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Effect of buffer strips and soil texture on runoff losses of flufenacet and isoxaflutole from maize fields

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Abstract

The influence of buffer strips and soil texture on runoff of flufenacet and isoxaflutole was studied for two years in Northern Italy. The efficacy of buffer strips was evaluated on six plots characterized by different soil textures; two plots had Riva soil (18.6% sand, 63.1% silt, 18.3% clay) while the remaining four plots had Tetto Frati (TF) soil (37.1% sand, 57% silt, 5.9% clay). Additionally, the width of the buffer strips, constituted of spontaneous vegetation grown after crop sowing, was also compared for their ability to abate runoff waters. Chemical residues in water following runoff events were investigated, as well as their dissipation in the soil. After the first runoff events, concentrations of herbicides in water samples collected from Riva plots were as much as four times lower in waters from TF plots. On average of two growing season, the field half-life of flufenacet in the upper soil layer (5 cm) ranged between 8.1 and 12.8 days in Riva soil, 8.5 and 9.3 days in TF soil. Isoxaflutole field half-life was less than 1 day. Buffer strip was very affective by the uniformity of the vegetative cover, particularly, at the beginning of the season. In TF plots, concentration differences were generally due to the presence or absence of the buffer strip, regardless of its width.

Keywords: Runoff, buffer strip, flufenacet, isoxaflutole, soil

Introduction

Diffuse water contamination by pesticides used on croplands has been reported in studies around the world. [1-3] The most frequently detected pollutants in surface and ground water are the most used in croplands and urban areas. Among the pesticides, herbicides and their metabolites are the most commonly detected substances in surface waters. In fact, the most recent monitoring campaign of the Piemonte region (Northwest Italy) conducted by the Regional Environmental Agency

Authority (ARPA) found that of the top 20 chemicals detected in surface water, 17 were herbicides or herbicide metabolites. [4] Similar results have been observed nationwide and worldwide. [5-8] In the last decade, protection and prevention of water resource contamination (surface and ground waters) has become a top priority of European policy as evidenced by the Directive on Sustainable Use of Pesticides (2009/128/EC) that mandates European Member States do more to reduce water pollution related to drift, runoff, and leaching of pesticides and other agricultural products.

Surface water contamination is mainly due to runoff from croplands and/or spray drift during pesticide application. The magnitude of the problem is highly related to several factors: rainfall intensity, pesticide characteristics, soil slope, and soil texture. Vegetative buffer strips (VBSs) are important tools to prevent runoff from entering the water stream and/or carrying away valuable sediment, organic materials, nutrients, and chemicals. In most cases, runoff events that occur shortly after herbicide application account for the largest losses. In general, intense rainfall shortly after application generally results in herbicide losses usually less than 0.5% of the amount applied, for most herbicides. [9]

Several field actions can be adopted to prevent diffuse pesticide pollution and/or nutrient losses via runoff and drift; however, a catchment scale approach is necessary to optimize efforts. To reduce pesticide transport via runoff, [10] in particular most mitigation efforts involve soil management and cropping practices, VBS use, retention and dispersion structures, proper pesticide use, and in some agriculture areas, attention to irrigation management. [11] Of course, each of these measures has a different impact on runoff relative to the local soil and climatic conditions.

In the case of VBSs, they are usually set up along streams, ponds, or lakes to prevent water pollution. VBSs have been a useful tool to reduce runoff and erosion, [10, 12, 13] and their efficacy is generally expressed as a percent reduction in pesticide concentration as compared to a non-buffered control. According to the literature, VBS effectiveness is generally above 50%. Typically, runoff volume retention (intended as infiltration) averages 45% (ranging between 0 and 100%) across different studies under both natural and simulated experimental conditions. [14]

69 Of particular interest is the Footprint Project which looked at the efficacy of buffer strips to reduce
70 pesticide runoff. [15] Buffer strips with widths ranging from 2 m to 21 m, the median reduction
71 observed in the pesticides considered ranged between 65% (2 m buffer strip) and 95% (21 m buffer
72 strip). The results presented by the FOCUS group working on a dataset from European studies only,
73 resulted in a reduced mean efficacy of 74% (pesticides in water phase) to 79% (sediment phase) for
74 buffer strip widths ranging from 1 to 20 m. [15] In an accurate review of the mitigation measures
75 available to prevent runoff and erosion of pesticides, Reichenberger et al. [10] found buffer strips
76 vary in effectiveness at the farm scale (from high to very low, according to the local conditions), but
77 they generally show a very high efficacy when adopted at the catchment scale. In some European
78 countries, the adoption of buffer strips between agricultural lands and waterways is already
79 mandatory (e.g. the introduction of 10m buffer strips along waterways from September 1 in
80 Denmark), [16] or included in EU cross-compliance measures (France and Italy).
81 Complementary to these results, many factors have been shown to influence VBS effectiveness:
82 slope, micro-topography, soil type, rainfall intensity, infiltration capacity, strip width, and irrigation
83 volume. Pesticide characteristics (solubility, K*oc*, and persistence), as well as soil texture, organic
84 content, and crop and tillage management also play important roles. [9, 17, 18, 19] Finally, buffer strips
85 filtration activity can vary with the specific PPP used, the sediment amount carried by runoff water
86 into the strip, the water retention time in the VBS, the soil infiltration rate, the uniformity of water
87 flow through the VBS, and maintenance of the strip itself. In general, however, the greater the width
88 of the buffer strip, the higher the runoff retention and infiltration capability, as well as the sediment
89 transport reduction. In the case of larger buffer strips, both infiltration and dilution of runoff flow
90 are promoted while the effect on sediment settling is less important. [20]
91 Despite the many studies that have investigated buffer strip efficacy to limit pesticide runoff, there
92 still remains a need for more research in this field because most of the studies have been carried out
93 on small plots. Furthermore, most studies were conducted under simulated rainfall and in a single
94 soil condition. The aim of this study was to evaluate the efficacy of buffer strips to mitigate the

runoff losses of flufenacet and isoxaflutole under natural rainfall conditions and in two different soil textures. Moreover, in one of the two soils, different buffer strip widths were compared. The two herbicides in the study are commonly used in Italy to control both grasses and broad-leaved weeds in several crops. Specifically, flufenacet is an oxyacetamide herbicide effective in pre- and early post-emergence against many grasses in corn, wheat, rice, tomato, soybean, potato, and sunflower. [21] Isoxaflutole is a broad spectrum proherbicide of the isoxazole family, used in pre-emergence or pre-plant mostly in maize and sugar-cane against grass and broad-leaved weed species. [21] A complete frame of the mode of action of isoxaflutole is reported by Pallet et al. [22] Both herbicides are applied on many important crops and in different periods of the year, so both carry a high potential to contaminate water resources.

Material and Methods

Experimental Site

The study was conducted at the experimental station of the Dipartimento di Scienze Agrarie, Forestali e Alimentari of Università di Torino, Italy. The station is located in the Po Valley in Northwest Italy in the municipality of Carmagnola (44° 53' 08.99'' N, 7° 41' 11.33'' E; WGS84) in an area traditionally cultivated with maize.

