Seasonal terbuthylazine monitoring in olive groves under conventional tillage

Seguimiento estacional de terbutilazina en un olivar sometido a laboreo tradicional
Monitorização sazonal da terbutilazina em olivais submetidos a lavoura convencional

ABSTRACT

During the last two decades there have been several herbicide pollution episodes of both surface and groundwater in areas where olive groves are established. These episodes always coincided with rainy periods. Understanding the evolution of herbicides in this type of plantation depending on the season of application is critical, especially when conventional tillage is used. Field monitoring of terbuthylazine in the first 2 cm of soil and in runoff water and sediment yield was carried out after winter and spring soil applications. Soil disappearance of terbuthylazine was associated with the first important rainfall event in both seasons (41 mm in spring and 30 mm in winter). At the end of the experiment (85 days and 103 mm rain in spring, and 107 days and 148 mm in winter), no terbuthylazine soil residues were found in winter, whereas 15% of terbuthylazine applied remained in spring. A higher percentage of the applied terbuthylazine in runoff water was recovered in winter (0.53%) than in spring (0.16%). However, no differences in terbuthylazine residues in sediment yields were observed (0.45% in spring and 0.46% winter). These data suggest that the dissipation of terbuthylazine from soil is related not only to the runoff process but also to other processes like leaching, which are more relevant at the end of the winter season.

RESUMEN

Durante las últimas dos décadas se han producido episodios de contaminación, tanto de aguas superficiales como subterráneas, por herbicidas usados en el olivar, coincidiendo con periodos de lluvia. De ahí la necesidad de conocer la evolución de algunos herbicidas en este tipo de cultivo dependiendo de su época de aplicación y, especialmente, cuando el sistema de laboreo usado es el laboreo tradicional. Se ha llevado a cabo un monitoreo del herbicida terbutilazina, tanto en los dos primeros centímetros de suelo como en las escorrientías y sedimentos producidos tras diferentes eventos de lluvia. La desaparición de terbutilazina del suelo está claramente asociada a los primeros eventos de lluvia importantes en ambas estaciones (41 mm en primavera y 30 mm en invierno). Al final del experimento (85 días y 103 mm en primavera, y 107 días y 148 mm en invierno) se recuperó el 15% de la terbutilazina aplicada en el suelo en primavera, mientras que en invierno no se encontraron residuos. Los porcentajes de terbutilazina recuperadas en escorrientía fueron también mayores en la campaña invernal (0.55%) que en la de primavera (0.17%), mientras que no se detectaron diferencias en las cantidades de terbutilazina recuperadas en los sedimentos entre ambas estaciones (0.45% y 0.46% en primavera e inverno, respectivamente). Estos datos ponen de manifiesto que la desaparición de terbutilazina no solo va a estar ligada a procesos de escorrientía sino también a procesos de lixiviación, más relevantes al final del periodo invernal.

RESUMO

Nas últimas décadas foram detetados alguns episódios de poluição com herbicidas em águas superficiais e subterrâneas, em áreas onde existem olivais coincidindo esses episódios com períodos de chuvas. Por esta razão, é necessário conhecer a evolução de alguns herbicidas nos olivais em função da sua aplicação sazonal. Isto é particularmente importante quando se usa a lavoura convencional. Para esse efeito, procedeu-se a monitorização do herbicida terbutilazina nos primeiros centímetros de solo, nas águas de escorriência e nos sedimentos produzidos após a corridência de várias

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chuvadas. O desaparecimento da terbutilazina do solo está associada à primeira precipitação em ambas as estações (41 mm na primavera e 30 mm no inverno). Até ao fim do ensaio de inverno, não foram recuperados do solo resíduos de terbutilazina, no entanto cerca de 15% da terbutilazina aplicada na primavera foi recuperada no fim do ensaio. No ensaio de escorrência a terbutilazina aplicada foi recuperada em maior percentagem no inverno (0,55%) do que na primavera (0,17%). No entanto, não ocorreram diferenças nas quantidades de terbutilazina nos sedimentos durante as duas estações. Isto está de acordo com os valores de escorrência e de sedimentos acumulados nos tanques em ambas as estações do ano. Estes dados mostram que o desaparecimento da terbutilazina do solo está relacionado esencialmente ao processo de lixiviação mais relevante no fim do período invernal e em menor extensão com a escorrência.

