

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

Buffer strip effect on terbuthylazine, desethyl-terbuthylazine and S-metolachlor runoff from maize fields in Northern Italy

This is the author's manuscript

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/99831> since

Published version:

DOI:10.1080/09593330.2012.680919

Terms of use:

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)

1 **Buffer strip effect on terbuthylazine, desethyl-terbuthylazine and S-**
2 **metolachlor runoff from maize fields in Northern Italy**

3
4 MARCO MILAN*, FRANCESCO VIDOTTO*, SERENELLA PIANO*, MICHÉLE NEGRE**, ALDO
5 FERRERO*

6
7 **Dipartimento di Agronomia, Selvicoltura e Gestione del Territorio, Università di Torino, Via Leonardo da*
8 *Vinci 44, 10095 Grugliasco (TO), Italy.*

9
10 ***Dipartimento di Valorizzazione e Protezione delle Risorse Agricole e Forestali, Università di Torino, Via*
11 *Leonardo da Vinci 44, 10095 Grugliasco (TO), Italy.*

12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30 *Correspondence:* Marco Milan, Dipartimento di Agronomia, Selvicoltura e Gestione del Territorio,
31 Università di Torino, Via Leonardo da Vinci 44, 10095 Grugliasco (TO), Italy. Tel: (+39)
32 0116705548; Fax: (+39) 0116708798; E-mail: marco.milan@unito.it
33

101 metolachlor and desethyl-terbuthylazine were measured during the growing seasons and their
102 dissipation in the soil was studied. Buffer strips are considered useful mitigation measure of
103 pesticide and sediment runoff in various environmental conditions. Better understanding the
104 efficacy of buffer strips in reducing pesticide runoff at a field-scale level may facilitate the adoption
105 of appropriate runoff mitigation measures by regional or national authorities.

106 **2. Materials and methods**

107 **2.1. Experimental design**

108 The study was carried out at the experimental station of the Dipartimento di Agronomia,
109 Selvicoltura e Gestione del Territorio of University of Turin, Italy. The experimental station is
110 located in the Po Valley in northwest Italy (44° 53' 08.99" N, 7° 41' 11.33" E; WGS84) in an area
111 traditionally cultivated with maize.

112 The experimental site consisted of two large plots cultivated with maize, each approximately 1050
113 m² (150x7 m) with a 0.5% slope (Figure 1). The plots were characterized by sandy loam soil
114 (68.77% sand, 26.79% silt, 4.45% clay), 0.9% organic matter, and a pH=7.63. One plot had an
115 untreated 6 m-wide vegetated buffer strip at the downstream head (buffered field; BF) while the
116 other plot had no buffer strip and was considered as the control (check field; CF). The buffer strip
117 was cultivated with maize, and weeds were allowed to grow freely. Weeds grown in the buffer strip
118 were representative of the common maize weeds of the North Italian area. They were mostly
119 represented by *Echinochloa crus-galli* (L.) P. Beauv., *Panicum dichotomiflorum* Michx.,
120 *Chenopodium album* L., *Portulaca oleracea* L., *Galinsoga quadriradiata* Cav., and *Poa pratensis*
121 L. Their density, expressed as percentage of soil coverage, ranged from 40% (ten days after the crop
122 sowing) to 100% during the rest of the season. Hand mowing was conducted as needed.

123 The measurements were carried out on the same plots during the 2007 and 2008 growing seasons,
124 which are regarded as temporal replications

125 **2.2 Chemicals studied**

126 Both plots, save the buffer strip, were treated with terbuthylazine (6-chloro-N-(1,1-dimethylethyl)-
127 N'-ethyl-1,3,5-triazine-2,4-diamine) and S-metolachlor (aRS,1S)-2-chloro-6'-ethyl-N-(2-methoxy-1-
128 methylethyl)acet-o-toluidide) at 843 g a.s. ha⁻¹ and 1400 g a.s. ha⁻¹, respectively by spray
129 application of 4.5 L ha⁻¹ of the herbicide Primagram Gold ® (Syngenta) using a conventional rear-
130 mounted boom sprayer adjusted to deliver 400 L ha⁻¹ of herbicide mixture. To avoid product
131 deposition from spray drift, the buffer strip was covered with a plastic film during herbicide
132 application. Physical-chemical properties of the studied substances are presented in Table 1.

133 **2.3 Agronomic practices**

134 In both experimental plots maize was cultivated according to local agronomic practices. Crop
135 sowing was carried out the 8 of April and 1 of April in 2007 and 2008, respectively.

136 Total rainfall measured during the growing season was 360 mm and 580 mm in 2007 and 2008,
137 respectively. Weather data were collected daily from the meteorological station located near the
138 experimental fields. Herbicides were applied in pre-emergence, within two days after sowing.

139 Over the two seasons, water was supplied as needed to the crop by a furrow irrigation system with
140 the exception of the second and the third 2007 irrigations, which were performed by a traveling-gun
141 sprinkler irrigation system. In 2007 the three irrigations were realized at July 10, July 24 and
142 August 8, respectively. In 2008 field were irrigated only two times at July 24 and August 7.

143 **2.4 Soil sampling**

144 Soil samples were collected using a stainless shovel in different positions of each treated area
145 immediately after spraying (to asses initial herbicide concentration, t_0) and at 1, 4, 28, 51 and 177
146 days after treatment (DAT) in 2007 and at 1, 4, 14, 28 and 47 DAT in 2008.

147 The samples were taken in the upper 5 cm of soil, with a 50 mm diameter soil core sampler. At each
148 sampling time, three bulk samples made, by 10 cores each, were randomly collected in both treated
149 areas. After collection, soil samples were stored at -20°C until chemical analysis.

150 **2.5 Water sampling**

151 Samples of runoff water were collected after each irrigation and rainfall (able to produce runoff).
152 Water samples were collected at 23, 60, 90 and 120 DAT in 2007 and at 9, 67, 74, 94, 112 and 127
153 DAT in 2008. A total of six samples (considered as replications) were collected after each runoff
154 event, three from the CF field and three from the BF field. The runoff flow from the plots was
155 measured using a triangular weir, placed on the downhill border of the field, with a notch angle of
156 28° , created according to the ISO rules (1433/1). The weirs were connected to automatic samplers
157 adjusted to collect, at each runoff event, a bulk sample made by 500 mL sub-samples gathered at
158 10-min intervals for the duration of the event. The end bulk samples had volumes ranging from 5 L
159 to 25 L, in relation to runoff event duration and intensity. Within about two hours from the end of
160 each event, three 0.5 L subsamples were derived from the bulk sample and stored at -20°C until
161 analysis.