Experimental Design

The study was carried out on six adjoining large plots cultivated with maize, each measuring 7 x 150m with a 0.5% slope (Fig. 1). Measurements were taken on the same plots during the 2009 and 2010 growing seasons, which are regarded as temporal replications.

Four plots (TF plots, from "Tetto Frati", which is the name of the hamlet where the station is located) were characterized by silty-loam soil original to the site (37.1% sand, 57% silt, 5.9% clay) with 1.3% organic matter and a pH=8. The remaining two plots (RIVA plots) were also a silty-loam

soil, but it was transferred from Riva municipality twenty years before (18.6% sand, 63.1% silt, 18.3% clay), with of organic matter and a pH=6,2.

At the downhill edges of each plot the runoff water was intercepted by a transversal drainage ditch. Each drainage ditch was connected to an independent automatic sampler. In 2010, the system was operated by flow metering devices, formed by a series of V-notch weirs fitted with magnetostrictive water level transmitters. The water level in the weirs was continuously recorded with a datalogger.

On the four TF plots, a control without a buffer strip (TF TEST) was compared to three plots with 2 m (TF2), 4 m (TF4), and 6 m (TF6)-wide vegetated buffer strips. The buffer strips were sowed with maize as was the rest part of the field; weeds were allowed to grow freely. Buffer strips were mowed as needed. Weeds grown in the buffer strip were representative of the common maize weeds of Northern Italian: *Echinochloa crus-galli* (L.) P. Beauv., *Panicum dichotomiflorum* Michx., *Chenopodium album* L., *Portulaca oleracea* L., *Trifolium repens* L., *Galinsoga quadriradiata* Cav., *Poa pratensis* L. and *Setaria viridis* L. Their density, expressed as percentage of soil coverage, ranged from 20% (a week post crop sowing) to 100% during the rest of the season. The buffer strips were mowed at least twice a year, after which the hay was removed. In the RIVA plots, a control *sans* buffer strip (RIVA TEST) was compared to a plot with a 6-m buffer strip (RIVA6). Characteristics of the buffer strip were similar to the buffers established in TF plots.

The plots were cultivated according to local agronomic practices, and the crop was sown on April 9 and April 20 in 2009 and 2010, respectively.

Herbicides were applied during pre-emergence, within three/four days after sowing, using a rear-mounted boom sprayer. Over the two growing seasons water was supplied as needed to the crop by a furrow irrigation system. In 2009, two irrigations were carried out on June 16 (37 m^3, average of the six plots) and August 3 (35 m^3), respectively; in 2010, fields were irrigated only once on July 21 (38 m^3).

Herbicides Studied

All plots, except the buffer strips, were treated with flufenacet (4'-fluoro-N-isopropyl-2-[5-(trifluoromethyl)-1,3,4-thiadiazol-2-yloxy]acetanilide) and isoxaflutole (5-cyclopropyl-1,2-oxazol-4-yl)(α,α,α-trifluoro-2-mesyl-p-tolyl)methanone) at 240 g a.i. ha^{-1} and 50 g a.s. ha^{-1}, respectively, by spray application of 500 g ha^{-1} of the commercial herbicide Merlin GP ® (Bayer CropScience Italia). To avoid deposition from spray drift, the buffer strip was covered with a plastic film during herbicide application. Table 1 shows the physical and chemical properties of the studied substances.

Soil sampling

Three soil samples were collected from the treated areas at various times: before herbicide application (to assess the residual previous soil contamination, t_{-1}), immediately after spraying (to asses initial herbicide concentrations, t_0), and at increasing intervals from herbicide application (at 0, 1, 7, 15, 40 and 90 days after treatment in 2009; and at 0, 3, 7, 17, 31, 42 and 90 days after treatment in 2010). Samples were taken from the upper 5 cm of the soil surface, with a 50 mm diameter soil core sampler. At each sampling time, and for each plot, 10 soil cores samples were randomly collected in the treated areas. After collection, soil samples were stored at -20°C until analysis.

Water sampling

Samples of runoff water were collected after each runoff event by automatic samplers adjusted to collect a bulk sample made by 500 mL sub-samples gathered at 10-min intervals for the duration of the event. The bulk samples had volumes ranging from 0.5 L to 25 L, which correlated to runoff event duration and intensity. Within about two hours from the end of each event, up to three 1 L subsamples were derived from the bulk sample and stored at -20°C until analysis. Water samples

were collected at 4, 5, 11, 12, 13, 62, 68, 77, 82, 93, 110, and 115 days after treatment (DAT) in 2009 and at 10, 11, 17, 44, 53, 54, 57, 89, and 110 DAT in 2010.

Herbicide Extraction and Analysis in the Soil

Flufenacet

The extraction of flufenacet from the soil was performed on 50 g samples. The samples were transferred into a 250 mL glass bottle (Duran, Germany) and 100 mL of acetone was added (J.T. Baker, USA). Thereafter, the solution was sonicated for 30 min in an ultrasonic bath (Sonorex RK 156BH, Germany). The sonicated solution was then passed through a 150 mm diameter Büchner funnel (Büchner, Germany) connected to a side-arm 250 mL flask (Duran, Germany) using a neoprene adapter with a tube to a vacuum pump (Supelco). Two filter paper disks (Perfecte 2®, Cartiera di Cordenons, Italy) were placed on the Büchner surface, then covered with a layer of celite (Celite 545 J.T. Baker). The soil and the glass bottle used for the extraction were washed with 50 mL of acetone and 50 mL of deionized water and the resulting volume was passed through the Büchner funnel. All the filtrate obtained was transferred into a 250 mL volumetric flask and adjusted to volume with deionized water. A final volume of 100 mL was then transferred to a 500 mL volumetric flask and adjusted to volume with deionized water. Herbicide extraction from this solution was carried out using solid phase extraction (SPE) cartridges. The cartridges (SupelcoSil LC-18, 6 mL, 0.5 g C18 sorbent material) were previously activated with 6 mL of n-hexane (J.T Baker, USA) and 6 mL of methanol (J.T. Baker, USA), and finally washed with 6 mL of deionized water. The entire volume (0.5 L) flowed through the cartridges under vacuum at a rate of 500 mL h^{-1}. The cartridges were let to dry. The adsorbed herbicide was eluted with n-hexane until a final volume of 5 mL was reached. The eluted volume of 5 mL was then filtered through a 0.2 µm nylon filter (Whatman, USA) to eliminate impurities. The final volume was dried under nitrogen flow by

a nitrogen generator (Claind, Italy) and recovered with 1 mL of n-hexane (Sigma Aldrich, Steinheim, Germany). Analysis was performed by GC-MS as described in the next paragraphs.

Isoxaflutole

The extraction of isoxaflutole from the soil was performed on 50 g samples. The samples were transferred into a 500 mL polyethylene bottle and 150 mL of a solution (80/20 v/v) of acetonitrile (Sigma Aldrich, Steinheim, Germany) and formic acid (0.8%) (Sigma Aldrich, Steinheim, Germany) was added. Thereafter, the solution was sonicated for 30 min in an ultrasonic bath (Sonorex RK 156BH, Germany). The sonicated solution was then transferred in a 250 mL vacuum flask through a funnel with its hole covered with a cotton stopper. The filtrates obtained were concentrated and dried in a rotary evaporator, then re-dissolved with 10 mL of a solution of acetonitrile and not-brought water (50/50 v/v). An aliquot of the eluted volume was transferred in the vials for the analysis. Analysis was performed by HPLC as indicated in the next paragraphs.

