SEASONAL DISTRIBUTION OF HERBICIDE AND INSECTICIDE RESIDUES IN THE WATER RESOURCES OF THE VINEYARD REGION OF LA RIOJA (SPAIN)

Eliseo Herrero-Hernández [a,*], M. Sonia Rodríguez-Cruz [a], Eva Pose-Juan [a], Sara Sánchez-González [a], M. Soledad Andrades [b], Maria J. Sánchez-Martín [a]

[a] *Institute of Natural Resources and Agrobiology of Salamanca (IRNASA-CSIC), Cordel de Merinas 40-52, 37008 Salamanca, Spain*

[b] *Departamento de Agricultura y Alimentación, Universidad de La Rioja, 51 Madre de Dios, 26006 Logroño, Spain*

*Corresponding author: E-mail: eliseo.herrero@irnasa.csic.es; Telephone: +34 923219606; Fax: +34 923219609

Abstract

Pesticides are needed to maintain high production in the vineyard area of La Rioja (Spain), and monitoring their spatial distribution is a priority for preserving the quality of natural resources. Accordingly, the purpose of this work was to conduct a study to evaluate the presence and seasonal distribution of herbicide and insecticide residues in ground and surface waters in this region. The monitoring network comprised 12 surface waters and 78 groundwaters, covering the three subareas (63,593 ha) into which the vineyard region is divided. The quality of natural waters was examined through the analysis of twenty-two herbicides, eight of their main degradation products, and eight insecticides. Pesticides were extracted by solid-phase extraction, and analysed by gas chromatography–mass spectrometry or by liquid-chromatography-mass spectrometry. The results reveal the presence of most of the herbicides and insecticides included in the study in one or more of the samples collected during the four campaigns. The herbicide terbuthylazine and its metabolite desethylterbuthylazine were the compounds more frequently detected (present in more than 65% of the samples across all the campaigns). Other compounds detected in more than 50% of the samples in one sampling campaign were the herbicides fluometuron, metolachlor, alachlor and ethofumesate. Insecticides were present in a small number of samples, with only pirimicarb being detected in more than 25% of the samples in March and June campaigns. The results reveal that the sum of compounds detected (mainly herbicides) was higher than 0.5 $\mu g\ L^{-1}$ in more than 50% of the samples, especially in the campaigns with the highest application of these compounds. A possible recovery of the quality of the waters was detected outside the periods of crop cultivation, although more monitoring programmes are needed to confirm this trend with a view to preventing and/or maintaining the sustainability of natural resources.

Keywords: pesticides; multi-residue analysis; surface water; groundwater; temporal evaluation; vineyards

1. Introduction

Water pollution due to the use of pesticides in agriculture is a priority issue that is currently a cause of global concern. Pesticides are needed to prevent and combat different weeds, pests and diseases, and improve crop quality and production. Their application in the environment may contaminate water resources, especially those located in intensive agricultural areas (Menezes Filho et al., 2010). An increasing number of herbicides, insecticides and fungicides have been detected in different watercourses (Masiá et al., 2015; Cotton et al., 2016; Rousis et al., 2017), some of which are destined for human consumption, so the protection of water quality has now become subject to more stringent legislation. The European Union has introduced strict directives to protect water quality, such as the REACH Regulation (EC, 2006) concerning the Registration, Evaluation, Authorization and Restriction of Chemicals, while Directive 2008/105/EC, on environmental quality standards in the field of water policy, provides a detail of priority substances (33) to be controlled in water, with pesticides making up a third of the list (EC, 2008). As regards the presence of these products in water, the maximum admissible concentration established by Directive 98/83/EC is 0.1 $\mu g L^{-1}$ for individual pesticides, and 0.5 $\mu g L^{-1}$ for the sum of pesticide concentration in drinking water (EC,1998).

The pollution of surface and groundwaters by pesticides is informed by the compounds' physicochemical characteristics (solubility in water, and their capacity to be retained by soil components and/or leached), the properties of the medium in which they are applied, their biotic (Barra Caracciolo et al., 2010) and abiotic degradation rate especially in reducing environments (Zeng et al., 2012), and climate and application technique as external factors.

Surface water contamination by pesticides is usually linked to the farming season, and its effect could be more temporal than that of groundwaters. Groundwater contamination by pesticides is more persistent being its biodegradation slower, and this may have a continuous toxicological effect on human health when used for public consumption (Kim et al., 2017).

Monitoring studies across the five continents have drawn attention to the potential that pesticides (herbicides, insecticides and fungicides) have to contaminate natural waters. Water contamination at different levels and by different compounds has been reported in several countries in Africa: Morocco (El Bakoury et al., 2008), Egypt (Nasr et al., 2009), Ghana (Agyapong et al., 2013), and the Republic of Benin (Pazou et al., 2014); the Americas: USA (Carriger et al., 2016), Costa Rica (Echeverría–Sáenz et al., 2012), Brazil (Milhome et al., 2015), and Argentina (De Gerónimo et al., 2014); Asia: Japan (Añasco et al., 2010), China (Zheng et al., 2016), India (Mamta et al., 2015), and Vietnam (Van Toan et al., 2013); and Oceania: Australia (Allinson et al., 2015) and New Zealand (Steward et al., 2014)). In Europe, different hydrogeological environments have been monitored in Germany (Reemtsma et al., 2013), France (Lopez et al., 2015), Italy (Montuori et al., 2016), Portugal (Cruzeiro et al., 2015), Denmark (Matamoros et al., 2012), and Greece (Papadakis et al., 2015), and levels of pesticides exceeding those permitted by EU legislation have been found to different extents in water resources beside agricultural areas growing different crops.

The overall cultivated area is Spain is around 17 million ha, and it is the second highest EU country in terms of agricultural activity by area (MAGRAMA, 2016). As a result, pollution due to the use of pesticides in agriculture merits special attention in different areas of the country. Some studies in the east of Spain have reported the presence in over 70% of the samples analysed of simazine, diuron and atrazine in wells used for providing irrigation and drinking waters (Postigo et al., 2010). They have also reported the presence of the insecticide chlorpyrifos and the herbicides terbuthylazine, and its degradation product deethylterbuthylazine, and diuron in over 0.1 $\mu g\ L^{-1}$ in different river basins, such as the rivers Llobregat (Masiá et al., 2015), Turia and Jucar (Ccanccapa et al., 2016a), Ebro (Ccanccapa et al., 2016b), and Guadalquivir (Hermosín et al., 2013), as well as in the Mar Menor lagoon (Moreno‒González et al., 2013) and waters in the Canary Islands (Estévez et al., 2012).

La Rioja (NW‒Spain) is a region of extensive agricultural activity, with areas dedicated mainly to cereals (40.4%), vineyards (34.6%) and olive and fruit trees (15.7%). The economy based on this activity is very important to this region, and in 2011 it was the sixth Spanish region with the highest investment per hectare in crop protection products, with a consumption of pesticides of 14 kg ha^{-1} (MAGRAMA, 2016). Vineyards are the main activity across a wide area of La Rioja classified as the Rioja Qualified Designation of Origen (DOCa Rioja). A substantial number of pesticides (herbicides, fungicides and insecticides) are being used in this wine‒growing area in different quantities depending on the weather. However, there are very few water monitoring studies on this area, with only a handful of sampling points and few compounds analysed (Navarro et al., 2010). Hildebrandt et al. (2008) have studied the presence of three triazines and their desethyl degradation products, metolachlor and metalaxyl, in the area where vineyards are the main crop, but the sampling points were too limited for a thorough assessment of the spatial water conditions.

Previous studies by the authors of this paper in the DOCa Rioja area have revealed the presence of herbicides, insecticides and fungicides in surface and groundwaters (Herrero–Hernández et al., 2012 and 2013) and in soils (Pose–Juan et al., 2015) in a high percentage of the analysed samples, even recording levels higher than permitted by EU legislation for drinking water. In addition, a temporal evaluation of fungicides in these waters has been carried out (Herrero–Hernández et al., 2016), reporting the presence of more than six fungicides in a third of the ground and surface waters in all the sampling campaigns. This research has flagged the need to evaluate the seasonal changes in other compounds used in the area as herbicides and insecticides. There is a clear lack of data regarding the presence of these compounds in the surface waters and groundwaters in this region, although their use is recommended in most of crops (herbicides) in farming or for pest control (insecticides) (MAPAMA, 2017).

Accordingly, the purpose of this work was to evaluate (i) the presence of twenty–two commonly used herbicides, eight of their main degradation products, and eight insecticides in surface and groundwaters in the vineyard areas of La Rioja (Spain), and (ii) the seasonal evolution of total concentrations of these compounds in different subareas. This involved monitoring 90 sampling points, including wells, springs, uptakes and rivers. Four campaigns were conducted over one year (September 2010, March 2011, June 2011, and September 2011). The quality of the waters was examined according to the levels **permitted by EU legislation for individual** (0.1 μg L^{-1}) or total **compounds** (0.5 μg L^{-1}), and the results could be useful for introducing strategic measures to maintain the sustainability of waters in this area.

2. Materials and methods

2.1. Chemicals

Standards of herbicides, their degradation products, and insecticides were purchased from Riedel-de-Haën (Seelze-Hannover, Germany), Fluka, and Dr. Ehrenstorfer (Augsburg, Germany) (purity ≥ 98%). These compounds belong to different chemical families, and have variable physicochemical properties (Table S1 in the Supplementary Material). Individual stock standard solutions (500 or 1000 μg mL^{-1}) for each one of the analytes were prepared in methanol, and then stored in the dark at 4 ºC. An intermediate working solution containing all the analytes in the same concentration (10 μg mL^{-1}) was prepared in methanol, and this mixture was used as spiking solution for the aqueous calibration standards. The organic solvents used for handling the standards and extractions (HPLC grade), methanol, acetonitrile and acetone, were obtained from Fisher Scientific (Loughborough, UK), being used as received. Ultra-high quality (UHQ) water was obtained with a Milli-Q water purification system (Millipore, Milford, MA, USA).

2.2. Study area and sample collection

Water samples were collected in 2-L brown glass bottles and transported to the laboratory in ice. Ninety sampling points were selected in the DOCa Rioja wine region in northern Spain, straddling the River Ebro (Fig. 1) and covering a total surface area of 63,593 ha. A description of the area can be found in previous papers published by the authors (Herrero-Hernández et al., 2013, 2016; Pose-Juan et al., 2015), as this work is part of a larger study conducted in this area to monitor the presence of pesticides and their seasonal changes in natural waters. Water samples (360 in total) were collected over a year in four consecutive campaigns: September 2010 (Sep–10), March 2011 (Mar–11), June 2011 (Jun–11) and September 2011 (Sep–11) from the three different subareas of Rioja Alavesa (ALV, 15 points), Rioja Alta (ALT, 34 points), and Rioja Baja (BAJ, 41 points). More detailed information about the sample collection procedure and area characteristics or sampling sites is included in the Supplementary Material (Table S2).

