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INTRA-ANNUAL TRENDS OF FUNGICIDES RESIDUES IN WATERS FROM VINEYARD AREAS IN LA RIOJA REGION OF NORTHERN SPAIN

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Abstract

The temporal trends of fungicides in surface and ground water in ninety samples, including both surface waters (12) and ground waters (78) from an extensive vineyard area located in La Rioja (Spain) were examined between September 2010 and September 2011. Fungicides are used in increasing amounts on vines in many countries, and they may reach the water resources. However, few data have been published on fungicides in waters, with herbicides being the more frequently monitored compounds. The presence, distribution and year-long evolution of seventeen fungicides widely used in the region and a degradation product were evaluated in waters during four sampling campaigns. All the fungicides included in the study were detected at one or more of the points sampled during the four campaigns. Metalaxyl, its metabolite CGA-92370, penconazole and tebuconazole were the fungicides detected in the greatest number of samples, although myclobutanil, CGA-92370 and triadimenol were detected at the highest concentrations. The highest levels of individual fungicides were found in Rioja Alavesa, with concentrations of up to 25.52 μg L^{-1}, and more than 40% of the samples recorded a total concentration of >0.5 μg L^{-1}. More than six fungicides were positively identified in a third of the ground and surface waters in all the sampling campaigns. There were no significant differences between the results obtained in the four sampling campaigns, and corroborated a pattern of diffuse contamination from the use of fungicides. The results confirm that natural waters in the study area are extremely vulnerable to contamination by fungicides, and highlight the need to implement strategies to prevent and control water contamination by these compounds.

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

1. Introduction

In agriculture, the more intensive use of pesticides to prevent and combat fungi, weeds and insects, the greater the potential discharge of these compounds into aquatic ecosystems. These products or their degradation products, may remain in the environment, and this has become a growing concern in recent years (Picó and Barceló, 2015; Ccanccapa et al., 2016; Teklu et al., 2016). Intensive agriculture combined with factors enhancing leaching and the hydrogeological characteristics of the unsaturated zone may lead to increased levels of pesticides in groundwater (Vryzas et al., 2012). As a result of this, a persistent threat to the environment and even to human health may occur, and it has required the drafting of strict directives by the European Commission (EC) to minimize the negative effects on the environment. Council Directive 98/83/EC (EC, 1998) set the limits for pesticides in water intended for human consumption at 0.1 μg L^{-1} for individual pesticides and 0.5 μg L^{-1} for the sum of all pesticides. More recently, EC Directive (EC, 2000, 2008) established a framework for Community action in the field of water policy, and approved a list of 33 priority compounds in the field of water policy. One-third of the compounds included on this list are pesticides, reflecting the EC's concern at the presence of these compounds in water (EC, 2013).

Fungicides are a group of pesticides used to combat fungi and (or) their spores. They can be chemical or biological, and act systemically or via contact with plant surfaces to prevent foliar diseases in a wide range of crops. The main market for fungicide is in Europe, where these compounds are critical components for the protection of grapevine and other crops (Oliver and Hewitt, 2014). According to data of FAOSTAT (2015) the use of fungicides and bactericides in the European Union was approximately 143500 t of active ingredients in 2013, which was higher than that in North America countries (85000 t of active ingredients).

A number of studies have reported fungicides in European waters. For example fungicides of the azole family have been found in samples from Swiss Midland lakes (Kahle et al., 2008); the metabolites of some fungicides (tolylfluanid, chlorothalonil, and trifloxystrobin) were found in waters from different areas in Germany (Reemtsma et al., 2013), and several fungicides were also detected by Gonçalves et al. (2007) in the waters of a vulnerable zone in Portugal, while carbendazim was the fungicide most frequently detected in several rivers and groundwaters influenced by agriculture in Serbia (Dujakovic et al., 2010).

Elsewhere azoxystrobin was the most frequently detected fungicide, followed by by metalaxyl, propiconazole, myclobutanil, and tebuconazole in southern and central USA (Battaglin et al. 2011). Also in the US, Reilly et al. (2012) detected at least one fungicide in 75% and 58% of the surface and ground waters, respectively, from three geographical areas of intense fungicide use. In Vietnam, isoprothiolane is the one most frequently detected in samples from locations influenced by rice growing (Van Toan et al., 2013), in Costa Rica it has been found in waters from an area impacted by nearby pineapple and banana plantations (Echeverria-Saenz et al., 2012), and in Australia it was shown the presence of residues of many different organic fungicides in the surface waters of a horticultural production catchment (Wightwick et al. 2012).

In Spain, the occurrence of a relatively low number of fungicides waters in different areas around the Mar Menor lagoon (SE Spain) (Moreno-González et al., 2013), in Andalusia (southern Spain) (Belmonte Vega et al., 2005) and in the Ebro River basin (Ccanccapa et al., 2016) have been found. Fungicides were also detected in soils from the La Rioja (northern, Spain), mainly metalaxyl and its metabolite, kresoxim-methyl and triadimenol (Pose-Juan et al., 2015). Metalaxyl, cyprodinil and penconazole were detected in the sediments and soils in different parts of Spain, such as a small river basin partially occupied by vineyards in Galicia (Bermúdez-Couso et al., 2007). Tebuconazole was detected in the basin of the River

Llobregat (Catalonia, Spain), although pesticide residues do not seem to pose a high risk to the local biota (Masiá et al., 2015). However, to date, there is clearly a lack of data regarding the presence and temporal evolution of fungicides in natural waters, especially in areas where they are widely used, such as agricultural zones where the main crop is vine.

Spain is the European country with the most land set aside for vineyards (14% of the total area), and is the third in terms of wine production, behind Italy and France (International Organisation of Vine and Wine - OIV, 2015). La Rioja is the fifth region in Spain in grape production. Its wines are protected by the oldest Qualified Designation of Origin (DOCa) in Spain. The DOCa Rioja is the Spanish market leader for fine wines, with nearly 40% of the total sales (Rioja DOCa - Qualified Designation of Origin, 2015). Hildebrandt et al. (2008) and Navarro et al. (2010) reported the presence of different pesticides (including fungicides) along the River Ebro, with some sampling points in La Rioja itself, although the monitoring was too sporadic to provide a clear picture of water conditions in this area. Previous studies we have carried out in this area have revealed the presence of a wide range of fungicides in surface and ground waters (Herrero-Hernández et al., 2012 and 2013). However, no study of the temporal variation of fungicides in surface and ground waters has been conducted, although one is required, considering the seasonal application of these compounds in vineyards and to other crops in this area.

The aim of this work was to study the intra-annual trends of fungicides widely used in vine cultivation in ground and surface waters from the wine-growing region of La Rioja (Spain), and evaluate the pollution of natural waters by these compounds according to the levels permitted by EU legislation (0.1 μg L^{-1}) (EC, 1998). Ninety sampling points, including wells, springs, uptakes and rivers, were sampled in the vineyard region of DOCa Rioja, and 17 fungicides were monitored in samples collected in four campaigns over the course of a year in order to explore the following: i) The temporal trends of the individual concentrations of fungicides in waters, ii) the temporal trends of the total concentrations of fungicides in waters, and iii) the variability of the fungicide concentrations in all the samples from different subareas and sampling campaigns.

2. Materials and methods

2.1. Chemicals

The standards of 17 fungicides and a degradation product were supplied by Fluka, Dr. Ehrenstorfer (Augsburg, Germany), Syngenta (Basel, Switzerland), and Riedel-de Haën (Seelze-Hannover, Germany) (minimum purity higher than 98%). The common names and physicochemical properties of the fungicides are listed in Table S1 in the Supplementary Material.

2.2. Characterization of the study area

The DOCa Rioja wine region is located in northern Spain, straddling the River Ebro (Fig. 1). The valley has a maximum width of around 40 km and an area of ~ 64,000 ha. It is covered by vineyards with the DOCa designation that occupy successive terraces to an altitude of around 700 m above sea level, and produce 280-300 million litres of wine per year. This area is divided into three subareas: Rioja Alta (ALT), with an Atlantic climate and chalky-clay, ferrous-clay or alluvial soils; Rioja Alavesa (ALV), with an Atlantic climate, and chalky-clay soils on terraces and small plots, and Rioja Baja (BJ), with a drier and warmer climate and alluvial and ferrous-clay soils (Herrero-Hernández et al., 2013). The region usually records mild temperatures between 7ºC and 20ºC and an annual rainfall between 300 and 400 mm (Rioja DOCa - Qualified Designation of Origin, 2015) with a rainfall pattern mainly winter dominated. The mobility of pesticides is favoured in the area because the soils generally have a low organic matter (OM) content (<1.5 %) and a sandy clay loam or sandy loam texture (Pose-Juan et al., 2015).