Herbicide Extraction and Analysis in the Water

Herbicides extraction from the water samples was carried out using solid phase extraction (SPE) cartridges. The cartridges (SupelcoSil LC-18, 6 mL, 0.5 g C18 sorbent material) were previously activated with 6 mL of acetonitrile (Sigma Aldrich, Steinheim, Germany) and then washed with 20 mL of distilled water. The entire volume (1 L) of the water sample flowed through the cartridges under vacuum at a flow of 500 mL h^{-1}. The cartridges were let to dry. The adsorbed herbicides were eluted with acetonitrile until a final volume of 5 mL was reached. The eluted volume of 5 mL was then filtered through a 0.20 µm nylon filter (Whatman, USA) to eliminate impurities. The final volume was dried under nitrogen flow by a nitrogen generator (Claind, Italy) and recovered with 1 mL of n-hexane (Sigma Aldrich, Steinheim, Germany). Analysis was performed by GC-MS.

High-performance liquid chromatography analysis

Analysis of isoxaflutole in soil was done by high-performance liquid chromatography (HPLC) using a Spectraphisics P2000 equipped with a C18 Varian Pursuit column (150 mm × 4.6 mm i.d., 5µm particle size), an ultra-violet (UV) detector at 270 nm for isoxaflutole, and a mobile phase composed by brought water with pH=2, and acetonitrile (50/50 v/v) with the flow rate set to 1 mL min^{-1}. Analytical-grade isoxaflutole supplied by Sigma Aldrich, Germany was used as the analytical standard.

Gas Chromatography Analysis

An Agilent 6890N GC and Agilent 5975 MS single-quadrupole, equipped with an MS detector, an autosampler (Agilent) and split-splitless injector, connected to an Agilent Chemstation was used. The Supelco Equity5 TM column (30 m x 0.25 mm i.d.) contained 5% diphenyl and 95% dimethyl siloxane. The MS source temperature was 270°C and the gas carrier was helium. Analytical-grade flufenacet and isoxaflutole, supplied by Sigma Aldrich, Germany, was used as the analytical standards. Retention times for flufenacet in the soil samples were 17.6 min and 16.3 min in 2009 and 2010, respectively. Retention times for flufenacet in the water were 22 min and 25.6 min in 2009 and 2010, respectively. Retention times for isoxaflutole in the water were 26.1 min and 17.7 min in 2009 and 2010, respectively. Retention times for isoxaflutole in the soil samples were 9.2 min and 9.8 min in 2009 and 2010, respectively.

Recovery and detection limits

The recovery tests for the extraction of the herbicides in the water were conducted both with tap water and surface water not contaminated. Three samples (500 mL) of not treated water were

contaminated with 1 mL of a stock solution 100 mg/L of flufenacet and isoxaflutole. The initial concentration was 0.2 mg/L. Extraction was carried out using SPE cartridges previously activated with 6mL of acetonitrile and then washed with 20 mL of distilled water. The same procedure was repeated contaminating other water samples with 1 mL of a stock solution 10 mg/L and 1 mL of a stock solution 1 mg/L of flufenacet and isoxaflutole.

The recovery tests for the extraction of the herbicides in the soil were conducted with two accession of the soil used in the experiment not contaminated. For each soil, three samples of soil (50 g) were contaminated with 100 µL of the stock solution 100 mg/L, with an initial concentration of 0.2 mg/L. The same procedure was carried out for flufenacet and isoxaflutole, but using the methods of extraction for each herbicide indicated in the previous paragraphs.

The mean recoveries of flufenacet and isoxaflutole in water were 98% and 87%, respectively; those in soil were 70% and 82 % for flufenacet and isoxaflutole, respectively. The limit of quantifications of the instrument (LOQ_i) achieved in the water samples were 0.08 µg L^{-1} for flufenacet and 0.1 µg L^{-1} isoxaflutole while the limit of quantification of the method (LOQ_m) were 5 µg kg^{-1} for both for flufenacet and isoxaflutole.

Statistical Analysis

A statistical analysis was employed to determine the significance of differences among the concentrations observed in the waters collected from the check and buffered fields at the different sampling times. The values presented are the means of the three data values. SPSS, version 17.00, (SPSS, IBM Corporation, 2008), was used for the statistical analysis. A Ryan-Eynot-Gabriel-Welsch-F test (*P <0.05) was employed to determine the statistical significance of differences among the concentrations observed in the waters collected from the check field and the buffered field at the different sampling time. Soil data were subjected to ANOVA to test effect of the year,

soil, days elapsed from the treatment (DAT) and the interaction between them. Flufenacet dissipation in the soil was fitted to a 2-parameter exponential decay model:

$Ct = C_0 e(-^{kt})$ [1]

where Ct is the concentration at time t, C_0 is the initial concentration, t is time, and k is the rate constant. Soil half-lives ($T_{1/2}$) values for flufenacet were calculated from the following equation:

$T_{1/2} = \ln (2/k)$ [2]

where *k* is the rate constant.

Model fitting was performed using the function *drm* of the add-on package *drc* of the R software. Data from 2009 and 2010 were first analyzed separately and then pooled to fit into a single model. The *anova* function of the R software was used to test if the pooled dataset was significantly better explained by single curves data separately (fitting both years and both soils) than by a single model fitting all data.

Rainfall Distribution and Runoff Events

Total rainfall measured during the crop growing seasons were 577 mm and 545 mm in 2009 and 2010, respectively. Weather data were collected daily from the meteorological station located near the experimental fields. In both years, the periods close to herbicide application were characterized by rainfall events that directly affected runoff losses and herbicide dissipation. The spring of 2009 was particularly rainy; in fact, a 282 mm rainfall was recorded in April. In the 2009 season, 13 runoff events were recorded while in 2010, 9 events were recorded.

Result and discussion

Herbicide Dissipation in the Soil

Flufenacet and isoxaflutole dissipation was studied in the soil of the treated areas. Persistence of both herbicides in the soil varied slightly between years, according to the different climatic conditions.

Flufenacet showed a rapid decay in both seasons (Figs. 2a and 2b). In 2009 the field dissipation half-life (DT_{50}) was 8.1 days in RIVA soil and 9.3 days in TF. During 2010 the persistence of flufenacet in the upper soil layers did not change significantly relative to the previous year, resulting in a soil half-life of 12.8 days in RIVA and 8.5 days on TF soil. In soil samples collected before the 2010 herbicide application, residues of flufenacet were below the detection limit. Also, the different rainfall pattern recorded in the two years during the first days after herbicide application did not significantly influence the flufenacet dissipation trend (Figs. 2a and 2b).

The statistical analysis conducted did not show a significant effect of the year and of the type of soil on the dissipation dynamics of flufenacet. The only significant factor was the time elapsed from the treatment (DAT). The data of the two years pooled in a single model revealed a DT_{50} of 10.2 days with a confidence interval (α=0.05) comprised between 6.4 to 14 days. As reported in the literature, flufenacet dissipation follows a first order kinetics. [23] In both years, three months after herbicide application on TF soil, flufenacet was below the limit of quantification. The only exception was in 2009 in RIVA soil when 90 days after treatment the concentration of the herbicide was still in the detectable range, but no higher than 29 $\mu g\ kg^{-1}$.

