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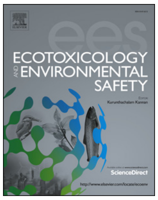

Behavior of quizalofop-p and its commercial products in water by liquid chromatography coupled to high resolution mass spectrometry

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ABSTRACT

A degradation study of quizalofop-p and its commercial products (quizalofop-p-ethyl, quizalofop-p-tefuryl and propaquizafop) in water samples has been performed using ultra high-performance liquid chromatography coupled to Orbitrap mass spectrometry (UHPLC-Orbitrap-MS). CHHQ (dihydroxychloroquinoxalin), CHQ (6-chloroquinoxalin-2-ol) and PPA ((R)-2-(4-hydroxyphenoxy)propionicacid) were the main metabolites of this active substance (quizalofop-p) in water. The degradation of the parent compound has been monitored in distilled water. Several commercial products (Panarex®, Master-D® and Dixon®) were used to evaluate the degradation of the target compounds into their metabolites. The concentration of the main active substances (quizalofop-p-tefuryl, quizalofop-p-ethyl and propaquizafop) decreased during the degradation studies, whereas the concentration of quizalofop-p increased. DT_{50} of the main active substances ranged from 10 days to 70 days for most of the analytes, so it can be concluded that compounds are medium-high persistent in this matrix. Metabolites, such as PPA, CHHQ and CHQ, were detected in water samples after 7 days of the application of the commercial products at concentrations higher than their limits of quantification (> 0.1 µg/L). CHQ was detected at 1400 µg/L after 75 days of the application of quizalofop-p-ethyl commercial product. CHHQ and CHQ were found at the highest concentrations at 7–45 days after the application of quizalofop-p-tefuryl, whereas PPA was detected at higher concentrations (up to 5.37 µg/L) in propaquizafop samples.

1. Introduction

Nowadays, one of the most relevant environmental issues is the occurrence of pesticide active substances and their metabolites in surface waters, wastewater effluents, and sediments (Ferrari et al., 2011). The increasing contamination of freshwater systems with industrial chemical compounds, which are released deliberately into the environment, is one of the key environmental problems society is facing today. More than one-third of the Earth's accessible renewable freshwater is used for agricultural, industrial and domestic purposes, and most of these activities lead to water contamination with numerous synthetic compounds. Chemical pollution of natural waters has already become a major public concern worldwide, since long-term effects on aquatic life and on human health are unknown (Loos et al., 2009).

Quizalofop-p, (*R*)-2-[4-(6-chloroquinoxalin-2-yloxy)phenoxy]propionic acid, is a systemic herbicide absorbed by the leaves with translocation throughout the plant. It is an aryloxyphenoxypropionate compound (Mantzos et al., 2016), used for post-emergence control of annual and perennial grass weeds in broad-leaved crops like beans, onions and potatoes (Roberts et al., 1998). Quizalofop-p has three different commercial products, quizalofop-p-ethyl (ethyl (2*R*)-2-{4-[(6-chloroquinoxalin-2-yl)oxy]phenoxy}-propanoate), quizalofop-p-tefuryl ((*RS*)-tetrahydrofurfuryl (R)-2-[4-(6-chloroquinoxalin-2-yloxy)phenoxy]propionate) and propaquizafop (2-[(Isopropylideneamino)oxy]ethyl(2R)-2-{4-[(6-chloro-2-quinoxalinyl)oxy]phenoxy}propanoate) (Fig. 1), and each compound is used for one specific application. All of these commercial products degrade to quizalofop-p under normal conditions in soils (López-Ruiz et al., 2017a) and a similar behavior could be expected in water. Moreover, this compound, quizalofop-p, can be degraded into different metabolites as CHHQ (dihydroxychloroquinoxalin), CHQ (6-chloroquinoxalin-2-ol) and PPA ((R)-2-(4-hydroxyphenoxy)propionic acid) (Fig. 2) that can be detected in soil, water, fruits, vegetables or air (EFSA European Food and Safety Authority, 2008).

The extraction of quizalofop-p and related compounds (quizalofop-p-ethyl, propaquizafop and quizalofop-p-tefuryl, metabolites not

