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(Article begins on next page)

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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

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

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

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

63 In the case of VBSs, they are usually set up along streams, ponds, or lakes to prevent water
64 pollution. VBSs have been a useful tool to reduce runoff and erosion, ^[10, 12, 13] and their efficacy is
65 generally expressed as a percent reduction in pesticide concentration as compared to a non-buffered
66 control. According to the literature, VBS effectiveness is generally above 50%. Typically, runoff
67 volume retention (intended as infiltration) averages 45% (ranging between 0 and 100%) across
68 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.

105

106 **Material and Methods**

107

108 *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.

113 *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

120 soil, but it was transferred from Riva municipality twenty years before (18.6% sand, 63.1% silt,
121 18.3% clay), with of organic matter and a pH=6,2.

122 At the downhill edges of each plot the runoff water was intercepted by a transversal drainage ditch.
123 Each drainage ditch was connected to an independent automatic sampler. In 2010, the system was
124 operated by flow metering devices, formed by a series of V-notch weirs fitted with magnetostrictive
125 water level transmitters. The water level in the weirs was continuously recorded with a datalogger.
126 On the four TF plots, a control without a buffer strip (TF TEST) was compared to three plots with 2
127 m (TF2), 4 m (TF4), and 6 m (TF6)-wide vegetated buffer strips. The buffer strips were sowed with
128 maize as was the rest part of the field; weeds were allowed to grow freely. Buffer strips were
129 mowed as needed. Weeds grown in the buffer strip were representative of the common maize weeds
130 of Northern Italian: *Echinochloa crus-galli* (L.) P. Beauv., *Panicum dichotomiflorum* Michx.,
131 *Chenopodium album* L., *Portulaca oleracea* L., *Trifolium repens* L., *Galinsoga quadriradiata* Cav.,
132 *Poa pratensis* L. and *Setaria viridis* L. Their density, expressed as percentage of soil coverage,
133 ranged from 20% (a week post crop sowing) to 100% during the rest of the season. The buffer strips
134 were mowed at least twice a year, after which the hay was removed. In the RIVA plots, a control
135 sans buffer strip (RIVA TEST) was compared to a plot with a 6-m buffer strip (RIVA6).
136 Characteristics of the buffer strip were similar to the buffers established in TF plots.
137 The plots were cultivated according to local agronomic practices, and the crop was sown on April 9
138 and April 20 in 2009 and 2010, respectively.

139 Herbicides were applied during pre-emergence, within three/four days after sowing, using a rear-
140 mounted boom sprayer. Over the two growing seasons water was supplied as needed to the crop by
141 a furrow irrigation system. In 2009, two irrigations were carried out on June 16 (37 m³, average of
142 the six plots) and August 3 (35 m³), respectively; in 2010, fields were irrigated only once on July 21
143 (38 m³).

144

145 ***Herbicides Studied***

146

147 All plots, except the buffer strips, were treated with flufenacet (4'-fluoro-N-isopropyl-2-[5-
148 (trifluoromethyl)-1,3,4-thiadiazol-2-yloxy]acetanilide) and isoxaflutole (5-cyclopropyl-1,2-oxazol-
149 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,
150 by spray application of 500 g ha⁻¹ of the commercial herbicide Merlin GP[®] (Bayer CropScience
151 Italia). To avoid deposition from spray drift, the buffer strip was covered with a plastic film during
152 herbicide application. Table 1 shows the physical and chemical properties of the studied substances.

153

154 **Soil sampling**

155

156 Three soil samples were collected from the treated areas at various times: before herbicide
157 application (to assess the residual previous soil contamination, t_{-1}), immediately after spraying (to
158 assess initial herbicide concentrations, t_0), and at increasing intervals from herbicide application (at
159 0, 1, 7, 15, 40 and 90 days after treatment in 2009; and at 0, 3, 7, 17, 31, 42 and 90 days after
160 treatment in 2010). Samples were taken from the upper 5 cm of the soil surface, with a 50 mm
161 diameter soil core sampler. At each sampling time, and for each plot, 10 soil cores samples were
162 randomly collected in the treated areas. After collection, soil samples were stored at -20°C until
163 analysis.

164

165 ***Water sampling***

166

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

172 were collected at 4, 5, 11, 12, 13, 62, 68, 77, 82, 93, 110, and 115 days after treatment (DAT) in
173 2009 and at 10, 11, 17, 44, 53, 54, 57, 89, and 110 DAT in 2010.