162 **2.6 Herbicide extraction and analysis**

163 **2.6.1 Soil**

164 The extraction of herbicides from the soil was performed on 25 g samples. The samples were
165 previously mixed with 10 g kieselguhr (Extrelut NT, Merck, Darmstadt, Germany), then added to
166 100 mL of a cyclohexane/ethyl acetate (Sigma Aldrich, Steinheim, Germany) solution (90:10:V/V).
167 Thereafter, the solution was mechanically agitated for thirty minutes. The liquid phase was

168 separated by filtration on anhydrous sodium sulfate. The extraction was repeated twice using 75 and
169 50 mL, respectively, of extraction solution and then shaking for 15 minutes. The filtrates obtained
170 from the three extractions were concentrated and dried in a rotary evaporator, then re-dissolved in 5
171 mL of acetonitrile.

172 *2.6.2 Water*

173 Herbicide extraction from water samples was carried out using solid phase extraction (SPE)
174 cartridges. The cartridges (SupelcoSil LC-18, 6 ml, 0.5 g C₁₈ sorbent material) were previously
175 activated with 6 ml of acetonitrile (Sigma Aldrich, Steinheim, Germany) and then washed with 6 ml
176 of distilled water. The entire volume (0.5 L) of the water sample flowed through the cartridges
177 under vacuum. The cartridges were let to dry. The adsorbed herbicides were eluted with acetonitrile
178 until a final volume of 5 mL was reached.

179 *2.6.3 HPLC analysis*

180 Analysis was performed by HPLC using a Spectraphysics P2000 equipped with a C18 Supelcosil™
181 LC-ABZ column (15 cm x 4.6 mm i.d., 5 μm particle sizes), a UV detector at 215 nm, a mobile
182 phase H₂O pH 3/CH₃CN 44/56, with the flow rate set to 1 mL min⁻¹. Analytical-grade S-
183 metolachlor, terbuthylazine and desethyl-terbuthylazine, supplied by Sigma Aldrich, Germany,
184 were used as analytical standards. Retention times were 8.19 min, 3.72 min and 12.0 min, for
185 terbuthylazine, desethyl-terbuthylazine and S-metolachlor, respectively.

186 *2.6.4 Recovery and detection limits*

187 The mean recoveries of terbuthylazine, desethyl-terbuthylazine and S-metolachlor in water were
188 98%, 86% and 87% respectively. The mean recoveries in soil were 70%, 85%, and 82 % for
189 terbuthylazine, desethyl-terbuthylazine and S-metolachlor, respectively. The detection limits
190 achieved in water samples were 0.08 μg L⁻¹ for terbuthylazine and S-metolachlor, and 0.05 μg L⁻¹
191 for desethyl-terbuthylazine. The detection limits achieved in soil were 5 μg kg⁻¹ for terbuthylazine
192 and S-metolachlor, and 2.80 μg kg⁻¹ for desethyl-terbuthylazine.

193 *2.7 Statistical analysis*

194 A Tuckey range test (α=0.05) was employed to determine the statistical significance of differences
195 among the concentrations observed in the waters collected from the check field and the buffered
196 field at the different sampling time. The values presented are the mean of three data. SPSS, version
197 17.00, (SPSS, IBM Corporation, 2008), was used for the statistical analysis.

198 **3. Results and discussion**

199 *3.1 Herbicide dissipation in the soil of treated areas*

200 The concentration of terbuthylazine and S-metolachlor in the top 5 cm soil layer showed a rapid
201 decay (Figure 2 and Figure 3) in each year. In general, the observed rapid degradation can be

202 attributed to the sampling procedure adopted in this study, in which only the superficial (5cm) soil
203 layer was sampled. However, the more rapid dissipation of the studied herbicides observed in 2008,
204 may also be due to the rainfall occurred in the last decades of April. The reduced intensity of the
205 rainfall just in one case produced a significant runoff (9 days after herbicide application),
206 nevertheless they promoted the movement of the studied molecule through the soil profile.

207 We found soil half-lives for S-metolachlor to be short with a range between 16 (2007) and 7 days
208 (2008). Our results agree with those of Youbin et al. [32], who reported that metolachlor
209 degradation was faster near the soil surface and that it increased as soil depth increased. Accinelli et
210 al. [33] too, found degradation to be faster in the upper (0-20 cm) soil depth compared to the sub-
211 surface layer. Other authors have reported longer field half-lives for metolachlor [33]; [34];
212 [35];[36], but their work referred to loamy soils in which a relevant amount of applied herbicide is
213 likely retained by the soil matrix. In consideration of the light soil texture at the experimental site,
214 we expected not only a lower persistence of S-metolachlor, but also a higher mobility of the
215 molecule throughout the soil profile.

216 Over the course of our two year study, the terbuthylazine-treated soil half-life values ranged from
217 12.1 (2007) to 8.9 days (2008). Terbuthylazine soil half-life ranges between 5 and 114 days
218 according to soil depth [37], soil characteristics, and soil temperatures [38]; [39];[40].

219 The higher rate of dissipation of this compound throughout sandy soil compared to clay soils is well
220 known. The soil matrix adsorbs only part of the molecule [41] resulting in a reduced degradation
221 [37]. Furthermore, terbuthylazine degradation appears to be more rapid in topsoil [37]. Despite
222 volatilization and photodegradation may reduce herbicide concentration in top soil [42], rainfall can
223 cause herbicides to move through the soil so much so that microbial degradation starts to be the
224 dominant factor in herbicide dissipation [9].

225 Despite several studies investigated the presence of desethyl-terbuthylazine in water environment,
226 less information are available on its behaviour into the soil. The soil half-life of triazine metabolites
227 are reported to be much higher than those of their parent compounds [43]. Nevertheless, compared
228 to the terbuthylazine, desethyl-terbuthylazine is more water soluble and less adsorbed to soil matrix.
229 These characteristics may have a great influence on the dissipation dynamics of this chemical,
230 particularly in permeable soils. In the present study, the desethyl-terbuthylazine formation was quite
231 rapid and varied greatly between the two years.

232 During the first year of the study (2007), desethyl-terbuthylazine concentration in soil reached the
233 maximum value at 28 DAT ($176.31 \mu\text{g kg}^{-1}$). However, even at 51 DAT its concentration was about
234 $21 \mu\text{g kg}^{-1}$; six months after herbicide application it was less than $4 \mu\text{g kg}^{-1}$. During 2008, desethyl-
235 terbuthylazine formation in the soil quickened and its peak value was registered 4 DAT ($218.47 \mu\text{g kg}^{-1}$)

236 kg⁻¹). Compared to the previous year, desethyl-terbuthylazine formation resulted more rapid. It is
237 important to note that in 2008 the first week after treatment was characterized by several light rains
238 which may have accelerated its formation. At 14 DAT the concentration of desethyl-terbuthylazine
239 was attested at 41.78 ! g kg⁻¹ while at its final sampling (47 DAT), it was no more than 5 ! g kg⁻¹.