2.3. Analytical methodology

Collected samples were filtered and processed as previously reported by Herrero–Hernández et al. (2012 and 2013). Briefly, a sample volume of 500 mL was percolated through a previously conditioned polymeric solid–phase extraction cartridge (Oasis HLB, 60 mg, Waters). Elution was performed with 4 mL of acetonitrile and then 4 mL of acetone. The organic phase obtained was evaporated to dryness, and the dry residues obtained were re–dissolved and analysed by gas chromatography–mass spectrometry (GC–MS) and by liquid–chromatography–mass spectrometry (LC–MS). Chromatographic conditions, data processing, and the validation of the methodology have previously been described by the authors (Herrero–Hernández et al. 2012, 2013). Quantification was performed by external calibration using matrix–matched standards (blank water samples spiked with standard analyte solutions). Sample analyses were run in duplicate and in most cases relative standard deviations of less than 10% were recorded. The quality control parameters are shown in Tables S3 and S4 in the Supplementary Material.

2.4. Data analysis

The data on the total concentrations of pesticides determined in water samples of different areas and at different sampling times were subjected to a two–way analysis of variance (ANOVA) to verify whether the effects of sampling time or areas and their interactions were significant. The least significant difference (LSD) test at a confidence level of 95% was used to separate means. Pearson correlations were also used to relate the concentrations of pesticides detected in waters. SPSS Statistics v22.0 software for Windows (IBM Inc., Chicago, ILL, USA) was used.

3. Results and discussion

3.1. Presence of herbicides and insecticides in water samples from the DOCa Rioja area.

The residues of the herbicides and insecticides studied were evaluated in the water samples for each campaign, determining the ranges and mean concentrations and the frequency of positive samples for each compound (Tables 1–3). The results indicate that most of the herbicides and insecticides included in the study were detected in one or more of the samples in all four campaigns, although some herbicides (metamitron, isoproturon, chlorsulfuron, flazasulfuron, and the hydroxylated metabolites of triazines) and some insecticides (acephate and cypermethrin) were not detected in any one of the four campaigns. Other compounds, such as the herbicides chloridazon, diclofop–methyl, chlorotoluron and its metabolite CMPU, alachlor, linuron, atrazine and the insecticides carbaryl, dimethoate, imidacloprid and methoxyfenozide, were detected only in certain areas or sampling campaigns. Fig. 2 shows the distribution of the total samples collected from the three subareas and in each sampling period according to the percentages of samples with non–detected pesticides, or with pesticides detected below or over the legally established limit for drinking water (0.1 μg L^{-1}) for triazine herbicides and some of their degradation products: (a) phenylurea and chloroacetanilide herbicides, (b) and insecticides (c).

The most ubiquitous compounds among the herbicides in all the sampling campaigns were terbuthylazine and its metabolite DET. These compounds were detected in more than 65% of the samples in each campaign, with terbuthylazine appearing in 95% of the samples in Jun–11. Other compounds were detected in more than 50% of the samples in a campaign (metolachlor in Sep–10, fluometuron and ethofumesate in Mar–11, and alachlor in Jun–11), and in more than 25% of the samples in one or more sampling campaigns (propazine, atrazine and terbutryn, diuron, linuron, metobromuron, lenacil and acetochlor) (Fig. 2 a,b). These results are consistent with the widespread application of these herbicides due to the intensive agriculture in the area studied. Moreover, different herbicides could be applied simultaneously in most crops in the area, as significant correlation coefficients ($p<0.05$) were found between the concentrations of some compounds, i.e., between triazine compounds (propazine, atrazine, terbuthylazine and terbutryn) and urea derivatives (diuron, linuron, metobromuron and fluometuron) or chloroacetamide (alachlor). It is assumed that these compounds were used at the recommended rates, although water contamination may occur due to their regular use in local crops, considering that the application of herbicides is part of normal agronomic practices for eliminating weeds in pre– or post–emergence.

The presence of the most ubiquitous compound, terbuthylazine, indicates its increased use in recent years. This herbicide behaves differently here than in previous studies (Hildebrandt et al., 2008; Postigo et al., 2010), where terbuthylazine concentrations were lower than those recorded here. This herbicide has been used to replace other triazines, such as atrazine and propazine, which were banned in the EU in 2004, and finally withdrawn from the market in Spain and Portugal in 2007 (EC, 2004). However, several years after this ban, atrazine and propazine were still being detected in water samples, together with the degradation products DEA and DIA. They were over 0.1 μg L^{-1} although their concentrations were always very low and appeared only in a few samples. The results on detections of atrazine in this work (≈ 30% of samples), and detected concentrations > 0.1 μg L^{-1} (≈ 5% of samples), together with the increase in its maximum concentrations in Mar–11 (Tables 1–3) and the higher concentration of its degradation products DEA and DIA in Jun–11 (Table 3), indicates that this herbicide was still being used. Triazines and their degradation products have been found in groundwaters in different areas of Spain. Atrazine, propazine, simazine and two degradation products of terbuthylazine have been found in the Llobregat river basin, where the main agricultural activities are vineyards and other crops such as artichokes, lettuce, and tomatoes, with the mean concentrations found in 2011 being higher than in 2010 for most of them (Masiá et al. 2015). Elsewhere, terbuthylazine and simazine have been found in the Guadalquivir river basin, where olive groves are the main crop (Hermosín et al., 2013). Atrazine, DEA, DIA, simazine, propazine, terbuthylazine and DET have also been detected in water samples from the Turia river basin (Ccanccapa et al., 2016a). In other European countries, triazines have frequently been detected in groundwater (atrazine, DEA and DIA) (Vryzas et al., 2012) and in surface waters (atrazine, DEA and simazine) (Thomatou et al., 2013) in Greece, in most of the tap water samples collected around Paris in France (atrazine, DEA and DIA, simazine, propazine, terbuthylazine and DET) (Cotton et al., 2016), and in drinking and groundwaters (atrazine, terbuthylazine, DEA, DIA and DET) around Zagreb in Croatia (Fingler et al., 2017).

The insecticides included in this study were detected in a smaller number of samples (including surface waters and groundwaters) (Tables 1–3 and Fig. 2c). Only pirimicarb was detected in more than 30–40% of the samples in Mar–11 and Jun–11, but it was not detected in concentrations over 0.1 μg L^{-1}. The rest of the insecticides included in the study were found in fewer than 20% of the samples, and only imidacloprid and methoxyfenozide were found in all the campaigns. The highest concentrations were found for methoxyfenozide, although the highest percentage of samples with concentrations > 0.1 μg L^{-1} was found for carbaryl (Fig. 2c). Significant correlations ($p<0.05$) were found between the concentrations of some insecticides, i.e., imidacloprid and pirimicarb or chlorpyrifos, indicating their simultaneously application. These compounds are applied for tackling *ad hoc* plagues in the different areas, and the simultaneous or repeated application of different compounds in similar crops in the area was possibly due to the recommendations made by the regional authorities and experts (Government of La Rioja, 2016). The insecticides found here were generally detected in other studies monitoring pesticide pollution caused by agricultural activities (Cruzeiro et al., 2015; Papadakis et al., 2015; Ccanccapa et al., 2016b), with the exception of carbaryl, which was scarcely monitored or detected.

In addition, it should be noted that the compounds found mainly in waters are characterized with GUS index values generally >2 or even >3, such as imidacloprid and methoxyfenozide or triazines (Table S1). Compounds with GUS index values >2.8 are classified as potential leachers, and this could explain their presence in waters, together with their specific and widespread use in local crops.

3.2 Spatial and temporal evaluation of herbicides and insecticides in water samples from the DOCa Rioja area

The total concentration of herbicides (Fig. 3a,b) and insecticides (Fig. 3c,d) was determined in ground and surface waters in the different subareas of La Rioja (ALV, ALT, and BAJ) and for each sampling period (Sep–10, Mar–11, Jun–11, and Sep–11). The herbicide concentration in groundwater was as follows: BAJ (214.3 μg L^{-1}) > ALV (142.1 μg L^{-1}) > ALT (64.21 μg L^{-1}). In turn, in surface waters it was as follows: ALV (12.27 μg L^{-1}) > BAJ (8.68 μg L^{-1}) > ALT (8.337 μg L^{-1}). These concentrations were generally higher in Mar–11 (ALV and ALT) and in Sep–10 (BAJ) for groundwaters, and in Mar–11 (ALV and ALT) and in Jun–11 (BAJ) for surface waters. However, the ANOVA for comparing the means in different areas and sampling times recorded only a significant difference between total herbicide concentration in the groundwaters of BAJ and ALT (LSD=31.84), and between the concentrations in Sep–10 or Mar–11 and Sep–11 (LSD=36.76), but the effect of both factors was not significant on the total herbicides at a 95% confidence level (area p=0.072, and sampling time p=0.121). However, area and sampling time had a significant effect in the total insecticide concentration in groundwaters, recording a peak concentration in ALV (LSD=1.415, p=0.0003) and in Jun–11 (LSD=1.624, p=0.0328) (Fig. 3c). No significant differences were found in total herbicide or insecticide concentrations in surface waters. It should be noted that the total amount of herbicides and insecticides peaks in the usual period of application of herbicides (March) and insecticides (June) in the three subareas. Only in BAJ were herbicide amounts higher in Sept–10, and this was due to the high degree of pollution of one of the samples in that period. The mishandling of products could be the cause of a point contamination detected at one site in this area.

The pollution in ALV was recorded in a lower number of waters (12 ground and three surface waters) than in BAJ (35 ground and six surface waters) or ALT (31 ground and three surface waters). The results show that herbicides were detected in all the water samples in all the campaigns in ALV (Table 1), while this did not occur in ALT or in BAJ, and no herbicides were detected in some waters samples in the four campaigns (Tables 2 and 3). In the case of insecticides, no sample was detected without any in Jun–11 in surface waters from ALV and ALT (Fig. 3d). ALV could therefore be considered the most polluted area in the DOCa Rioja, despite being the smallest of the three areas in question. ALV accounts for 20.8% of the total area (63,593 ha), with vineyards being the main crop (11,500 ha). ALT and BAJ are larger, accounting for 30.3% and 35.7%, respectively, and they include other crops apart from vineyards, such as cereals, and olive and fruit trees (Fig. 1).

The higher pollution in ALV may be due to the application of a greater amount of pesticides, although this information is not available. Furthermore, the vulnerability of soils to pollution could be a factor, as the mobility and/or persistence of these compounds in soils depend on their properties and soil characteristics (Marín–Benito et al., 2009; Rodríguez–Cruz et al., 2012). Soil texture and composition were generally similar in the DOCa Rioja area, although a greater or lesser percentage of porous lithology might characterise the different subareas (Fig. 1) and affect the potential persistence of herbicides and insecticides and their mobility to waters (Pose–Juan et al., 2015).