174

175 ***Herbicide Extraction and Analysis in the Soil***

176

177 *Flufenacet*

178

179 The extraction of flufenacet from the soil was performed on 50 g samples. The samples were
180 transferred into a 250 mL glass bottle (Duran, Germany) and 100 mL of acetone was added (J.T.
181 Baker, USA). Thereafter, the solution was sonicated for 30 min in an ultrasonic bath (Sonorex RK
182 156BH, Germany). The sonicated solution was then passed through a 150 mm diameter Büchner
183 funnel (Büchner, Germany) connected to a side-arm 250 mL flask (Duran, Germany) using a
184 neoprene adapter with a tube to a vacuum pump (Supelco). Two filter paper disks (Perfecte 2[®],
185 Cartiera di Cordenons, Italy) were placed on the Büchner surface, then covered with a layer of celite
186 (Celite 545 J.T. Baker). The soil and the glass bottle used for the extraction were washed with 50
187 mL of acetone and 50 mL of deionized water and the resulting volume was passed through the
188 Büchner funnel. All the filtrate obtained was transferred into a 250 mL volumetric flask and
189 adjusted to volume with deionized water. A final volume of 100 mL was then transferred to a 500
190 mL volumetric flask and adjusted to volume with deionized water. Herbicide extraction from this
191 solution was carried out using solid phase extraction (SPE) cartridges. The cartridges (SupelcoSil
192 LC-18, 6 mL, 0.5 g C18 sorbent material) were previously activated with 6 mL of n-hexane (J.T.
193 Baker, USA) and 6 mL of methanol (J.T. Baker, USA), and finally washed with 6 mL of deionized
194 water. The entire volume (0.5 L) flowed through the cartridges under vacuum at a rate of 500 mL h⁻¹.
195 ¹. The cartridges were let to dry. The adsorbed herbicide was eluted with n-hexane until a final
196 volume of 5 mL was reached. The eluted volume of 5 mL was then filtered through a 0.2 µm nylon
197 filter (Whatman, USA) to eliminate impurities. The final volume was dried under nitrogen flow by

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

200

201 *Isoxaflutole*

202

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

212

213 ***Herbicide Extraction and Analysis in the Water***

214

215 Herbicides extraction from the water samples was carried out using solid phase extraction (SPE)
216 cartridges. The cartridges (SupelcoSil LC-18, 6 mL, 0.5 g C18 sorbent material) were previously
217 activated with 6 mL of acetonitrile (Sigma Aldrich, Steinheim, Germany) and then washed with
218 20 mL of distilled water. The entire volume (1 L) of the water sample flowed through the cartridges
219 under vacuum at a flow of 500 mL h⁻¹. The cartridges were let to dry. The adsorbed herbicides were
220 eluted with acetonitrile until a final volume of 5 mL was reached. The eluted volume of 5 mL was
221 then filtered through a 0.20 µm nylon filter (Whatman, USA) to eliminate impurities. The final
222 volume was dried under nitrogen flow by a nitrogen generator (Claind, Italy) and recovered with 1
223 mL of n-hexane (Sigma Aldrich, Steinheim, Germany). Analysis was performed by GC-MS.

224 ***High-performance liquid chromatography analysis***

225

226 Analysis of isoxaflutole in soil was done by high-performance liquid chromatography (HPLC)
227 using a Spectraphysics P2000 equipped with a C18 Varian Pursuit column (150 mm × 4.6 mm i.d.,
228 5µm particle size), an ultra-violet (UV) detector at 270 nm for isoxaflutole, and a mobile phase
229 composed by brought water with pH=2, and acetonitrile (50/50 v/v) with the flow rate set to 1 mL
230 min⁻¹. Analytical-grade isoxaflutole supplied by Sigma Aldrich, Germany was used as the
231 analytical standard.

232

233 ***Gas Chromatography Analysis***

234

235 An Agilent 6890N GC and Agilent 5975 MS single-quadrupole, equipped with an MS detector, an
236 autosampler (Agilent) and split-splitless injector, connected to an Agilent Chemstation was used.
237 The Supelco Equity5 TM column (30 m x 0.25 mm i.d.) contained 5% diphenyl and 95% dimethyl
238 siloxane. The MS source temperature was 270°C and the gas carrier was helium. Analytical-grade
239 flufenacet and isoxaflutole, supplied by Sigma Aldrich, Germany, was used as the analytical
240 standards. Retention times for flufenacet in the soil samples were 17.6 min and 16.3 min in 2009
241 and 2010, respectively. Retention times for flufenacet in the water were 22 min and 25.6 min in
242 2009 and 2010, respectively. Retention times for isoxaflutole in the water were 26.1 min and 17.7
243 min in 2009 and 2010, respectively. Retention times for isoxaflutole in the soil samples were 9.2
244 min and 9.8 min in 2009 and 2010, respectively.

