Science of the Total Environment 607–608 (2017) 204–213

Contents lists available at ScienceDirect

Science of the Total Environment

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

Degradation studies of quizalofop-p and related compounds in soils using liquid chromatography coupled to low and high resolution mass analyzers

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HIGHLIGHTS

- LC-Orbitrap was used for degradation studies of quizalofop and related compounds.
- Degradation studies of different quizalofop-related products were evaluated.
- Enantiomeric determination of quizalofop has been investigated using LC-QqQ.
- The dissipation of quizalofop in two types of soils has been studied.

GRAPHICAL ABSTRACT

ARTICLE INFO

Article history:
Received 8 May 2017
Received in revised form 29 June 2017
Accepted 29 June 2017
Available online 27 July 2017

Editor: Jay Gan

Keywords:
Quizalofop-p
Metabolites
Propaquizafop
UHPLC-Orbitrap-MS
Degradation study
Enantiomeric separation

ABSTRACT

A comprehensive degradation study of quizalofop-p, quizalofop-p-ethyl, quizalofop-p-tefuryl and propaquizafop in soil samples have been firstly performed using ultra high performance liquid chromatography coupled to Orbitrap mass spectrometry (UHPLC-Orbitrap-MS). Thus, metabolites or degradation products, such as CHHQ (dihydroxychloroquinoxalin), CHQ (6-chloroquinoxalin-2-ol), PPA ((*R*)-2-(4-hydroxyphenoxy)propionic acid) and 2,3-dihydroxyquinoxaline were also monitored. An extraction procedure based on QuEChERS procedure was used. Acidified water (0.1 M hydrochloric acid) and acidified acetonitrile (1% acetic acid, (v/v)) were used as extraction solvents, and magnesium sulfate and sodium chloride were used as salts. Dispersive solid phase extraction with C_{18} as sorbent, was needed as a clean-up step. 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. Dissipation rates of half-live of quizalofop-p were also evaluated, and it was observed that this compound is easily degraded, obtaining values lower than 1 day. Taking into account that quizalofop-p is the *R* enantiomer of quizalofop, a chiral separation was performed by liquid chromatography coupled to tandem mass spectrometry, concluding that in samples containing quizalofop-p-tefuryl, there was a 15% contribution from the *S* enantiomer and a 85% contribution from the *R* enantiomer. Metabolites such as PPA, CHHQ and CHQ were detected in soil samples after 15 days of application commercial product at concentrations between the limits of detection (LOD) and the limits of quantification (LOQ). CHQ and CHHQ were detected at concentrations higher than the LOQ in samples after 50 and 80 days of application, with their concentration increasing during this time up to 500%.

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http://dx.doi.org/10.1016/j.scitotenv.2017.06.261
0048-9697/

1. Introduction

Quizalofop-p, also known as (*R*)-2-[4-(6-chloroquinoxalin-2-yloxy)phenoxy]propionic acid, is an aryloxyphenoxypropionate compound. It is a systemic herbicide, absorbed by the leaves with translocation throughout the plant (Mantzos et al., 2016), and it is commonly used for post-emergence control of annual and perennial grass weeds in broad-leaved crops like soya beans (Roberts et al., 1998). This compound is the *R* enantiomer of quizalofop (2-[4-(6-chloroquinoxalin-2-yloxy)phenoxy]propionic acid), which is the parent compound, and its use as pesticide has not been approved. Nevertheless its metabolites can be used as phytosanitary products (European Union, 2002). Quizalofop-p is the main active substance of quizalofop, and other compounds such as quizalofop-p-ethyl (ethyl (2*R*)-2-{4-[(6-chloroquinoxalin-2-yl)oxy]phenoxy}-propanoate) and quizalofop-p-tefuryl ((*RS*)-tetrahydrofurfuryl (*R*)-2-[4-(6-chloroquinoxalin-2-yloxy)phenoxy]propionate) can be used as main substances of commercial products. Another metabolite related to quizalofop is propaquizafop (2-[(Isopropylideneamino)oxy]ethyl(2*R*)-2-{4-[(6-chloro-2-quinoxalinyl)oxy]phenoxy}propanoate). This compound is an isopropylideneamino ester of quizalofop that has been scarcely evaluated. In addition, there are a number of common metabolites to all of this compounds, which can be detected in soil, water, crops or air as CHHQ (dihydroxychloroquinoxalin), CHQ (6-chloroquinoxalin-2-ol), PPA ((*R*)-2-(4-hydroxyphenoxy)propionic acid) and 2,3-dihydroxyquinoxaline (EFSA (European Food and Safety Authority), 2008).

Up to now, the maximum residue limit (MRL) in food commodities for quizalofop-p has only included the parent compound, quizalofop, which has not been authorized as herbicide, whereas propaquizafop has an independent MRL ("Pesticide database,", n.d.).

Up to our knowledge, the few papers that have studied this herbicide, quizalofop-p, and its metabolites were mainly focused on the chiral study and the degradation of the parent compound (Li et al., 2012; Liang et al., 2014; Ma et al., 2016), whereas in multiresidue methods focused studies the parent compound is included but not the metabolites (Kaczyński et al., 2016; Karasali et al., 2016; Lazartigues et al., 2011; Mantzos et al., 2016; Marchese et al., 2001). Therefore, more studies focused on the dissipation of quizalofop and related products are needed for determining the metabolites that could appear during the degradation of the parent compounds.