The rapid flufenacet field dissipation can be attributed partly to the sampling procedure adopted, in which only the superficial soil layer was sampled. This result agrees with Rouchaud et al., [24] who found no flufenacet residues after the wheat harvest in summer and after the corn harvest during the fall in the 0-20 cm soil layer with a similar LOQ. In top soil, the dissipation dynamics are generally faster compared to that of deeper soil layers. Furthermore, the microbial degradation which is the principal means of dissipation of flufenacet in soil must be considered. Since microbial activity is enhanced during the spring, a shorter half-life could be expected at that time. Soil half-lives for aerobic microbial degradation have ranged from 10 to 34 days in varying soil types at

approximately 1.0 ppm at 20-21°C. [25] In a study conducted by Rouchaud et al., [26] the half-life of flufenacet in different soil ranged between 66±3.9 days and 44±2.2 days. However, their study was conducted on soils characterized by a history of organic fertilization and thus with a highest organic matter content. [26] Persistence was also affected by the time of herbicide application, with high persistence after fall applications. According to Gupta and Gajbhiye [23] flufenacet half-life ranged from 10.1 to 30.1 days on three different Indian soils. Dissipation studies conducted in Italy and France have reported soil half-lives of 13-16 days when applied during early spring and of 15-53 days during spring application. Autumn applications are generally characterized by longer persistence periods. [27, 28] Soil moisture content and pH affected flufenacet dissipation less. Conversely, the type of soil, its adsorption capacity, and the rate of application can have a significant effect on dissipation behavior. Gupta and Gajbhiye [23] observed that dissipation of flufenacet is slower in soil with high adsorption capacity and less desorption.

The isoxaflutole soil half-life observed over the two years in the treated areas of the two soils studied was short, less than 1 day, and soil dissipation resulted faster in TF soils compared to Riva soil. In general isoxaflutole dissipation follows a first order kinetic. [29] The field dissipation half-lives in this study are similar to those reported by other studies conducted worldwide: from 0.5 to 4 days, [27] from 1.4 to 3 days, [30] and from 0.5 to 2.4 days. [28] Other documents indicate the field half-life was less than 2 days [29] while Papiernik et al., [31] reported a soil half-life for the sum of isoxaflutole+diketonitrile as within 8 to 14 days in the top 1 m of three different soils. Our result agreed with other studies [32] and is explained by the abiotically-governed transformation of isoxaflutole into the active form diketonitrile, which is the key step in the dissipation pathway of the herbicide. [33]

In this study, the observed rapid dissipation can be partially attributed to the sampling procedure; only the superficial (5 cm) soil layer was sampled.

Furthermore, during 2009, a cumulative amount of 46.2 mm of rain was recorded during the week preceding herbicide application (Fig. 2a). The higher water content of the soil observed just before

352 the treatment had likely facilitated the conversion of isoxaflutole into proherbicide diketonitrile. In
353 2010, the soil surface was very dry at spraying due the absence of rainfall in the previous weeks.
354 According to Taylor et al., [34] under dry conditions, isoxaflutole is very stable and unavailable, and
355 it persists more at the surface. [35] However, a succeeding rainfall might promote the rapid
356 transformation of isoxaflutole into its active form. Indeed, this condition was verified during 2010,
357 when the soil was dry before treatment, but just 6 hours after treatment, a light rain occurred and
358 caused transformation of the parent compound. Pallet et al. [35] observed that the shorter half-life
359 recorded for isoxaflutole under increased moisture content might relate to the need of isoxaflutole to
360 be in solution in order to be transformed into diketonitrile.
361 Conversion of isoxaflutole to diketonitrile is rapid and become faster with higher temperatures,
362 higher soil moisture levels, and at basic pH. [33] Since the higher clay content of RIVA soil did not
363 affect the sorption of the molecule, [36] the diverse and low persistence might instead be associated
364 with the differing pH of the two soils. Mitra et al. [36] and Rouchaud et al. [37] observed faster
365 dissipation of isoxaflutole at basic pHs. In the present study, TF soil has a sub-alkaline reaction (pH
366 8.2) while the pH of RIVA soil is sub-acid (6.2) (Table 1). Hence, the slightly faster dissipation
367 observed in TF soil over the two years might result from the combined effects of soil reaction and
368 different soil moisture at the time of herbicide application.
369 As previously indicated, the two soils studied had similar low organic matter content, but they
370 differed in pH and clay content. These two parameters may affect the soil dissipation of many
371 pesticides, including isoxaflutole. A study conducted by Mitra et al., [36] pointed out that sorption of
372 isoxaflutole was not influenced by clay content. [38] On the contrary, it was highly related to organic
373 matter content [39] and to the soil pH. [39, 40] Specifically, sorption of isoxaflutole increases with
374 increasing organic matter content, and sorption increases at decreasing pH. [36] Beltrán et al. [41] has
375 discussed the influence of soil pH on the dissipation reaction rate of isoxaflutole, and they found
376 that the isomerization of IFT into DKN is rapid, depends strongly on pH, and is governed by a
377 chemical process.

Dissolved Flufenacet in Runoff Water

The runoff of flufenacet was studied during the growing seasons in relation to rainfall and irrigation occurrences. In Table 2 are listed all the runoff events that occurred and the subsequent concentrations of flufenacet detected. The different rainfall distributions affected the transport of flufenacet and isoxaflutole, and thus runoff losses. In particular, several rainfall events occurred early after herbicide application causing relevant runoff outflows.

In both years, the highest flufenacet concentrations in runoff waters were measured during the runoff events that occurred in the first two weeks after application. This is consistent with several studies [18,42] that showed that major losses occur during runoff events close to herbicide application. [2, 9, 43-47]

Flufenacet was found in all samples collected with significant differences in the plots containing buffer strips and related to soil texture differences. The first runoff event occurred only four days after herbicide application. As shown in Table 2, during 2009 the presence of the buffer strip did not affect the amount of flufenacet transported much. The highest concentrations detected in TF plots ranged between 9.2 $\mu g\ L^{-1}$ (TF2) and 14.9 $\mu g\ L^{-1}$ (TF4) with no significant difference among plots. These concentrations were four times lower than those found in the RIVA runoff waters (Table 2). In spite of this, the presence of the buffer did not significantly reduce the amount of flufenacet transported. The lack of a clear effect of the buffer to reduce the transported dissolved flufenacet was likely due to the low weed coverage (around 20%) at that time.