2.3. Sample collection and analytical methodology

A total of ninety water samples were collected from three different agricultural areas in the three different subareas of Rioja Alavesa (15 points), Rioja Alta (34 points), and Rioja Baja (41 points). Twelve samples were surface waters (two on the River Ebro at the end of La Rioja region, six on the main tributaries, one on the Lodosa canal, and three on small rivers), and seventy-eight samples were groundwaters from private wells (44) with depths <10 m (39) or >10 m (5), and uptakes or springs (Herrero-Hernández et al., 2013). Table S2 in the Supplementary Material provides the characteristics of the sampling points in terms of water type (surface or ground water) and water depth (well, spring, uptake or river), crop cultivated and watering use. The wells were located inside the cultivated fields or next to them, and they were generally used for irrigation purposes. Samples were collected manually or after 10 min of water pumping, using the pipes and the electrical pumps used by the farmer in each case. They were collected over a year in four sampling campaigns: September 2010 (Sept-10), March 2011 (Mar-11), June 2011 (Jun-11) and September 2011 (Sept-11).

All the water samples were collected in 2 L brown glass bottles and transported to the laboratory in iceboxes. They were filtered through nitrocellulose screens with Minisart NY 25 filter 0.45 μm (Sartorius Stedim Biotech, Germany), and fungicides were removed by solid-phase extraction after a SPE preconcentration step with polymeric cartridges (Oasis HLB, 60 mg, Waters). Samples analysis was carried out by gas chromatography–mass spectrometry (GC–MS) or by liquid-chromatography-mass spectrometry (LC–MS), as indicated in Herrero-Hernandez et al. (2012 and 2013). The analytical conditions and quality control parameters are shown in Tables S3 and S4, respectively, in the Supplementary Material.

2.4. Statistical analysis and data processing

Pearson correlations were calculated to relate the concentrations of fungicides in waters and the properties of fungicides. Principal component analysis (PCA) was used as a tool to explore the data variability of the fungicide concentrations in all the samples from different subareas and sampling times. This multivariate data analysis transforms the set of possible correlated measured variables into a reduced set of a few uncorrelated variables, and it is used to facilitate the assessment of the potential contamination sources from data obtained in large-scale monitoring studies. A total of 6480 results were evaluated from the analysis of 360 samples. The matrix of scores and the matrix of loadings were obtained to give information, respectively, on the distribution of patterns or sources of contamination among samples (map of samples) and on the contribution of the original variables to each one of these contamination patterns or sources (map of variables). IBM SPSS Statistics 22 software was used for data processing.

3. Results and discussion

3.1. Intra-annual evolution of the individual concentrations of fungicides in waters in DOCa Rioja

Residual concentrations of fungicides were detected in most of the samples analysed in the three subareas of DOCa Rioja (Tables 1-4), although there were several points where fungicides were detected in any of the sampling periods. All the fungicides were detected in one or more of the four sampling campaigns, and most of them were detected in one or more of the samples; only iprovalicarb and cyproconazole were not detected in any sample in September 2010 and March 2011, respectively. Other compounds were detected in five or fewer samples, such as nuarimol, trifloxystrobin and dimethomorph in March 2011, nuarimol and trifloxystrobin in June 2011, and iprovalicarb, azoxystrobin and dimethomorph in September 2011 (See Tables 1-4). These results confirm how vulnerable the natural waters in the study area are to contamination by fungicides due to their widespread use in vineyards - the main crop. There was, nonetheless, a high percentage of sampling points that met the EU quality standard for individual compounds, with concentration levels below 0.1 μg L^{-1} according to the percentages of total samples in which the fungicides were not detected, or were detected below or above this legally established limit (See Fig. 2)

The most abundant and ubiquitous compounds detected in the first sampling campaign (Sept-10) were metalaxyl (52 samples, 12 of them with concentrations > 0.1 μg L^{-1} (52/12) and a maximum concentration (Cmax) of 1.299 μg L^{-1}), its metabolite CGA-92370 (51/8, and Cmax of 16.47 μg L^{-1}), penconazole (43/13 and Cmax of 0.342 μg L^{-1}), tebuconazole (42/14 and Cmax of 1.968 μg L^{-1}) and kresoxim-methyl (40/16 and Cmax of 0.287 μg L^{-1}). Other compounds detected in this sampling in high concentrations were myclobutanyl, azoxystrobin and triadimenol, at Cmax of 12.61, 4.778 and 4.332 μg L^{-1} respectively. In all cases, these Cmax were detected in samples from Rioja Alavesa.

Some of these compounds, such as tebuconazole (67/3 and Cmax of 3.236 μg L^{-1}), metalaxyl (45/12 and Cmax of 8.015 μg L^{-1}), kresoxim-methyl (45/7 and Cmax of 0.574 μg L^{-1}), and penconazole (41/5 and Cmax of 3.683 μg L^{-1}), were also the most ubiquitous compounds in the sampling campaign carried out in Mar-11, together with pyrimethanil (58/6 and Cmax of 0.234 μg L^{-1}) and triadimenol (40/12 and Cmax of 3.103 μg L^{-1}). The metabolite of metalaxyl and myclobutanyl were the other compounds detected in high concentrations (Cmax of 7.226 and 7.208 μg L^{-1}, respectively). Cmax data were recorded for tebuconazole, myclobutanil, triadimenol, metalaxyl and its metabolite in Rioja Alavesa, for penconazole, triadimenol and metalaxyl in Rioja Alta, and for metalaxyl and triadimenol in Rioja Baja.

The same fungicides were also detected in the sampling campaigns carried out in Jun-11 (metalaxyl (59/19 and Cmax of 18.85 μg L^{-1}), its metabolite CGA-92370 (55/9 and Cmax of 1.643 μg L^{-1}), and triadimenol (34/14 and Cmax of 8.470 μg L^{-1}), together with azoxystrobin (50/3 and Cmax of 0.463 μg L^{-1}) and myclobutanil (33/18 and Cmax of 3.091 μg L^{-1}); and in the last sampling campaign carried out in Sept-11, penconazole (47/12 and Cmax of 0.476 μg L^{-1}), metalaxyl (39/8 and Cmax of 1.848 μg L^{-1}), cyproconazole (39/4 and Cmax of 0.154 μg L^{-1}), tebuconazole (37/7 and Cmax of 3.023 μg L^{-1}) and myclobutanil (33/6 and Cmax of 5.068 μg L^{-1}). High concentrations were also detected in Rioja Alavesa and in Rioja Alta in the June-11 and Sep-11 sampling campaigns (Tables 1-4).

It is evident that metalaxyl, its metabolite CGA-92370, penconazole and tebuconazole were the fungicides detected in a greater number of samples, although myclobutanil, CGA-92370 and triadimenol were detected in higher concentrations. Fig. 3 shows the evolution of the sum of concentrations of these compounds in all the samples over the four campaigns in the three subareas of DOCa Rioja. Peak concentrations were found in March (penconazole and tebuconazole), June (metalaxyl and myclobutanil), and September (CGA-92370, myclobutanil, triadimenol and tebuconazole), and they could be related to the application of these fungicides following the recommendations made by the authorities and experts for tackling *ad hoc* diseases in the different areas (Gobierno de La Rioja, 2016). The highest fungicide concentrations were obtained for samples located in Rioja Alavesa, except for penconazole, which recorded a concentration peak in Rioja Alta.

A certain relationship was found between water solubility, GUS index or Kow, and the total concentrations of these fungicides, although it was significant only for water solubility (excluding metalaxyl) in the June sampling ($r=0.88$, $p<0.10$), for the GUS index in the September sampling ($r=0.82$, $p<0.10$), and for Kow ($r=-0.94$ and -0.99 ($p<0.01$)) in the March and June samplings, respectively. However, no significant correlations were found for these parameters when all the fungicides were considered jointly.

Residues of the fungicides included in this study were also detected in surface waters in the province of Almería (SE Spain) (pyrimethanil, myclobutanil, benalaxyl, nuarimol, tebuconazole and azoxystrobin) (Ruiz Gil et al., 2008). Furthermore, the levels of fungicides found are similar to those reported in other European agricultural regions in Germany (Berenzen et al., 2005) and Greece, where triadimenol, cyproconazole, pyrimethanil and benalaxyl were detected in several water samples (Thomatou et al., 2013), and more recently, fungicides have been detected in 14% of the samples in the basin of Lake Vistonis, with metalaxyl being the compound found in higher concentrations (Papadakis et al., 2015).

Other studies found residues of some of the fungicides included in this work in several agricultural regions in countries as Argentina (tebuconazole with a mean concentration of 0.033 μg L^{-1}) (De Geronimo et al., 2014), Costa Rica (myclobutanil, triadimenol, cyprodinil and metalaxyl reaching values of 0.082 μg L^{-1} for metalaxyl) (Echeverría-Sáenz et al., 2012), Brazil (tebuconazole, azoxystrobin and trifloxystrobin reaching concentrations up to 0.037 μg $L^{−1}$ in river water samples) (Montagner et al., 2014), USA in samples from streams, ponds, and shallow groundwaters in areas of intense fungicide use (azoxystrobin, pyrimethanil, cyprodinil and dimethomorph with concentrations up to 0.180 μg L^{-1} (Reilly et al., 2012) and in water samples from streams in 13 states (azoxystrobin, metalaxyl, myclobutanil, tebuconazole and trifloxystrobin with concentrations up to 1.13 μg L^{-1}) (Battaglin et al., 2011), and Australis in the surface water samples (myclobutanil, pyrimethanil, cyproconazole, trifloxystrobin, and fenarimol at concentrations >0.2 μg $L^{−1}$) (Wightwick et al. 2012).