245

246 ***Recovery and detection limits***

247

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

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

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

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

265

266 *Statistical Analysis*

267

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

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

277
$$C_t = C_0 e^{-kt} \quad [1]$$

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

280
$$T_{1/2} = \ln(2/k) \quad [2]$$

281 where k is the rate constant.

282 Model fitting was performed using the function *drm* of the add-on package *drc* of the R software.

283 Data from 2009 and 2010 were first analyzed separately and then pooled to fit into a single model.

284 The *anova* function of the R software was used to test if the pooled dataset was significantly better
285 explained by single curves data separately (fitting both years and both soils) than by a single model
286 fitting all data.

287

288 ***Rainfall Distribution and Runoff Events***

289

290 Total rainfall measured during the crop growing seasons were 577 mm and 545 mm in 2009 and
291 2010, respectively. Weather data were collected daily from the meteorological station located near
292 the experimental fields. In both years, the periods close to herbicide application were characterized
293 by rainfall events that directly affected runoff losses and herbicide dissipation. The spring of 2009
294 was particularly rainy; in fact, a 282 mm rainfall was recorded in April. In the 2009 season, 13
295 runoff events were recorded while in 2010, 9 events were recorded.

296

297 **Result and discussion**

298

299 ***Herbicide Dissipation in the Soil***

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

303 Flufenacet showed a rapid decay in both seasons (Figs. 2a and 2b). In 2009 the field dissipation
304 half-life (DT_{50}) was 8.1 days in RIVA soil and 9.3 days in TF. During 2010 the persistence of
305 flufenacet in the upper soil layers did not change significantly relative to the previous year, resulting
306 in a soil half-life of 12.8 days in RIVA and 8.5 days on TF soil. In soil samples collected before the
307 2010 herbicide application, residues of flufenacet were below the detection limit. Also, the different
308 rainfall pattern recorded in the two years during the first days after herbicide application did not
309 significantly influence the flufenacet dissipation trend (Figs. 2a and 2b).

310 The statistical analysis conducted did not show a significant effect of the year and of the type of soil
311 on the dissipation dynamics of flufenacet. The only significant factor was the time elapsed from the
312 treatment (DAT). The data of the two years pooled in a single model revealed a DT_{50} of 10.2 days
313 with a confidence interval ($\alpha=0.05$) comprised between 6.4 to 14 days. As reported in the literature,
314 flufenacet dissipation follows a first order kinetics. ^[23] In both years, three months after herbicide
315 application on TF soil, flufenacet was below the limit of quantification. The only exception was in
316 2009 in RIVA soil when 90 days after treatment the concentration of the herbicide was still in the
317 detectable range, but no higher than 29 $\mu\text{g kg}^{-1}$.

318 The rapid flufenacet field dissipation can be attributed partly to the sampling procedure adopted, in
319 which only the superficial soil layer was sampled. This result agrees with Rouchaud et al., ^[24] who
320 found no flufenacet residues after the wheat harvest in summer and after the corn harvest during the
321 fall in the 0-20 cm soil layer with a similar LOQ. In top soil, the dissipation dynamics are generally
322 faster compared to that of deeper soil layers. Furthermore, the microbial degradation which is the
323 principal means of dissipation of flufenacet in soil must be considered. Since microbial activity is
324 enhanced during the spring, a shorter half-life could be expected at that time. Soil half-lives for
325 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

the treatment had likely facilitated the conversion of isoxaflutole into proherbicide diketonitrile. In 2010, the soil surface was very dry at spraying due the absence of rainfall in the previous weeks. According to Taylor et al.,^[34] under dry conditions, isoxaflutole is very stable and unavailable, and it persists more at the surface.^[35] However, a succeeding rainfall might promote the rapid transformation of isoxaflutole into its active form. Indeed, this condition was verified during 2010, when the soil was dry before treatment, but just 6 hours after treatment, a light rain occurred and caused transformation of the parent compound. Pallet et al.^[35] observed that the shorter half-life recorded for isoxaflutole under increased moisture content might relate to the need of isoxaflutole to be in solution in order to be transformed into diketonitrile.

Conversion of isoxaflutole to diketonitrile is rapid and become faster with higher temperatures, higher soil moisture levels, and at basic pH.^[33] Since the higher clay content of RIVA soil did not affect the sorption of the molecule,^[36] the diverse and low persistence might instead be associated with the differing pH of the two soils. Mitra et al.^[36] and Rouchaud et al.^[37] observed faster dissipation of isoxaflutole at basic pHs. In the present study, TF soil has a sub-alkaline reaction (pH 8.2) while the pH of RIVA soil is sub-acid (6.2) (Table 1). Hence, the slightly faster dissipation observed in TF soil over the two years might result from the combined effects of soil reaction and different soil moisture at the time of herbicide application.