Thereafter, a continuous rainfall occurred between 11^{th} and 13^{th} day after treatment, which resulted in a runoff event that endured during the entire rain period. At the beginning of this event, the flufenacet concentrations were lower than in the first event, but by the end of it (at 13 DAT), a concentration increase was observed, particularly in runoff waters that flowed from RIVA plots (Table 2). One explanation for this observation might be that after three days of rain, all soil macropores were saturated by water, and that runoff overcame the infiltration rate. Then, in the second week of June (at 62 DAT), fields were watered by furrow irrigation. The flufenacet

404 concentrations in runoff waters from the RIVA fields ranged between 15 μg L^{-1} (RIVA TEST) and
405 5.9 μg L^{-1} (RIVA6) while runoff water flows from TF plots was no higher than 0.5 μg L^{-1} (Table 2).
406 Beginning with 68 DAT, the presence of a buffer strip generally resulted in reduced losses of
407 flufenacet via runoff from TF plots, except for runoff events at 77 DAT (heavy thunderstorm) and
408 110 DAT (second irrigation). On the other hand, flufenacet was always detected in runoff waters
409 that flowed from RIVA TEST and RIVA6; those detected in RIVA6 were always lower than in the
410 test plot. Four months after herbicide application, residues of flufenacet were found only in runoff
411 waters from TF TEST (0.2 μg L^{-1}), RIVA TEST (0.3 μg L^{-1}), and RIVA6 (0.2 μg L^{-1}).
412 In 2010, the first runoff event occurred at 11 DAT. As shown in Table 2, the highest concentrations
413 were observed in runoff waters from TF TEST and RIVA TEST. These concentrations were
414 remarkably lower than those observed at the first runoff event in the previous year. This difference
415 is probably due to higher weed coverage of the buffer (about 60%) compared to that of 2009
416 (indicate the percentage here for comparison). In addition, a rainfall of 10.2 mm occurred just 12
417 hours after herbicide application, caused no field runoff, but favored the chemical movement
418 through the soil profile. Two weeks after spraying, flufenacet residues in runoff waters from RIVA
419 plots ranged between 2.7 μg L^{-1} (RIVA TEST) and 1.6 μg L^{-1} (RIVA6) as opposed to values for
420 runoff waters from the TF plots between 0.6 μg L^{-1} and 0.9 μg L^{-1} (Table 2).
421 Flufenacet concentrations in runoff water decreased gradually over the next runoff events and at 53
422 DAT, no flufenacet residues were found in the waters that flowed from TF plots. The herbicide was
423 still present in runoff waters from RIVA plots up to a month after spraying, with no significant
424 differences among plots. Next, a storm of 69.6 mm at 110 DAT caused the complete flooding of the
425 structures where the sampling devices were located, and made it impossible to collect any runoff
426 samples. No residue of flufenacet was found in the samples collected following a rainfall that
427 occurred few days later (113 DAT).
428 One way to predict the fate of pesticides in the environment is to analyze key parameters, such as
429 K_{oc}, solubility, persistence, and pH stability. As pesticides bind differently to clay particles and to

organic matter, studying their K_{oc} (K of organic carbon) is an effective measure of adsorption to organic matter or to soil carbon that may help to explain the behavior of a specific pesticide in a defined environmental compartment. In general, pesticides with higher K_{oc} values are more bound to the soil coefficient contrary to those with lower K_{oc}. The latter tend to be transported more with water than on sediment. [13] As indicated in the review of flufenacet performed by the European Commission, the mean K_{oc} for flufenacet is 202 for OC content > 0.23%. [27] Consistent with this information, we found flufenacet to move off fields more easily with water than when attached to sediment.

In this study, concentration differences measured in the water of the two soils clearly highlighted the effect of soil texture on the amount of flufenacet transported. Soil texture affects infiltration rates and runoff is generally more pronounced in fine-textured soil. [45] RIVA soil has more silt and more clay compared to TF soil (Section). Silty soils are very vulnerable to surface runoff due to the changeable behavior of their particles during seasonal changes, [10] and their tendency to develop a superficial crust. Crusting and compaction influence the infiltration rate, favor runoff, and increase the initial concentrations of pesticides. [45] The higher concentrations recorded throughout the season in runoff waters from RIVA plots might be related to these considerations.

Dissolved Isoxaflutole in Runoff Water

The presence of isoxaflutole in runoff waters was assessed in the same temporal interval as that of flufenacet. As for flufenacet, the highest isoxaflutole concentrations were detected during the first runoff event in waters from the plots without buffer. In 2009, at the first event (4 DAT), the highest isoxaflutole concentrations were detected in RIVA plots, where they ranged between 5 $\mu g\ L^{-1}$ (RIVA TEST) and 2.90 $\mu g\ L^{-1}$ (RIVA6). In TF plot runoff, they did not exceed 0.16 $\mu g\ L^{-1}$ (TF TEST). In the runoff events that occurred later in the season, isoxaflutole was present in runoff waters from TF4 only at 6 DAT (0.13 $\mu g\ L^{-1}$) and TF6 waters were always below the LOQ. In water

456 samples collected from TF2 and TF TEST, isoxaflutole was generally below the LOQ with the
457 exception of some samples (Table 3). In contrast, during all of 2010, isoxaflutole was found only in
458 runoff waters from RIVA TEST (0.10 μg L^{-1}) collected at the first runoff event (10 DAT).
459 As isoxaflutole is rapidly converted into diketonitrile, its presence in the dissolved phase of runoff
460 waters appears to be unlikely. The frequency of the detection of isoxaflutole, atrazine, and their
461 respective metabolites in 10 Iowa rivers that drain important croplands, Meyer et al. [48] found
462 isoxaflutole in only 4 samples out of 75 collected, and only in the period post planting.
463 Furthermore, the study found diketonitrile and benzoic acid (both isoxaflutole metabolites) in 56
464 and 43 samples out of 75 collected, respectively which confirmed rapid transformation of the parent
465 compound. [48] Our results showed that if a runoff event occurs in the first weeks after herbicide
466 application, significant amounts of this herbicide can be transported via runoff waters, despite its
467 low water solubility (6.2 mg L^{-1}). [49] The differences in the concentrations of isoxaflutole in runoff
468 waters, observed over the two years, are likely to be related to the different rainfall pattern occurred.
469 As discussed in the Section 3.1, under dry conditions, isoxaflutole is very stable and unavailable,
470 and it persists more at the surface. [34, 35] Thus, in 2009 the driest condition of the soil had probably
471 delayed the conversion of isoxaflutole into diketonitrile. In 2010, the soil was dry too at the time of
472 spraying, but a rainfall occurred few hours later without causing runoff, promoted the conversion of
473 the herbicide in the metabolite. However, a succeeding rainfall might promote the rapid
474 transformation of isoxaflutole into its active form. In synthesis, isoxaflutole, due to its low
475 application rate and likely for its rapid conversion to metabolite, was always found at lower
476 concentrations and mostly in runoff waters collected at early runoff events after application. Our
477 results evidenced also that soil texture did greatly affect the amount of isoxaflutole transported by
478 water.
479
480 ***Efficiency of the Vegetative Buffer Strip***
481

In general the runoff mitigation effect of a buffer strip decreases as the ratio between the field area and the buffer area increases. [50] Larger buffer strips mitigate sediment transport; for more soluble pesticides, the effect might be limited. Also, buffer strips are most effective against nutrients and pesticides bound to sediments and less effectiveness on predominantly-dissolved chemicals. [51, 52] Among the various conditions of our study, we found that with a 6 m buffer strip, the most favorable ratio (25:1) we could attain was with isoxaflutole on RIVA soil.

