Science of the Total Environment 472 (2014) 767–777

Contents lists available at ScienceDirect

Science of the Total Environment

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

Persistence of oxyfluorfen in soil, runoff water, sediment and plants of a sunflower cultivation

N. Mantzos [a,c], A. Karakitsou [b], D. Hela [b], G. Patakioutas [a], E. Leneti [a], I. Konstantinou [c,*]

[a] Faculty of Agricultural Technology, T.E.I. of Epirus, 47100 Arta, Greece
[b] Department of Business Administration of Food and Agricultural Products, University of Patras, Agrinio 30100, Greece
[c] Department of Environmental and Natural Resources Management, University of Patras, Agrinio 30100, Greece

HIGHLIGHTS

- Field dissipation and transport of oxyfluorfen were studied in sunflower cultivation.
- Soil dissipation is described more adequately by first-order kinetics.
- Residual concentrations of oxyfluorfen in soil depth under 10 cm were very low.
- Oxyfluorfen presented limited mobility through runoff and leaching processes.
- Low levels of residual concentrations were detected in sunflower plants.

ARTICLE INFO

Article history:
Received 9 September 2013
Received in revised form 2 November 2013
Accepted 3 November 2013
Available online 10 December 2013

Keywords:
Oxyfluorfen
Sunflower
Soil dissipation
Runoff water
Sediment

ABSTRACT

A field dissipation and transport study of oxyfluorfen in a sunflower cultivation under Mediterranean conditions have been conducted in silty clay plots (cultivated and uncultivated) with two surface slopes (1% and 5%). The soil dissipation and transport of oxyfluorfen in runoff water and sediment, as well as the uptake by sunflower plants, were investigated over a period of 191 days. Among different kinetic models assayed, soil dissipation rate of oxyfluorfen was better described by first-order kinetics. The average half-life was 45 and 45.5 days in cultivated plots with soil slopes 5% and 1% respectively, and 50.9 and 52.9 days in uncultivated plots with soil slopes 5% and 1%. The herbicide was detected below the 10 cm soil layer 45 days after application (DAA). Limited amounts of oxyfluorfen were moved with runoff water and the cumulative losses from tilled and untilled plots with slope 5% were estimated at 0.007% and 0.005% of the initial applied active ingredient, while for the plots with slope of 1%, the respective values were 0.002% and 0.001%. The maximum concentration of oxyfluorfen in sediment ranged from 1.46 $\mu g\ g^{-1}$ in cultivated plot with soil slope 1% to 2.33 $\mu g\ g^{-1}$ in uncultivated plot with soil slope 5%. The cumulative losses from tilled and untilled plots with slope 5% were estimated at 0.217% and 0.170% while for the plots with slope of 1%, the respective values were 0.055% and 0.025%. Oxyfluorfen was detected in sunflower plants until the day of harvest; maximum concentrations in stems and leaves (0.042 $\mu g\ g^{-1}$) were observed 33 DAA and in roots (0.025 $\mu g\ g^{-1}$) 36 DAA. In conclusion, oxyfluorfen hardly moves into silty clay soil and exhibited low run-off potential so it represents a low risk herbicide for the contamination of ground and adjacent water resources.

1. Introduction

During the last decades the growing concern for greenhouse gas emissions, climate change and fuel demands have resulted in an increased interest in biomass and other energy sources that are potentially CO_2-neutral and therefore less polluting. The European Union aims to increase the share of renewable energy in the transport sector up to 10% by 2020 (EC, 2009), 5% of which is proposed to be covered by food-based biofuels (EC. European Commision, 2012). Sunflower (*Helianthus annuus*) is cultivated worldwide in more than 26 million hectares, 4.3 of which in EU (FAOSTAT. Food and Agriculture Organization of the United Nations, 2011) for edible oil and biofuel production. The interest in sunflower cultivation may increase as the development of new technologies enables biofuel production from sunflower stalks (Ruiz et al., 2013). In Greece the plant is cultivated in an area of about 59,000 ha (FAOSTAT. Food and Agriculture Organization of the United Nations, 2011) and has been proposed as an alternative cultivation in order to replace other conventional crops such as tobacco and cotton (Skoulou et al., 2011).