240 ***3.2 Dissolved herbicides in runoff water***

241 Residues of the three studied substances were detected in the water flushed in the sampling system
242 of each experimental plot after runoff events that were due to rainfall or irrigation. The sampling
243 was carried out on the same plots in 2007 and 2008 which are regarded as temporal replications.
244 The outflows produced after every rainfall or irrigation able to produce runoff were accurately
245 measured (Table 2). In our investigation, we found concentrations of terbuthylazine, desethyl-
246 terbuthylazine, and S-metolachlor in runoff waters to be related to the time elapsed between
247 herbicide application and runoff events. The highest values during the seasons were observed in
248 water samples collected from CF.

249 In 2007 the first instance occurred 23 days after herbicide application (DAT); concentrations of
250 terbuthylazine, desethyl-terbuthylazine, and S-metolachlor in the water flow from BF were 95%
251 lower than those detected from CF. Several studies have similarly reported that major losses result
252 when rainfall occurs close to herbicide application [13]; [7]; [15]. The second important runoff
253 event occurred at 60 DAT. In this instance, large concentrations of terbuthylazine and desethyl-
254 terbuthylazine (13.5 ! g L⁻¹ and 15.9 ! g L⁻¹, respectively) were found in runoff water collected from
255 CF while S-metolachlor was not detected in either plots. In comparison to the previous event, the
256 resulting concentrations were about one order of magnitude lower, and no runoff was recorded from
257 the BF (Table 2).

258 Several irrigation events followed these rainfalls. Furrow irrigation, at 90 DAT, caused water runoff
259 in both fields. Measurements indicated terbuthylazine and desethyl-terbuthylazine concentrations in
260 BF runoff were about 9 and 3 times lower, respectively, than those detected in CF. The following
261 two runoff events were due to irrigations performed by a traveling-gun sprinkler irrigation system
262 The second irrigation occurred at 104 DAT, but no runoff resulted. The third irrigation, at 120
263 DAT, led to runoff in CF only. In this cases, the observed runoff volumes were far lower than those
264 usually expected, which was most likely related to the higher amount of water infiltrated with a
265 sprinkler versus furrow irrigation system. However, approximately 8 hours after irrigation, a severe
266 storm caused an important runoff in both plots. Terbuthylazine and desethyl-terbuthylazine
267 concentrations increased noticeably compared to previous runoff measurements. We postulate that
268 the just-previous irrigation had already raised the water content of the soil. Then, when the storm

269 came, conditions favored runoff and allowed transport of the herbicide fraction adsorbed on the
270 sediment [44]; [45].

271 In 2008, the first runoff event was registered after an important rainfall at 9 DAT, but a resulting
272 outflow was recorded only from CF (Table 2). While this runoff event occurred closer to herbicide
273 application (9 DAT) than did the first event in 2007 (23 DAT), resulting chemical concentrations
274 detected in the runoff samples were lower than those detected in 2007. The rainfall occurred in the
275 first days after herbicide application may have stimulated herbicides dissipation as well as the
276 movement of the compounds in the deep layers of the soil. Effectively, in 2008, peak of desethyl-
277 terbuthylazine in soil, was reached at 4 DAT, while in 2007 peak value of desethyl-terbuthylazine
278 was registered at 28 DAT, few days after the first event of runoff. The second important runoff
279 event, also due to a rainfall, occurred at 67 DAT. Concentrations of the studied chemicals decreased
280 relative to the previous rainfall and were measured at 2.1 ! g L^{-1} for terbuthylazine, 0.9 ! g L^{-1} for
281 desethyl-terbuthylazine, and 0.6 ! g L^{-1} for S-metolachlor. These concentrations appear to be much
282 smaller respect to those observed during the runoff event occurred in 2007, at a similar time from
283 herbicide application (60 DAT). The reason is attributable to the particularly rainy spring
284 registered, which probably has facilitated the movement of the chemicals deep into the soil. The
285 next two runoff events occurred at 74 DAT and 94 DAT; both were rainfall related. In these runoff
286 events, S-metolachlor concentrations, regardless of field, were always below the determination limit
287 while terbuthylazine and desethyl-terbuthylazine continued to be found in water flows from both
288 fields. In any case, concentrations of the two chemicals observed in outflows from BF were,
289 generally, lower than those found in water from CF.

290 Furrow irrigation at 112 DAT produced a significant runoff. Terbuthylazine and desethyl-
291 terbuthylazine were found in concentration above the detection limits only in outflows from CF.
292 Two weeks later (127 DAT), in the water samples collected after the second irrigation, desethyl-
293 terbuthylazine was detected in water sample from CF and BF field at similar concentrations, while
294 no more terbuthylazine was found (Table 2). In both years, desethyl-terbuthylazine was present in
295 concentration above the detection limit until the latest sampling; either in runoff waters from CF
296 plot that BF plot. The presence of the metabolite in the water that crossed the buffer strip suggests
297 there may have been transport from the treated area or degradation of the parent compound
298 transported through the buffer strip during an earlier runoff event. However, desethyl-terbuthylazine
299 seems show a potential longer risk of water contamination.

300 ***3.3 Efficiency of the vegetative buffer strip***

301 The ratio of field area to strip area in buffered plot was 25:1. Other studies were conducted with
302 higher ratios by other authors [46]; [47]. A higher field/filter ratio may reduce the efficacy of buffer

303 strip particularly in case of accentuated slope. However, as reported in section 2.1, our experimental
304 fields have a limited slope.

305 In Table 3 are reported the runoff events, the water volumes applied during irrigations and the
306 corresponding measured runoff volumes in 2007 and 2008. In general, higher runoff volumes were
307 observed in CF indicating that the buffer strip successfully reduced runoff volumes. Nevertheless,
308 as shown in Table 3, in some cases runoff volume measured in buffered plots were higher than in
309 the control plot. Operating on a field scale, a modification of soil roughness, perhaps for a weed
310 spots, may affect the outflow behavior along the field.

311 Buffer strips reduce runoff volumes by slowing water speed, which in turn, promotes water
312 infiltration into the soil [18]; [48]; [49]. As observed in the two years, the different cover offered by
313 spontaneous vegetation during the season may affect buffer strip efficiency.

