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Herbicide monitoring in soil, runoff waters and sediments in an olive orchard

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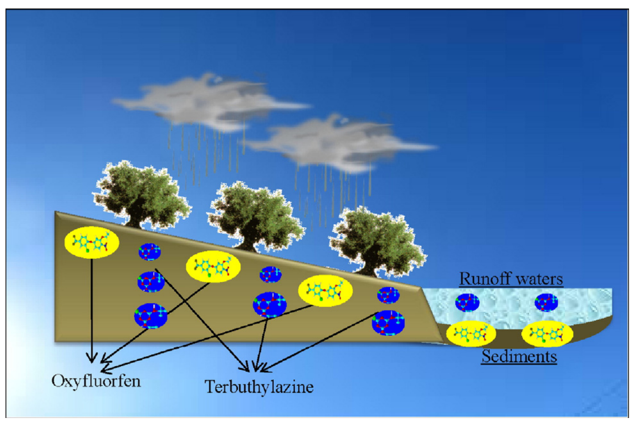
HIGHLIGHTS

- We monitored two herbicides in olive orchard field under real rainfall conditions.
- Terbuthylazine was less persistent in the first 2 cm of soil compared to oxyfluorfen.
- Terbuthylazine concentration in runoff was low.
- Oxyfluorfen recovered from sediments was 37.69% higher than terbuthylazine.
- Oxyfluorfen on sediments favour long term water contamination.

GRAPHICAL ABSTRACT



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ABSTRACT

Occurrences of surface water contamination by herbicides in areas where olive orchards are established reveal a need to understand soil processes affecting herbicide fate at field scale for this popular Mediterranean crop. A monitoring study with two herbicides (terbuthylazine and oxyfluorfen) in the first 2 cm of soil, runoff waters, and sediments, was carried out after under natural rainfall conditions following winter herbicide application. At the end of the 107 day field experiment, no residues of the soil applied terbuthylazine were recovered, whereas 42% of the oxyfluorfen applied remained in the top soil. Very low levels of both herbicides were measured in runoff waters; however, concentrations were slightly higher for terbuthylazine (0.53% of applied) than for oxyfluorfen (0.03% of applied), relating to their respective water solubilities. Congruent with soil residue data, 38.15% of the applied oxyfluorfen was found in runoff-sediment, compared to only 0.46% for terbuthylazine. Accordingly, the herbicide soil distribution coefficients measured within runoff field tanks was much greater for oxyfluorfen ($K_d = 3098$) than for terbuthylazine ($K_d = 1.57$). The herbicide oxyfluorfen is co-transported with sediment in runoff, remaining trapped and/or adsorbed to soil particle aggregates, due in part to its low water solubility. In contrast, terbuthylazine soil dissipation may be associated more so with leaching processes, favored by its high water solubility, low sorption, and slow degradation. By comparing these two herbicides, our results reaffirm the importance of herbicide physico-chemical properties in dictating their behavior in soil and also

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suggest that herbicides with low solubility, as seen in the case oxyfluorfen, remain susceptible to offsite transport associated with sediments.

1. Introduction

The negative environmental impact of pesticides remains a topic of concern, especially when rivers, reservoirs, and ground waters are contaminated, as this can influence human health. Pesticide contamination is particularly problematic in the Mediterranean region near olive orchards and affects multiple olive oil producing countries including Italy, Greece, Tunisia, Turkey, Morocco, and Spain, the number one producer in the world. In Southern Spain almost 30% of the total cropped land is occupied by olive trees (Gómez-Calero and Giráldez, 2009), which has recently been linked to surface and ground water pollution from herbicides (Hermosín et al., 2013). The high contamination risk in this area is due in part to the Mediterranean climate, i.e. long hot and dry periods followed by short cold seasons with heavy rainfall. Typically, the rainy period coincides with olive tree herbicide applications, increasing the risk of non-point transport to water bodies. Other characteristics favoring herbicide transport are: a) low olive tree density, b) limited soil cover by vegetation, and c) slopes ranging from 10 to 30% (Gómez-Calero and Giráldez, 2009), all of which enhance runoff and loss of chemicals adsorbed to soil particles with erosion. This is of particular concern in the Guadalquivir River Valley (Andalucia, Spain), where olive cropping areas are commonly located near large water reservoirs used for human consumption.

