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(Article begins on next page)

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

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Abstract

The effectiveness of a 6m-wide vegetative buffer strip for reducing runoff of S-metolachlor, terbuthylazine and desethyl-terbuthylazine was studied in 2007-2008 in Northern Italy. Two cultivated fields, with and without the buffer strip, were compared. Residues of the chemicals were investigated in runoff water collected after runoff events and their dissipation in the soil was studied. The highest concentration of the chemicals in water occurred in samples collected from the unbuffered field at the first runoff events. Losses of terbuthylazine and S-metolachlor in runoff waters were particularly high in 2007 (2.6% and 0.9% of the amount applied, respectively). Soil half-life of terbuthylazine and S-metolachlor ranged between 13.5 and 8.9 days and 16 and 7 days, respectively. Presence of desethyl-terbuthylazine was related to parent compound degradation. The buffer strip allowed important reduction of chemicals content in water (>90%), in particular during the first runoff events.

Keywords: runoff, buffer strip, terbuthylazine, desethyl-terbuthylazine, S-metolachlor, herbicide

1. Introduction

Both surface and ground water can be contaminated by agrochemicals used to protect crops from pests and diseases [1]; [2]; [3]; [4]; [5]; [6]. Prevention, or at least mitigation, of herbicidal runoff water contamination is a major environmental challenge facing both Italy and Europe. In fact, the European Water Framework Directive (2000/60EC) established severe limits on the pesticide levels that could be found in environmental and drinking waters. Individual compounds and the total across all pesticides were set to a maximum of 0.10 µg/L and 0.50 µg/L, respectively. Now, the introduction of the Directive on sustainable use of pesticides (2009/128/EC) will require that European Member States do more efforts to reduce water pollution associated with drift, runoff, and leaching of Plant Protection Products (PPPs). Vegetative buffer strips (VBSs), the subject of the study described here, are one defense that may be helpful in efforts to curb the deleterious effects of runoff and its consequent water contamination.

Runoff, the flow of water, sediments, organic materials, and chemicals over the soil surface, is one of the main ways through which agrochemicals may reach surface waters [7]. The magnitude of this phenomenon is highly related to several factors: the amount of rainfall occurring after pesticide application, pesticide characteristics, and soil slope and texture [8]; [9]; [10]; [11]. Runoff events that occur shortly after to herbicide application account for the largest losses [12]; [13]; [7]; [9]; [14]; [15]; [6]. Notwithstanding severe rainfall shortly after application, total herbicide losses are small—generally, less than 0.5% of the amount applied for most herbicides [16].

67   Vegetative buffer strips (VBSs) are the major tool to prevent runoff from entering the water stream

68   and/or carrying away sediments, organic materials, nutrients, and chemicals [17]; [18]; [19]; [20];

69   [21]; [22] . VBSs are usually set up along creeks, streams, ponds, or lakes to prevent water pollution

70   of their waters [19]; [23]; [24]; [25]. VBS efficacy is generally expressed as a percent reduction in

71   PPP concentration as compared to a non-buffered control. According to the literature, VBS

72   effectiveness is generally above 50% [26]; [20]; [11]. Typically, runoff volume retention (intended

73   as infiltration), have averaged 45% (with ranges between 0 and 100%) across different studies

74   under both natural and simulated experimental conditions [27].

75   Many and diverse factors have been shown to influence the success of VBSs. The primary

76   determinant of VBS efficacy is its design. The minimum VBS width that will yield an acceptable

77   level of effectiveness must be dimensioned relative to slope steepness and correlated to its primary

78   function (to reduce sediment transport or increase infiltration). The USDA recommends buffer strip

79   widths of at least 6 m for sediment and strongly adsorbed PPPs. Similarly, the same agency

80   recommends at least 30 m for dissolved compounds—nitrate as well as weakly and moderately

81   adsorbed PPPs. Since several species can be profitably seeded in a buffer strip, multi-species VBSs

82   are preferable to those composed of a single-species because a combination of plant species

83   generally results in stronger mitigation capacity [28].