314 Terbutylazine and S-metolachlor are transported both in water phase than in the solid phase,
315 adsorbed to eroded soil particles [50]. Nevertheless, the soil texture of the plots in this study we
316 quantify the amount of terbutylazine and S-metolachlor dissolved in the runoff water lost during
317 each growing season expressed as percentage of the total amount applied. It was calculated by
318 multiplying volume of runoff by mean concentration of dissolved herbicides (Runoff Volume [m³]
319 x Concentration [! g L⁻¹]) determined in the samples at each event. Overall, the greatest losses were
320 recorded following the first runoff event after herbicide application both in the check field and field
321 with the buffer strip. Our results agree with those previously reported by other authors [13]; [7];
322 [15]; [6]. We found that for CF during 2007, 2.5% of total applied terbutylazine and 0.80% of
323 distributed S-metolachlor were lost to runoff during the growing season. It is important to note that
324 in this season, 93% and 80% of the total losses of terbutylazine and S-metolachlor, respectively,
325 were recorded during the first runoff event (23 DAT). As Wauchope [50] suggests, this runoff event
326 could be defined, in the case of terbutylazine, as *catastrophic* since it produced runoff losses of 2%
327 or more of the applied amount. By contrast, the buffered field lost only 0.014% of total applied
328 terbutylazine while no metolachlor losses were observed during the season. In 2008, CF had runoff
329 losses of only 0.11% and 0.05% of terbutylazine and S-metolachlor, respectively. Overall the
330 season, total losses of the two compounds from BF were 0.006% for terbutylazine, while no S-
331 metolachlor losses were measured. These low values might be due to two facts the first 2008 runoff
332 event (9 DAT) produced lower runoff outflows and the buffer strip was well covered by weeds.

333 **4. Conclusions**

334 The present experiment assessed the effect of a 6 m wide buffer strip on movement of two
335 herbicides (terbutylazine and S-metolachlor) and one metabolite (desethyl-terbutylazine) by
336 runoff. We found that the highest concentrations of chemicals were transported by outflows when

337 runoff events occurred close to herbicide application. These findings, as reported by other studies,
338 confirmed that terbuthylazine, desethyl-terbuthylazine, and S-metolachlor are easily transported
339 through runoff water. The presence of a buffer strip allowed important reduction (>90%) of
340 chemicals content in water, in particular during the first runoff events.

341 Terbuthylazine and S-metolachlor total losses in dissolved water phase were particularly high in
342 2007, as much as 2.6% and 0.9% of the amount applied, respectively. Desethyl-terbuthylazine was
343 detected in runoff waters at higher amount in the first runoff events and in general, it resulted
344 detected in runoff waters longer than the other two chemicals. The risk of surface water
345 contamination by S-metolachlor is highest early after herbicide application. Its high water solubility
346 favors its presence throughout the soil profile, but it makes it easily transportable by runoff into
347 surface waters early after its application. For the studied herbicides, rainfall close to the time of
348 herbicide application (within 14 days) may cause a significant transfer of compounds via runoff.

349 Degradation of molecules in the study was fast, particularly in 2008. This is probably because of the
350 shallow depth of sampling, the characteristics of the soil particle size and to the rainy spring in
351 2008. Despite several studies investigated the presence of desethyl-terbuthylazine in water
352 environment, less information are available on its behaviour into the soil. Fate of desethyl-
353 terbuthylazine in soil was strictly related to parent compound degradation and it was influenced by
354 occurrence of rainfall events.

355 The present study demonstrated that even in sandy loam soils, transfers of S-metolachlor,
356 terbuthylazine and desethyl-terbuthylazine with runoff waters may occur. Although herbicides with
357 high mobility and low K_d were more vulnerable to leaching, they certainly can be easily transported
358 by runoff during the first weeks after herbicide distribution.

359 These results also showed that on plain fields, 6 m buffer strips can play an important role in the
360 reduction of water body contamination for the herbicides studied here, in particular. Even if buffer
361 strip did not completely stop the runoff transport, the concentrations of the chemicals studied in
362 runoff waters were greatly reduced, particularly at the first runoff events when the amounts
363 transported are high. This can significantly contribute to the reduction of water outflow and to total
364 herbicides transported.

365 In conclusion, buffer strips could be considered as useful mitigation measure of pesticide runoff and
366 its adoption should be supported by national authorities.

367 **Acknowledgements**

368 This study was financially supported by the Agricultural Department of the Regione Piemonte,
369 Italy. The authors thank experimental station technicians for their valuable contributions in the field
370 operations. Appreciation is further extended to the members of the group in Sustainable Weed

371 Management of the Department of Agronomy, Forest and Land Management of the University of
372 Turin, which helped the authors during the study.

373 **References**

- 374 [1]Griffini, O., Bao, M. L., Barbieri, C., Burrini, D., & Pantani, F., B. Environ. Contam. Tox. ,
375 **59**(2), 202 (1997). <http://dx.doi.org/10.1007/s001289900465>.
- 376 [2]Guzzella, L., Pozzoni, F., & Giuliano, G., Environ. Pollut., **142**(2), 344 (2006).
377 <http://dx.doi.org/10.1016/j.envpol.2005.10.037>.
- 378 [3]Larson, J. S., Gilliom R. J., Capel P. D., U.S. GEOLOGICAL SURVEY, **98**(4222), 1 (1999).
- 379 [4]Paris, P., De santis T., Esposito D., Pace Emanuele, Romoli D., & S., U., Report 2007-2008-
380 Istituto per la Sicurezza e la Protezione Ambientale (ISPRA), Roma, Italy (2010).
- 381 [5]Parris, K., Int. J. Water Resour. Dev., **27**(1), 33 (2011).
382 <http://dx.doi.org/10.1080/07900627.2010.531898>.
- 383 [6]Riise, G., Lundekvam, H., Wu, Q. L., Haugen, L. E., & Mulder, J., Environ. Geochem. Heal.
384 **26**(2), 269 (2004). <http://dx.doi.org/10.1023/B:EGAH.0000039590.84335.d6>.
- 385 [7]Leonard, R. A., Movement of pesticides into surface waters Pesticides in the soil - Environment:
386 processes, impacts and modelling. Soil Society of America Book Series (Vol. 2, pp. 303
387 (1990).
- 388 [8]Carter, A., Pesticide Outlook, 11(4), 149 (2000). <http://dx.doi.org/10.1039/b006243j>.
- 389 [9]Mueller, T. C., Shaw, D. R., & Witt, W. W., Weed Technol., **13**(2), 341 (1999).
- 390 [10]Wauchope, R. D., Graney, R. L., Cryer, S., Eadsforth, C., Klein, A. W., & D., R. K., Pure Appl.
391 Chem., **67**(12), 2089 (1995). <http://dx.doi.org/10.1351/pac199567122089>.
- 392 [11]Webster, E. P., & Shaw, D. R., Weed Sci., **44** (3), 662 (1996).
- 393 [12]Balsari, P., Marucco P., Tamagnone M., Ferrero A., Vidotto F., Tesio F., et al., Report: Ricerca
394 e sperimentazione nella difesa delle colture - Sintesi delle attività 2007-2010. Regione
395 Piemonte - Assessorato Agricoltura, Foreste, Caccia e Pesca - Direzione agricoltura, Torino,
396 Italia, (2010).
- 397 [13]Gaynor, J. D., MacTavish, D. C., & Findlay, W. I., J. Environ. Qual., **24**(2), 246 (1995).
398 <http://dx.doi.org/10.2134/jeq1995.00472425002400020006x>.
- 399 [14]Müller, K., Trollove, M., James, T. K., & Rahman, A., Aust. J. Soil Res., **42**(1), 17 (2004).
400 <http://dx.doi.org/10.1071/SR03090>.
- 401 [15]Ng, H. Y. F., & Clegg, S. B., Sci. Tot. Environ, **193**(3), 215 (1997),
402 [http://dx.doi.org/10.1016/S0048-9697\(96\)05342-9](http://dx.doi.org/10.1016/S0048-9697(96)05342-9).
- 403 [16]Wauchope R.D., J. Environ. Qual., **7**(4), 459 (1978).
404 <http://dx.doi.org/10.2134/jeq1978.74459x>.