Box and whisker plots (Fig. 4 and 5) were obtained for the dispersion of the total concentrations of herbicides or insecticides in ground and surface waters for each area and sampling period. These plots represent the 25th, 50th and 75th percentiles (horizontal lines in the box), the minimum and maximum values, but no more than 1.5 times the distance of the box (its whiskers), the outliers or values less than or equal to 3, and more than 1.5 times the distance of the box outside the quartile (o) and the extremes or values more than three times the distance of the box outside the quartile (*). The dispersion of the herbicide and insecticide concentrations found in between 25% and 50% of the samples was lower than in 50% to 75%, of the samples, with a lower dispersion of concentrations in 25% of the samples with the lowest concentrations than in 25% of the samples with the highest concentrations. These plots for samples from three areas and for all four campaigns also indicate that, in general, the peak values of the medians of total concentration without considering the outlier values correspond to the samples collected in the three areas in Mar–11 (herbicides) (Fig. 4) and Jun–11 (insecticides) (Fig. 5). This median is especially high in the case of ALV, 0.853 μg L^{-1} for groundwaters, and in ALT or BAJ for surface waters (Fig. 4), although the number of samples here was very low, with this value exceeding the limit for the total amount of pesticides (0.5 μg L^{-1}) permitted by EU legislation. In the case of insecticides (Fig. 5), these median values are considerably lower, peaking in the Jun–11 sampling campaign in the three areas for both ground and surface waters.

In addition, the samples with the highest values of herbicides corresponded to groundwaters (Fig. 4 a–c) collected from Rioja Baja (BAJ–G16) in Sep–10 (81.72 μg L^{-1}), Mar–11 (20.42 μg L^{-1}), and Jun–11 (23.74 μg L^{-1}), and BAJ–G28 in Mar–11 (25.60 μg L^{-1})); from Rioja Alavesa (ALV–G11 in Mar–11 (27.79 μg L^{-1}) and in Jun–11 (20.87 μg L^{-1}), ALV–G2 in Sep–10 (19.17 μg L^{-1}) and in Sept–10 ALV–G1 (10.98 μg L^{-1})), and from Rioja Alta (ALT–G20) in Mar–11 (9.912 μg L^{-1}). These high concentrations were provided by terbuthylazine, DET and fluometuron (especially in BAJ–G16 in Sep–10), and to a lesser extent by diuron (Sep–10) and alachlor (Jun–11).

In the case of insecticides (Fig. 5 a–c), the samples with the highest concentrations were ALV–G1 with methoxyfenozide in all four sampling periods and ALT–G11, ALT–G15, and BAJ–G31 with concentrations of carbaryl or imidacloprid over the limit established by EU legislation for individual pesticides, although the concentrations were always lower than for herbicides. These samples were generally from wells < 5 m in depth close to vineyards, cereal crops and fruit tree orchards. These water sources were not used for human consumption, but mostly for irrigation.

3.3. Evaluation of the quality of water samples from the DOCa Rioja area according to European legislation

A different number of herbicides or insecticides were detected in each water sample, with the total concentration of all of them being the indicator for evaluating water quality. Fig. 6 shows the co–occurrence of different herbicides or insecticides in the water samples collected in the four campaigns. Between eleven and fifteen herbicides were detected in several samples in the four campaigns, while only two insecticides were detected in Sept–10, three in Mar–11 and Sept–11, and more than four in Jun–11. The results indicate that no herbicides were detected in 8% (Sept–10), 6% (Mar–11), 1% (Jun–11) and 6% (Sept–11) of the samples. However, more than five herbicides were detected in 40% (Sept–10), 45% (Mar–11), 48% (Jun–11) and 35% (Sept–11) of samples. More than fifteen herbicides were detected in 1% of the samples (Sep–11) (Fig. 6). In the case of insecticides, the results indicate that no insecticides were detected in 63% (Sept–10), 61% (Mar–11), 42% (Jun–11) and 80% (Sept–11) of the samples, while two or more insecticides were detected in 7% (Sept–10), 10% (Mar–11), 27% (Jun–11) (including 1% of samples with more than four insecticides), and 3% (Sept–11) (Fig 6).

According to the number and concentration of each herbicide and insecticide, an evaluation of the quality of the water samples was carried out for each area of DOCa Rioja in accordance with the European Directive (EC, 2008), which sets a limit of 0.1 $\mu g\ L^{-1}$ for the individual concentration of pesticides, or of 0.5 $\mu g\ L^{-1}$ for the total concentration of pesticides in drinking water. Table 4 shows the number of water samples (ground and surface waters) with no pesticides detected, and the number of water samples that meet one or other of the criteria laid down in EU legislation or both of them in the three subareas in DOCa Rioja for different sampling periods. The number of samples meeting both criteria and an individual one was the same. However, the number of samples that meet the criterion for total concentration was always higher. This indicates that although the number of pesticides (mainly herbicides) was high, most of them were present in low concentrations. It should be noted that the number of samples complying with EU legislation in 2011 decreases in the March and June campaigns, being higher in the September ones. Comparing both September campaigns, an increase in the number of samples complying with EU legislation was observed in the three subareas in 2011, indicating a possible recovery of water quality. However, seasonal rainfall or other weather conditions might be involved in this improvement, and more monitoring programmes with an adequately designed monitoring well network would be needed to confirm this trend.

4. Conclusions

This study reports the evolution of herbicide and insecticide concentrations in ground and surface waters in the DOCa Rioja vineyard region over the course of a year. All the samples collected contained some of the herbicides or insecticides studied in one or more of the four campaigns (Sept–10, Mar–11, June–11, and Sept–11). The significant correlation coefficients ($p<0.05$) found between the concentrations of some herbicides evidence the simultaneous application of different chemicals in most of the crops in the area under study. In addition, all the samples collected in Rioja Alavesa were contaminated with some herbicides and/or insecticides in all four campaigns, and this is the most contaminated area, while in the case of Rioja Alta and Rioja Baja some samples were not contaminated with any pesticides at all. The percentage of samples with a high number of pesticides is consistent with the widespread use of herbicides and a less extended use of insecticides. Furthermore, the increase in the detection of herbicides and insecticides corresponded with their application period (herbicides in March and insecticides in June). The number of samples complying with European legislation in both the individual and total concentration of pesticides increased over the sampling periods. This could indicate a possible recovery of water quality outside the periods of crop growth, although more monitoring programmes are needed to confirm this improvement. The findings in this study provide valuable information, highlighting the need to carry out additional biotic and abiotic degradation studies and to implement strategies for effective water protection. On the other hand future studies should also be expanded to degradation products of these compounds, less considered in these evaluations, in order to reach a more real risk assessment as a result of the use of pesticides in agriculture.

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consumption (0.1 μg L^{-1}) in the four sampling campaigns: Sept–2010 (1), Mar–11 (2), Jun–11 (3) and Sep–11 (4). Plots correspond to triazine herbicides (a), other herbicides (b) and insecticides (c)

Fig. 3. Distribution of the total amount of herbicides (a,b) and insecticides (c,d) in ground and surface waters of the three subareas in the four sampling campaigns.

Fig. 4. Box and whisker plots of the range of total concentration of herbicides detected in each sample of ground (–G) and surface (–S) waters of the three subareas of DOCa Rioja (ALV = Rioja Alavesa; ALT = Rioja Alta and BAJ = Rioja Baja) in the four sampling campaigns.

Fig. 5. Box and whisker plots of the range of total concentration of insecticides detected in each sample of ground (–G) and surface (–S) waters of the three subareas of DOCa Rioja (ALV = Rioja Alavesa; ALT = Rioja Alta and BAJ = Rioja Baja) in the four sampling campaigns.

Fig. 6. Co–occurrence of herbicides and insecticides in water samples collected in each sampling campaign.

Table 1. Concentrations of herbicides and insecticides (μg L^{-1}) (range and mean values) and positive samples detection frequency (number/%) in the samples taken in La Rioja Alavesa area in the different sampling periods.

Compounds	Sep–10 (n=15 samples)			Mar–11 (n=15 samples)			Jun–11 (n=15 samples)			Sep–11 (n=12 samples)		
	Range	Mean	FD (%)	Range	Mean	FD (%)	Range	Mean	FD (%)	Range	Mean	FD (%)
Propazine	0.015/0.103	0.050	7/47	0.018/0.043	0.024	7/47	0.018/0.055	0.031	5/33	0.002/0.013	0.007	5/42
Terbuthylazine	0.003/5.387	0.737	13/87	0.025/12.60	2.386	12/80	0.021/6.829	0.812	15/100	0.007/1.448	0.232	12/100
Deethylterbuthylazine	0.017/4.360	0.630	13/87	0.013/1.385	0.289	13/87	0.022/1.891	0.347	14/93	0.015/2.209	0.456	11/92
Simazine	0.061/0.207	0.134	2/13	0.019/0.171	0.097	3/20	0.047/0.078	0.064	3/20	0.092	0.092	1/8
Atrazine	0.008/0.032	0.018	7/47	0.034/0.214	0.092	4/27	0.016/0.066	0.048	3/20	–	–	–
Deethylatrazine	0.008/0.019	0.014	3/20	0.032	0.032	1/7	0.009	0.009	1/7	0.007/0.017	0.012	2/17
Deisopropylatrazine	0.016/0.092	0.043	3/20	0.032/0.086	0.058	5/33	0.025/0.031	0.028	2/13	0.016	0.016	1/8
Terbutryn	0.024/2.749	0.480	7/47	0.037/0.665	0.173	5/33	0.017/0.587	0.173	4/27	0.014/0.701	0.262	3/25
Metribuzin	0.067	0.067	1/7	0.170	0.170	1/7	0.019/0.144	0.083	3/20	0.047/0.063	0.055	2/17
Fluometuron	0.027/0.522	0.172	9/60	0.035/12.72	0.999	15/100	0.015/2.601	0.496	7/47	0.043/0.772	0.274	5/42
Diuron	0.354/5.008	2.681	2/13	0.013/1.512	0.344	7/47	0.015/0.926	0.364	4/27	0.040/1.414	0.789	3/25
Linuron	0.047/0.074	0.056	3/20	0.034/0.118	0.080	4/27	0.103	1.103	1/7	–	–	–
Lenacil	0.012/4.005	0.960	5/33	0.013/1.612	0.367	8/53	0.082/1.046	0.301	9/60	0.018/1.432	0.653	4/33
Metobromuron	0.017/0.143	0.080	2/13	0.011/0.033	0.022	2/13	0.012/0.016	0.014	3/20	0.015/0.056	0.036	2/17
Acetochlor	0.003/0.084	0.036	3/20	0.064/0.195	0.129	8/53	0.048	0.048	1/7	0.019/0.076	0.052	4/33
Metolachlor	0.017/0.263	0.089	10/67	0.028/0.034	0.032	3/20	0.041/0.138	0.082	3/20	0.025/0.047	0.038	5/42
Ethofumesate	0.189	0.189	1/7	0.018/0.057	0.029	11/73	0.008/0.074	0.025	7/47	0.006/0.048	0.025	4/33
Chloridazon	–	–	–	–	–	–	0.024/0.028	0.026	2/13	–	–	–
Dichlofop–methyl	0.024/0.112	0.058	4/27	–	–	–	–	–	–	0.022/0.093	0.053	4/33
Alachlor	0.039/0.193	0.114	4/27	–	–	–	0.019/8.928	1.269	13/87	0.034/1.628	0.650	4/33
Chlorotoluron	–	–	–	–	–	–	–	–	–	–	–	–
CMPU	0.218	0.218	1/7	–	–	–	–	–	–	–	–	–
Dimethoate	–	–	–	–	–	–	0.052/0.084	0.070	3/20	0.039	0.039	1/8
Pirimicarb	0.014/0.037	0.023	3/20	0.026/0.037	0.030	7/47	0.019/0.043	0.028	7/47	–	–	–
Imidacloprid	0.003	0.003	1/7	–	–	–	0.052/0.084	0.070	4/27	–	–	–
Chropyrifos	–	–	–	–	–	–	–	–	–	–	–	–
Methoxyfenozide	0.555/3.823	2.189	2/13	0.179/4.806	2.493	2/13	0.260/4.654	2.457	2/13	0.010/2.979	1.520	2/17
Carbaryl	0.071/0.141	0.097	3/20	–	–	–	0.044/1.865	0.785	4/27	0.056/0.823	0.418	3/25

Table 2. Concentrations of herbicides and insecticides (μg L^{-1}) (range and mean values) and positive samples detection frequency (number/%) in the samples taken in La Rioja Alta area in the different sampling periods.