84   Secondary to design, but not without consequence, are numerous other factors affecting VBS

85   effectiveness. The surrounding cropland characteristics and environmental conditions play roles:

86   slope, micro-topography, soil type, rainfall intensity, infiltration capacity, strip width, and irrigation

87   volume [29]; [30]; [14]; [31]. Pesticide characteristics (solubility, Koc, and persistence) as well as

88   soil texture, organic content, and crop and tillage management also show great influence [27]; [30];

89   [31]. Finally, VBS filtration activity can vary with the specific PPPs used, the sediment amount

90   carried by runoff water into the strip, the water retention time in the VBS, the soil infiltration rate,

91   the uniformity of water flow through the VBS, and maintenance of the strip itself [29]; [25].

92   Although many studies on buffer strips have been conducted, there is a need for more research in

93   this field. Most of the studies have been conducted at the field scale but on small plots and the

94   behavior of metabolites has not been investigated. The objective of this experiment was to

95   determine the effectiveness of 6 m wide VBSs for reducing off-site movement by runoff of two

96   herbicides (S-metolachlor and terbuthylazine and one metabolite, desethyl-terbuthylazine) from

97   maize fields. Terbuthylazine and S-metolachlor are selective herbicides widely applied to maize for

98   the control of broadleaved weed and grasses, respectively. These two herbicides, together with

99   desethyl-terbuthylazine, the main metabolite of terbuthylazine, are among the most frequently

100   found chemicals in surface and ground water [2]; [3]; [4]. Losses by runoff of terbuthylazine, S-

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

2. Materials and methods

2.1. Experimental design

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

The experimental site consisted of two large plots cultivated with maize, each approximately 1050 m^2 (150x7 m) with a 0.5% slope (Figure 1). The plots were characterized by sandy loam soil (68.77% sand, 26.79% silt, 4.45% clay), 0.9% organic matter, and a pH=7.63. One plot had an untreated 6 m-wide vegetated buffer strip at the downstream head (buffered field; BF) while the other plot had no buffer strip and was considered as the control (check field; CF). The buffer strip was cultivated with maize, and weeds were allowed to grow freely. Weeds grown in the buffer strip were representative of the common maize weeds of the North Italian area. They were mostly represented by *Echinochloa crus-galli* (L.) P. Beauv., *Panicum dichotomiflorum* Michx., *Chenopodium album* L., *Portulaca oleracea* L., *Galinsoga quadriradiata* Cav., and *Poa pratensis* L. Their density, expressed as percentage of soil coverage, ranged from 40% (ten days after the crop sowing) to 100% during the rest of the season. Hand mowing was conducted as needed.

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

2.2 Chemicals studied

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

2.3 Agronomic practices

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

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

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

2.4 Soil sampling

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

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

2.5 Water sampling

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

2.6 Herbicide extraction and analysis

2.6.1 Soil

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

168 separated by filtration on anidrous 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 C_{18} 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 Spectraphisics P2000 equipped with a C18 Supelcosil ^{TM}

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 plhase H_2O pH 3/CH_3CN 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 trough 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 (176.31µg kg^{-1}). However, even at 51 DAT its concentration was about

234   21 µg kg^{-1}; six months after herbicide application it was less than 4 µg kg^{-1}. During 2008, desethyl-

235   terbuthylazine formation in the soil quickened and its peak value was registered 4 DAT (218.47 µg

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 µg kg^{-1} while at its final sampling (47 DAT), it was no more than 5 µg 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 µg L^{-1} and 15.9 µg 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 μg L^{-1} for terbuthylazine, 0.9 μg L^{-1} for
281 desethyl-terbuthylazine, and 0.6 μg 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 Terbuthylazine 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 terbuthylazine 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 [m^3]

319 x Concentration [$\mu g \, L^{-1}$]) 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 terbuthylazine 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 terbuthylazine 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 terbuthylazine, 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 terbuthylazine while no metolachlor losses were observed during the season. In 2008, CF had runoff

329 losses of only 0.11% and 0.05% of terbuthylazine and S-metolachlor, respectively. Overall the

330 season, total losses of the two compounds from BF were 0.006% for terbuthylazine, 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 (terbuthylazine and S-metolachlor) and one metabolite (desethyl-terbuthylazine) 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 Kd 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.

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References

[1]Griffini, O., Bao, M. L., Barbieri, C., Burrini, D., & Pantani, F., B. Environ. Contam. Tox. , **59**(2), 202 (1997). http://dx.doi.org/10.1007/s001289900465.

