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Impact of herbicides used in olive groves on waters of the Guadalquivir river basin (southern Spain)

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ABSTRACT

A long-term programme was carried out to monitor the water concentrations of at least 4 of 6 herbicides (atrazine, simazine, terbuthylazine, diuron, oxyfluorfen, and diflufenican) and 2 of their metabolites (desethylatrazine and desethylsimazine) and relate them to the impact of olive crops in the Guadalquivir river basin. The mean surface water concentrations found were mostly above the UE recommended limit for drinking water (0.1 $\mu g\,L^{-1}$), but showed a decrease with time: diuron from 2.36 $\mu g\,L^{-1}$ in 2003 to 0.03 $\mu g\,L^{-1}$ in 2010, and terbuthylazine from 0.89 $\mu g\,L^{-1}$ in 2008 to 0.20 $\mu g\,L^{-1}$ in 2010. The mean herbicide concentrations for groundwaters were lower than those for surface waters, but some were still above the limit for drinking water: diuron ranged from 0.39 $\mu g\,L^{-1}$ in 2003 to 0.01 $\mu g\,L^{-1}$ in 2010, and terbuthylazine from 0.70 $\mu g\,L^{-1}$ in 2008 to 0.22 $\mu g\,L^{-1}$ in 2010. The maximum herbicide water concentrations, in both surface and ground waters, were measured in winter and spring, coinciding with rainfall periods. Herbicide concentrations were found to be related: (a) to soil runoff processes in surface waters and (b) to leaching or preferential flow through soil into groundwaters. Herbicide solubility, half-life, and field dose were also related with their respective water levels. The acceptable evolution of herbicide concentration in surface waters from 2002 to 2010 is associated to the current regional and national regulations and actions, which should be maintained.

1. Introduction

A number of authors have reported the presence of pesticides in waters at various sites in Spain, mainly related with a wide range of agricultural practices affecting rivers, reservoirs, wetlands, and groundwater (Espigares et al., 1997; Belmonte-Vega et al., 2005; Sanchez-Camazano et al., 2005; Bermudez-Couso et al., 2007; Arias-Estevez et al., 2008; Hildebrandt et al., 2008). However, most of these studies monitored only a short period of time and did not focus on a specific crop. Some works have recently drawn attention to pesticide levels in Europe (Kreuger, 1998; Haarstad and Ludvigsen, 2007; Loos et al., 2010) and in different Spanish rivers or wetlands in relation to particular crops (Belmonte-Vega et al., 2005; Sanchez-Camazano et al., 2005; Hildebrandt et al., 2008; Barba-Brioso et al., 2010; Palma et al., 2009; Köck-Schulmeyer et al., 2011). Some of these studies, in areas close to (Palma et al., 2009) or in (Espigares et al., 1997; Belmonte-Vega et al., 2005; Barba-Brioso et al., 2010) southern Spain, reported very high concentrations of herbicides used in olive crops. At the same time, long-term monitoring is very useful because it enables correlating various factors such as regional farming practices with climatic and geographical conditions (Kreuger, 1998) and even suggesting some improvement in crop management practices (Haarstad and Ludvigsen, 2007; Davis et al., 2011).

The olive is a crop historically related to the Mediterranean region, and more than 95% of the world olive production is located in Mediterranean countries; in Andalusia, southern Spain, the 1.5 Mha of olive groves occupies almost 30% of its total cropped land (Gómez-Calero, 2009). In the last decade, Common Agricultural Policy in Europe (CAP-EU) has enhanced agricultural production, prompting farmers to intensify their exploitations (Metzidakis et al., 2008; Testi et al., 2009). This has resulted in some negative effects on the environment, such as water scarcity and quality (Espigares et al., 1997; de Graaff and Eppink, 1999; Belmonte-Vega et al., 2005; Gomez et al., 2009; Lecina et al., 2010; Palma et al., 2009; Barba-Brioso et al., 2010). Olive production, like that of other crops, is strongly dependent on pesticide use due to climatic and soil conditions that favour pests and weeds. The Spanish case of the olive crop is of special concern because most of the land under cultivation is concentrated in the Guadalquivir valley, from the north-eastern edge to the south-western, with a slope of 10–30% and on poor soils (Gómez-Calero, 2009), with several surface water reservoirs devoted to human consumption. In addition, the rainfall

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coincides with the cropping season, when herbicides are applied to the soil to keep it clean of weeds and to facilitate harvesting of the olive fruits. These conditions increase herbicide being lost from the soil and entering, by non-point diffusion transport processes, bodies of water (Kookana et al., 1998; Arias-Estevez et al., 2008). Hence, in years of heavy rainfall, such as in 2001–2005 in southern Spain, there were several public alarms as a result of very high levels of the herbicides used in olive groves being detected in surface water reservoirs meant for human consumption. Although certain management techniques, such as controlled release formulations (Cruz-Guzman et al., 2004; Trigo et al., 2009), organic residue amendments (Cox et al., 1997; Cabrera et al., 2008), or field green covers (Gomez-Calero and Giraldez, 2009; Moreno et al., 2009; Zuazo et al., 2011), have been suggested as environmentally sustainable solutions for the presence of olive crop herbicides in waters, no systematic report on their presence can be found in the scientific bibliography.