- 405 [17]CORPEN. (2007). Report, Comite d'orientation pour des pratiques agricoles respectueuses de
406 l'environnement. Group zone tampons, Premiere edition, Paris, 1997.
407 [http://www.developpement-](http://www.developpement-durable.gouv.fr/IMG/pdf/DGALN_fonctions_environn_zones_temp_bd.pdf)
408 [durable.gouv.fr/IMG/pdf/DGALN_fonctions_environn_zones_temp_bd.pdf](http://www.developpement-durable.gouv.fr/IMG/pdf/DGALN_fonctions_environn_zones_temp_bd.pdf).
- 409 [18]Krutz, L. J., Senseman, S. A., Zablutowicz, R. M., & Matocha, M. A., *Weed Sci.*, **53**(3),353
410 (2005). <http://dx.doi.org/10.1614/WS-03-079R2>.
- 411 [19]Lacas, J. G., Voltz, M., Gouy, V., Carluer, N., & Gril, J. J., *Agronomie*, **25**(2), 253 (2005).
- 412 [20]USDA, United States Department of Agriculture- Natural Conservation Service (2000).
413 <http://www.in.nrcs.usda.gov/technical/agronomy/newconbuf.pdf>.
- 414 [21]Zanin, G., Otto S., Masin R., Ferrero A., Milan M., Vidotto F., Proceedings of Conference on :
415 Protezione dei corpi idrici superficiali dall'inquinamento da agrofarmaci. Società Italiana per
416 la Ricerca sulla Flora Infestante (SIRFI), Bologna, Italia, 2009, pp. 55 (2009).
- 417 [22]Reichemberger S., Bach M., Skitschak A., Frede H. G., *Sci. Tot. Environ.*, **384** (1-3), 1 (2007).
- 418 [23]Norris, V., *Water Resour. Manag.*, **7**(4), 257 (1993). <http://dx.doi.org/10.1007/BF00872284>.
- 419 [24]Patty, L., Real, B., & Gril, J., *J. Pestic. Sci.*, **49**(3), 243 (1997).
420 [http://dx.doi.org/10.1002/\(SICI\)1096-9063\(199703\)49:3<243::AID-PS510>3.0.CO;2-8](http://dx.doi.org/10.1002/(SICI)1096-9063(199703)49:3<243::AID-PS510>3.0.CO;2-8).
- 421 [25]Smith, A. M., Iowa State University, University Extension, 4. (1999)
422 <http://www.extension.iastate.edu/Publications/PM1507.pdf> 7
- 423 [26]Rankins, J., A., Shaw, D. R., & Boyette, M., *Weed Sci.*, **49**(5), 647 (2001).
424 [http://dx.doi.org/10.1614/0043-1745\(2001\)049\[0647:PGFSFR\]2.0.CO;2](http://dx.doi.org/10.1614/0043-1745(2001)049[0647:PGFSFR]2.0.CO;2).
- 425 [27]Arora, K., Mickelson, S. K., Helmers, M. J., & Baker, J. L., *J. Amer. Water Resour. Assoc.*,
426 **46**(3), 618 (2010).
- 427 [28]Shultz, R. C., Wray P. H., Colletti J. P., Isehart T. M., Rodrigues C. A., Kueh A. (1997).
428 University Extension, Iowa State University, 1 (1997).
429 <http://www.extension.iastate.edu/Publications/PM1626b.pdf>
- 430 [29]Carter, A. D., *Weed Res.*, **40**(1), 113 (2000). [http://dx.doi.org/10.1046/j.1365-](http://dx.doi.org/10.1046/j.1365-3180.2000.00157.x)
431 [3180.2000.00157.x](http://dx.doi.org/10.1046/j.1365-3180.2000.00157.x).
- 432 [30]Gustafson D. I., *Environ. Toxicol. Chem.*, **8**(4), 339 (1989).
433 <http://dx.doi.org/10.1002/etc.5620080411>.
- 434 [31]Patakioutas, G. I., & Albanis, T. A., *Int. J. Environ. An. Ch.*, **84**(1-3), 103 (2004).
435 <http://dx.doi.org/10.1080/03067310310001593747>.
- 436 [32]Youbin, S., Kazuhiro, T., Akio, I., & Dongmei, Z., *Pest Manag. Sci.*, **65**(9), 956 (2009).
437 <http://dx.doi.org/10.1002/ps.1779>.