The Table 4 reports the runoff events and the corresponding measured runoff volumes during 2010. The higher runoff volumes were generally observed in plots lacking buffer strips, which demonstrated the positive effect of the buffer. This was particularly true for RIVA plots; it was less evident in TF plots. In these plots, runoff volumes measured in buffered plots were, at times, higher than in the control plot. If operating on a field scale, then some modification must be made for the soil unevenness that characterizes large plots. Weed spots might also have affected the runoff flow behavior through the field. Overall, the maximum runoff flows were always measured on RIVA plots, which indicated the high bent of that soil type to surface runoff.

Buffer strip efficacy was evaluated in absolute terms by considering both the observed concentrations in water samples, and by calculating the total losses in relation to the runoff volumes recorded during 2010. Total losses were calculated for flufenacet only, as isoxaflutole was always below the quantification limit. Flufenacet is transported both in the water phase and in the solid phase and adsorbed to particles eroded from the soil surface. For our purposes, only the amounts of herbicides dissolved in runoff waters were considered for the calculation. Total losses were calculated for each event by multiplying the volume of runoff by the mean concentration of dissolved herbicide (Runoff Volume [m^3] x Concentration [$\mu g\ L^{-1}$]). It was expressed as a percentage of the total amount o f herbicide applied. In the case of concentrations below LOQ, and even considering actual concentrations as equal to LOQ, total losses showed only a negligible difference in the adopted calculation.

As expected, our results indicated that RIVA plots accounted for the highest losses in 2010; they were 0.40% in RIVA TEST and 0.23% in RIVA 6m. Alternatively, TF plot total losses were largely lower, ranging between 0.07% (TF TEST) and 0.01% (TF2 and TF6). According to Whauchope, [9] runoff losses of these magnitudes can be considered "*intermediate*." Overall, most of the losses were due to the first runoff events both in the buffered and non-buffered plots. The total losses were not calculated during 2009; however, given the high concentrations observed in the first runoff events, it is reasonable to assume that flufenacet and isoxaflutole had larger losses during this season.

As indicated in the Material and Methods section, the buffer strip was not specifically sowed, but it was represented by spontaneous vegetation grown after crop sowing. In both seasons, the first runoff event occurred early after herbicide spraying. Being that the buffer strip vegetation was comprised only of spontaneous weeds, its coverage was insufficient to fully counter runoff flows, particularly during 2009. A buffer strip acts by reducing flow velocity and increasing infiltration; thereby, it reduces the total pesticides transported. [53] However, in 2009, during the first runoff events, the presence of the buffer strip in all plots did not significantly affect the amount of pesticides transported, especially for flufenacet. Presence of a buffer strip showed a certain effect late in the season (Table 2), when the vegetation cover of the buffer became more dense and uniform. This behavior was observed especially in RIVA plots. During 2010, the presence of the buffer strip significantly affected the amount of herbicide transport, both on RIVA and TF plots.

The effect of the different buffer strip widths in reducing runoff in TF plots can be extrapolated from Table 3. During both years, the width of the buffer seems unrelated to improved buffer performance, as detected concentrations did not differ greatly between the compared plots. Buffer strip efficiency was found to be greatly affected by the uniformity of the vegetative cover, in particular at the beginning of the season. On TF plots, differences in the concentrations were generally due the presence/absence of buffer strips, regardless of its width. Similar behavior was observed by Tingle et al. [53]

Conclusions

Flufenacet and isoxaflutole can be easily transported with runoff waters. In both years, the highest concentrations were found in water samples collected after the first runoff events. Flufenacet was always found in runoff waters at concentrations higher than isoxaflutole. In general, flufenacet losses were larger and extended further into the season. The study evidenced the strong effect of soil texture on the amount of flufenacet and isoxaflutole transported. Both soils were silty-loam textured, but they differed in their soil properties affecting the amount of each herbicide available for surface runoff. Flufenacet did not persist longer in the top soil surface. On TF plots, concentration differences were generally due the presence/absence of buffer strips, regardless of buffer strip width. It was also observed that buffer strip efficiency was greatly affected by the degree of development of the spontaneous vegetative cover, particularly at the beginning of the growing season. This problem could be avoided by sowing a mix of grasses (such as *Festuca* spp. and *Lolium* spp.) on the buffer strip surface early in the season to ensure better coverage.

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701 # Figure captions

702 **Figure 1**: Experimental layout adopted. A: sampling devices.

703 **Figure 2**. Flufenacet concentrations (μg kg^{-1}) in soil of treated areas in 2009 (a) and 2010 (b).