1. Introduction

The negative environmental impact of pesticide use remains a topic of interest, mainly due to its great influence on human health especially when rivers, reservoirs and ground waters are affected. Those impacts may be severe when a given crop is concentrated in an extensive monoculture area, as is usual with rice, vineyards and olives. These three cultivars require diverse and intense pesticide treatment (herbicide, insecticide and fungicide) throughout the crop cycle (Espigares et al. 1997; Padovani et al. 2006; Bermúdez-Couso et al. 2007; Hermosín et al. 2013). Olive crops are located in countries of the Mediterranean basin, especially southern Spain where almost 30% of its total cropped land is occupied by olive trees (Gómez and Giráldez 2009). This crop has intrinsic characteristics that can be linked to surface and ground waters pollution episodes by pesticides (Hermosín et al. 2010; Hermosín et al. 2013): a) olive crops are established in areas with very adverse climate conditions like long hot and dry periods followed by short cold seasons with heavy rainfall events (Mediterranean climate), b) the rainy period coincides with olive tree herbicide applications during harvesting (beginning of winter) and flowering (spring), thus increasing possibility of non-point diffusion transport of pesticides to waterbodies, c) most of the olives groves are planted on poor soils under conventional tillage with slope in the 10-30% range (Francia-Martínez et al. 2006; Gómez and Giráldez 2009) and d) low plant density combined with scarce soil vegetation cover enhances erosion processes and the loss of chemicals adsorbed to soil particles by runoff. For those reasons, the Spanish case of the olive crop is of special concern, and in addition, most of the land under cultivation is concentrated in the Guadalquivir valley with several surface water reservoirs devoted to human consumption.

Conventional tillage, no tillage with herbicide used to maintain bare soil and no tillage with cover crops are the most studied managements (Pastor et al. 2000; Sánchez-Moreno et al. 2014). However, they are focused on soil erosion, fertility and water conservation studies. Low or non-tillage managements are gaining importance in olive orchards (Franco and Calatrava 2012), but conventional tillage is still maintained in many areas like Southern Spain. There are few works which monitored herbicide as conventional tillage in olive orchards (Sanchez-Moreno et al. 2014), although other crops have been taken into account in this type of study (Atucha et al. 2013; Mantzos et al. 2014). There are several aspects associated to conventional tillage that could have a great influence on soil pesticide dissipation such as seasonal application and chemical characteristics of the pesticides (Navarro et
al. 2008, Hermosín et al. 2013). Therefore, our objectives were to monitor soil herbicide content, runoff and sediment yield during two different seasons, spring and winter, for one year and to assess the relation of the herbicide depletion with soil processes affecting herbicide losses. The herbicide chosen for this study was terbuthylazine because it has been widely used in olive orchards and it has been strongly related to several episodes of reservoirs contamination in Andalusian olive groves areas. Hermosín et al. (2013) reported very high level of surface and ground water contamination with terbuthylazine in olive crop areas.

2. Materials and Methods

2.1. Soil and herbicide properties

Field herbicide monitoring was carried out on an olive farm located in western Seville, Spain, 37° 20' 33.6'' N 6° 13' 44'' W. The olive plantation was established with the table olive variety Gordal planted at 8 x 6 m. The slope is uniform in a north-west direction with an average steepness of 11%. This area has a Mediterranean climate characterized by heavy rain concentrated in late fall and winter, and followed by a dry period during the rest of the year. Two plots of 60 x 4 m, devoted to conventional tillage (CT) from 2003, were used as replicates.

| Table 1. Physico-chemical soil properties |
|-------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Sand (%) | Silt (%) | Clay (%) | Texture | pH | CE (mS/cm) | CaCO₃ (%) | OC (%) | OM (%) | N (%) | C/N |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 55 | 28 | 17 | Sandy loam | 8.40 | 0.10 | 28 | 0.78 | 1.34 | 0.06 | 13 |