- 438 [33]Accinelli, C., Dinelli, G., Vicari, A., & Catizone, P., *Biol. Fert. Soils*, **33**(6), 495 (2001).
439 <http://dx.doi.org/10.1007/s003740100358>.
- 440 [34]Dinelli, G., Accinelli, C., Vicari, A., & Catizone, P., *J. Agri. Food Chem.*, **48**(7), 3037 (2000).
441 <http://dx.doi.org/10.1021/jf991057b>.
- 442 [35]Walker, A., & Brown, P. A., *B. Environ. Contam. Tox.*, **34**(2), 143 (1985).
443 <http://dx.doi.org/10.1007/BF01609716>
- 444 [36]Wauchope, R. D., Buttler, T. M., Hornsby, A. G., Augustijn-Beckers, P. W. M., & Burt, J. P.,
445 *Rev. Environ. Contam. T.*, **123**, 1 (1992). http://dx.doi.org/10.1007/978-1-4612-2862-2_1.
- 446 [37]Sarmah, A. K., Close, M. E., & Mason, N. W. H., *J. Environ. Sci. Heal. B.*, **44**(4), 325-336,
447 (2009). <http://dx.doi.org/10.1080/03601230902800960>.
- 448 [38]Dousset, S., Mouvet, C., & Schiavon, M., *Pest. Sci.*, **49**(1), 9 (1997).
449 [http://dx.doi.org/10.1002/\(SICI\)1096-9063\(199701\)49:1<9::AID-PS472>3.0.CO;2-F](http://dx.doi.org/10.1002/(SICI)1096-9063(199701)49:1<9::AID-PS472>3.0.CO;2-F).
- 450 [39]James, T. K., Rahman, A., Holland, P. T., McNaughton, D. E., & Heiermann, M., presented at
451 the Plant Protection Conference, Proceedings of 51st N.Z., (1998).
- 452 [40]Sahid, I., & Teoh, S., *B. Environ. Contam. Tox.*, **52**(2), 226 (1994).
453 <http://dx.doi.org/10.1007/BF00198492>.
- 454 [41]Langenbach, T., Schroll, R., & Scheunert, I., *Chemosphere*, **45**(3), 387 (2001).
455 [http://dx.doi.org/10.1016/S0045-6535\(00\)00548-8](http://dx.doi.org/10.1016/S0045-6535(00)00548-8).
- 456 [42]Gerstl, Z., Sluszny, C., Alayof, A., & Graber, E. R., *Sci. Tot. Environ.*, **196**(2), 119 (1997).
457 [http://dx.doi.org/10.1016/S0048-9697\(96\)05406-X](http://dx.doi.org/10.1016/S0048-9697(96)05406-X).
- 458 [43]Bottoni, P., Keizer, J., & Funari, E., *Chemosphere*, **32**(7), 1401 (1996).
459 [http://dx.doi.org/10.1016/0045-6535\(96\)00049-5](http://dx.doi.org/10.1016/0045-6535(96)00049-5).
- 460 [44]Asmussen, L. E., White, J., A. W., Hauser, E. W., & Sheridan, J. M., *J. Environ. Qual.*, **6**(2),
461 159 (1977). <http://dx.doi.org/10.2134/jeq1977.00472425000600020011x>.
- 462 [45]Rohde, W. A., Asmussen, L. E., Hauser, E. W., Wauchope, R. D., & Allison, H. D., *J. Environ.*
463 *Qual.*, **9**(1), 37 (1980). <http://dx.doi.org/10.2134/jeq1980.00472425000900010011x>.
- 464 [46]Arora K., Mickelson S.K., Baker J.L., *T. Am. Soc. Agric. Engi.*, **46** (3), 635 (2003).
- 465 [47]Boyd P. M., Baker J.L., Mickelson S.K., Ahmed S.I., *T. Am. Soc. Agric. Engi.*, **46** (3), pp. 675
466 (2003).
- 467 [48]Krutz, L. J., Senseman, S. A., McInnes, K. J., Zuberer, D. A., & Tierney, D. P., *J. Agri. Food*
468 *Chem.*, **51**(25), 7379 (2003). <http://dx.doi.org/10.1021/jf0348572>.
- 469 [49]Le Bissonnais, Y., Lecomte, V., & Cerdan, O., *Agronomie*, **24**(3), 129 (2004).
470 <http://dx.doi.org/10.1051/agro:2004010>.

471 [50]Pätzold, S., Klein, C., & Brümmer, G. W., Soil Use Manage., **23**(3), 294 (2007).

472 <http://dx.doi.org/10.1111/j.1475-2743.2007.00097.x>.