3.2. Intra-annual evolution of the total concentration of fungicides in waters in DOCa Rioja

The temporal evolution of the total concentration of fungicides was studied to establish the ‘good chemical status’ of surface and ground waters according to the European Directive (EC, 2008). This Directive establishes a limit of 0.5 μg L^{-1} for the aggregate concentration of pesticides to be applied to drinking water. In groundwater (Fig. 4), the results in Sept-10 showed up to 11 samples in Rioja Alta (35%) with ∑concentration of fungicides above 0.5 μg L^{-1}, and a number of samples in Rioja Alavesa (2) and Rioja Baja (1) with ∑concentrations above 25 μg L^{-1}. In Mar-11, up to nine samples were detected in Rioja Alta (29%) with ∑concentration of fungicides above 0.5 μg L^{-1}, as well as samples with concentrations >15 μg L^{-1} in Rioja Alavesa (2), and >10 μg L^{-1} in Rioja Alta (1) and Rioja Baja (1). In Jun-11, up to nine samples were detected in Rioja Alta (29%) containing fungicide concentrations above 0.5 μg L^{-1}, and samples with concentrations above 8 μg L^{-1} were found in Rioja Alavesa (3) and Rioja Baja (1). In the last sampling campaign (Sept-11), up to five samples were found in Rioja Baja (17%) containing fungicides adding up to more than 0.5 μg L^{-1}, and there were three samples in Rioja Alavesa with concentrations above 9 μg L^{-1}.

No significant relationship was found between the depth of the groundwater and the total content of fungicides. The wells deeper than 10 m recorded, in general, the lowest content of fungicides although it was not possible to find relationships with parameters of soils or local hydrologic conditions. However it was observed that less polluted groundwaters corresponded to wells located in areas where the main crops are fruit trees, cereals, etc. with lower amounts of fungicides than in vineyard are applied. On the other hand it worth noting that the high levels of total concentration over the four sampling campaigns in Rioja Alavesa (2), Rioja Alta (1) and Rioja Baja (1) were found at the same sampling points. They correspond to groundwater samples from shallow wells (1-3 m) in areas where the vineyard is the only crop and this may be due to improper handling of these products in the vicinity of wells.

In surface waters, the results obtained in the four sampling periods indicated ∑concentrations of fungicides above 0.5 μg L^{-1} in 0-2 samples (0-66%) in Rioja Alavesa, in 2-3 samples (33-100%) in Rioja Alta, and in 1-2 samples (16-66%) in Rioja Baja.

This total concentration of fungicides in waters is generally due to the presence of a different number of compounds. In groundwaters, the results indicate that no fungicides were detected in just seven of the 78 samples in Sept-10, eight in Mar-11, two in Jun-11 and seventeen in Sept-11, but more than six fungicides were detected in a higher number of samples (29 in Sept-10, 23 in Mar-11, 25 in Jun-11, and 23 in Sept-11) (Fig 5a). In surface waters, the number of samples positively identifying more than six fungicides was four in Sept-10, five in Mar-11 and Jun-11, and six in Sept-11 (Fig 5b). The percentage of samples with a high number of fungicides (29-37% of groundwaters and 33-50% of surface waters) again highlights the widespread use of different compounds on local crops (vines and fruits) due to the different diseases affecting them, which are mainly Downy mildew (*Plasmapora viticola*), *Botrytis cinerea*, and Powdery mildew (*Uncinula necator)*.

3.3. Principal component analysis

Principal component analysis (PCA) was used as a multivariate analysis tool to explore the relationships among the concentrations of fungicides measured in different subareas and sampling campaigns, and evaluate their variability. The results indicate that all the variables are explained to a greater or lesser extent by the factors obtained from the analysis. In agreement with the explained total variance, the number of principal components (PCs) with eigenvalues >1 that better explain the variables were six and five, respectively, for ground and surface waters. These PCs explain 70.93% of the variance of fungicide data from groundwater samples, whereas a higher variance (73.79%) was explained by the data from surface water samples. Similar variances were explained when data were arranged by subarea or sampling campaign.

For groundwater, the first PC explained 25.38% of the total data variance, and for surface waters this first PC explained 25.71% of the variance (Table 5). In general, all the loadings were positive and high, indicating a pattern of diffuse contamination from the use of fungicides in the areas studied. This first PC was mainly explained for groundwaters by the presence of myclobutanil, tebuconazole and dimethomorph, and for surface waters by the presence of cyprodinil and pyrimethanil, while other fungicides made a lower contribution to PC1. Certain variables, such as triadimenol, metalaxyl or its metabolite CGA-92370, recorded a greater loading in other PCs (Table 5). The results indicate that CGA-92370 and metalaxyl did not dominate similar PCs, although CGA-92370 is produced by the degradation of metalaxyl.

Score plots for PC1 vs. PC2, representing the distribution of sampling sites from different subareas and sampling campaigns corresponding to groundwaters (Fig. 6a) and surface waters (Fig. 6b) as well as the distribution of sampling sites from different campaigns corresponding to ground and surface waters (Fig. 7) were only included. Score plots for data distributed in other limited regions of space encompassed by different well-defined PC axes are not shown because they are not relevant. The distribution of variables in different groundwaters was fairly uniform around the origin of the axis, although some sites in Rioja Alavesa and Rioja Alta are outstanding (Fig. 6a). The variables from Rioja Alavesa groundwaters stand out in all the sampling campaigns, whereas the variables from Rioja Alta groundwaters only do so in the Mar-11 sampling. This agrees with the high values found for metalaxyl, CGA-92370, tebuconazole, triadimenol and myclobutanil in some sites in Rioja Alavesa, and penconazole in some sites in Rioja Alta. The outstanding points in the Mar-11 sampling might indicate residual contamination from previous campaigns at certain hot spots. The variables were also uniformly distributed around the origin of the axis, with some sites standing out in different surface waters. In this case, Rioja Alta sites recorded greater variability in the four sampling campaigns, whereas they were only outstanding for Rioja Alavesa in the Jun-11 sampling.

The variables are distributed around the origin of the axis in different surface waters, whereas they are distributed in the lower quadrant with only some outstanding points through the upper right quadrant in groundwaters in all the sampling campaigns (Fig. 7). Surface water recorded lower levels of fungicides than groundwaters and a lower detection rate. These results could be explained by the behavior (sorption and leaching) of fungicides in soils which is depending on the characteristics of soils and fungicides. In a previous study a significant correlation was found between residues of some fungicides in soils from Rioja region and soil characteristics (Pose-Juan et al., 2015). This finding was also reported in other studies on the distribution of pesticides in other areas (Hildebrandt et al., 2008), and it was explained by the rapid degradation of pesticides in surface water, whereas a lower degradation of these compounds could occur in groundwater, making this medium more vulnerable, especially when groundwater is used for human consumption.

4. Conclusions

The study carried out between September 2010 and September 2011 along the wine growing region of La Rioja showed the great diversity of fungicides in the study area and its occurrence in water samples with a dispersed pattern of fungicide concentrations. All the fungicides included in the study were detected in one or more of the four sampling campaigns, and most of them were detected in one or more of the samples in all the campaigns. Metalaxyl, its metabolite CGA-92370, penconazole and tebuconazole were the most frequently detected fungicides, although myclobutanil, CGA-92370 and triadimenol were detected in higher concentrations. These results are consistent with the widespread use of these compounds which are those more applied following information provided by local farmers. The highest concentrations of fungicides were obtained in samples located in Rioja Alavesa regard other zones of the study area, except penconazole with the highest total concentration located in Rioja Alta. Up to 40%, 35% and 25% of groundwaters with a total concentration of fungicides >0.5 μg L^{-1} were detected in the areas studied, and approximately a quarter of the total waters recorded more than six fungicides in all the sampling campaigns. Furthermore, the concentrations in groundwaters were greater than in surface waters in all cases, and samples not too deep located close to vineyard showed the higher concentrations. This could indicate an easier percolation of fungicides in these cases and highlight the need to implement strategies to enhance the retention of these compounds by soils for effective water protection given the imperative use of these compounds in agriculture. The use of biobeds during the handling of pesticides or the washing of equipment and the application of organic amendments to soils may be some of these strategies.

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Figure captions

Figure 1. Map of the Rioja DOCa wine-growing region in Spain including the sampling points (taken from “Plan Nacional de ortofotografía aérea de España”).

Figure 2. Distribution of samples with no detected fungicides or detected in concentrations below or over the limit established by European Directives for human consumption (0.1 μg L^{-1}) in different sampling campaigns: September 2010 (a), March 2011 (b), June 2011 (c) and September 2011 (d).

Figure 3. Changes of total concentrations of the most frequently detected fungicides: metalaxyl, its metabolite CGA-92370, myclobutanil, triadimenol, penconazole and tebuconazole detected in all sampling sites of the different subareas of La Rioja.