Oxyfluorfen [2-chloro-α,α,α-trifluoro-*p*-tolyl 3-ethoxy-4-nitrophenyl ether] is a common used pre- or post-emergent herbicide for broadleaved

* Corresponding author. Tel.: +30 2641074186; fax: +30 2641074176.
E-mail addresses: iokonst@upatras.gr, iokonst@cc.uoi.gr (I. Konstantinou).

0048-9697/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.scitotenv.2013.11.016

and grassy weeds in a variety of field crops (Sondhia, 2009). In Greece, oxyfluorfen is registered for vegetables, vines, industrial crops and aromatic plants, citrus as well as pome and stone fruits orchards. Particularly in sunflower where few herbicides are registered, oxyfluorfen has the broader spectrum of activity (GMRDF. Greek Ministry of Rural Development and Food, 2011). The compound belongs to the diphenyl ether chemical group and has low water solubility (0.116 mg/L at 20 °C), and low vapor pressure (0.026 mPa at 25 °C), high K_{oc} (log K_{oc} = 3.46–4.13) and high K_{ow} (logK_{ow} = 4.86).

Based on the above physicochemical properties, oxyfluorfen is very well-sorbed to most soils, and binding is peaking in soils with high percentage of organic matter and clay; thus, is considered as slightly mobile to immobile in soil (EFSA. European Food Safety Authority, 2010; USEPA. United States Environmental Protection Agency, 2002). The most likely route of oxyfluorfen dissipation is soil binding. The main mechanism for degradation in soils is photodegradation. Evaporation on the other hand is more common in soils with higher moisture (Sondhia, 2009; USEPA. United States Environmental Protection Agency, 2002). Oxyfluorfen is considered to have medium to very high soil persistence, with a field half-life of about 37–172 days (EFSA. European Food Safety Authority, 2010).

Oxyfluorfen can contaminate surface water through spray drift and runoff (USEPA. United States Environmental Protection Agency, 2002) and is assessed as very toxic to aquatic organisms (EFSA. European Food Safety Authority, 2010). It is stable to hydrolysis at pH 4 to 9 but degrades rapidly under sunlight in aqueous solution. Because oxyfluorfen is nearly insoluble in water and has a tendency to adsorb on to soil, it will be sorbed to suspended particles or sediments. It is hardly removable within treated plants and it is metabolized very slowly, but since it is not readily taken up by roots, residues in plants are generally very low (EXTOXNET. Extension Toxicology Network, 1996).

Some field studies have investigated the environmental fate of oxyfluorfen. Most of them centered their analysis on soil dissipation and on the persistence of oxyfluorfen residues in crops: Alister et al. (2009) look into bare soil under different environmental conditions; Das et al. (2003) and Sondhia (2009) examine paddy fields and rice crops; Ying and Williams (1999, 2000a, 2000b) investigate vineyard soils, grapes and wine, while Milanova and Grigorov (1996) focus on the soil of a peach orchard. Limited data have been reported about the presence of the compound in run-off water (Goodwin and Beach, 2001; Keese et al., 1994) as well as in run-off and sediment (Riley et al., 1994). However no data exists in literature regarding the dissipation of oxyfluorfen in sunflower cultivation. Furthermore, although many studies exist in literature concerning dissipation of pesticides in soil, plants and water of certain cultivations (Li et al., 2012; Ramesh and Maheswari, 2004; Wang et al., 2007), there is a lack of data regarding pesticides fate on all substrates of a cultivation including runoff sediment. Pesticides can be absorbed onto soil particles during the sediment generation and transport processes. Therefore, sediment losses after rainfall or irrigation events become an important factor on pesticide environmental fate (Chen et al., 2004).

This work presents the results of an integrated field dissipation and transport study in order to investigate the distribution and movement of oxyfluorfen in a sunflower cultivation under Mediterranean conditions. The objective of the study was to investigate the persistence of oxyfluorfen in tilled and untilled (bare) soil, and the transport by runoff water and sediment, taking into account soil inclination, as well as the accumulation of oxyfluorfen in sunflower plants.