[2]Guzzella, L., Pozzoni, F., & Giuliano, G., Environ. Pollut., **142**(2), 344 (2006). http://dx.doi.org/10.1016/j.envpol.2005.10.037.

[3]Larson, J. S., Gilliom R. J., Capel P. D., U.S. GEOLOGICAL SURVEY, **98**(4222), 1 (1999).

[4]Paris, P., De santis T., Esposito D., Pace Emanuele, Romoli D., & S., U., Report 2007-2008- Istituto per la Sicurezza e la Protezione Ambientale (ISPRA), Roma, Italy (2010).

[5]Parris, K., Int. J. Water Resour. Dev., **27**(1), 33 (2011). http://dx.doi.org/10.1080/07900627.2010.531898.

[6]Riise, G., Lundekvam, H., Wu, Q. L., Haugen, L. E., & Mulder, J., Environ. Geochem. Heal. **26**(2), 269 (2004). http://dx.doi.org/10.1023/B:EGAH.0000039590.84335.d6.

[7]Leonard, R. A., Movement of pesticides into surface waters Pesticides in the soil - Environment: processes, impacts and modelling. Soil Society of America Book Series (Vol. 2, pp. 303 (1990).

[8]Carter, A., Pesticide Outlook, 11(4), 149 (2000). http://dx.doi.org/10.1039/b006243j.

[9]Mueller, T. C., Shaw, D. R., & Witt, W. W., Weed Technol., **13**(2), 341 (1999).

[10]Wauchope, R. D., Graney, R. L., Cryer, S., Eadsforth, C., Klein, A. W., & D., R. K., Pure Appl. Chem., **67**(12), 2089 (1995). http://dx.doi.org/10.1351/pac199567122089.

[11]Webster, E. P., & Shaw, D. R., Weed Sci., **44** (3), 662 (1996).

[12]Balsari, P., Marucco P., Tamagnone M., Ferrero A., Vidotto F., Tesio F., et al., Report: Ricerca e sperimentazione nella difesa delle colture - Sintesi delle attività 2007-2010. Regione Piemonte - Assessorato Agricoltura, Foreste, Caccia e Pesca - Direzione agricoltura, Torino, Italia, (2010).

[13]Gaynor, J. D., MacTavish, D. C., & Findlay, W. I., J. Environ. Qual., **24**(2), 246 (1995). http://dx.doi.org/10.2134/jeq1995.00472425002400020006x.

[14]Müller, K., Trolove, M., James, T. K., & Rahman, A., Aust. J. Soil Res., **42**(1), 17 (2004). http://dx.doi.org/10.1071/SR03090.

[15]Ng, H. Y. F., & Clegg, S. B., Sci. Tot. Environ, **193**(3), 215 (1997), http://dx.doi.org/10.1016/S0048-9697(96)05342-9.

[16]Wauchope R.D., J. Environ. Qual., **7**(4), 459 (1978). http://dx.doi.org/10.2134/jeq1978.74459x.

405 [17]CORPEN. (2007). Report, Comite d'orientation pour des pratiques agricoles respectueuses de
406   l'environement.   Group   zone   tampons,   Premiere   edition,   Paris,   1997.
407   http://www.developpement-
408   durable.gouv.fr/IMG/pdf/DGALN_fonctions_environn_zones_temp_bd.pdf.
409 [18]Krutz, L. J., Senseman, S. A., Zablotowicz, 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.
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.
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-
431   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.

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.

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.

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.

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).