Compounds	Sep–10 (n=34 samples)			Mar–11 (n=34 samples)			Jun–11 (n=34 samples)			Sep–11 (n=30 samples)		
	Range	Mean	FD (%)	Range	Mean	FD (%)	Range	Mean	FD (%)	Range	Mean	FD (%)
Propazine	0.012/0.182	0.046	21/62	0.019/0.081	0.032	12/35	0.010/0.648	0.162	5/15	0.009/0.063	0.031	14/47
Terbuthylazine	0.003/1.899	0.256	27/79	0.028/6.118	0.527	22/65	0.027/0.438	0.109	31/91	0.008/0.242	0.062	29/97
Deethylterbuthylazine	0.009/1.839	0.125	29/85	0.012/0.203	0.049	28/82	0.009/0.143	0.047	27/79	0.015/0.146	0.044	21/70
Simazine	0.069/0.114	0.092	2/6	0.045/0.067	0.054	4/12	0.066/0.069	0.067	2/6	0.019/0.043	0.031	2/7
Atrazine	0.007/0.055	0.020	14/41	0.030/0.110	0.053	10/29	0.028/0.065	0.043	6/18	0.006/0.028	0.018	5/17
Deethylatrazine	0.011/0.022	0.017	6/15	0.013/0.106	0.055	5/15	0.101	0.101	1/3	0.005/0.046	0.016	4/13
Deisopropylatrazine	0.014/0.033	0.024	2/6	0.056/0.145	0.101	2/6	0.132	0.132	1/3	0.156	0.156	1/3
Terbutryn	0.006/0.164	0.064	15/44	0.037/0.042	0.040	3/9	0.024/0.025	0.025	2/6	0.006/0.055	0.023	10/33
Metribuzin	0.017/0.026	0.021	2/6	0.044/0.059	0.051	2/6	0.018/0.074	0.056	4/12	0.036/0.098	0.058	3/10
Fluometuron	0.005/0.489	0.099	13/38	0.031/3.599	0.326	28/82	0.009/0.694	0.113	17/50	0.012/0.216	0.065	5/17
Diuron	0.051/0.607	0.329	2/6	0.009/0.110	0.046	5/15	0.018/0.192	0.065	5/15	0.017/0.153	0.070	3/10
Linuron	0.043/0.101	0.073	6/18	0.022/0.153	0.070	12/35	0.107/0.277	0.192	2/6	0.022/0.031	0.026	3/10
Lenacil	0.016/0.669	0.144	8/24	0.015/0.303	0.099	9/26	0.030/0.380	0.113	13/38	0.013/0.726	0.133	9/30
Metobromuron	0.011/0.290	0.142	5/15	0.019/0.086	0.052	2/6	0.008/0.082	0.032	9/26	0.019/0.092	0.051	4/13
Acetochlor	0.014/0.113	0.053	8/24	0.022/0.183	0.108	14/41	0.010/0.084	0.033	7/21	0.011/0.043	0.025	4/13
Metolachlor	0.022/0.276	0.075	23/68	0.024/0.068	0.039	4/12	0.010/0.076	0.043	9/26	0.027/0.105	0.066	10/33
Ethofumesate	0.031/0.211	0.095	8/24	0.013/0.061	0.026	20/59	0.013/0.168	0.050	10/29	0.004/0.161	0.071	4/13
Chloridazon	–	–	–	–	–	–	0.027/0.039	0.033	7/21	0.020	0.020	1/3
Dichlofop–methyl	0.017/0.203	0.110	2/6	–	–	–	–	–	–	–	–	–
Alachlor	0.077/0.297	0.142	7/21	0.029/0.031	0.030	2/6	0.019/0.648	0.108	24/71	0.062/0.476	0.232	4/13
Chlorotoluron	–	–	–	–	–	–	0.022	0.022	1/3	–	–	–
CMPU	–	–	–	–	–	–	–	–	–	0.045/0.119	0.082	2/7
Dimethoate	–	–	–	–	–	–	0.024/0.089	0.057	6/17	0.019	0.019	1/3
Pirimicarb	0.023/0.065	0.046	7/20	0.019/0.031	0.028	12/35	0.009/0.041	0.027	13/37	0.029	0.029	1/3
Imidacloprid	0.033	0.033	1/3	0.043/0.656	0.350	2/6	0.047/0.074	0.056	4/11	0.252	0.252	1/3
Chlorpyrifos	–	–	–	0.015/0.128	0.072	3/9	–	–	–	–	–	–
Methoxyfenozide	–	–	–	0.036/0.132	0.084	2/6	0.054/0.108	0.081	2/6	–	–	–
Carbaryl	0.014/0.082	0.057	3/9	–	–	–	0.045/0.503	0.166	6/17	0.080/0.091	0.087	3/10

Table 3. Concentrations of herbicides and insecticides (μg L^{-1}) (range and mean values) and positive samples detection frequency (number/%) in the samples taken in La Rioja Baja area in the different sampling periods.

Compounds	Sep–10 (n=41 samples)			Mar–11 (n=41 samples)			Jun–11 (n=41 samples)			Sep–11 (n=40 samples)		
	Range	Mean	FD (%)	Range	Mean	FD (%)	Range	Mean	FD (%)	Range	Mean	FD (%)
Propazine	0.014/0.112	0.047	14/33	0.020/0.194	0.075	14/33	0.008/0.156	0.042	6/14	0.006/0.043	0.021	11/27
Terbuthylazine	0.006/34.04	1.205	32/76	0.011/9.900	0.948	24/56	0.028/6.174	0.251	38/88	0.005/1.322	0.084	31/76
Deethylterbuthylazine	0.007/30.48	0.993	34/81	0.011/5.192	0.232	32/74	0.012/1.625	0.113	29/67	0.016/2.193	0.138	24/59
Simazine	0.085	0.085	1/2	0.021/0.082	0.055	5/12	0.040/0.075	0.055	5/12	0.017	0.017	1/2
Atrazine	0.007/0.028	0.015	12/29	0.014/0.333	0.075	13/30	0.031/0.136	0.056	14/33	0.005/0.015	0.009	3/7
Deethylatrazine	0.012/0.068	0.040	4/10	0.016/0.092	0.048	5/12	0.382/2.469	1.426	2/5	0.004/0.031	0.011	5/12
Deisopropylatrazine	0.023/0.539	0.281	2/5	0.042/0.642	0.342	2/5	1.045	1.045	1/2	0.147	0.147	1/2
Terbutryn	0.006/0.107	0.054	13/31	0.036/0.042	0.038	7/16	0.024/0.034	0.029	2/5	0.002/0.025	0.014	15/37
Metribuzin	0.062/0.159	0.111	2/5	–	–	–	0.039/0.082	0.060	2/5	0.045	0.045	1/2
Fluometuron	0.004/16.13	1.189	14/33	0.045/18.36	1.672	25/58	0.009/2.473	0.449	10/23	0.014/0.256	0.069	7/17
Diuron	0.015/0.036	0.026	3/7	0.005/0.247	0.062	11/26	0.019/0.046	0.032	4/9	0.024/0.036	0.031	3/7
Linuron	0.061/0.143	0.102	2/5	0.017/0.198	0.060	12/28	0.042/0.217	0.091	4/9	0.021/0.032	0.027	3/7
Lenacil	0.007/0.388	0.107	9/21	0.058/0.541	0.172	10/23	0.046/0.293	0.097	16/37	0.004/0.133	0.059	8/20
Metobromuron	0.022/0.139	0.088	4/10	0.003/0.116	0.036	8/19	0.002/0.089	0.028	10/23	0.011/0.227	0.079	8/20
Acetochlor	0.021/0.077	0.055	4/10	0.093/0.224	0.149	5/12	0.018/0.099	0.063	3/7	0.024/0.055	0.039	6/15
Metolachlor	0.012/1.106	0.104	20/48	0.025/0.163	0.083	3/7	0.017/0.144	0.054	14/33	0.000/0.085	0.032	22/54
Ethofumesate	0.002/0.159	0.085	7/17	0.017/0.058	0.030	22/51	0.005/0.128	0.044	13/30	0.001/0.115	0.048	8/20
Chloridazon	–	–	–	–	–	–	0.034	0.034	1/2	0.007	0.007	1/2
Dichlofop–methyl	0.025/0.037	0.031	5/12	–	–	–	–	–	–	0.016/0.039	0.027	3/7
Alachlor	0.034/0.138	0.099	3/7	0.030	0.030	1/2	0.013/11.98	0.619	24/56	0.013/0.520	0.139	6/15
Chlorotoluron	–	–	–	–	–	–	0.015	0.015	1/2	–	–	–
CMPU	–	–	–	–	–	–	–	–	–	–	–	–
Dimethoate	–	–	–	0.018/0.054	0.031	4/10	0.043/0.071	0.057	5/12	–	–	–
Pirimicarb	0.018/0.061	0.042	8/19	0.025/0.036	0.029	12/29	0.013/0.036	0.027	18/43	–	–	–
Imidacloprid	0.0080.216	0.057	5/12	0.025/0.052	0.037	4/10	0.015/0.204	0.086	8/19	0.039/0.076	0.058	2/5
Chlorpyrifos	–	–	–	–	–	–	0.117	0.117	1/2	–	–	–
Methoxyfenocide	–	–	–	–	–	–	–	–	–	–	–	–
Carbaryl	0.084/0.298	0.151	5/12	–	–	–	0.017/0.450	0.197	7/17	0.026/0.139	0.074	6/15

Table 4. Detection frequency of samples with no pesticides detected, that satisfy EU legislation for individua
total concentration of pesticides ([C] < 0.5 μg L^{-1}) (EC, 1998), or for both conditions in the three subareas
campaigns.