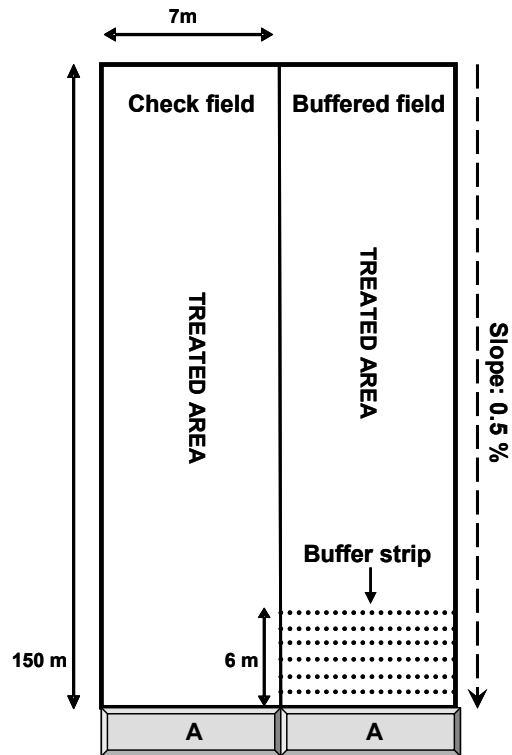
473

474

475

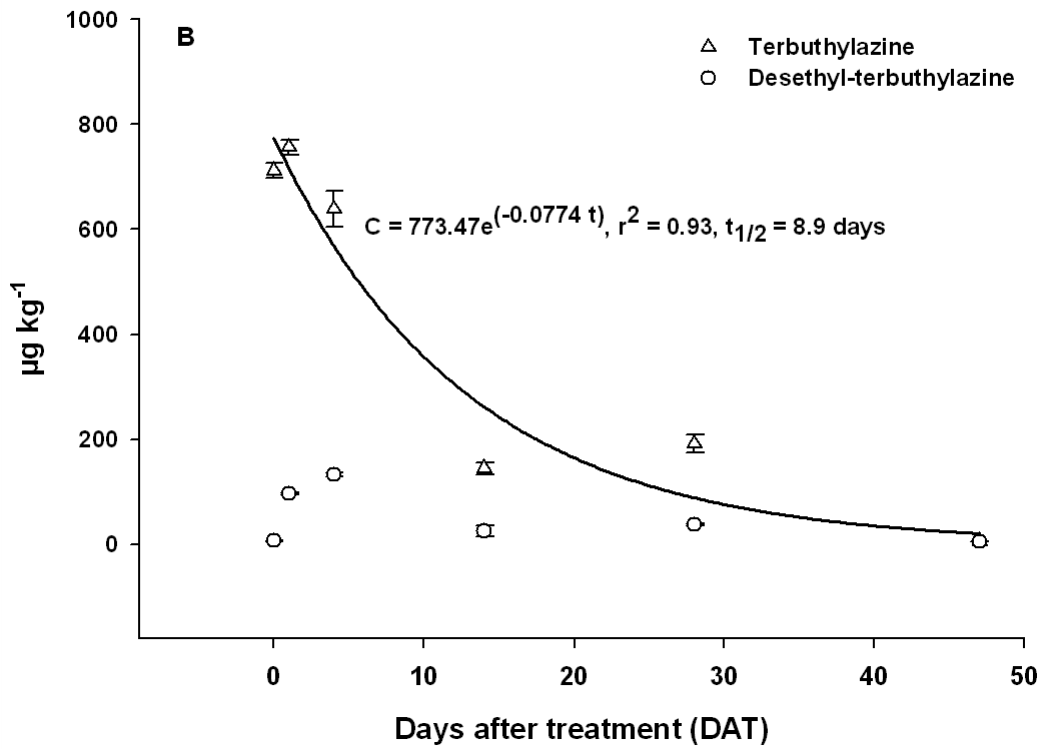
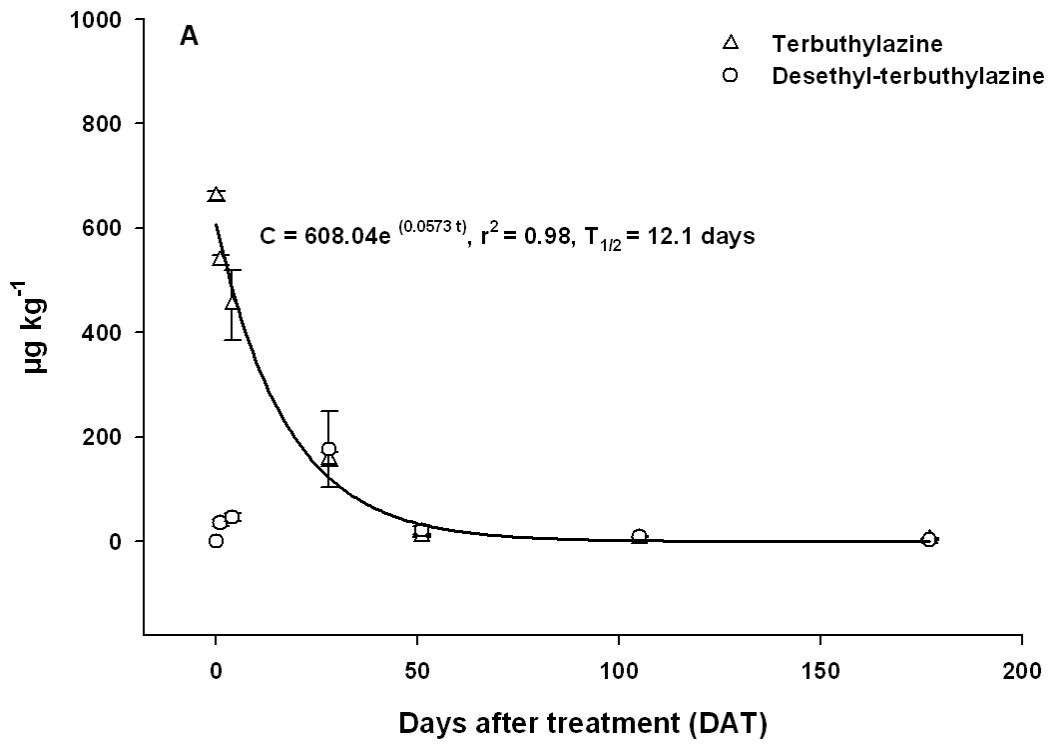
476

477

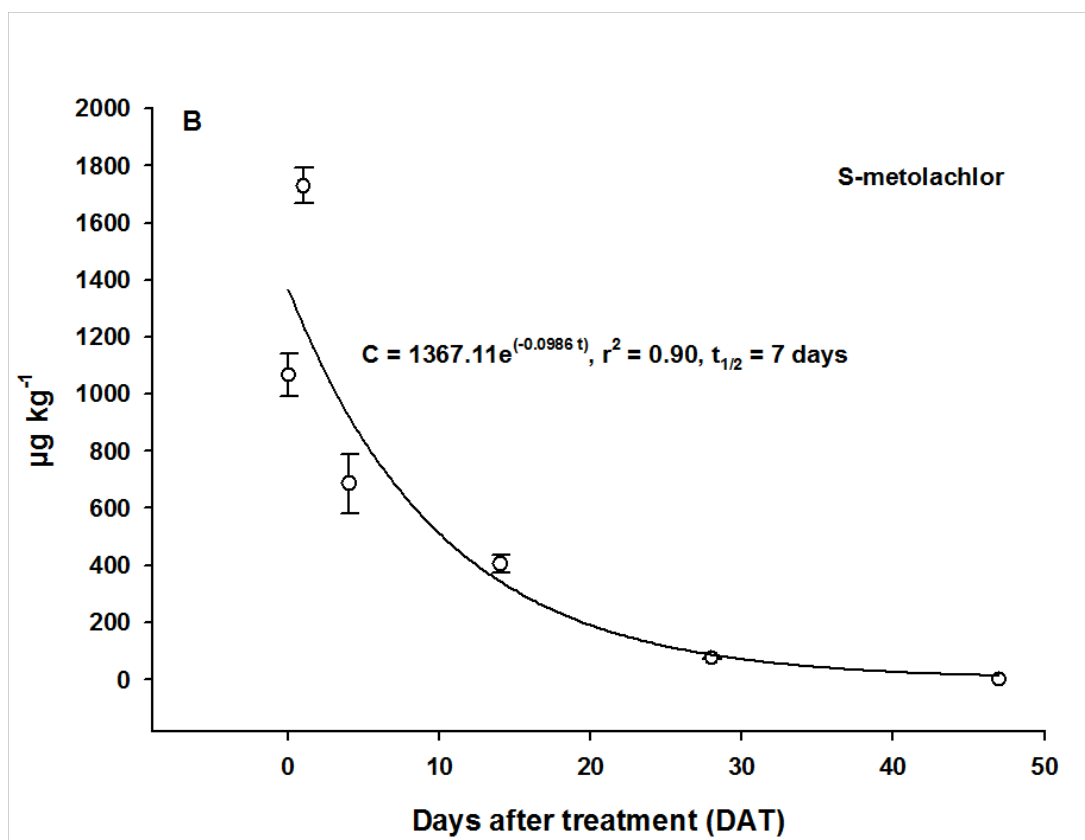
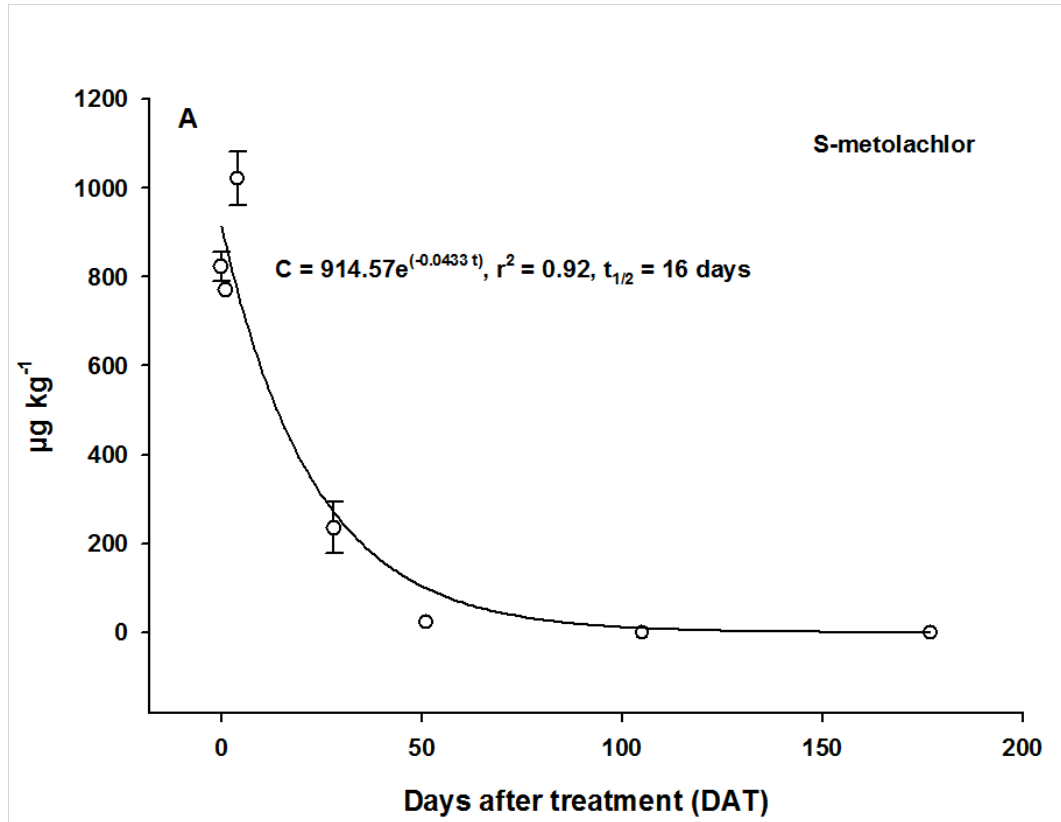