Terbuthylazine soil applications were carried out in two different seasons: spring (March 2012) and late fall (November 2012). Both applications corresponded with those actually done on olive tree plantations (Fernández-Escobar and Barranco 2008). In the first case, herbicide field monitoring was accomplished in the spring season (from March 14th to June 6th) whereas in the second case, herbicide field monitoring was accomplished in the late fall and winter (from November 26th to March 3rd). In this last case, most of the experimental study was achieved in winter and so is referred to for the rest of the work as the “winter season”. Terbuthylazine (6-chloro-N-(1,1-dimethyl)-N´-ethyl-1,3,5-triazine-2,4-diamine) is an herbicide used as pre- or post-emergence weed control with a water solubility of 6.6 mg l⁻¹, vapor pressure of 0.15 mPa at 25°C (non-volatile), octanol:water partition coefficient (K<sub>OW</sub> or logP) of 3.21, a DT₅₀ field range of 22.0-74.4 days (medium persistence), Kf (Freundlich sorption parameter) value of 2.1-10.5 and GUS value 3.07 (high leaching potential), according to the Pesticide Properties Database (PPDB 2012). Commercial product was applied to the plots as Cuña (terbuthylazine 50% w/v) at a field dose of 2 L ha⁻¹. The herbicide application was carried out with a back-pack sprayer using 16 L of commercial product applied at 6 passes per minute until full coverage of the plot. In the years prior to our study, paraquat 12% and diquat 8%
at a rate of 4 L ha⁻¹ were applied to these plots. Also, the soil surface in the tree line was kept bare through the periodical use of herbicides fluroxipir and flazasulfuron.

2.2. Herbicide monitoring

Herbicide monitoring of CT plots involved soil sampling, as well as sampling of runoff and sediment accumulated in collection tanks, in two different seasons (spring and winter). In the case of soil sampling, only a part of the treated area was sampled, in order to discard heterogeneity produced at the beginning and end of herbicide application (Figure 1). Three soil samples, spaced 1 m each, were taken from every tree at 2.5 m from the tree trunk. The soil samples were taken with a core sampler of 6 cm diameter and 2 cm depth. The first 2 cm of soil were chosen for soil sampling because the depletion of some compounds such as Br by runoff occurred principally in the upper 1.5-2 cm of soil (Ahuja and Lehman 1983). The soil sampling was carried out at 0, 7, 15, 30, 55 and 85 days after herbicide application in spring season, and at 0, 7, 15, 44, 66, 91 and 107 days after herbicide application in winter season. In the laboratory, 20 g of air dried and sieved soil samples were mixed to obtain 60 g of one composite sample. Duplicates of this composite sample were extracted and analyzed by HPLC to determine pesticide soil residues.
Runoff and sediment yields generated in each plot were collected in three fiberglass tanks (Figure 1) with flow splitters (ratio 1:15) allowing measurement of up to 230 mm of runoff. An automatic weather station was also located in this sampling site. The tank sampling was done as described by Gómez et al. (2009). Briefly, the collection of water and sediment in the tank was done on the first working day after a single large rain event, or several rain pulses or events. Runoff volume and wet sediment weight were measured directly in the tanks. A well-mixed water and sediment sample was taken from each tank for laboratory analysis of herbicide residues by GC-MS.

2.3. Herbicide extraction and analysis of samples

a) Soil samples. Herbicide extraction from soil samples was carried out with 5 g of soil to which 10 ml of methanol was added. After shaking 24 h, centrifugation (8,000 r.p.m., 10 min) was accomplished and supernatants were filtered (0.45 µm) prior to analysis of herbicide residues by HPLC. Previously it was checked that this extraction method gave a recovery efficiency of 94% and a Relative Standard Deviation (RSD) value of 1.30% ($n = 8$).

The chromatographic system consisted of a photo diode array detector (2996 PDA) and a Waters (Milford, MA) 1525 system equipped with 717 autosampler. The column was a Nova-Pack C18 column (150 mm length × 3.9 mm i.d.) with mobile phase of 50:50 acetonitrile/water at a flow rate of 1 ml min$^{-1}$, 25 µl injection volume and UV detection at 220 nm. External calibration curves with standard solutions between 0.1 and 2 mg L$^{-1}$ were used in the calculations. The linear calibration resulted in correlation coefficients greater than 0.99 and the limit of quantification (LOQ) of the analytical method for the determination of terbuthylazine was 0.05 mg L$^{-1}$.