	Rioja Alavesa				Rioja Alta				
	Sep–10	Mar–11	Jun–11	Sep–11	Sep–10	Mar–11	Jun–11	Sep–11	Se
No detected pesticides	0 / 15[a]	0 / 15	0 / 15	0 / 12	3 / 34	1 / 34	1 / 34	0 / 30	3
[C] < 0.1	5 / 15	5 / 15	3 / 15	8 / 12	17 / 34	15 / 34	17 / 34	20 / 30	23
Σ[C] < 0.5	8 / 15	7 / 15	6 / 15	8 / 12	23 / 34	22 / 34	21 / 34	23 / 30	28
EU legislation	5 / 15	5 / 15	3 / 15	8 / 12	17 / 34	15 / 34	17 / 34	20 / 30	23

[a] Number of samples that satisfy the criteria indicated in each line / Total number of samples for that area

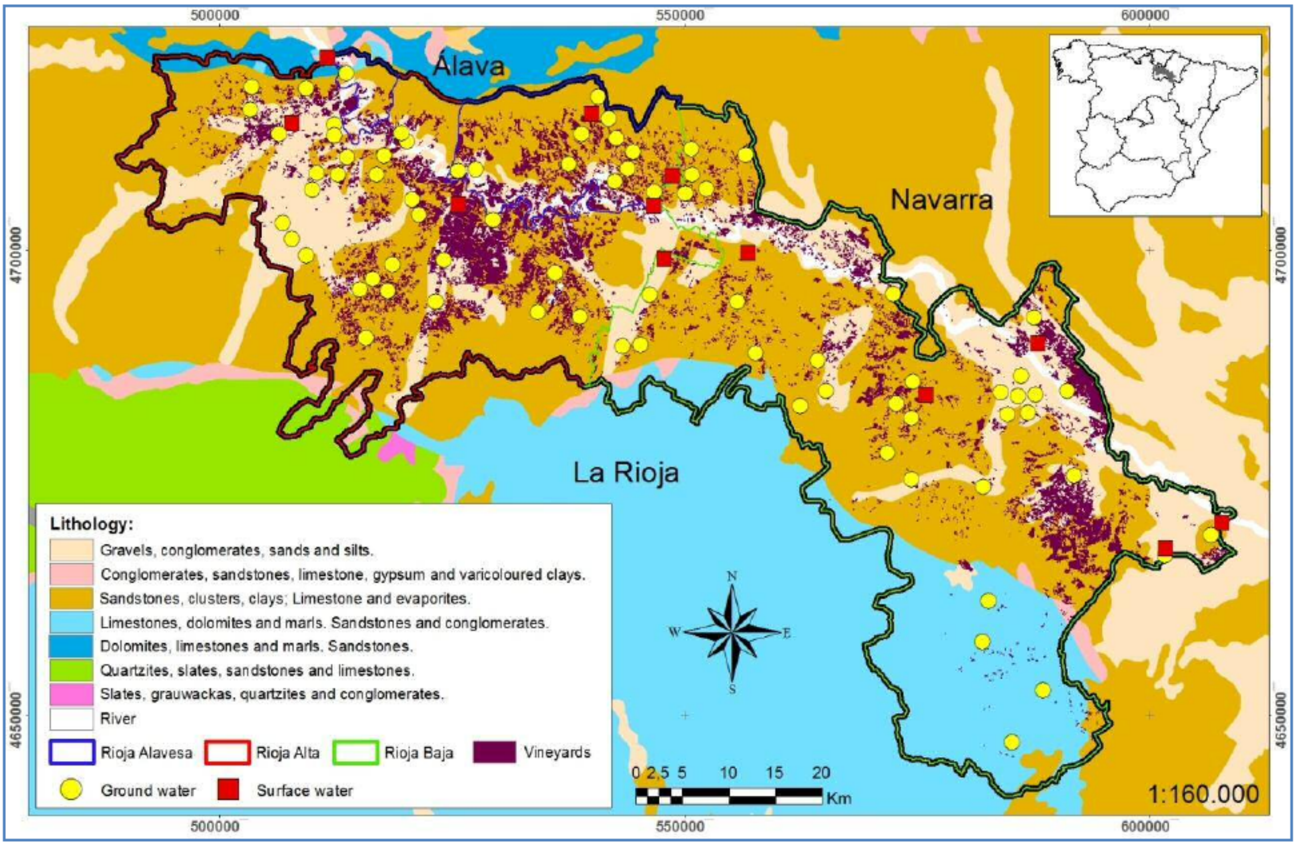
500000
550000
600000
4700000
4650000
Álava
Navarra
La Rioja
Lithology:
Gravels, conglomerates, sands and silts.
Conglomerates, sandstones, limestone, gypsum and varicoloured clays.
Sandstones, clusters, clays; Limestone and evaporites.
Limestones, dolomites and marls. Sandstones and conglomerates.
Dolomites, limestones and marls. Sandstones.
Quartzites, slates, sandstones and limestones.
Slates, grauwackas, quartzites and conglomerates.
River
Rioja Alavesa
Rioja Alta
Rioja Baja
Vineyards
Ground water
Surface water
N
W
E
S
0 2,5 5 10 15 20
Km
1:160.000

Fig. 1.

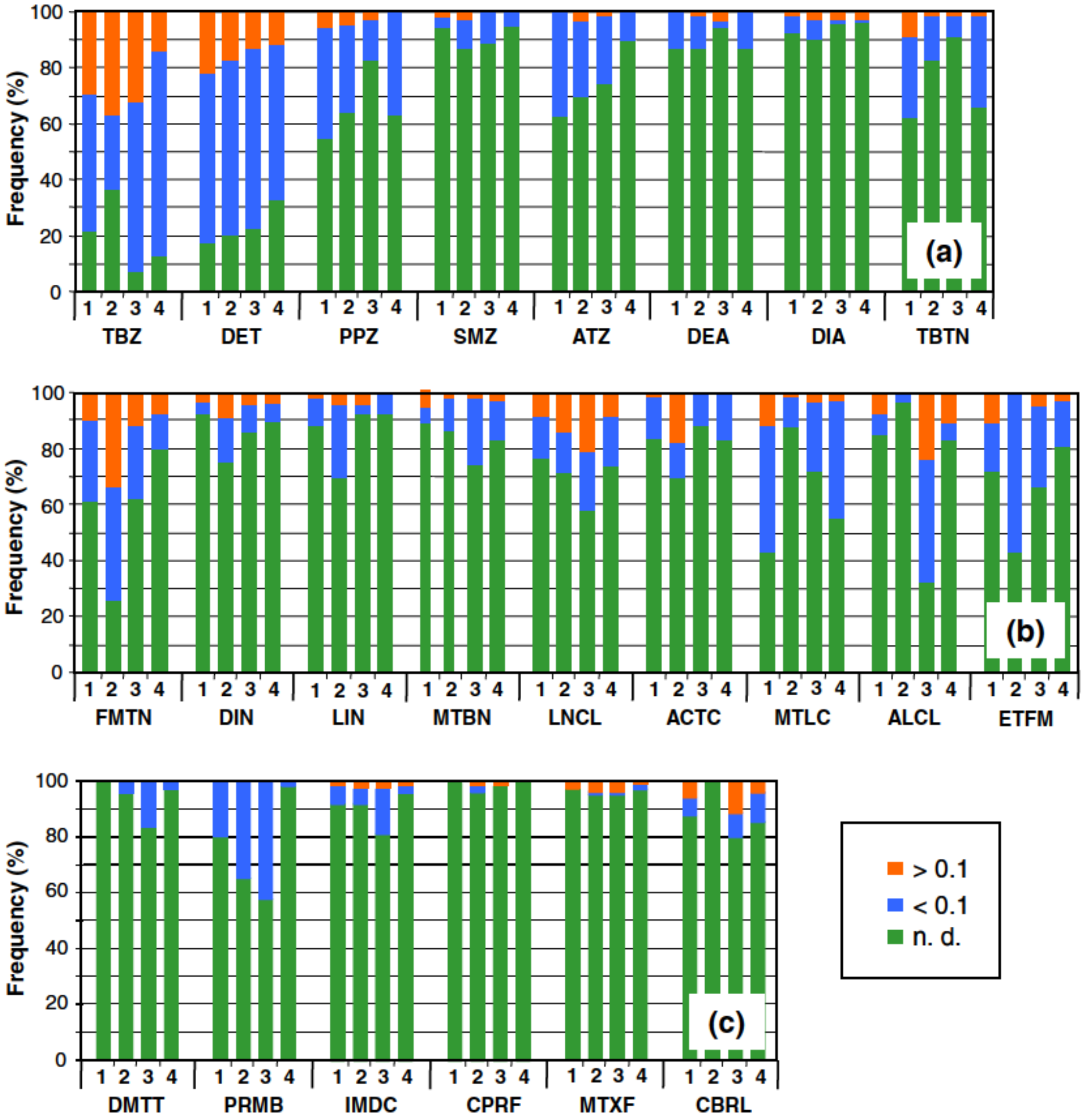
Frequency (%)
0
20
40
60
80
100
1 2 3 4
TBZ
DET
PPZ
SMZ
ATZ
DEA
DIA
TBTN
(a)
FMTN
DIN
LIN
MTBN
LNCL
ACTC
MTLC
ALCL
ETFM
(b)
DMTT
PRMB
IMDC
CPRF
MTXF
CBRL
(c)
> 0.1
< 0.1
n. d.

Fig. 2

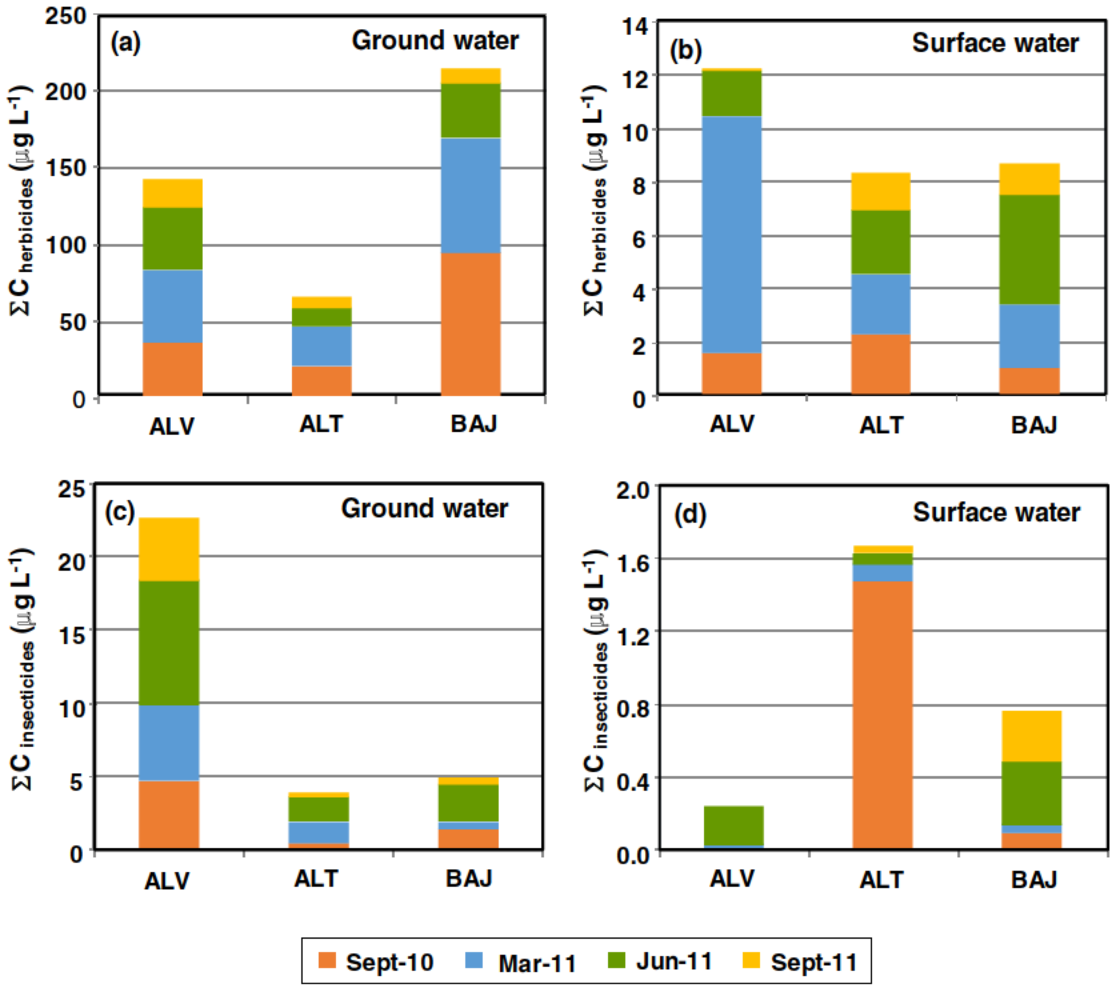
(a)
Ground water
ΣC herbicides (µg L⁻¹)
0
50
100
150
200
250
ALV
ALT
BAJ
(b)
Surface water
ΣC herbicides (µg L⁻¹)
0
2
4
6
8
10
12
14
ALV
ALT
BAJ
(c)
Ground water
ΣC insecticides (µg L⁻¹)
0
5
10
15
20
25
ALV
ALT
BAJ
(d)
Surface water
ΣC insecticides (µg L⁻¹)
0.0
0.4
0.8
1.2
1.6
2.0
ALV
ALT
BAJ
Sept-10
Mar-11
Jun-11
Sept-11