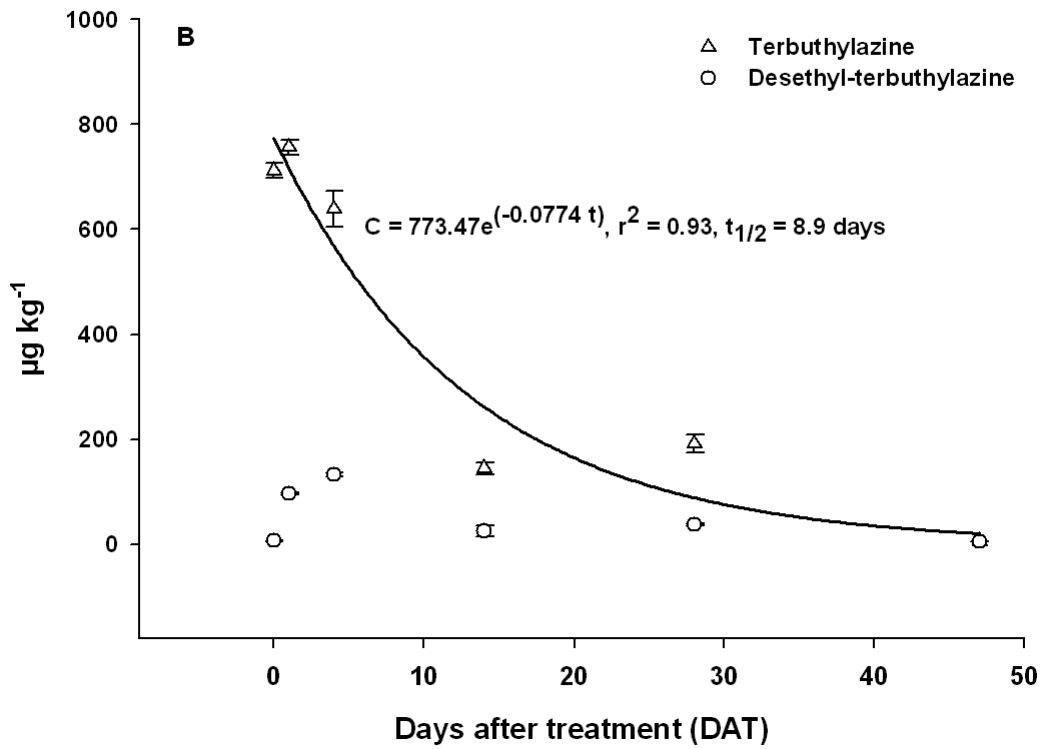472 http://dx.doi.org/10.1111/j.1475-2743.2007.00097.x.
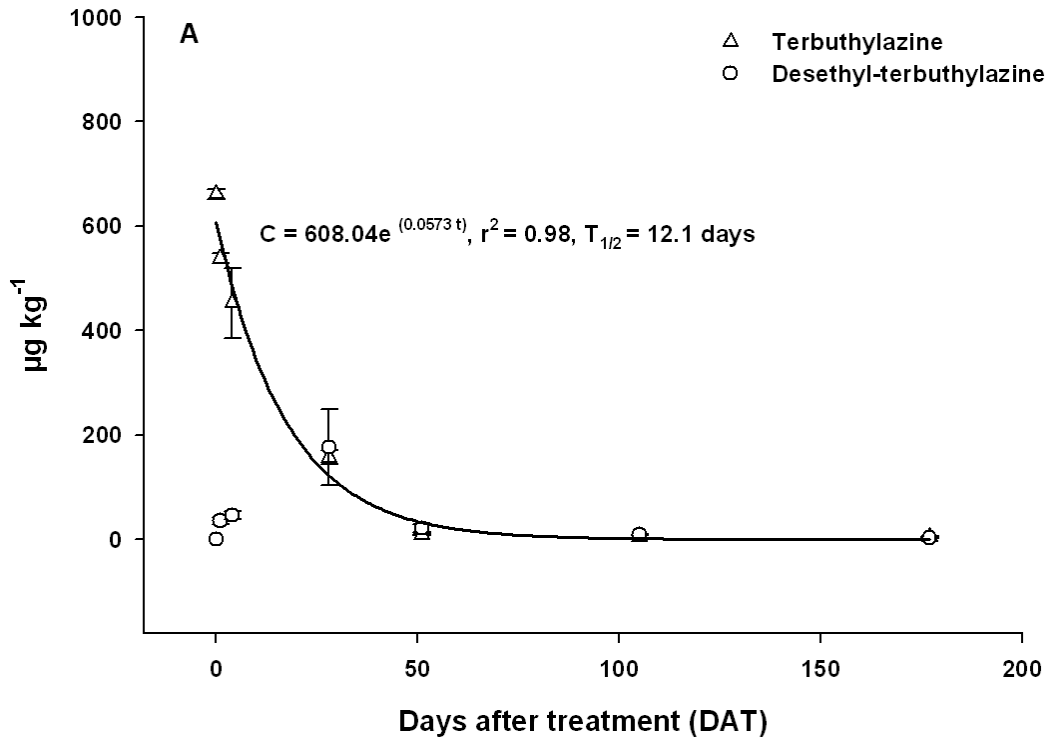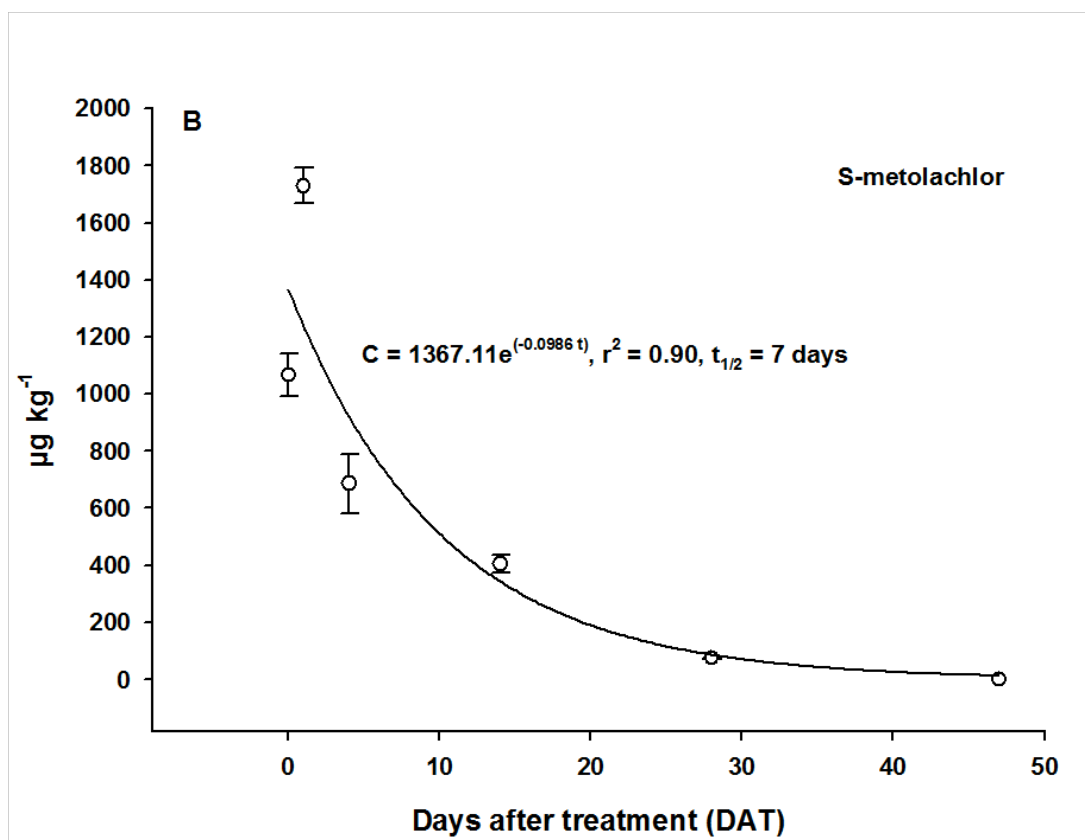