Figure 4. Distribution of ground (a) and surface water (b) samples with total concentration of fungicides below or over the limit established by European Directives for human consumption (0.5 μg L^{-1}) in different sampling campaigns in the three subareas of La Rioja.

Figure 5. Percentage of ground (a) and surface water (b) samples with different number of fungicides detected for the four sampling campaigns in the three subareas of La Rioja.

Figure 6. Scores plot for PC1 vs. PC2 showing data distribution of ground waters (a) and surface waters (b) for all the sampling campaigns in the subareas of Rioja Alavesa (ALV), Rioja Alta (ALT) and Rioja Baja (BJ).

Figure 7. Scores plot for PC1 vs. PC2 showing data distribution depending on the type of water for all the sampling campaigns in the three subareas of La Rioja (GW, groundwater; SW, surface water).

Table 1

Number of positive samples (or samples with some compound detected) with concentrations below and over 0.1 μg L^{-1} and average and maximum concentrations for the fungicides detected in the different areas of study in September 2010.

Pesticide	Rioja Alavesa (n = 15)				Rioja Alta (n = 34)				Rioja Baja (n = 41)			
	Positive samples		Concentration (μg L^{-1})		Positive samples		Concentration (μg L^{-1})		Positive samples		Concentration (μg L^{-1})	
	C < 0.1	C > 0.1	Average±SD	C_{max}	C < 0.1	C > 0.1	Average±SD	C_{max}	C < 0.1	C > 0.1	Average±SD	C_{max}
Cymoxanil	0	0	0	0	1	2	0.257±0.193	0.449	4	2	0.089±0.073	0.222
Pyrimethanil	3	3	0.125±0.107	0.331	8	8	0.167±0.167	0.590	10	4	0.089±0.130	0.478
Cyprodinil	2	2	0.109±0.104	0.249	5	4	0.124±0.109	0.352	2	3	0.126±0.087	0.247
Iprovalicarb	0	0	-	-	0	0	-	-	0	0	-	-
Metalaxyl	8	4	0.278±0.480	1.299	15	7	0.105±0.160	0.590	17	1	0.051±0.099	0.435
CGA 92370	7	5	1.853±4.805	16.47	17	1	0.051±0.099	0.435	19	2	0.062±0.148	0.637
Penconazole	6	3	0.095±0.116	0.342	14	3	0.064±0.066	0.209	10	7	0.084±0.070	0.222
Myclobutanil	2	2	3.487±6.107	12.61	7	3	0.087±0.068	0.239	5	4	0.162±0.232	0.750
Triadimenol	6	2	0.903±1.661	4.332	5	0	0.037±0.015	0.063	10	0	0.034±0.012	0.045
Flutriafol	2	0	0.018±0.006	0.022	10	0	0.034±0.012	0.045	8	0	0.021±0.012	0.042
Tebuconazole	4	4	0.321±0.667	1.968	11	4	0.086±0.041	0.164	13	6	0.084±0.048	0.206
Kresoxim-methyl	4	3	0.109±0.094	0.279	7	6	0.124±0.082	0.287	13	7	0.078±0.071	0.206
Nuarimol	3	1	0.100±0.088	0.162	11	4	0.076±0.061	0.202	8	3	0.064±0.048	0.167
Benalaxyl	1	1	0.094±0.073	0.146	10	2	0.089±0.091	0.325	4	6	0.108±0.062	0.214
Azoxyxtrobin	3	3	0.878±1.911	4.778	7	3	0.085±0.058	0.209	7	1	0.058±0.029	0.103
Trifloxystrobin	4	0	0.037±0.028	0.077	7	0	0.053±0.015	0.075	10	0	0.036±0.026	0.086
Dimethomorph	3	2	0.067±0.071	0.170	10	0	0.036±0.019	0.075	6	0	0.023±0.008	0.036
Cyproconazole	1	0	-	0.094	12	0	0.052±0.024	0.092	14	1	0.049±0.025	0.102

Table 2

Number of positive samples (or samples with some compound detected) with concentrations below and over 0.1 μg L^{-1} and average and maximum concentrations for the fungicides detected in the different areas of study in March 2011.

Pesticide	Rioja Alavesa (n = 15)				Rioja Alta (n = 34)				Rioja Baja (n = 41)			
	Positive samples		Concentration (μg L^{-1})		Positive samples		Concentration (μg L^{-1})		Positive samples		Concentration (μg L^{-1})	
	C < 0.1	C > 0.1	Average±SD	C_{max}	C < 0.1	C > 0.1	Average±SD	C_{max}	C < 0.1	C > 0.1	Average±SD	C_{max}
Cymoxanil	0	0	-	-	5	2	0.189±0.315	0.900	0	2	0.166±0.075	0.219
Pyrimethanil	3	3	0.058±0.016	0.089	22	2	0.057±0.041	0.234	27	1	0.049±0.016	0.105
Cyprodinil	2	0	0.080±0.005	0.084	5	4	0.159±0.219	0.737	5	0	0.052±0.033	0.084
Iprovalicarb	2	1	0.077±0.030	0.111	4	1	0.107±0.118	0.315	1	1	0.147±0.080	0.204
Metalaxyl	7	2	0.536±1.139	3.396	14	5	0.204±0.610	2.707	12	5	0.526±1.931	8.015
CGA 92370	3	4	1.566±2.785	7.226	9	4	0.068±0.042	0.164	8	4	0.185±0.300	1.089
Penconazole	9	0	0.052±0.033	0.089	15	4	0.286±0.843	3.683	12	1	0.050±0.089	0.338
Myclobutanil	3	5	1.033±2.498	7.208	4	9	0.189±0.137	0.474	6	7	0.148±0.147	0.404
Triadimenol	5	2	0.573±0.965	2.476	10	4	0.274±0.755	2.889	13	6	0.277±0.698	3.103
Flutriafol	7	1	0.058±0.033	0.100	7	1	0.106±0.154	0.484	4	0	0.038±0.009	0.046
Tebuconazole	13	1	0.270±0.854	3.236	26	0	0.042±0.019	0.093	25	2	0.054±0.041	0.205
Kresoxim-methyl	8	1	0.078±0.054	0.212	16	3	0.088±0.122	0.574	14	3	0.075±0.047	0.232
Nuarimol	2	0	0.071±0.025	0.089	1	0	0.034	0.034	2	0	0.045±0.003	0.048
Benalaxyl	2	0	0.037±0.007	0.043	3	0	0.063±0.017	0.081	3	0	0.054±0.033	0.091
Azoxystrobin	1	1	0.493±0.636	0.943	5	0	0.042±0.023	0.074	3	0	0.042±0.025	0.070
Trifloxystrobin	0	0	-	-	2	1	0.166±0.236	0.439	1	0	0.025	0.025
Dimethomorph	0	2	0.222±0.069	0.271	0	0	-	-	1	0	0.013	0.013
Cyproconazole	0	0	-	-	0	0	-	-	0	0	-	-

Table 3

Number of positive samples (or samples with some compound detected) with concentrations below and over 0.1 μg L^{-1} and average and maximum concentrations for the fungicides detected in the different areas of study in June 2011.

Pesticide	Rioja Alavesa (n = 15)				Rioja Alta (n = 34)				Rioja Baja (n = 41)			
	Positive samples		Concentration (μg L^{-1})		Positive samples		Concentration (μg L^{-1})		Positive samples		Concentration (μg L^{-1})	
	C < 0.1	C > 0.1	Average±SD	C_{max}	C < 0.1	C > 0.1	Average±SD	C_{max}	C < 0.1	C > 0.1	Average±SD	C_{max}
Cymoxanil	4	1	0.176±0.277	0.670	4	1	0.083±0.048	0.163	3	3	0.117±0.109	0.313
Pyrimethanil	3	0	0.044±0.022	0.068	7	1	0.050±0.045	0.143	3	2	0.093±0.058	0.169
Cyprodinil	6	0	0.018±0.009	0.029	13	0	0.021±0.016	0.051	7	0	0.019±0.008	0.028
Iprovalicarb	5	1	0.094±0.021	0.133	8	1	0.076±0.027	0.135	13	2	0.074±0.021	0.110
Metalaxyl	6	6	2.194±5.416	18.85	14	9	0.117±0.132	0.613	20	4	0.169±0.351	1.607
CGA 92370	8	3	0.326±0.577	1.643	20	2	0.066±0.055	0.230	18	4	0.070±0.063	0.245
Penconazole	3	4	0.161±0.143	0.429	6	5	0.139±0.104	0.336	8	5	0.119±0.117	0.363
Myclobutanil	0	6	0.759±1.154	3.091	1	9	0.183±0.118	0.374	14	3	0.083±0.074	0.307
Triadimenol	5	4	0.762±1.690	5.218	0	8	1.218±2.930	8.470	15	2	0.139±0.322	1.362
Flutriafol	3	0	0.037±0.006	0.042	6	0	0.038±0.009	0.054	8	0	0.035±0.013	0.054
Tebuconazole	7	1	0.160±0.374	1.086	5	0	0.044±0.021	0.079	7	1	0.060±0.081	0.254
Kresoxim-methyl	6	0	0.053±0.022	0.083	11	1	0.066±0.024	0.105	11	2	0.089±0.108	0.428
Nuarimol	1	1	0.102±0.066	0.149	2	0	0.055±0.049	0.089	0	1	0.114	0.114
Benalaxyl	4	1	0.057±0.062	0.167	8	2	0.045±0.041	0.135	8	1	0.060±0.031	0.125
Azoxystrobin	9	1	0.078±0.136	0.463	17	2	0.046±0.051	0.241	21	0	0.030±0.012	0.067
Trifloxystrobin	1	0	0.089	0.089	1	0	0.052	0.052	1	1	0.103±0.085	0.163
Dimethomorph	3	2	0.087±0.108	0.238	6	1	0.028±0.036	0.109	6	0	0.019±0.022	0.061
Cyproconazole	4	1	0.200±0.343	0.811	3	0	0.046±0.017	0.066	0	2	0.277±0.217	0.430