Fig. 3

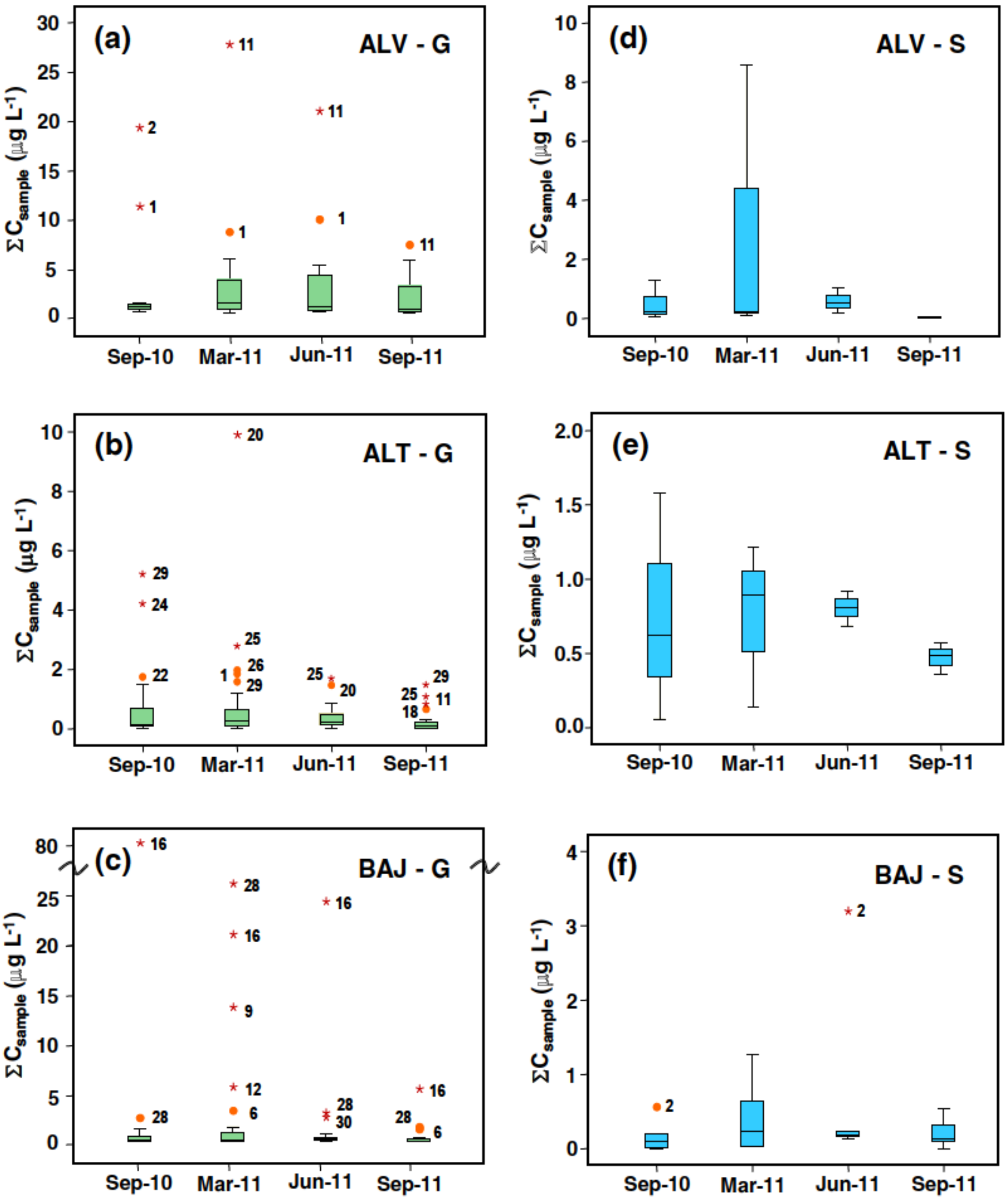
(a)
ALV - G
(b)
ALT - G
(c)
BAJ - G
(d)
ALV - S
(e)
ALT - S
(f)
BAJ - S
ΣC$_{sample}$ (µg L^{-1})
Sep-10
Mar-11
Jun-11
Sep-11
0
5
10
15
20
25
30
80
0
2
4
6
8
10
0.0
0.5
1.0
1.5
2.0
1
3
4
11
2
1
1
11
29
24
22
20
25
26
29
20
25
29
11
18
16
28
16
9
12
6
28
30
16
28
6
2

Fig. 4

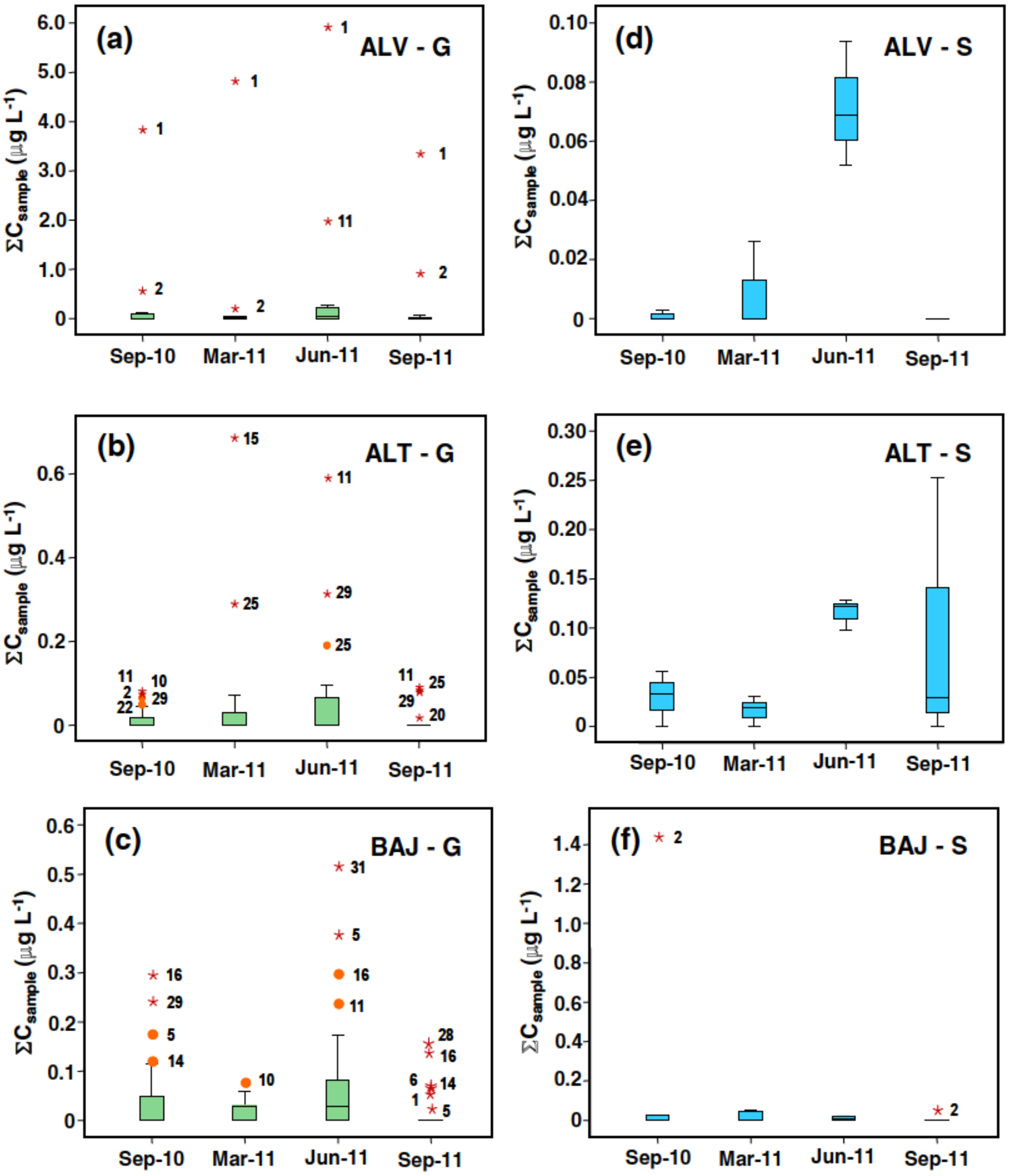
(a)
ALV - G
ΣC_sample (µg L-1)
6.0
5.0
4.0
3.0
2.0
1.0
0
1
1
1
1
11
2
2
2
Sep-10
Mar-11
Jun-11
Sep-11
(d)
ALV - S
ΣC_sample (µg L-1)
0.10
0.08
0.06
0.04
0.02
0
Sep-10
Mar-11
Jun-11
Sep-11
(b)
ALT - G
ΣC_sample (µg L-1)
0.6
0.4
0.2
0
15
11
25
29
25
11
10
2
29
22
11
25
29
20
Sep-10
Mar-11
Jun-11
Sep-11
(e)
ALT - S
ΣC_sample (µg L-1)
0.30
0.25
0.20
0.15
0.10
0.05
0
Sep-10
Mar-11
Jun-11
Sep-11
(c)
BAJ - G
ΣC_sample (µg L-1)
0.6
0.5
0.4
0.3
0.2
0.1
0
31
5
16
11
16
29
5
14
10
28
16
6
14
1
5
Sep-10
Mar-11
Jun-11
Sep-11
(f)
BAJ - S
ΣC_sample (µg L-1)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
2
2
Sep-10
Mar-11
Jun-11
Sep-11