This work reports, for the first time, the monitoring of water concentrations of herbicides used in olive groves in the Guadalquivir catchment in Andalusia (southern Spain), and their relationships with olive crop presence, soil-water processes, and the relevant regulations. Although olive production is the most important crop in southern Spain, there has been no specific study on the water herbicide presence relating to this crop in this region. Espigares et al. (1997) drew attention to the very high concentration of very toxic pesticides (organochlorine and organophosphorous insecticides) in waters of the Guadalquivir river basin, and which in some cases, such as DDT, had long been prohibited. That study monitored only one year and with regard to improving water treatment and human health. Long-term monitoring studies on herbicide presence in waters are needed not only to identify the source of pollution but also to look at designing future remediation. They should also provide historical data on water herbicide levels in order to develop new technological management strategies in a crop to enhance the sustainability. In addition, because most drinking water in Spain comes from surface water reservoirs, such studies can be useful in developing strategies to minimize the adverse impact of pesticides or in evaluating changes in pesticide policies of national or regional governments (Haarstad and Ludvigsen, 2007; Davis et al., 2011), or in the treatment of drinking water (Espigares et al., 1997).

2. Experimental

2.1. Chemicals

The chemicals monitored were those summarized in Table 1. With the exception of dimethoate, all of them are herbicides used pre- and/or post-emergence, mainly just before the olive harvesting season in October–December and in the olive flowering period, late-spring, to avoid water and nutrient competition. The insecticide dimethoate is used in summer to early autumn to control the various olive-attacking insects. Some of the herbicides were banned during the study (atrazine and simazine in 2002 and diuron in 2008–2009, while the use of terbuthylazine was limited in 2009, when it was prohibited in the olive integrated production system which increased from 10% to more than 25% in the study period), and others (oxyfluorfen and diflufenican) became increasingly used. Therefore, the chemicals were monitored in two groups during corresponding periods: (a) the first period (2002–2008, with the exception of 2004, which was not sampled), they were the herbicides atrazine, simazine, terbuthylazine, and diuron, together with their metabolites desethylsimazine and desethylterbuthylazine; and (b) the second period (2009–2010), they were the herbicides diuron, terbuthylazine, oxyfluorfen, and diflufenican, together with the insecticide dimethoate.

2.2. Sampling area and sample collection

The sampled rivers and springs were located in agricultural areas cultivated mainly with olive trees, and all of them feeding or connected to the Guadalquivir river basin. The mean annual precipitation in this basin is 580 mm, with some dry periods (2–5 years) below 400 mm. The rainfall mainly occurs in late autumn to early winter and in late winter to early spring. The geology mainly comprises limestones, dolomites, and sandstones. The soil characteristics are diverse, ranging from lithosols to poor sandy soils, prone to erosion (mainly in the eastern part) to deep, silty, heavy fertile soils in the western depression part.

The sample sites were selected after an hydrogeological study of this area performed by Pulido-Bosh and Calaforra (2000), whose main criteria were: (a) surface area devoted to the target crop (olives), (b) use rates and total usage of the target products, (c) vulnerability of upper aquifers to diffuse pollution in both typical and worst-case scenarios, (d) representative sites in streams, rivers and some reservoirs for surface water and (e) availability of representative wells and springs in the area, including a sound knowledge of their hydrogeological characteristics and easy access for sampling. The location is given in Fig. 1 and the description in Table 2. The deep of sampling was: (a) for surface waters 0–1 m and (b) for groundwater, in the case of the well 4–7 m and in the cases of boreholes or springs at public fountain in the tap and or at the beginning of the spring itself. The sampling schedule was based on fixed time intervals (August, November–December, and March–April), although in some years, additional sampling dates were included depending on the occurrence of very hard rain events.

The mean year precipitation during the period studied in the Guadalquivir River basin was of 640 mm, with a minimum value of 358 in 2003 and a maximum value of 990 mm in 2010. These data were given by AEMET and they were used to relate with water concentrations measured. Although olive crop have been traditionally a non-irrigated cultivar, in the last 15–20 years drip-irrigation olive groves have increased dramatically in Andalucía (Testi et al., 2009), enhanced by CAP-EU (Metzidakis et al., 2008). The irrigation in the area of study could range from 0 to 40%. However, since irrigation period is from May to September (the dry-period) and by drip-irrigation system, this irrigation water has not influence in the run-off and leaching process affecting soil applied herbicides (Testi et al., 2009).

2.3. Sample processing and analysis

The sample analysis method used was changed during the study period because of changes in the chemicals monitored in the final two years, and the availability of additional techniques. In particular, the inclusion of oxyfluorfen and diflufenican required more-accurate techniques for their monitoring, which were available at Cordoba University Services (SCAI, www.uco.es/research). Thus, the samples were analyzed in the two periods as follows:

2.3.1. Period 2002–2008

Solid-phase extraction (SPE) and liquid chromatographic techniques were applied to quantify the pesticides. Automated SPE was performed with the Visiprep SPE Vacuum Manifold (SUPELCO, Bellefonte, PA) apparatus. The cartridges (Supelclean ENVI-18 SPE Tubes, SUPELCO) contained 500 mg of C18 bonded silica material with a capacity of 6 mL. Methanol (4 mL) and water (4 mL) were used for conditioning the cartridge. Four replicates of 250 mL of water sample were passed through the corresponding cartridges at a flow-rate of 2.5 mL min^{-1}. Water residues from the cartridges were removed (10 min under a flow of nitrogen). Elution was carried out with 4 mL of ethyl acetate at a flow-rate of 1 mL min^{-1}. Evaporation of the solvent was performed under a stream of