Table 4

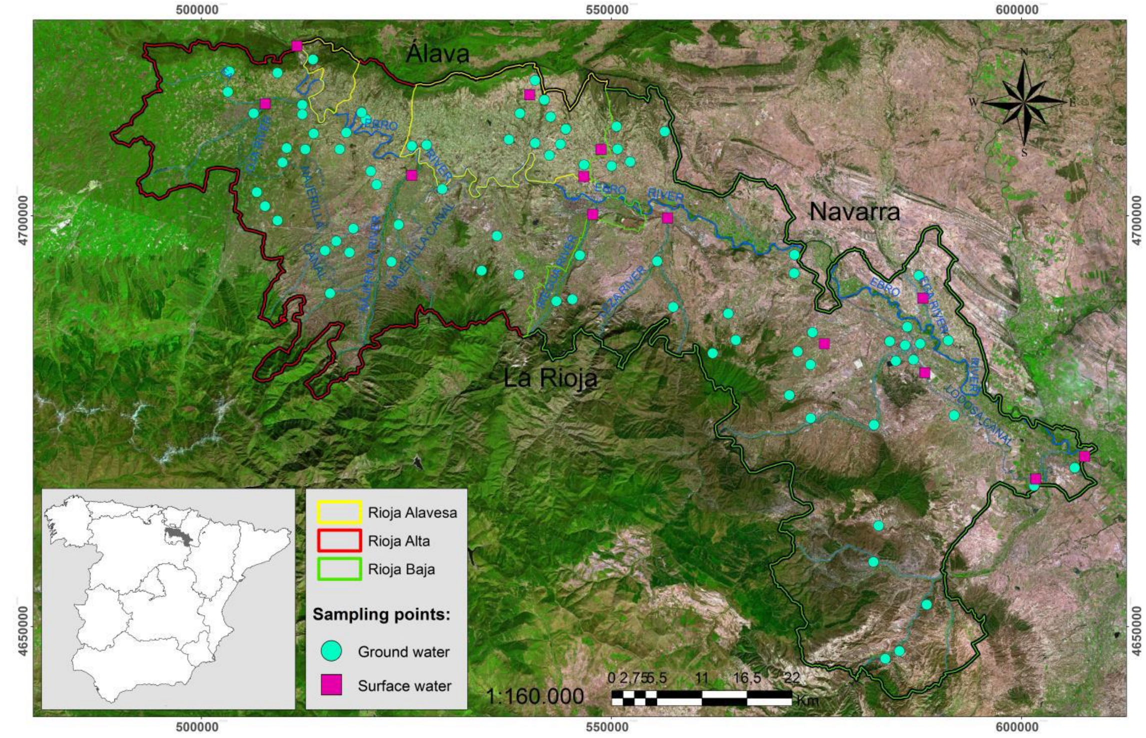
Number of positive samples (or samples with some compound detected) with concentrations below and over 0.1 μg L^{-1} and average and maximum concentrations for the fungicides detected in the different areas of study in September 2011.

Pesticide	Rioja Alavesa (n = 12)				Rioja Alta (n = 30)				Rioja Baja (n = 40)			
	Positive samples		Concentration (μg L^{-1})		Positive samples		Concentration (μg L^{-1})		Positive samples		Concentration (μg L^{-1})	
	C < 0.1	C > 0.1	Average±SD	C_{max}	C < 0.1	C > 0.1	Average±SD	C_{max}	C < 0.1	C > 0.1	Average±SD	C_{max}
Cymoxanil	0	0	-	-	2	0	0.069±0.028	0.088	3	1	0.076±0.022	0.102
Pyrimethanil	4	2	0.075±0.069	0.172	10	2	0.046±0.041	0.113	10	2	0.059±0.040	0.140
Cyprodinil	3	1	0.262±0.480	0.981	11	2	0.071±0.037	0.155	9	1	0.056±0.035	0.121
Iprovalicarb	0	0	-	-	2	0	0.036±0.009	0.042	0	0	-	-
Metalaxyl	5	3	0.421±0.649	1.848	13	2	0.092±0.162	0.666	13	3	0.139±0.333	1.353
CGA 92370	3	4	3.968±7.305	19.97	8	2	0.106±0.094	0.358	6	1	0.070±0.036	0.130
Penconazole	6	3	0.113±0.142	0.476	11	4	0.066±0.041	0.153	18	5	0.063±0.069	0.281
Myclobutanil	2	4	1.603±2.244	5.068	11	0	0.041±0.024	0.082	14	2	0.065±0.054	0.195
Triadimenol	3	4	4.049±9.491	25.52	5	3	0.076±0.058	0.173	9	5	0.112±0.171	0.682
Flutriafol	3	0	0.016±0.015	0.034	4	1	0.052±0.064	0.166	6	1	0.044±0.039	0.110
Tebuconazole	1	3	1.319±1.337	3.023	15	3	0.061±0.043	0.160	14	1	0.055±0.035	0.165
Kresoxim-methyl	2	2	0.120±0.085	0.237	2	9	0.144±0.084	0.362	8	5	0.084±0.043	0.151
Nuarimol	0	0	-	-	0	2	0.201±0.016	0.212	4	2	0.070±0.041	0.120
Benalaxyl	1	1	0.173±0.182	0.302	3	3	0.091±0.054	0.149	6	0	0.036±0.013	0.045
Azoxystrobin	0	2	0.271±0.026	0.289	1	0	0.024	0.024	0	0	-	-
Trifloxystrobin	1	0	0.022	0.022	3	0	0.037±0.022	0.061	9	0	0.043±0.018	0.077
Dimethomorph	1	2	0.196±0.119	0.320	0	0	-	-	0	0	-	-
Cyproconazole	6	1	0.055±0.037	0.107	15	2	0.053±0.036	0.154	14	1	0.052±0.028	0.109

Table 5

Principal component matrix with the loadings to each of the PCs.

	Ground waters						Surface waters				
Variable	PC1	PC2	PC3	PC4	PC5	PC6	PC1	PC2	PC3	PC4	PC5
Cymoxanil	0.056	0.050	0.075	-0.183	0.480	0.007	0.454	0.148	0.634	-0.241	0.061
Pyrimethanil	0.506	0.111	0.045	-0.110	0.514	-0.202	0.664	0.010	0.472	-0.371	0.241
Cyprodinil	0.573	-0.151	-0.319	-0.389	0.244	-0.092	0.701	-0.102	0.536	-0.132	0.052
Iprovalicarb	0.320	0.540	0.101	0.097	-0.397	-0.046	-0.108	0.363	0.212	0.536	-0.048
Metalaxyl	0.326	-0.005	-0.372	-0.060	-0.174	0.635	0.374	0.652	-0.461	0.111	-0.097
CGA 92370	0.542	-0.373	-0.037	0.655	0.108	-0.018	0.303	0.267	-0.380	0.069	0.746
Penconazole	0.590	0.728	-0.070	0.039	-0.118	-0.038	0.644	0.433	-0.271	-0.146	-0.249
Myclobutanil	0.669	-0.382	0.212	-0.038	-0.231	-0.211	0.600	0.387	-0.388	-0.252	-0.123
Triadimenol	0.585	-0.243	-0.558	-0.295	-0.068	0.242	0.345	-0.014	-0.330	0.450	0.665
Flutriafol	0.415	0.724	-0.129	0.097	-0.089	0.019	0.544	-0.467	-0.028	0.388	-0.149
Tebuconazole	0.724	-0.463	-0.019	-0.212	-0.160	-0.213	0.660	-0.258	0.115	0.088	0.282
Kresoxim-methyl	0.575	0.421	0.185	-0.054	0.247	0.075	0.645	-0.347	0.169	0.148	0.111
Nuarimol	0.083	0.053	0.413	-0.127	0.297	0.581	0.652	-0.170	-0.458	0.274	-0.367
Benalaxyl	0.489	-0.163	0.536	-0.034	0.193	0.050	0.436	-0.396	0.048	0.085	-0.233
Azoxyxtrobin	0.302	-0.189	-0.219	0.781	0.256	0.134	0.157	0.534	0.485	0.552	-0.132
Trifloxystrobin	0.503	0.714	-0.001	0.062	0.029	-0.126	0.648	0.410	-0.050	-0.424	-0.215
Dimethomorph	0.785	-0.461	0.033	0.007	-0.147	-0.039	0.037	0.450	0.377	0.686	-0.117
Cyproconazole	0.327	-0.139	0.600	-0.011	-0.374	0.240	0.379	-0.603	-0.252	0.308	-0.230
%Variance	25.38	16.25	8.55	7.88	7.07	5.80	25.71	14.48	13.03	11.77	8.806