Fig. 5

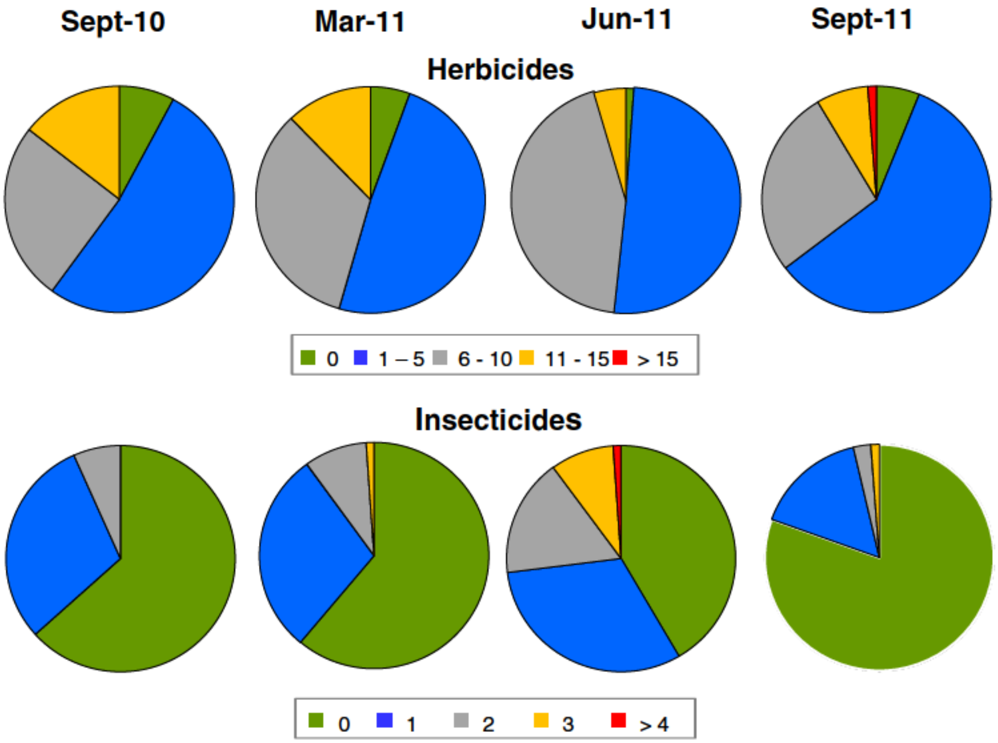
Sept-10
Mar-11
Jun-11
Sept-11
Herbicides
0
1 – 5
6 - 10
11 - 15
> 15
Insecticides
0
1
2
3
> 4

Fig. 6

2. Materials and methods

2.1. Chemicals

Table S1. Common names, physicochemical properties and application dose of herbicides and insecticides selected for the study.

Pesticide	Abbreviation	Field of use	Solubility (mg L^{-1})	Log Kow	GUS index	DT$_{50}$ (days)	Application Dose^{a}(g ha^{-1})
Atrazine	ATZ	Herbicide	35	2.7	3.75	66	990-2520
Deisopropylatrazine	DIA	Prod. Degr.	670	1.15	-		-
Deethylatrazine	DEA	Prod. Degr.	3200	-	3.54	150	-
2-Hidroxyatrazine	HA	Prod. Degr.	-	-	-	-	-
DeisopropylhydroxyATZ	DIHA	Prod. Degr.	-	-	-	-	-
DeethylhydroxyATZ	DEHA	Prod. Degr	-	-	-	-	-
Simazine	SMZ	Herbicide	5	2.3	3.35	-	2250-3600
Propazine	PPZ	Herbicide	8.6	3.95	3.84	135	1800-2000
Terbuthylazine	TBZ	Herbicide	6.6	3.4	3.07	75.1	1000
Deethylterbuthylazine	DET	Prod. Degr.	327.1	-	3.54	53.8	-
2-Hidroxyterbuthylazine	HT	Prod. Degr.	7.19	-	4.59	453	-
Terbutryn	TBTN	Herbicide	22	3.65	1.31	74	1750-2500
Metribuzin	MTBZ	Herbicide	1165	1.65	2.57	11.5	525
Chlorsulfuron	CLSN	Herbicide	12500	-0.99	5.38	51.4	10.5-15
Flazasulfuron	FZSN	Herbicide	2100	-0.06	2.34	8	25-50
Chloridazon	CLDZ	Herbicide	422	1.19	2.54	43.1	1935-3225
Metamitron	MTMN	Herbicide	1770	0.85	3.09	19	2800-4900
Lenacil	LNCL	Herbicide	2.9	1.69	4.25	14.4	500-625
Isoproturon	IPTN	Herbicide	70.2	2.5	2.07	12	1500-2000
Chlorotoluron	CLTN	Herbicide	74	2.5	2.79	59	1500-2750
1-(3-chloro,4-methylphenyl) urea	CMPU	Prod. Degr.	-	-	-	-	-
Metobromuron	MTBN	Herbicide	330	2.41	2.52	-	2000
Fluometuron	FMTN	Herbicide	111	2.18	4.19	124	1250-2000
Diuron	DIU	Herbicide	35.6	2.87	1.83	75.5	400-2400
Ethofumesate	ETFM	Herbicide	50	2.7	3.38	97	1000-1500
Linuron	LIN	Herbicide	63.8	3	2.03	87	1000-2500
Alachlor	ALCL	Herbicide	240	3.09	2.19	35	1920-2880
Acetochlor	ACTC	Herbicide	282	4.14	2.07	10.6	1680-2016
Metolachlor	MTLC	Herbicide	530	3.4	3.32	15	893-1258
Dichlofop-methyl	DCFM	Herbicide	0.39	4.8	0	0.31	900-1080
Acephate	ACFT	Insecticide	790000	-0.85	1.76	-	150-600
Carbaryl	CBRL	Insecticide	9.1	2.36	2.02	16	1500-2500
Chlorpyrifos	CPRF	Insecticide	1.05	4.7	0.15	76	144-768
Dimethoate	DMTT	Insecticide	39800	0.704	1.05	2.6	600-900
Imidacloprid	IMDC	Insecticide	610	0.57	3.76	187	100
Methoxyfenocide	MTXF	Insecticide	3.3	3.72	3.02	718	192-240
Pirimicarb	PRMB	Insecticide	3100	1.7	2.73	86	150-200
Cypermethryn	CPMN	Insecticide	0.009	5.3	-1.66	68	330-660

^{a}Data taken from PPDB (2017) and De Liñan and De Liñán (2016).

2.2. Study area and sample collection

The Rioja DOCa wine region is located in northern Spain, straddling the River Ebro. Fig. 1 shows a map of the area. The local terrain perfectly delimits the region and sets it apart from the surrounding area. Its 63,593 hectares of vineyards are divided between three provinces on the Upper Ebro - La Rioja (43,885 ha), Alava (12,934 ha) and Navarre (6,774 ha). One hundred kilometres separate Haro, the westernmost town, from Alfaro, the easternmost. The valley has a maximum width of about 40 km, being covered in vineyards that occupy successive terraces to an altitude of around 700 m above sea level. The whole area benefits from the confluence of two climates, Atlantic and Mediterranean, which provide mild temperatures between 7ºC and 20ºC and an annual rainfall between 300 and 400 mm. with a rainfall pattern mainly winter dominated.

The region itself is divided into three sub-areas: Rioja Alavesa, which is significantly influenced by the Atlantic climate, and its soils, in general, are chalky-clay in terraces and small plots; Rioja Alta, with the climate being also mainly Atlantic, while the soils are chalky-clay, ferrous-clay or alluvial and, finally, Rioja Baja, with a drier and warmer climate and alluvial and ferrous-clay soil types. In general, the soils have low OM content (<2 %), a sandy clay loam or sandy loam texture and pH is slightly alkaline favouring the mobility of pesticides in the area. Water availability is moderate during summer (Rioja DOCa - Qualified Designation of Origin, 2016).

Besides vineyards, the other crops in this area are cereals, fruit trees, sugar beet and potatoes (Government of La Rioja, 2014). Table S2 shows the main characteristics of the sampling sites, including the hydrogeological units or aquifers where the samples are located, the type of crops and the existence or not of irrigation in the surrounding areas that could influence the type and levels of pesticides detected. The number of wells and springs in Rioja Alta and Rioja Alavesa is higher than in Rioja Baja, where irrigation is provided by river water (Lodosa canal). However, the wells in Rioja Baja are deeper than in the other two regions, where the water table can be just a few meters below the surface.

Water samples were collected in 2 L amber glass bottles and transported to the laboratory in iceboxes. Within four days, the samples were filtered through nitrocellulose screens with 0.45 μm pore size membranes (Millipore), being kept refrigerated at 4 ºC in the dark prior to extraction. The extracts were analysed within two weeks of collection.

A total of ninety water samples were collected from different areas affected by agricultural development throughout the three different sub-areas of Rioja Alavesa (15 points), Rioja Alta (34 points) and Rioja Baja (41 points) (Fig. 1 and Table S2). Twelve of these samples corresponded to surface waters (two on the River Ebro at opposite ends of La Rioja region, six more on the main tributaries, one more on the Lodosa canal and three more on small rivers) and seventy-eight samples corresponded to groundwaters from privately dug wells with different depths varying between 1 and 15 m, in general, and public sources or springs. Only three samples came from depths of between 17 and 60 m (Table S2). The dug wells were located inside the cultivated fields or next to them, being generally used for irrigation purposes. Samples were collected manually or pumped, depending on the well type.

Table S2. Characteristics of the sampling points monitored in the three subareas studied in La Rioja region.