b) Water and sediment samples: Water samples were analysed by liquid/liquid extraction adding 15 ml of dichloromethane to 15 ml of water samples. After 30 min shaking, the solution was allowed to decant during 24 h and 10 ml of dichloromethane were removed and evaporated to dryness by rotary evaporation. The final extract was recovered with 1 ml of cyclohexane and analyzed by GC-MS. 2 g of dried sediment samples were extracted with 20 ml of acetonitrile. After shaking for 20 min, and sonication for another 10 min, samples were centrifuged 5 min at 4200 r.p.m. and supernatants removed for evaporating with a rotary evaporator until dryness. Final extract was recovered with 2 ml of cyclohexane and analyzed by GC-MS. Both extraction procedures were previously assayed with spiked water and soil giving a yield of 74% (RSD of 5% and $n = 4$) and 90% (RSD of 19% and $n = 4$), respectively.

GC-MS analytical conditions were as follows: Gas chromatographic performance was conducted using CLARUS 500 (Perkin Elmer) and chromatographic separation was performed on Elite-5ms UI column (30 mm x 0.25 mm, 0.25 m film thickness, Perkin Elmer). The column oven temperature was set to 70 ºC, then increased to 180 ºC at 25 ºC/min$^{-1}$, and held for 5 min, then rapped to 300 ºC at 12 ºC/min, and held for 5 min, with helium gas flowing at 1 ml min$^{-1}$. The injection volume was 4 µl. MS was conducted with a single quadrupole Mass Spectrometer (Clarus Mass Spectrometer, Perkin Elmer) in electron impact ionization (EI). The MS source conditions were transfer line temperature 280 ºC and ion source temperature 240 ºC. Linearity was assessed by the determination coefficient ($r^2$) of a calibration curve that was created based on six points of different concentrations of terbuthylazine standards ranging from 0.01 to 1 µg ml$^{-1}$. The LOD and LOQ were determined using signal-to-noise ratios of 3 and 10, respectively.

All the results obtained were expressed in percentage of herbicide recovered from the total of herbicide applied. Standard error was calculated from the replicates of every sample and represented in tables as parentheses, and in graphs as error bars. Also, a statistic analysis of t-Student was performed in the first cm of soil, runoff water and sediments samples.
3. Results and Discussion

3.1. Rainfall events and runoff and sediment yield

Rainfall occurred during field herbicide monitoring, as individual and total events, are presented in Table 2 and 3 for spring and winter seasons, respectively. Three rainfall events were recorded in spring season, whereas six rainfall events were recorded in winter season. Total values of rainfall events were 103 mm in spring season and 148 mm in winter season. Along the entire study, the highest rainfall event (55 mm) was in the winter season, 107 days after field herbicide application. This is in agreement with the seasonal precipitation pattern of the Mediterranean region characterized by scarce but often high intensity rainfall in winter.

Table 2. Individual and total rainfall events, and runoff and sediments, recorded during the spring season

<table>
<thead>
<tr>
<th>Days*</th>
<th>Rainfall (mm)</th>
<th>Runoff (mm)</th>
<th>Sediments (T ha⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>41</td>
<td>0.89 (± 0.385)ᵃ</td>
<td>2.45 (± 0.624)</td>
</tr>
<tr>
<td>55</td>
<td>34</td>
<td>1.09 (± 0.179)</td>
<td>3.57 (± 0.330)</td>
</tr>
<tr>
<td>85</td>
<td>28</td>
<td>1.34 (± 0.062)</td>
<td>2.36 (± 0.437)</td>
</tr>
<tr>
<td>Total</td>
<td>103</td>
<td>3.32 (± 0.626)</td>
<td>8.38 (± 1.391)</td>
</tr>
</tbody>
</table>

ᵃDays after herbicide application; ᵇNumbers in parentheses correspond to the standard error.