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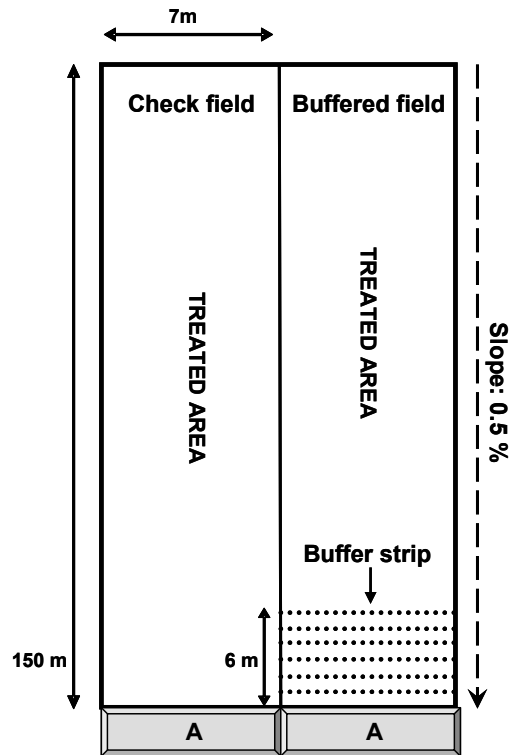
478 **Figure 1: Experimental layout adopted. A: weirs and automatic samplers.**