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4700000
4650000
Álava
Navarra
La Rioja
EBRO
RIVER
Rioja Alavesa
Rioja Alta
Rioja Baja
Sampling points:
Ground water
Surface water
1:160.000
0 2,75 5,5 11 16,5 22
Km

Figure 1

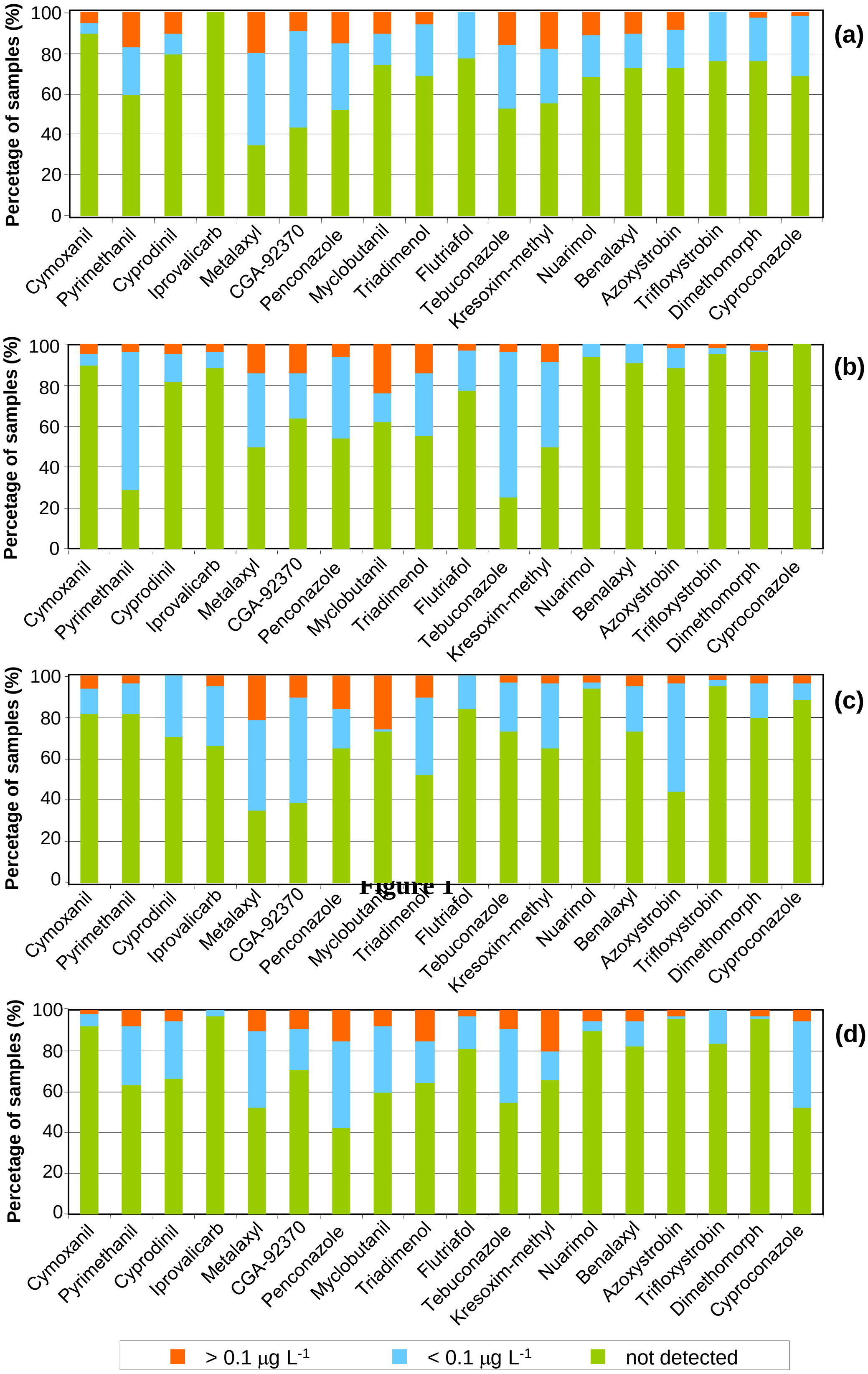

(a)
(b)
(c)
(d)
Percetage of samples (%)
0
20
40
60
80
100
Cymoxanil
Pyrimethanil
Cyprodinil
Iprovalicarb
Metalaxyl
CGA-92370
Penconazole
Myclobutanil
Triadimenol
Flutriafol
Tebuconazole
Kresoxim-methyl
Nuarimol
Benalaxyl
Azoxystrobin
Trifloxystrobin
Dimethomorph
Cyproconazole
> 0.1 µg L-1
< 0.1 µg L-1
not detected

Figure 2

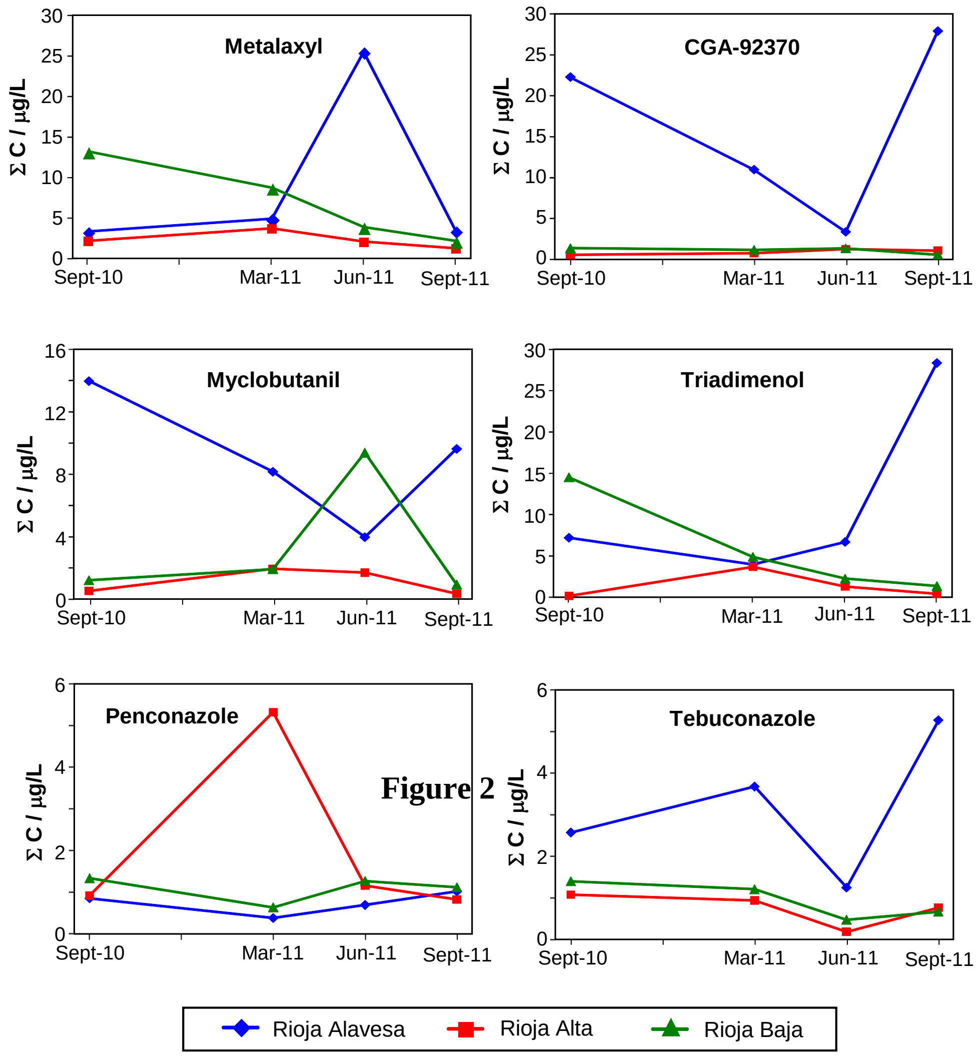
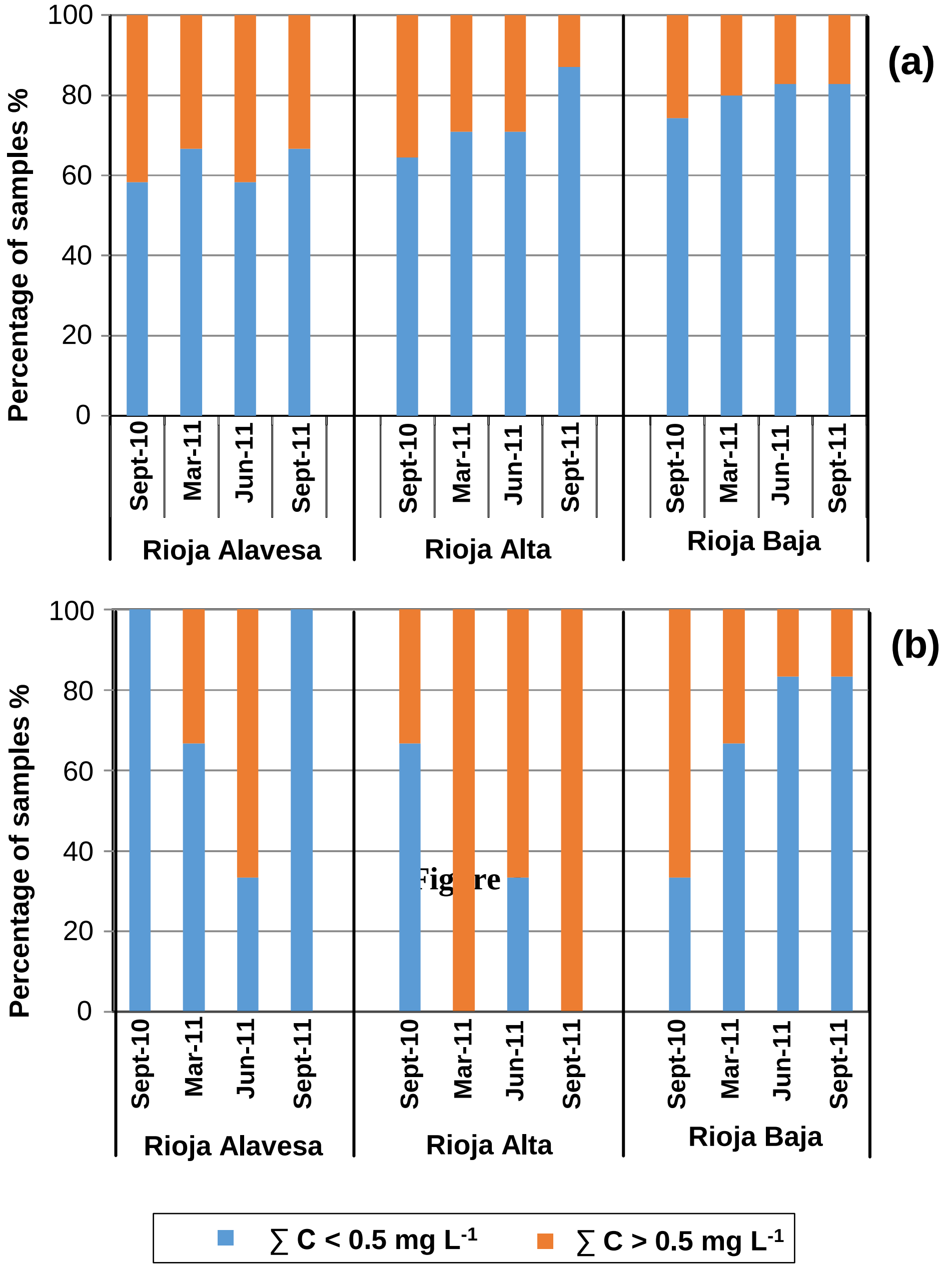