Sampling point	Water type	Water depth (m)	Characteristics of the area	
			Crops cultivated	Watering
Rioja Alavesa				
ALV-G1	Groundwater	1-2	Vineyards	Yes
ALV-G2	Groundwater	1-2	Vineyards	Yes
ALV-G3	Groundwater	<5	Cereals and vineyards	No
ALV-G4	Groundwater	Spring	Vineyards	No
ALV-G5	Groundwater	Uptake	Vineyards	No
ALV-G6	Groundwater	Spring	Vineyards	No
ALV-G7	Groundwater	Spring	Vineyards and olives	No
ALV-G8	Groundwater	<5	Vineyards	Yes
ALV-G9	Groundwater	3	Vineyards and cereals	No
ALV-G10	Groundwater	Spring	Vineyards	No
ALV-G11	Groundwater	<5	Vineyards	No
ALV-G12	Groundwater	Spring	Vineyards and cereals	No
ALV-S1	Surface water (Moreda river)	-	Vineyards and olives	No
ALV-S2	Surface water (Oyón river)	-	Vineyards	-
ALV-S3	Surface water (Viñaspre river)	-	Vineyards and orchard	-
Rioja Alta				
ALT-G1	Groundwater	Spring	Vineyards and cereals	No
ALT-G2	Groundwater	Uptake	Vineyards and cereals	No
ALT-G3	Groundwater	Uptake	Vineyards and cereals	No
ALT-G4	Groundwater	Spring	Vineyards and cereals	No
ALT-G5	Groundwater	Uptake	Cereals, vineyards and beet	No
ALT-G6	Groundwater	8	Cereals, vineyards and beet	No
ALT-G7	Groundwater	<5	Vineyards, cereals and beet	No
ALT-G8	Groundwater	2-3	Vineyards and cereals	No
ALT-G9	Groundwater	Spring	Vineyards and cereals	No
ALT-G10	Groundwater	Uptake	Vineyards	No
ALT-G11	Groundwater	5-10	Vineyards and cereals	No
ALT-G12	Groundwater	<5	Vineyards and fruit trees	No
ALT-G13	Groundwater	Uptake	Vineyards	No
ALT-G14	Groundwater	5-10	Vineyards and cereals	No
ALT-G15	Groundwater	<5	Vineyards, cereals and fruit trees	Sometimes
ALT-G16	Groundwater	Uptake	Cereals and vineyards	No
ALT-G17	Groundwater	Uptake	Vineyards	No
ALT-G18	Groundwater	Uptake	Vineyards and orchards	Si
ALT-G19	Groundwater	Uptake	Vineyards and cereals	No
ALT-G20	Groundwater	<5	Vineyards and cereals	Yes, drip
ALT-G21	Groundwater	Uptake	Vineyards and orchards	Yes
ALT-G22	Groundwater	Spring	Vineyards and orchards	Yes
ALT-G23	Groundwater	5-10	Vineyards	No
ALT-G24	Groundwater	Uptake	Vineyards	No
ALT-G25	Groundwater	3	Vineyards	No
ALT-G26	Groundwater	45	Vineyards and orchards	No
ALT-G27	Groundwater	Spring	Vineyards and cereals	No
ALT-G28	Groundwater	Spring	Vineyards and orchards	No
ALT-G29	Groundwater	5-6	Vineyards	No
ALT-G30	Groundwater	Uptake	Vineyards and cereals	No
ALT-G31	Groundwater	2-3	Vineyards, cereals and potatoes	Yes
ALT-S1	Surface water (Ebro river)	-	Vineyards, olive and fruits	
ALT-S2	Surface water (Najerilla river)	-	Vineyards	
ALT-S3	Surface water (Oja river)	-	Vineyards	

Sampling point	Water type	Water depth (m)	Characteristics of the area	
			Crops cultivated	Watering
Rioja Baja				
BJ-G1	Groundwater	Spring	Vineyards	No
BJ-G2	Groundwater	60	Vineyards	Yes, drip
BJ-G3	Groundwater	Spring	Fruit trees and orchards	Yes
BJ-G4	Groundwater	Uptake	Fruit trees	Yes
BJ-G5	Groundwater	<3	Olive trees	Yes, drip
BJ-G6	Groundwater	3-4	Vineyards	No
BJ-G7	Groundwater	Spring	Fruit trees	No
BJ-G8	Groundwater	2-3	Vineyards	Yes, drip
BJ-G9	Groundwater	3	Vineyards	Yes, drip
BJ-G10	Groundwater	4-5	Vineyards	Yes, drip
BJ-G11	Groundwater	5	Vineyards and fruit trees	Yes
BJ-G12	Groundwater	3-4	Vineyards	No
BJ-G13	Groundwater	<5	Orchards	Yes
BJ-G14	Groundwater	5-6	Vineyards and olives	No
BJ-G15	Groundwater	Spring	Vineyards	Yes, drip
BJ-G16	Groundwater	3-4	Vineyards and cereals	Sometimes
BJ-G17	Groundwater	17	Fruit trees and orchards	Yes
BJ-G18	Groundwater	7-9	Vineyards and olives	Yes, drip
BJ-G19	Groundwater	8-10	Vineyards and olives	Yes, drip
BJ-G20	Groundwater	> 10	Vineyards	No
BJ-G21	Groundwater	> 10	Olive trees	No
BJ-G22	Groundwater	> 10	Orchards	Yes
BJ-G23	Groundwater	Spring	Vineyards, cereals and olives	No
BJ-G24	Groundwater	5-10	Vineyards and cereals	No
BJ-G25	Groundwater	5-6	Orchards	Yes
BJ-G26	Groundwater	Spring	Vineyards and cereals	No
BJ-G27	Groundwater	Spring	Vineyards, cereals and olives	No
BJ-G28	Groundwater	<5	Vineyards	No
BJ-G29	Groundwater	3-4	Vineyards	Yes
BJ-G30	Groundwater	Spring	Vineyards	No
BJ-G31	Groundwater	3-4	Vineyards, cereals, fruit trees	No
BJ-G32	Groundwater	6-8	Vineyards	No
BJ-G33	Groundwater	Spring	Vineyards and olives	No
BJ-G34	Groundwater	6-8	Vineyards	No
BJ-G35	Groundwater	5-6	Vineyards	Yes, drip
BJ-S1	Surface water (Lodosa canal)	-	Vineyards and fruit trees	
BJ-S2	Surface water (Ebro river)	-	Vineyards	
BJ-S3	Surface water (Ega river)	-	Vineyards	
BJ-S4	Surface water (Iregua river)	-	Vineyards	
BJ-S5	Surface water (Leza river)	-	Vineyards	
BJ-S6	Surface water (Villar de Arnedo river)	-	Vineyards	

2.3. Analytical methodology

Table S3. Quality control parameters of the SPE-LC-MS method applied to the analysis of herbicides and insecticides in surface and ground waters.

Pesticide	SIM ion m/z	V cone (V)	RT (min)	Recovery[a] (%)	RSD (%)	r^2 (0.1-2.0 μg L^{-1})[b]	LOD[c] (μg L^{-1})	LOQ[d] (μg L^{-1})
Chlorsulfuron	358.1	20	4.52	67	11	0.990	0.025	0.071
Flazasulfuron	408.2	20	5	71	12	0.993	0.041	0.106
DIHA	156.1	25	6.6	63	14	0.991	0.046	0.112
Acephate	184.1	15	6.9	68	10	0.990	0.064	0.147
DEHA	170.1	25	7.3	67	15	0.996	0.048	0.107
DIA	174.2	25	9.3	82	8	0.999	0.013	0.034
Imidacloprid	256.2	15	9.3	103	7	0.991	0.019	0.048
Chloridazon	222.1	30	10.3	86	14	0.993	0.021	0.058
Dimethoate	230.2	15	10.5	80	18	0.996	0.023	0.054
Metamitron	203.2	25	10.6	69	16	0.990	0.019	0.030
HA	198.1	25	10.8	71	10	0.997	0.037	0.065
DEA	188.1	25	11.1	81	15	0.997	0.021	0.064
HT	212.2	25	12.9	76	11	0.990	0.027	0.080
Metribuzin	215.1	20	13.2	65	12	0.991	0.01	0.024
CMPU	185.1	20	13.5	90	10	0.994	0.039	0.089
DET	202.2	20	13.5	84	9	0.994	0.016	0.046
Carbaryl	202.2	15	14.0	81	11	0.996	0.022	0.069
Lenacil	235.2	15	14.9	94	5	0.996	0.026	0.061
Isoproturon	207.2	25	15.2	78	13	0.990	0.021	0.065
Chlorotoluron	213.2	20	15.5	85	13	0.993	0.015	0.040
Atrazine	216.1	30	16.0	86	7	0.993	0.011	0.040
Metobromuron	259.1	20	16.1	77	5	0.996	0.018	0.061
Fluometuron	233.2	20	16.2	87	8	0.993	0.019	0.047
Pirimicarb	239.2	20	16.8	69	12	0.996	0.012	0.028
Diuron	233.2	25	17.0	93	10	0.992	0.013	0.041
Propazine	230.2	25	18.7	74	12	0.995	0.022	0.058
Terbuthylazine	230.2	25	19.1	81	9	0.996	0.011	0.038
Ethofumesate	287.2	20	19.2	70	10	0.993	0.015	0.048
Methoxyfenozide	369.3	20	20.5	73	10	0.998	0.016	0.042
Linuron	250.1	20	20.6	69	11	0.995	0.023	0.061
Metolachlor	284.2	15	22.1	78	14	0.990	0.020	0.038
Dichlofop-methyl	341.2	15	22.3	-	-	0.990	0.098	0.215
Chlorpyrifos	350.1	20	27.3	65	12	0.991	0.031	0.055
Cypermethrin	416.2	20	27.6	-	-	0.991	0.094	0.207

[a] Calculated from the replicated analysis ($n = 5$) of spiked (0.1 μg L^{-1}) groundwater samples; [b] Linear calibration range; [c] LOD Detection limit for a signal-to-noise ratio of 3. [d] LOQ Quantification limit for a signal-to-noise ratio of 10

Table S4. Quality control parameters of the SPE-GC-MS method applied to the analysis of herbicides and insecticides in surface and ground waters.

Compound	RT (min)	Monitored ions (Abundance)		Recovery^a (%)	RSD^a (%)	r^2 (0.1-1.5^b µg L^{-1})	LOD^c (µg L^{-1})	LOQ^d (µg L^{-1})
		Target (m/z)	Qualifier Ions (m/z)					
Fluometuron	4.5	174	219 (794)/187 (536)	94	12	0.997	0.018	0.058
Metobromuron	7.8	229	231 (995)/199 (497)	85	15	0.991	0.026	0.059
DET	8.3	186	188 (319)/83 (287)	99	19	0.991	0.008	0.025
DEA	8.4	172	174 (321)/187 (315)	85	14	0.997	0.018	0.053
DIA	8.6	173	158 (870)/145 (751)	81	16	0.990	0.011	0.038
Propazine	8.8	214	229 (659)/172 (622)	79	15	0.996	0.012	0.037
Atrazine	9.2	200	215 (591)/58 (389)	81	14	0.997	0.016	0.048
Terbuthylazine	9.3	214	43 (574)/173 (512)	81	13	0.994	0.004	0.011
Simazine	9.5	201	44 (795)/186 (624)	79	16	0.992	0.013	0.034
Dimethoate	10.4	87	93 (535)/125 (454)	83	17	0.990	0.037	0.087
Acetochlor	10.9	59	146 (839)/162 (696)	82	15	0.993	0.014	0.033
Alachlor	11.4	45	160 (378)/188 (304)	108	12	0.998	0.020	0.058
Pirimicarb	11.5	166	72 (877)/238 (237)	75	15	0.996	0.014	0.039
Metolachlor	13.1	162	238 (469)/45 (197)	81	15	0.998	0.008	0.023
Terbutryn	13.2	226	185 (838)/170 (629)	68	17	0.996	0.026	0.073
Metribuzin	13.3	198	57 (216)/199 (190)	81	18	0.998	0.021	0.064
Ethofumesate	14.0	207	161 (752)/137 (376)	78	12	0.996	0.010	0.028
Metamitron	25.2	104	202 (864)/174 (456)	75	13	0.992	0.019	0.054
Lenacil	26.0	153	53 (90)/154 (86)	97	14	0.999	0.017	0.043

[a] Calculated from the replicated analysis (n = 6) of spiked (0.1 µg L^{-1}) groundwater samples; [b] Linear calibration range. [c] LOD Detection limit for a signal-to-noise ratio of 3. [d] LOQ Quantification limit for a signal-to-noise ratio of 10.

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