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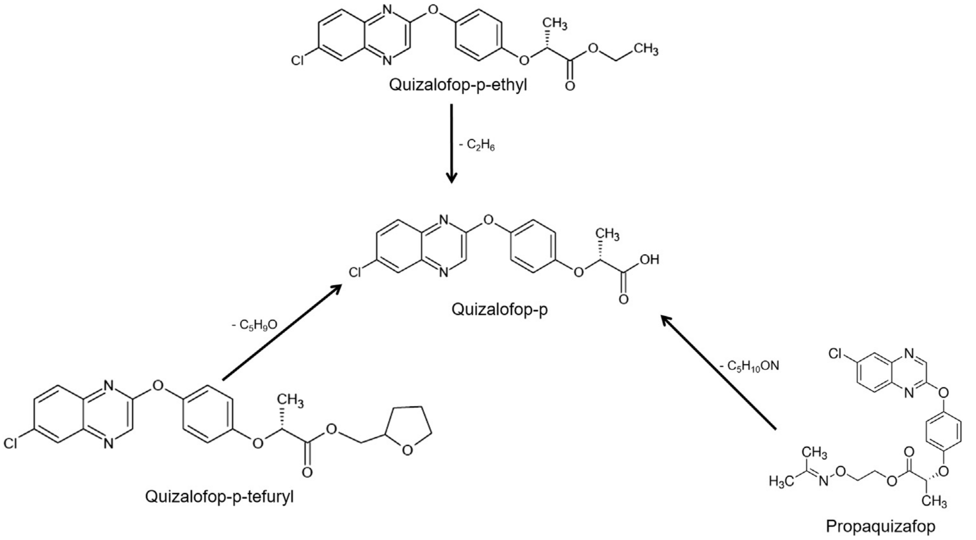

Fig. 1. Transformation scheme of the commercial products in the main active substance, quizalofop-p.

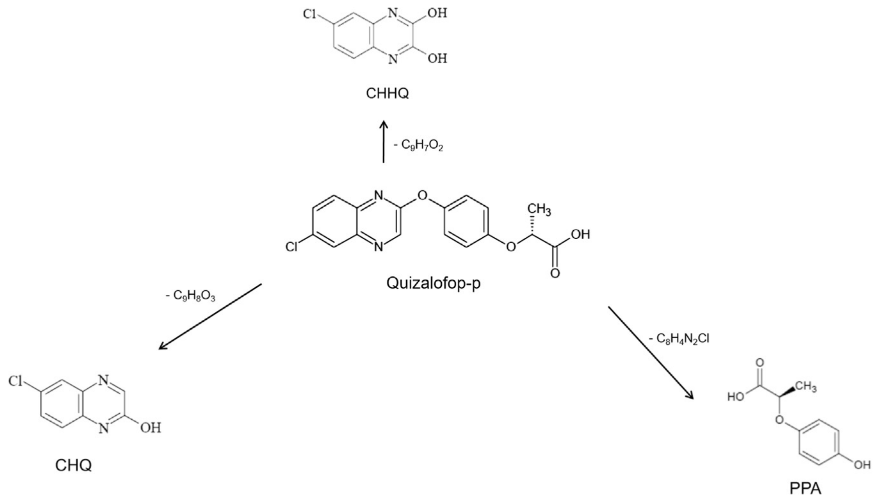

Fig. 2. Transformation scheme of the main active substance in its main metabolites.

included) from water samples has generally been performed by solid phase extraction (SPE), using Oasis HLB cartridges (Mantzos et al., 2016, 2013), strata X cartridges (Lazartigues et al., 2011) and multi-walled carbon nanotubes (MWCNTs) (Luo et al., 2014). For the elution of the compounds, several solvents as ethyl acetate (AcOEt) (Mantzos et al., 2016, 2013) and acetonitrile (ACN) (Lazartigues et al., 2011), or methanol (MEOH) containing 0.1 M chlorhydric acid (Luo et al., 2014) have been used.

Determination has been carried out by liquid chromatography coupled to mass spectrometry (LC-MS) (Lazartigues et al., 2011; Luo et al., 2014), but gas chromatography coupled to mass spectrometry was also applied in some studies (Mantzos et al., 2016, 2013). However, LC coupled to high resolution mass spectrometry (LC-HRMS) has only been used in a previous study (López-Ruiz et al., 2017a). For this reason, the development of a method based on HRMS for water sample analysis is important because the technique has a lot of possibilities. It allows analytical strategies that combine: (a) target analysis (determination of specific priority analytes included in a database, for which standards are available); (b) post-run target or retrospective screening analysis based on an accurate customized mass database of known parent molecules and some diagnostic fragment ions or isotopic pattern, and (c) non-target analysis, which is commonly performed applying several software tools (Coscollà et al., 2014; López-Ruiz et al., 2017b). Despite these benefits, LC-HRMS has several drawbacks as the high cost of the analyzer compared with a triple quadrupole analyzer, as well as well-trained staff and suitable software are needed.

This is the first time that degradation of quizalofop-p and its commercial products in water has been studied, considering that most of the previous studies have been focused on soils (López-Ruiz et al., 2017a) or only the main active substance had been studied in soils (Li et al., 2012; Ma et al., 2016) or rats (Liang et al., 2014). Thus, the main purpose of this study is the evaluation of the behavior of quizalofop-p and related compounds in water, monitoring the degradation of these compounds into metabolites. For that purpose, an analytical method has been developed and validated for the quantitative determination of quizalofop-p and metabolites applying UHPLC coupled to Orbitrap-MS for the identification of the compounds, applying target and non-target approaches for the detection of known and potential unknown metabolites of quizalofop-p.

2. Materials and methods

2.1. Material and reagents

Quizalofop (CAS registry No. 76578–12-6, purity 97,1%), quizalofop-p (CAS registry No. 94051–08-8, purity > 99%), quizalofop-p-