Metalaxyl
CGA-92370
Myclobutanil
Triadimenol
Penconazole
Tebuconazole
Σ C / µg/L
Sept-10
Mar-11
Jun-11
Sept-11
Figure 2
Rioja Alavesa
Rioja Alta
Rioja Baja

Figure 3



(a)
Percentage of samples %
100
80
60
40
20
0
Sept-10
Mar-11
Jun-11
Sept-11
Rioja Alavesa
Rioja Alta
Rioja Baja
(b)
∑ C < 0.5 mg L-1
∑ C > 0.5 mg L-1

Figure 4.

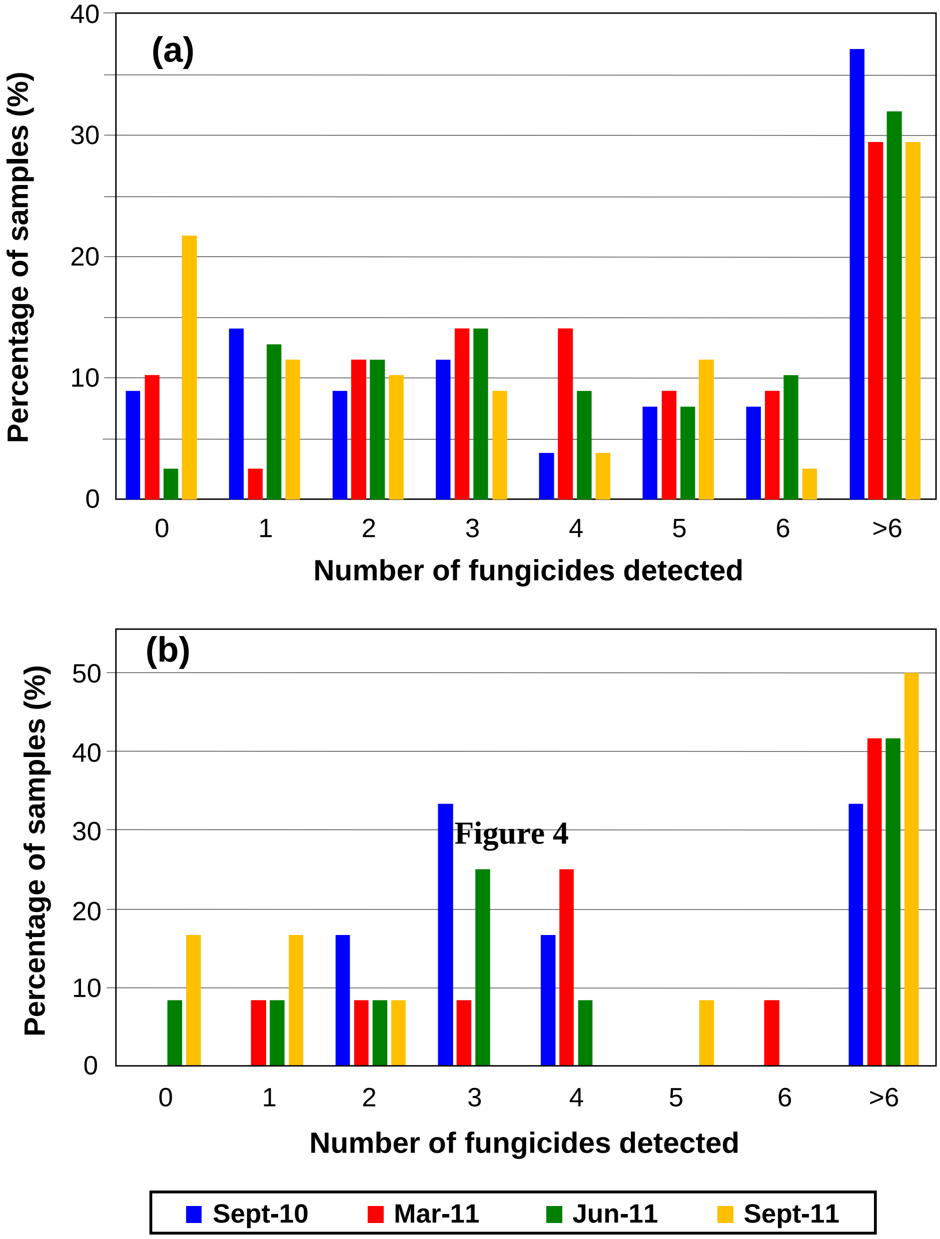

(a)
Percentage of samples (%)
0
10
20
30
40
0
1
2
3
4
5
6
>6
Number of fungicides detected
(b)
Percentage of samples (%)
0
10
20
30
40
50
Figure 4
0
1
2
3
4
5
6
>6
Number of fungicides detected
Sept-10
Mar-11
Jun-11
Sept-11

Figure 5.