2. Materials and methods

2.1. Chemicals

Standards of oxyfluorfen (99.8% purity) were obtained from Riedel-de-Haën (Pestanal) (Seelze, Germany). HPLC-grade acetonitrile (AcN), methanol (MeOH), ethyl acetate (EtOAc) and water, anhydrous magnesium sulfate ($MgSO_4$), sodium chloride (NaCl), sodium sulfate (Na_2SO_4), sodium citrate tribasic dehydrate and sodium citrate dibasic sesquihydrate were purchased from Sigma-Aldrich (Steinheim, Germany). Primary secondary amine (PSA, 40–60 μm in size), graphitized carbon black (GCB, 40–60 μm in size) and octadecyl silica (C_{18}, 40–60 μm in size) sorbents were supplied by Supelco (Bellefonte, PA, USA). Oasis HLB solid phase cartridges (6 mL, 200 mg) were from Waters (Mildford, MA, USA).

Table 1
Main physicochemical characteristics of soil and sediment collected from the experimental field.

Depth (cm)	EC (mS/cm)	pH (water)	Clay (%)	Silt (%)	Sand (%)	OC (%)	$CaCO_3$ (%)
0–10	0.4	7.9	46.1	39.0	14.9	2.8	11.6
10–20	0.4	7.9	45.2	44.0	10.9	2.4	11.8
Sediment	0.5	7.7	42.5	50.0	7.4	4.1	10.7

2.2. Experimental design and sampling

2.2.1. Field experiment design and soil characterization

The experimental field was located in the area of Arta (latitude 39°07N, longitude 20°56E) in North-Western Greece in a site with no history of pesticide use for the last 10 years. The soil of the field was alluvial silty clay (SiC) and its physicochemical characteristics are shown in Table 1. The determination of soil and sediment EC and pH was conducted in soil/water extract 1:2.5 and in soil/water suspension 1:2.5, respectively. The grain size distribution analysis was conducted with Bouyoucos hydrometer method, $CaCO_3$ was determined with the Bernard calcimeter and organic carbon with the Walkley–Black method. Sorption coefficient of oxyfluorfen in plots soil was determined (K_f = 120.9; logK_{oc} = 3.63) following the procedures described elsewhere (Konstantinou and Albanis, 2000) based on Freundlich adsorption isotherm model. The total area of the field was approximately 700 m^2 and it was divided in two groups of six plots each with a plot dimension of 4 × 10 m. One group of plots was used for sunflower cultivation, when the other included the control plots, where the pesticide was applied without cultivation (bare soil plots). Two different slopes (1% and 5%), with three plots in each slope, were formed in each group as follows: topsoil (0–30 cm) from the same field was transferred to the experimental plots and the slopes were carved out with the use of an opto-mechanical theodolite (Fet 500, Geo-Fennel, Baunatal, Germany). One meter distance was maintained between the plots. The three sides of the plots were protected by soil boundaries and metal sheet boarders to a level of ~40 cm height. In the fourth side, the lower one, a runoff and sediment collector was established. The runoff drainage flow was collected with plastic gutters (4 m long), which routed the runoff, via a plastic pipe, in two plastic barrels serially connected, 170 L capacity in total. A Tichelmann irrigation system was established. Two photographs of the experimental plots before and after planting are shown in Fig. S1. Sunflower seeds were sown by hand at 22 cm apart in rows (row to row distance of 0.7 m; 280 seeds per plot). After sowing, 2 kg of a complex fertilizer (220 g N, 131 g P and 249 g K) was added in every plot. Two (2) days after sowing, oxyfluorfen was applied as a water emulsion of the commercial EC formulation LAPAFARM 24 EC (24%, w/v) at the rate of 233 g ha^{-1}, as recommended. For the application of the pesticide, a portable backpack sprayer (RS5B, Zenoah Komatsu, Japan) equipped with a broom type nozzle and operated at a constant pressure was used. Before use the spraying device was calibrated in respect to spray beam and pumping volume per time unit. In addition many trials were conducted in order to ensure that a constant spraying volume was applied per soil surface unit. Finally the pesticide application was executed longwise in every plot in a repetitive pattern, in order to ensure a uniform distribution.