704 Arithmetic mean of three bulk replications ±SD.

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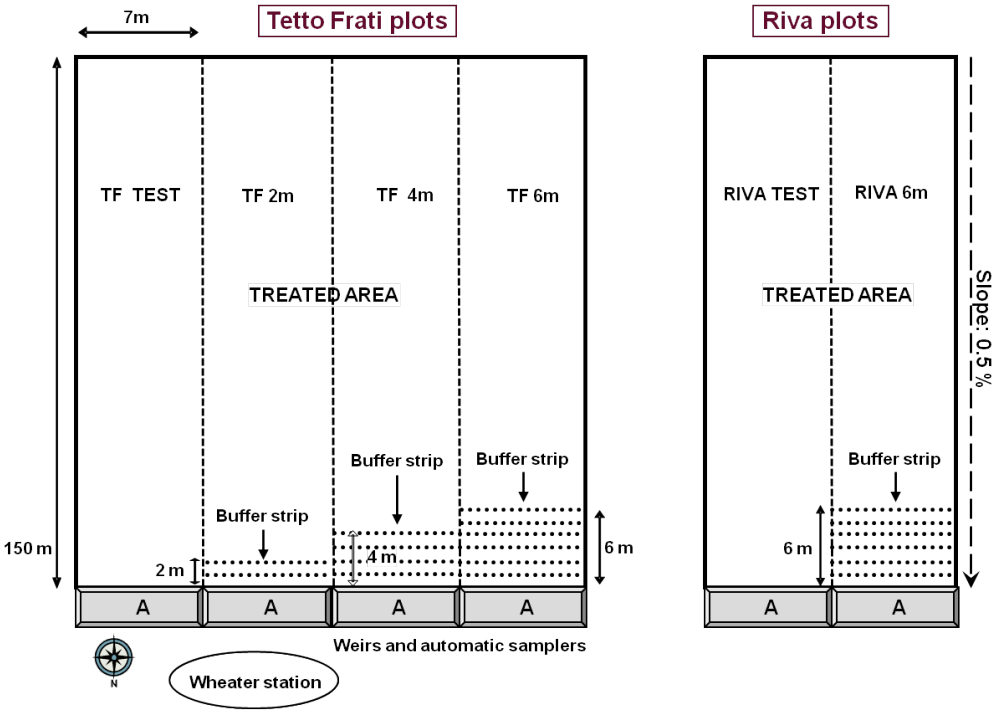
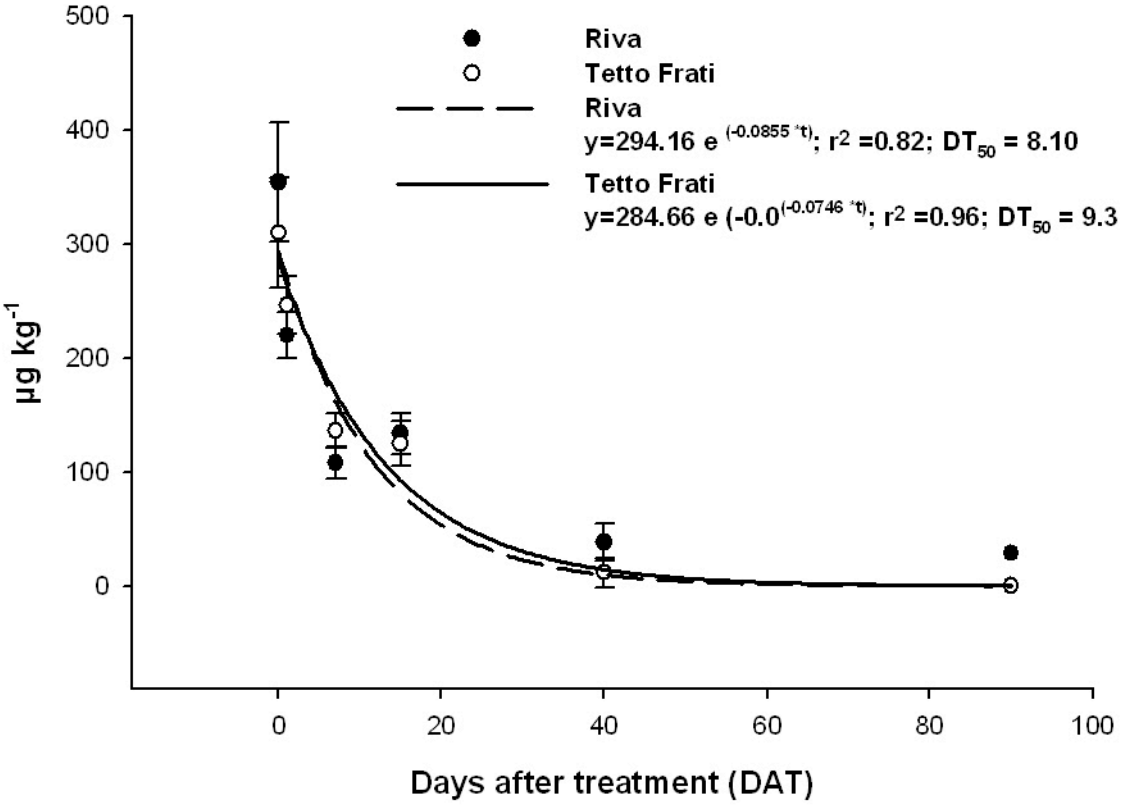
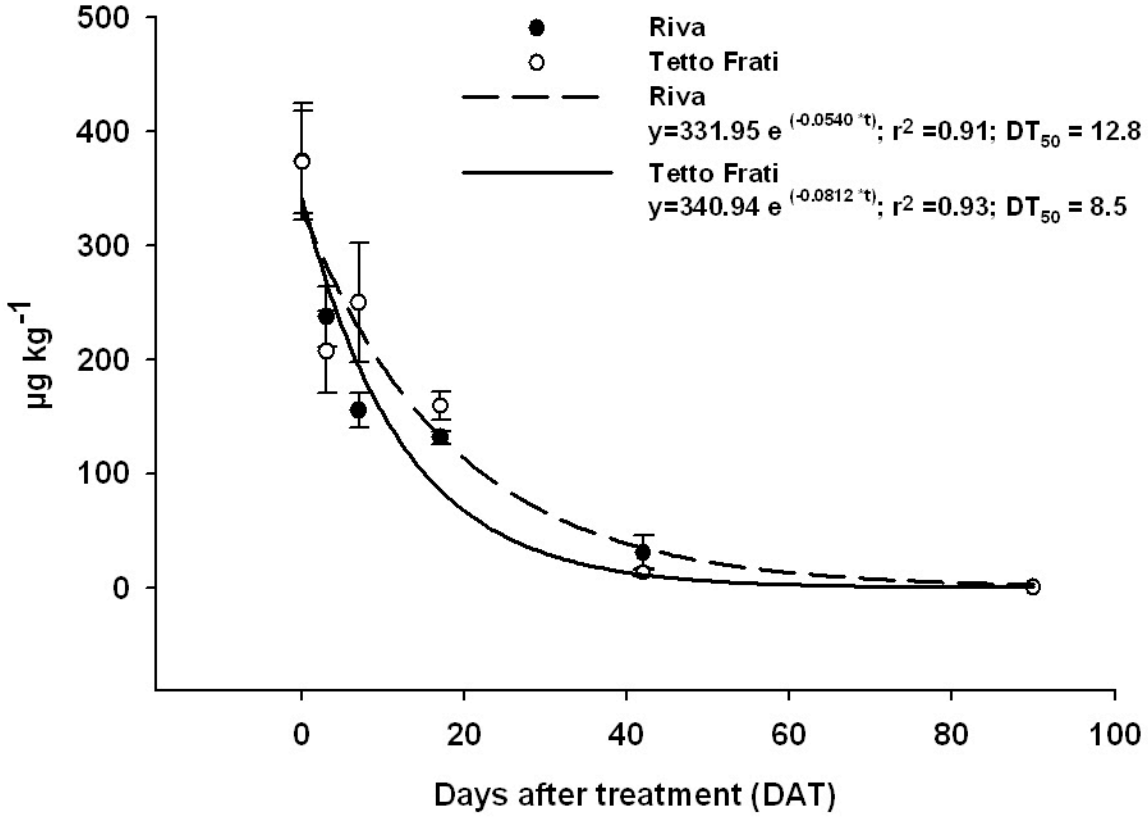

7m
Tetto Frati plots
Riva plots
TF TEST
TF 2m
TF 4m
TF 6m
TREATED AREA
RIVA TEST
RIVA 6m
TREATED AREA
Slope: 0.5 %
Buffer strip
Buffer strip
Buffer strip
Buffer strip
150 m
2 m
4 m
6 m
6 m
A
A
A
A
A
A
Weirs and automatic samplers
N
Wheater station

Fig. 1


Riva
Tetto Frati
Riva
y=294.16 e (-0.0855 *t); r2 =0.82; DT50 = 8.10
Tetto Frati
y=284.66 e (-0.0(-0.0746 *t); r2 =0.96; DT50 = 9.3
µg kg-1
500
400
300
200
100
0
0
20
40
60
80
100
Days after treatment (DAT)

a



b

733 **Fig. 2**

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736 **Table 1.** Physico-chemical properties of flufenacet and isoxaflutole. Source: PPDB, The Pesticide
737 Properties Database, AERU, University of Hertfordshire, 2009.

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Herbicides	Water solubility ($mg\ L^{-1}$)	Koc ($mL\ g^{-1}$)	DT50 in field (days)	GUS
Flufenacet	56	401	40	2.4
Isoxaflutole	6.2	145	1.3	0.6

739 *Note: GUS = Ground water ubiquity score*

740 **Table 2.** Concentration of flufenacet detected in water samples collected after each runoff event in 2009 and 2010. Values are expressed in µg L^{-1}.