Multiple factors influence the transport of herbicides in soil such as application timing and herbicide chemical characteristics. Studies monitoring the presence of herbicides in water have confirmed the importance of these factors (Hermosín et al., 2013; Sánchez-González et al., 2013; Bozzo et al., 2013; Robles-Molina et al., 2014); however, there are very few "in situ" studies on how soil processes affect soil applied herbicides, and none have been performed in olive orchards. Previous water monitoring studies have reported the widespread presence of triazine herbicides, including terbuthylazine, a commonly used herbicide in olive production. For this reason, oxyfluorfen, a low water soluble herbicide, was introduced as an alternative for use in olive orchards in recent years; however, reports of oxyfluorfen contamination suggest further research is required to assess the fate and transport of this herbicide. Hermosín et al. (2013) related the presence of various pesticides in surface and ground waters, including both terbuthylazine and oxyfluorfen, to rain events and runoff/leaching processes. Additionally, herbicide field application rate and water solubility affected their presence in water. Hermosín et al. (2013) found terbuthylazine at very high concentrations in surface as in ground waters, whereas oxyfluorfen was present at low concentrations. Calderon et al. (2015a) recently published an article on seasonal monitoring of terbuthylazine in soil and runoff and observed the highest herbicide losses in the winter season coinciding with high rainfall, leading to surface and ground water contamination. While general pesticide monitoring studies in runoff waters and sediments are common (Mantzos et al., 2014; Pose-Juan et al., 2015), none have been performed at field scale in olive groves and under natural rainfall conditions.

The present study compares the behavior of two herbicides used in olive orchards, terbuthylazine and oxyfluorfen, with different physicochemical properties and similar field application rates. This study was carried out during the winter season when the principal soil herbicide application in olive orchards is made and herbicide concentrations several times higher than safer critical limit for water quality have been found (Hermosín et al., 2013). We aim to provide real field data to assess soil processes and herbicide characteristics that are relevant in herbicide loss by erosion and leaching under natural rainfall conditions. The goal is to ultimately provide information for designing tools to prevent or minimize water pollution associated with olive production, which has been previously shown to be a serious problem (Hermosín et al., 2013).

2. Materials and methods

2.1. Soil and herbicide properties

Field experiment location and site description are shown in Calderon et al. (2015a). Two 60 × 4 m plots under conventional tillage (CT) were used as replicates for the herbicide monitoring experiments (Fig. 1). A plot without herbicide treatment was left between the studied plots in order to avoid cross contamination during herbicide application. Soil tillage management consisted of regular chisel plow passes (2–3 times a year at 10–15 cm depth). These passes were carried out at the end of fall and mid-spring, depending on plant growth and were performed as mechanical control of weeds. In the years prior to our study, paraquat and diquat were applied to these plots for chemical weed control. Physicochemical properties of the soils were determined by the Analysis Service of IRNAS (Sevilla, Spain). Soil pH was measured as a 1:2.5 (*w*/*w*) ratio soil:deionized water suspension. Texture was determined by the Bouyoucos hydrometer method, carbonates by the Bernard calcimeter method, and organic carbon (OC) by the Walkley and Black method. The main physicochemical properties are: sand: 55%; silt: 28%; clay: 17%; texture: sandy loam; pH: 8.40; electrical conductivity (E.C.): 0.10 mS cm^{-1}; $CaCO_3$: 28%; organic matter (OM): 1.34%.

Terbuthylazine (6-chloro-*N*-(1.1-dimethyl)-*N′*-ethyl-1,3,5-triazine-2,4-diamine) is an herbicide used for pre- or post-emergence weed control, and oxyfluorfen (2-chloro-4-trifluoromethylphenyl-3-ethoxy-4-nitrophenyl ether) is a selective herbicide used in the control of annual broad-leaved weeds by pre- or post-emergence application. The main chemical properties of the herbicides according to Pesticide Properties DataBase (PPDB, 2016) are summarized in Table 1. Commercial products were applied to the CT plots as Cuña® (terbuthylazine 50% *w*/*v*) and Goal Supreme® (oxyfluorfen 48% *w*/*v*) at recommended rates of 2 L ha^{-1} (commercial product) for both herbicides. 48 mL of commercial product were mixed with water to prepare 16 L of spray liquid which was applied with a back-pack sprayer at 6 passes per minute until the plot was fully covered. Herbicide soil application was carried out on November 26, 2012 and monitored through March 13, 2013, covering the winter season. The tree lines on either side of the experimental plots (outside of sampling area) were kept bare for olive harvesting throughout by periodical use of herbicides fluroxypyr and flazasulfuron.

2.2. Herbicide monitoring

Herbicide monitoring of CT plots consisted of several soil samplings, in addition to the collection of runoff waters and sediments accumulated in collection tanks throughout the winter season (Fig. 1). Prior to herbicide application, soil samples were collected to quantify possible terbuthylazine soil residues remaining from spring application (Calderon et al., 2015a). Twenty filter paper disks (12.5 cm diameter) were placed randomly on each of the two CT plots before herbicide application and were collected immediately after application. The wetted filter paper disks were placed in glass vials and extracted with methanol to determine the exact herbicide doses applied to each plot. Soil sampling was carried out in the shaded regions of Fig. 1, in order to discard the heterogeneity produced at the beginning and end of herbicide application. Three soil samples, spaced 1 m apart, were taken at the site of every tree 2.5 m from the tree trunk. A total of 36 soil samples were