Table 3. Individual and total rainfall events, and runoff and sediments, recorded during the winter season

<table>
<thead>
<tr>
<th>Days*</th>
<th>Rainfall (mm)</th>
<th>Runoff (mm)</th>
<th>Sediments (T ha⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>14</td>
<td>0.05 (± 0.009)ᵇ</td>
<td>0.98 (± 0.001)</td>
</tr>
<tr>
<td>22</td>
<td>10</td>
<td>0.02 (± 0.001)</td>
<td>-</td>
</tr>
<tr>
<td>44</td>
<td>9</td>
<td>0.86 (± 0.004)</td>
<td>1.44 (± 0.004)</td>
</tr>
<tr>
<td>66</td>
<td>30</td>
<td>1.31 (± 0.026)</td>
<td>1.37 (± 0.003)</td>
</tr>
<tr>
<td>91</td>
<td>30</td>
<td>1.61 (± 0.015)</td>
<td>2.80 (± 0.001)</td>
</tr>
<tr>
<td>107</td>
<td>55</td>
<td>1.65 (± 0.066)</td>
<td>2.74 (± 0.004)</td>
</tr>
<tr>
<td>Total</td>
<td>148</td>
<td>5.50 (± 0.121)</td>
<td>9.33 (± 0.013)</td>
</tr>
</tbody>
</table>

ᵃDays after herbicide application; ᵇNumbers in parentheses correspond to the standard error; ᶜNo sediments recovered in tanks.

Runoff water and sediment yield that accumulated in tanks during the spring and winter experiments are also summarized in Table 2 and 3. In the case of the spring season more runoff was recovered after lower rainfall events (1.34 mm after 28 mm) compared to other events that occurred in the same season (0.89 mm after 41 mm), whereas in winter, the runoff pattern was directly proportional to rainfall recorded (Table 3). Runoff data presented a large inter-seasonal variability, which is normal as it is controlled not only by rainfall characteristics but also soil conditions such as soil moisture and the period since last tillage.

Sediment yield (Table 2 and 3) was lower in the spring (8.38 T ha⁻¹) than winter season (9.33 T ha⁻¹).
in agreement with the total rainfall that occurred in both seasons. However, the difference found in sediments was not very marked compared to the large difference observed in runoff between both seasons. This could be due to the effect of recent tillage (February) prior to the spring herbicide application, which enhanced soil losses at higher rainfall and resulted in a higher sediment concentration than in winter. In any case, the olive orchard has intrinsic characteristics (cultivation on steep slopes with Mediterranean climate) that together with low soil organic matter make the olive crop environment easily erodible. Dunjó et al. (2004), found that the cultivated olive tree environment brought about the highest runoff and sediment yield compared to other Mediterranean environments.

3.2. Herbicide field monitoring

Terbutylazine monitoring in the first 2 cm of soil, in spring and winter, is represented in Figure 2. Terbutylazine followed the same soil dissipation tendency in both seasons, matching the highest decrease of herbicide in soil with the first important rainfall events (41 mm in spring and 30 mm in winter), regardless of the season. These rainfall events occurred 30 and 66 days after herbicide application in spring and winter, respectively. From this point, terbutylazine residues in soil followed a smooth further decrease in both seasons. At the end of soil monitoring experiment, 15% of the terbutylazine applied was recovered in spring (85 days), whereas no terbutylazine was recovered in winter (107 days). The data obtained from herbicide soil monitoring were fitted to a first-order kinetic, with both the linear regression equation and half-life (DT50) also represented in Figure 2. R² values higher than 0.7 indicate a good fit to this first order kinetic (Beulke and Brown 2001). Terbutylazine DT50 obtained from this experiment was 34 and 18 days in the spring and winter seasons respectively. In winter, the number of rainfall events was higher compared to those of spring, which could be determining for the low terbutylazine half-life in winter. In any case, both half-lives observed are in the same range as those found by others authors (Tomlin 2006).

