from Merck (Damstadt, Germany). Iron (III) perchlorate hexahydrate (reagent grade) and humic acids sodium salt (technical grade) were purchased from Alfa Aesar GmbH (Karlsruhe, Germany) and Aldrich (Steinheim, Germany), respectively.

Aqueous stock solutions of sethoxydim and sethoxydim formulation (100 mg L^{-1}) were prepared by dissolving the appropriate amount of the analytical standard or commercial formulation Poast® in ultrapure water. In the case of sethoxydim formulation, it was also necessary to dissolve in a minimum amount of acetonitrile

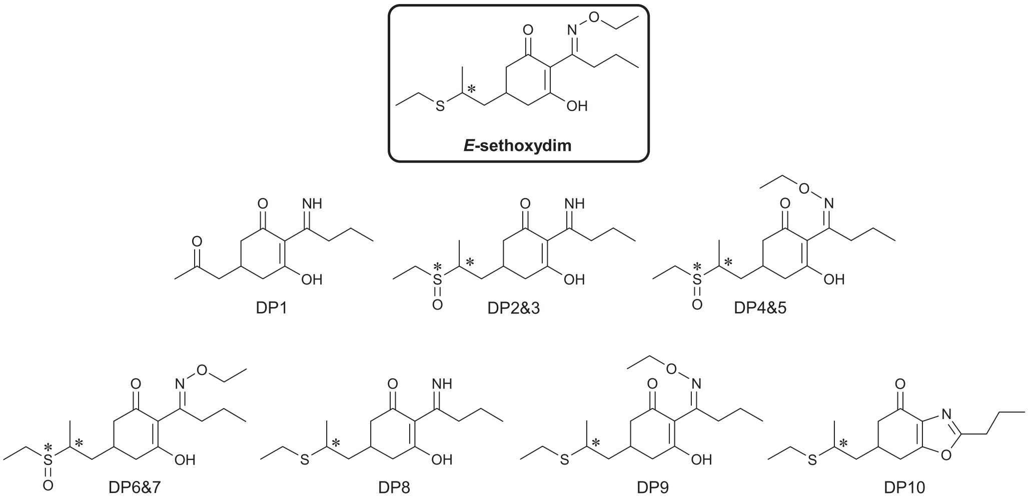

Fig. 1. Identified photodegradation products (DP1-DP10) during the photolysis of the herbicide sethoxydim in ultrapure water (Sevilla-Morán et al., 2014).