The extraction of quizalofop and quizalofop-p-ethyl in soil has been usually performed by solid-liquid extraction followed by a dehydration step (Ma et al., 2016; Li et al., 2012). When multiresidue methods are used, the extraction method applied is the European version of QuEChERS (Mantzos et al., 2013), using acetone or acetonitrile as extraction solvent.

For the analysis of the target compounds, liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) is the most used analytical technique (Kaczyński et al., 2016; Karasali et al., 2016; Lazartigues et al., 2011; Marchese et al., 2001; Saha et al., 2015), but LC-UV has also been utilized (Guillén-Casla et al., 2011; Ma et al., 2016; Li et al., 2012) especially for the enantioselective degradation of quizalofop-p-ethyl. Up to our knowledge, there are no studies using high-resolution mass spectrometry (HRMS) for the analysis of these compounds. This could be explained by the high cost of these analyzers and the fact that they have not been implemented in routine laboratories yet. Nevertheless HRMS instruments, such as Orbitrap, have several advantages because they operate in the full scan mode (theoretically, no limitations in the number of monitored compounds) and the Independent Data Acquisition (IDA) mode enables the detection of a wide range of compounds at low concentration levels in complex sample matrices with high mass accuracy (Gómez-Pérez et al., 2012). This powerful analytical tool allows for the development of analytical strategies that combine: (a) target analysis (determination of specific priority analytes 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 (Coscollà et al., 2014). For these reasons, in this study, HRMS is used for the detection of target compounds (parent compounds and known metabolites) as a result of the degradation of quizalofop-p and related compounds in soils under field conditions.

The aim of this study is to understand the dissipation behavior of quizalofop and related compounds in soils, monitoring the parent compound and the appearance of metabolites due to the scarce studies focused on this issue. For that purpose, a new analytical method has been developed and validated for the quantitative determination of quizalofop and metabolites applying UHPLC coupled to Orbitrap-MS. Moreover, HPLC-QqQ-MS/MS was used for the enantiomeric separation of quizalofop.

2. Materials and methods

2.1. Equipment, material and reagents

Quizalofop (CAS registry No. 76578-12-6, purity 97,1%), quizalofop-p-ethyl (CAS registry No. 100646-51-3, purity 98,4%), quizalofop-p-tefuryl (CAS registry No. 200509-41-7, purity >99%), propaquizafop (CAS registry No. 111479-05-1, purity >99%), quizalofop-p (CAS registry No. 94051-08-8, purity >99%), 2,3-dihydroxyquinoxaline (CAS registry No. 15804-19-0, purity >99%) and PPA (CAS registry No. 94050-90-5, purity >99%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). CHHQ (CAS Registry No. 6639-79-8, purity ≥99%) and CHQ (CAS Registry No. 2427-71-6, purity >99%) were purchased from Cymit (Barcelona, Spain).

Commercial products, like Dixon® (propaquizafop 10% (v/v)) and Master-D® (quizalofop-p-ethyl 5% (v/v)) were purchased in Planeta Huerto (Alicante, Spain), while Panarex® (quizalofop-p-tefuryl 4% (v/v)) was donated by Massó S.A. (Barcelona, Spain).

Stock standard solutions of 1000 mg/L were prepared by dissolving 10 mg of the pure compound in 10 mL of acetonitrile (ACN), except for 2,3-dihydroxyquinoxaline, CHQ and CHHQ, which were prepared in a mixture of ACN:water (50:50 (v/v)). Intermediate solution of the compounds (10 mg/L) was prepared by taking 100 μL of each stock solution and diluting up to 10 mL with acetonitrile in a volumetric flask. Stock solution was stored at −21 °C and intermediate solutions were stored at 4 °C. Stock solution were stable for a year and the intermediate solution for 2 months.

ACN (LC-MS grade) and formic acid were acquired from Fluka (St. Louis, MO, USA). Water (LC-MS grade) and hydrochloric acid were acquired from J.T. Baker (Deventer, The Netherlands) and acetic acid was obtained from Panreac (Barcelona, Spain). Isopropanol, ethanol and *n*-hexane (LC-MS grade) were obtained from Sigma-Aldrich. Ammonium acetate and magnesium sulfate (Sigma-Aldrich), sodium chloride (J.T. Baker) and C_{18} (Supelco, Bellefonte, PA, USA) were used during the extraction procedure and for the preparation of the mobile phase.

A mixture of acetic acid, caffeine, Met–Arg–Phe–Ala–acetate salt and Ultramark 1621 (ProteoMass LTQ/FT-hybrid ESI positive), and a mixture of acetic acid, sodium dodecyl sulfate, taurocholic acid sodium salt hydrat and Ultramark 1621 (fluorinated phosphazines) (ProteoMass LTQ/FT-Hybrid ESI negative) from Thermo-Fisher (Waltham, MA, USA) were employed for the accurate mass calibration of the Orbitrap analyzer.

For the treatment and preparation of samples, an analytical balance AB204-S from Mettler Toledo (Greifensee, Switzerland), a vortex mixer WX from Velp Scientifica (Usmate, Italy), a Reax 2 rotary agitator from Heidolph (Schwabach, Germany) and a Centronic BL II centrifuge from J.P. Selecta (Barcelona, Spain) were used.

2.2. UHPLC-Orbitrap-MS analysis

For chromatographic analysis Thermo Fisher Scientific Transcend 600 LC (Thermo Scientific Transcend™, Thermo Fisher Scientific, San Jose, CA, USA) was used.