Figure 2. Terbutylazine evolution in the first 2 cm of soil during the spring and winter season, linear regression equation and half-life (DT50) calculated from soil monitoring data. The representation of terbutylazine data correspond to the average values of the data recorded in two CT plot replicates.
Figure 3 represents the percentage of total applied terbuthylazine recovered in runoff water and sediments, collected during the spring and winter seasons. Only three samples were taken in spring because no runoff water and sediment yield were obtained from previous rainfall events, whereas in winter, 6 samples were taken. In spring, the highest amount of terbuthylazine recovered in runoff water (0.12%) and sediments (0.35%) was after 30 days of herbicide application, corresponding to the highest rainfall event that occurred in this season. In winter, the highest amount of terbuthylazine recovered in runoff water (0.20%) was after 66 days of herbicide application, whereas in sediments (0.23%) this occurred 14 days after herbicide application. In general, the largest amounts of terbuthylazine recovered in runoff were always in the sediments during the spring experiment. However, during the winter experiment, large amounts of terbuthylazine were recovered both in the runoff waters and the sediments, depending on the sampling time. In fact, after 66 days of herbicide application, terbuthylazine was recovered only in runoff waters, coinciding with the first important rainfall event that occurred during winter season. This rainfall event could have some effect on the solubilization of terbuthylazine, enhancing its transport in the aqueous runoff phase. In any case, the highest amount of terbuthylazine recovered in runoff corresponded to the sediments, in both seasons. This can be explained because after terbuthylazine soil application, it remains free on the soil surface or associated with fine soil particles and thus, be transported on sediments after important rain events (Agassi et al. 1995).

It is important to note the large variability between data of soil dissipation and runoff from plots replicates. After a t-Student statistic analysis of average values, the results obtained from terbuthylazine soil dissipation in the first 2 cm and runoff waters during spring and winter seasons were significantly different at P > 0.95. However, the results obtained from runoff sediments during both seasons were not significantly different. Authors like Gómez et al. (2001) assume the 50% of variability is due to spatial variability of $K_s$, surface storage, and the depth to claypan, and the other 50% to variability in rainfall among plots and measurements error in runoff.

Figure 3. Terbuthylazine (% of total applied) recovered in runoff waters and sediments, in spring and in winter seasons. The representation of terbuthylazine data correspond to the average values of the data recorded in the two replicates of CT plots.
When we compare the data obtained from monitoring of terbuthylazine in the first 2 cm of soil and the data obtained from runoff waters and sediments, for the spring season the highest disappearance of terbuthylazine from soil coincides with the highest content of terbuthylazine in runoff water and sediments (30 days). In the winter application, relevant concentration of terbuthylazine in runoff water was measured after 66 days, matching with the highest disappearance of herbicide from the first cm of soil. However, this fact did not occur with regard to the content of terbuthylazine in sediments in winter season. In any case, these amounts of terbuthylazine (runoff water and sediments) are too small to explain the depletion of terbuthylazine from soil observed during the monitoring of the first 2 cm of soil. Therefore other processes such as volatilization, leaching or degradation, in addition to runoff, may be involved in terbuthylazine soil dissipation.

Terbuthylazine soil losses due to volatilization processes are usually too low (0.26-0.65% of applied) (Schroll et al. 1999) to explain the high dissipation found in this work. Degradation and leaching processes have been demonstrated to be important pathways of terbuthylazine soil disappearance. In fact, triazine herbicides are easily degradable under some particular conditions of soil moisture and temperature (Barriuso and Houot 1996) and to have a high leaching potential, especially in soils with low organic matter (Toiber-Yasur et al. 1999). In order to know the effect of these processes in terbuthylazine soil dissipation, incubation and leaching experiments at lab scales were carried out with this same soil (Calderón et al. 2013). These degradation experiments do not have great relevance in terbuthylazine depletion from the soil studied in this work. Almost 80% of the herbicide applied remained in soil after 62 days of study. However in the experiment achieved in soil columns, high leaching of terbuthylazine was observed in this soil because 70% of the herbicide applied was recovered in leachates after 53 days of study. These findings are in agreement with the high amount of terbuthylazine, exceeding the limits established by the EU for drinking waters, found in groundwater close to olive orchard and after rainfall events occurred shortly after herbicide application (Hermosin et al. 2013). For that reason, we consider leaching and, in less extent degradation and runoff, like the main process responsible of terbuthylazine soil dissipation. Nevertheless, although low terbuthylazine losses in runoff have been observed in this study, traces of this herbicide from different runoff points can become important sources of water contamination in areas where olive orchard are established and under this type of soil management.

4. Conclusions

Soil losses of terbuthylazine associated with runoff water and sediments were low. Terbuthylazine soil depletion is closely related to rain events. The depletion could be related to leaching processes and to a lesser extent runoff, both being more severe in winter than in spring. The highest terbuthylazine surface and groundwater contamination potential is clearly associated with the winter herbicide application for harvesting in olive orchards.

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