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

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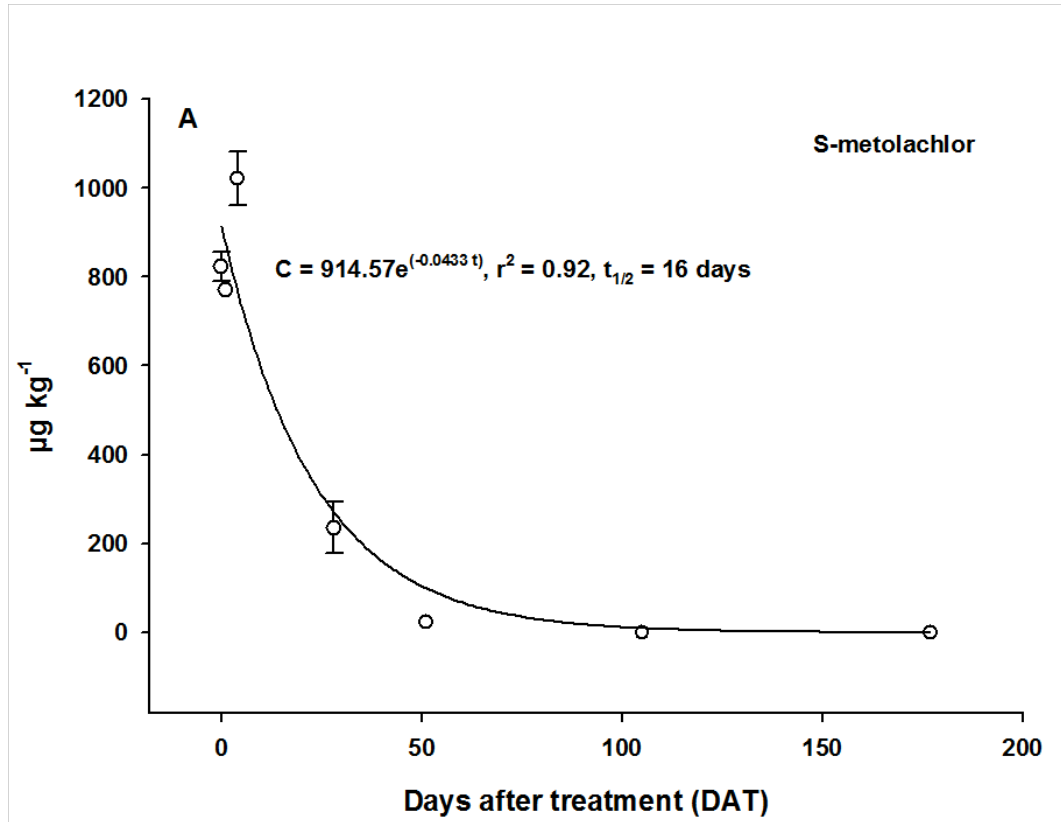
484 **Figure 3: S-metolachlor concentrations (µg kg⁻¹) in soil of treated areas in 2007 (A) and 2008 (B). Arithmetic**
485 **mean of three bulk replications ± SE.**

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

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489

490 **Table 2: Concentration of terbuthylazine, desethyl-terbuthylazine, and S-metolachlor detected in water samples**
491 **collected after each runoff event in 2007 and 2008. Values are expressed in μg L^{-1}. Arithmetic mean of three**
492 **replications ± SE. Same-letter values are not significantly different (Tuckey's range test; α=0.05).**

DAT	Check field (μg L -1)			Field with buffer strip (μg L -1)		
2007	**TBA**	**DTA**	**MET**	**TBA**	**DTA**	**MET**
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 *Note 1: DAT (days after treatment); TBA (terbuthylazine); DTA (desethyl-terbuthylazine); MET (S-metolachlor); NR (no runoff; R*
494 *(Rainfall); I (Irrigation); LOD=0.08 μg L -1 for TBA and MET, 0.05 μg L -1 for DTA; LOQ=0.23 μg L -1 for TBA and MET, 0.14*
495 *μg L -1 for DTA.*
496
497

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 (m^3)		Runoff volume (m^3)	
			CF	BF	CF	BF
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

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

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