478 **Figure 1: Experimental layout adopted. A: weirs and automatic samplers.**

479



481 Figure 2: Terbutylazine and desethyl-terbutylazine concentrations (µg kg⁻¹) in soil of treated areas in 2007 (A)
 482 e 2008 (B). Arithmetic mean of three bulk replications ± SE.



484 Figure 3: S-metolachlor concentrations ($\mu\text{g kg}^{-1}$) in soil of treated areas in 2007 (A) and 2008 (B). Arithmetic
485 mean of three bulk replications \pm SE.

486 **Table 1. Physico-chemical properties of terbuthylazine, desethyl-terbuthylazine, and S-metolachlor (PPDB, The**
487 **Pesticide Properties Database, AERU, University of Hertfordshire, 2009).**

	Terbuthylazine	Desethyl-terbuthylazine	S-metolachlor
Water solubility (mg L⁻¹)	6.6	327.1	480
Koc (ml g⁻¹)	231	121	226.1
DT50 in field (days)	22.4	28.6	21
GUS index	3.07	3.5	1.9

488

489

490
491
492

Table 2: Concentration of terbuthylazine, desethyl-terbuthylazine, and S-metolachlor detected in water samples collected after each runoff event in 2007 and 2008. Values are expressed in $\mu\text{g L}^{-1}$. Arithmetic mean of three replications \pm SE. Same-letter values are not significantly different (Tuckey's range test; $\alpha=0.05$).

DAT	Check field ($\mu\text{g L}^{-1}$)			Field with buffer strip ($\mu\text{g L}^{-1}$)		
	TBA	DTA	MET	TBA	DTA	MET
2007						
23 (R)	136.2 (11.5) a	43.5 (1.6) a	80.4 (1.7)	0.8 (0.1) b	0.9 (0.1) b	< LOD
60 (R)	13.5 (1.5)	15.9 (1.1)	< LOD	NR	NR	NR
90 (I)	6.6 (0.2) a	4.4 (1.3) a	< LOD	0.5 (0.2) b	1.3 (0.2) b	< LOD
120 (I)	0.9 (0.1)	0.2 (0.1)	< LOD	NR	NR	NR
120 (R)	3.1 (0.2)	2.5 (0.1) a	< LOD	< LOQ	0.5 (0.1) b	< LOD
2008						
9 (R)	40.6 (0.6)	11.4 (0.2)	66.7 (0.5)	NR	NR	NR
67 (R)	2.1 (0.1)	0.9 (0.0) a	0.6 (0.2)	< LOQ	0.4 (0.1) b	< LOD
74 (R)	1.2 (1.0) a	0.8 (0.1) a	< LOD	0.5 (0.2) b	0.4 (0.1) b	< LOD
94 (R)	0.9 (0.1)	2.1 (0.1) a	< LOD	< LOD	1.0 (0.0) b	< LOD
112 (I)	0.2 (0.5)	< LOD	< LOD	< LOD	< LOD	< LOD
127 (I)	< LOD	< LOQ	< LOD	< LOD	< LOQ	< LOD

493
494
495
496
497

Note 1: DAT (days after treatment); TBA (terbuthylazine); DTA (desethyl-terbuthylazine); MET (S-metolachlor); NR (no runoff; R (Rainfall); I (Irrigation); LOD=0.08 $\mu\text{g L}^{-1}$ for TBA and MET, 0.05 $\mu\text{g L}^{-1}$ for DTA; LOQ=0.23 $\mu\text{g L}^{-1}$ for TBA and MET, 0.14 $\mu\text{g L}^{-1}$ for DTA.

498 **Table 3: Runoff events, water volumes applied during irrigations and corresponding measured runoff volumes**
 499 **in 2007 and 2008.**

DAT	Precipitation (mm)	Temperature °C	Irrigation volume (m³)		Runoff volume (m³)	
2007						
23 (R)	44.4	10.7	-	-	15.2	13.9
60 (R)	34.7	21.2	-	-	9.5	7.9
90 (I)	-	17.8	51	47	1.5	1.1
104 (I)	-	22.9	48	49	NR	NR
120 (I)	-	18.8	49	50	0.2	-
120 (R)	24.2	18.8			3.5	1.4
2008						
9 (R)	12.6	10.6	-	-	0.9	NR
67 (R)	61.6	17.2	-	-	25.1	24.6
74 (R)	30.6	15.9	-	-	7.2	5.3
94 (R)	23.2	21.9	-	-	2.9	0.7
112 (I)	-	20.9	33	42	2.2	3.7
127 (I)	-	23.2	37	39	3.2	4.4

Note 2: DAT (days after treatment); NR: no runoff; R: Rainfall; I: Irrigation

500

501