As previously indicated, the two soils studied had similar low organic matter content, but they differed in pH and clay content. These two parameters may affect the soil dissipation of many pesticides, including isoxaflutole. A study conducted by Mitra et al.,^[36] pointed out that sorption of isoxaflutole was not influenced by clay content.^[38] On the contrary, it was highly related to organic matter content^[39] and to the soil pH.^[39, 40] Specifically, sorption of isoxaflutole increases with increasing organic matter content, and sorption increases at decreasing pH.^[36] Beltrán et al.^[41] has discussed the influence of soil pH on the dissipation reaction rate of isoxaflutole, and they found that the isomerization of IFT into DKN is rapid, depends strongly on pH, and is governed by a chemical process.

378 ***Dissolved Flufenacet in Runoff Water***

379 The runoff of flufenacet was studied during the growing seasons in relation to rainfall and irrigation
380 occurrences. In Table 2 are listed all the runoff events that occurred and the subsequent

381 concentrations of flufenacet detected. The different rainfall distributions affected the transport of
382 flufenacet and isoxaflutole, and thus runoff losses. In particular, several rainfall events occurred
383 early after herbicide application causing relevant runoff outflows.

384 In both years, the highest flufenacet concentrations in runoff waters were measured during the
385 runoff events that occurred in the first two weeks after application. This is consistent with several
386 studies ^[18,42] that showed that major losses occur during runoff events close to herbicide application.
387 [2, 9, 43-47]

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

397 Thereafter, a continuous rainfall occurred between 11th and 13th day after treatment, which resulted
398 in a runoff event that endured during the entire rain period. At the beginning of this event, the
399 flufenacet concentrations were lower than in the first event, but by the end of it (at 13 DAT), a
400 concentration increase was observed, particularly in runoff waters that flowed from RIVA plots
401 (Table 2). One explanation for this observation might be that after three days of rain, all soil
402 macropores were saturated by water, and that runoff overcame the infiltration rate. Then, in the
403 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 $\mu\text{g L}^{-1}$ (RIVA TEST) and
405 5.9 $\mu\text{g L}^{-1}$ (RIVA6) while runoff water flows from TF plots was no higher than 0.5 $\mu\text{g L}^{-1}$ (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 $\mu\text{g L}^{-1}$), RIVA TEST (0.3 $\mu\text{g L}^{-1}$), and RIVA6 (0.2 $\mu\text{g L}^{-1}$).
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 $\mu\text{g L}^{-1}$ (RIVA TEST) and 1.6 $\mu\text{g L}^{-1}$ (RIVA6) as opposed to values for
420 runoff waters from the TF plots between 0.6 $\mu\text{g L}^{-1}$ and 0.9 $\mu\text{g L}^{-1}$ (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

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

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

446

447 ***Dissolved Isoxaflutole in Runoff Water***

448

449 The presence of isoxaflutole in runoff waters was assessed in the same temporal interval as that of
450 flufenacet. As for flufenacet, the highest isoxaflutole concentrations were detected during the first
451 runoff event in waters from the plots without buffer. In 2009, at the first event (4 DAT), the highest
452 isoxaflutole concentrations were detected in RIVA plots, where they ranged between 5 $\mu\text{g L}^{-1}$
453 (RIVA TEST) and 2.90 $\mu\text{g L}^{-1}$ (RIVA6). In TF plot runoff, they did not exceed 0.16 $\mu\text{g L}^{-1}$ (TF
454 TEST). In the runoff events that occurred later in the season, isoxaflutole was present in runoff
455 waters from TF4 only at 6 DAT (0.13 $\mu\text{g L}^{-1}$) 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 ($0.10 \mu\text{g L}^{-1}$) 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

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

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

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

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

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

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

533

534 **Conclusions**

535

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

548

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550

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556

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Figure captions

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

Figure 2. Flufenacet concentrations ($\mu\text{g kg}^{-1}$) in soil of treated areas in 2009 (a) and 2010 (b).
Arithmetic mean of three bulk replications $\pm$ SD.

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725 **Fig. 1**

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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

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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 $\mu\text{g L}^{-1}$.
 741 Arithmetic mean of three replications $\pm$ 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 $\mu\text{g L}^{-1}$ 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 $\mu\text{g L}^{-1}$.

747 Arithmetic mean of three replications $\pm$ 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) = $0.02 \mu\text{g L}^{-1}$. 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						
54	23.2	53.7	50.6	53.0	56.3	87.0	78.5
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

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Note 3: DAT (days after treatment); NR: no runoff; I: Irrigation; nm: not measured; * Irrigation volumes were: RIVATEST: 38.7 m³;

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RIVA6:44.0 m³; TFTEST: 34.6 m³ TF2: 39.4 m³ TF4: 37.6; TF6 35.3 m³ TF

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