741 Arithmetic mean of three replications ± SE. Same-letter values are not significantly different [REGWF test (*P <0.05)].

DAT	Precipitation mm	Temperature °C	Flufenacet concentration in the runoff water (µg L^{-1})					
			TFTEST	TF2	TF4	TF6	RIVATEST	RIVA6
				2009				
4	23.6	9.3	13.7 ±5.5 b	9.2 ±3.1 b	14.9 ±3.6 b	13.5 ±8 b	66.3 ±10.2 a	57.2 ±3.8 a
5	23.2	10.7	13.7±3.1 c	6.4±0.8 d	12.3±1.2 c	6.3±1.5 d	67±2.6 b	91.7±10.2 a
11*	33.2	10.1	1.5	1.5	6.1	4.6	41.4	42.5
12	63.4	9.5	2.4±0.2 d	2.1±0.6 d	3.9±0.9 c	1.3±0.2 d	19.5±0.8 a	16 b
12			3.5±1.2 b	3±0.2 b	3.8±0.8 b	4.4±0.7 b	10.8±1.1 a	14.3±3.2 a
13	9.2	11.8	5.4±0.8 c	2.7±0.4 c	9.1±0.2 c	4.9±1.8 c	64.7±3.6 a	57.5±4.3 b
62 (I)	-	24.5	0.4±0.3 a	0.3±0.3 a	0.3±0.1 a	0.5±0.4 c	15±3.5 a	5.8±1.9 b
68	14	18.2	0.8±0.3 b	< LOQ	< LOQ	< LOQ	1.5±0.1 a	1.0±0.0 b
77	46.8	23.2	0.4±0.10 b	0.1±0.3 b	0.3±0.1 b	0.5±0.1 b	1.9±0.4 a	1.7±0.4 a
82	28.6	23.5	0.1±0.0 c	< LOQ	< LOQ	0.1±0.0	0.5±0.0 a	0.3±0.1 b
93	39	22.4	0.2±0.1 bc	< LOQ	< LOQ	< LOQ	0.4±0.01 c	0.3±0.0 bc
110 (I)	-	25.1	0.2±0.1 bc	0.2±0.1	0.2±0.2 a	0.5±0.6 a	0.9±0.9 c	0.7±0.3 bc
115	30	22.7	0.2±0.0 b	< LOQ	< LOQ	< LOQ	0.3±0.0 a	0.2±0.0 b
				2010				
10	25.4	13.8	13.0±7.5 a	0.6±0.4 b	2.7±1.6 b	0.2±0.1 b	10.4±5.9 a	0.7±0.4 b
11	42.6	11.4	1.0±0.7 c	0.7±0.3 d	0.8±0.5 c	0.3±0.2 d	6.2±3.6 a	4.2±2.4 b
17	11.2	15.4	0.9±0.5 c	0.7±0.4 c	0.9±0.5 c	0.6±0.3 c	2.7± 1.5 a	1.6±0.9 a
44	37.6	22.0	0.3±0.2 c	0.2±0.1 c	0.2±0.1 c	0.2±0.1 c	0.5±0.2 a	0.4±0.3
53	72.8	17.1	0.1±0.1 a	< LOQ	0.1±0.1 a	0.1±0.1 a	0.2±0.2 a	0.1±0.2 a
54	23.2	18.9	< LOQ	< LOQ	< LOQ	< LOQ	0.1± a	0.1± a
57	12.8	17.7	< LOQ	< LOQ	< LOQ	< LOQ	0.1± a	0.1± a
89 (I)	I	23.9	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
110	69.6	17.3	nc	nc	nc	nc	nc	nc

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743 *Note 1: DAT (days after herbicide treatment); I (Irrigation); LOQ (Limit of quantification) =0.05 µg L -1 for flufenacet. nc: not collected * Arithmetic mean of two data.*

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746 **Table 3.** Concentration of isoxaflutole detected in water samples collected after each runoff event in 2009 and 2010. Values are expressed in µg L^{-1}.

747 Arithmetic mean of three replications ± SE. Same-letter values are not significantly different [REGWF test (*P <0.05)].

DAT	Precipitations mm	Temperature °C	Isoxaflutole concentration in the runoff water (µg L^{-1})					
			TFTEST	TF2	TF4	TF6	RIVATEST	RIVA6
---------- 2009----------								
4	23.6	9.3	0.16 (0.01) c	< LOQ	0.08 (0.06) c	< LOQ	5 (3.30) a	2.87 (0.45) b
5	23.2	10.7	0.20 (0.03) c	< LOQ	0.13 (0.07) c	< LOQ	4.17 (0.61) a	0.99 (0.18) b
11*	33.2	10.1	< LOQ	< LOQ	< LOQ	< LOQ	0.75 (0.31) a	0.92 (0.32) a
12	63.4	9.5	< LOQ	< LOQ	< LOQ	< LOQ	0.34 (0.02) a	0.11 (0.09) b
12			< LOQ	< LOQ	< LOQ	< LOQ	0.42 (0.03) a	0.35 (0.26) a
13	9.2	11.8	0.13 (0.01) b	< LOQ	< LOQ	< LOQ	1.14 (0.23) a	1.24 (0.15) a
62 (I)	-	24.5	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
68	14	18.2	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
77	46.8	23.2	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
82	28.6	23.5	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
93	39	22.4	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
110 (I)	-	25.1	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
115	30	22.7	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
---------- 2010----------								
10	25.4	13.8	< LOQ	< LOQ	<LOQ	< LOQ	0.10 (0.05)	< LOQ
11	42.6	11.4	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
17	11.2	15.4	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
44	37.6	22.0	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
53	72.8	17.1	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
54	23.2	18.9	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
57	12.8	17.7	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
89 (I)	-	23.9	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
110	69.6	17.3	nc	nc	nc	nc	nc	nc

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749 *Note 2: DAT (days after treatment); I (Irrigation); LOQ (Limit of quantification) = 0.02 µg L -1. nc: not collected * Arithmetic mean of two data.*

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Table 4. Rainfall events and corresponding measured runoff volumes in 2010.

DAT	Rainfall (mm)	Runoff (m^3)					
		TFTEST	TF2	TF4	TF6	RIVATEST	RIVA6
10	25.4	1.0	0.9	1.0	0.8	1.2	0.8
11	42.6	1.5	1.3	2.5	2.6	11	9.6
17	11.2	0.9	0.5	1.5	0.8	2.8	1.6
44	37.6	7.2	8.0	7.0	6.5	7.8	7.7
53	72.8	53.7	50.6	53.0	56.3	87.0	78.5
54	23.2						
57	12.8	1.8	1.9	1.8	0.8	3.4	1.6
89 (I)	I*	16.7	16.6	14.5	11.9	21.5	17.5
110	69.6	nm	nm	nm	nm	nm	nm

Note 3: DAT (days after treatment); NR: no runoff; I: Irrigation; nm: not measured; Irrigation volumes were: RIVATEST: 38.7 m^3; RIVA6:44.0 m^3; TFTEST: 34.6 m^3 TF2: 39.4 m^3 TF4: 37.6; TF6 35.3 m^3 TF*