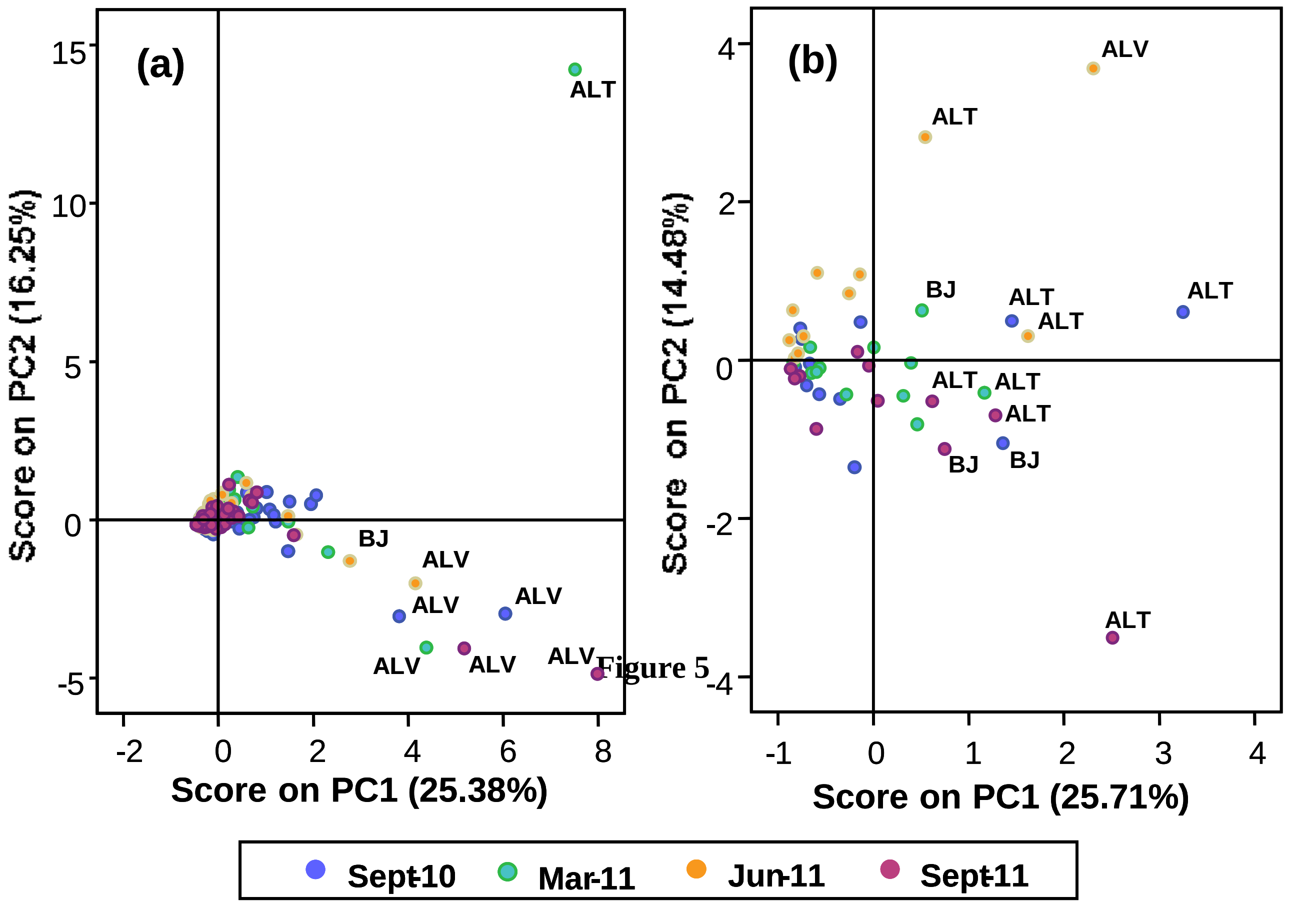
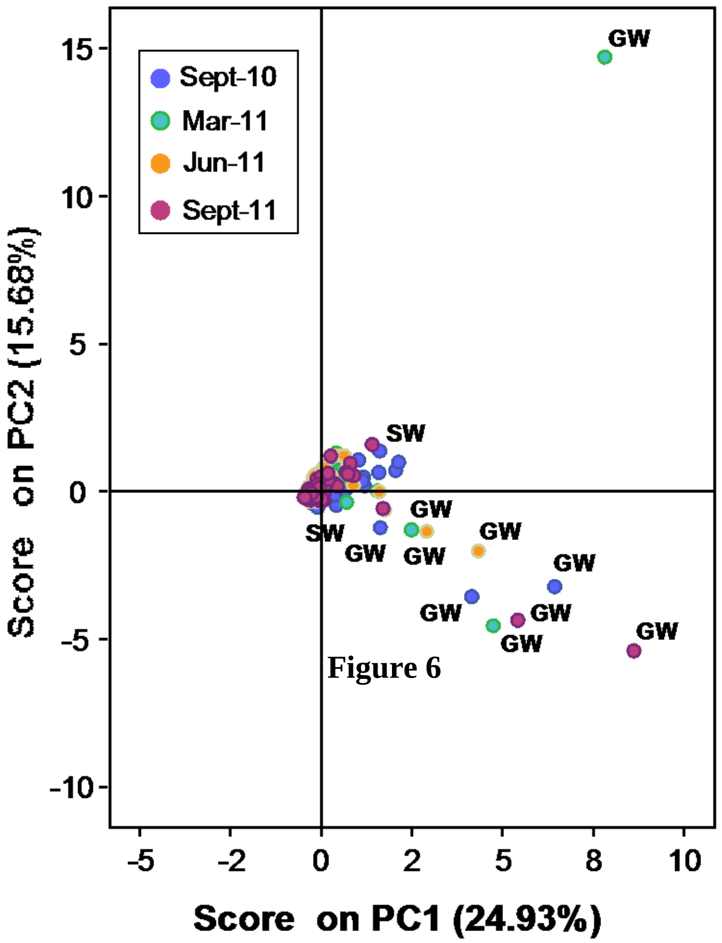


Figure 5

Figure 6



Sept-10
Mar-11
Jun-11
Sept-11
GW
SW
SW
GW
GW
GW
GW
GW
GW
GW
GW
GW
Figure 6
15
10
5
0
-5
-10
Score on PC2 (15.68%)
-5
-2
0
2
5
8
10
Score on PC1 (24.93%)

Figure 7

Supplementary Material

INTRA-ANNUAL TRENDS OF FUNGICIDES RESIDUES IN WATERS FROM VINEYARD AREAS IN LA RIOJA REGION OF NORTHERN SPAIN

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Nº Pages: 7

Nº Tables: 4

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

Pesticide	Water Solubility ($mg\ L^{-1}$)	GUS index	Log Kow	DT50	Application Dose[a] ($g\ ha^{-1}$)
Cymoxanil	780	0.34	0.67	1.4	90-120
Pyrimethanil	121	2.65	2.84	55	1750-2000
Cyprodinil	13	1.2	4.0	53	375
Iprovalicarb	17.8	2.35	3.2	10.5	120-150
Metalaxyl	8400	2.11	1.65	42	200-300
CGA 92370	-	-	-	-	-
Penconazole	73.0	1.51	3.72	117	25-75
Myclobutanil	132	3.54	2.89	365	62
Triadimenol	72.0	3.75	3.18	136.7	100-250
Flutriafol	95.0	5.29	2.3	1587	125
Tebuconazole	36.0	2.0	3.7	365	125-250
Kresoxim-methyl	2.0	1.82	3.4	0.87	<300
Nuarimol	26	3.52	3.18	344	150
Benalaxyl	28.6	0.51	3.54	75	150-210
Azoxystrobin	6.0	2.53	2.5	84.5	250
Trifloxystrobin	0.61	0.53	4.5	2	75-180
Dimethomorph	28.95	2.56	2.68	56.7	1500
Cyproconazole	93	3.25	3.09	142	<1

[a] Data taken from PPDB (2015) and De Liñán and De Liñán (2008).

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

Sampling point	Water type	Water depth (m)	Characteristics of the area	
			Crops cultivated	Watering
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	
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-S2	Surface water (Lodosa canal)	-	Vineyards and fruit trees	
BJ-S3	Surface water (Ebro river)	-	Vineyards	
BJ-S4	Surface water (Ega river)	-	Vineyards	
BJ-S5	Surface water (Iregua river)	-	Vineyards	
BJ-S6	Surface water (Leza river)	-	Vineyards	
BJ-S7	Surface water (Villar de Arnedo river)	-	Vineyards	

Table S3. Conditions for analytical determination and quality control parameters of the SPE-LC-MS method applied to the analysis of fungicides in surface and ground waters.

Fungicide	SIM ion m/z	V cone (V)	SIM window	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})
Cymoxanil	199.2	35	1	8.3	76	13	0.991	0.022	0.069
Cyproconazole	292.2	20	4	18.3	76	13	0.992	0.021	0.059
Azoxystrobin	404.2	25	4	18.3	85	11	0.995	0.017	0.052
Iprovalicarb	321.3	20	5	19.9	86	7	0.995	0.016	0.037
Dimethomorph	388.2	25	5	20.6	82	12	0.995	0.017	0.062
Benalaxyl	326.2	25	6	25.2	89	15	0.992	0.015	0.048
Cyprodinil	226.2	40	6	25.5	73	9	0.994	0.018	0.043
Trifloxystrobin	409.1	20	6	26.9	64	7	0.991	0.016	0.037

[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. Conditions for analytical determination and quality control parameters of the SPE-GC-MS method applied to the analysis of fungicides in surface and ground waters.

Compound	SIM window	RT (min)	Monitored ions (Abundance) Target (m/z) Qualifier Ions (m/z)	Recovery[a] (%)	RSD[a] (%)	r^2 (0.1-1.5[b] μg L^{-1})	LOD[c] (μg L^{-1})	LOQ[d] (μg L^{-1})
CGA 92370	1	7.3	148 120 (572)/91 (322)	78	17			
Pyrimethanil	3	10.0	198 199	65	14	0.992	0.031	0.078
Metalaxyl	4	12.9	45 206 (326)/132 (299)	108	12	0.997	0.001	0.006
Penconazole	5	16.3	248 159 (851)/161 (577)	83	14	0.996	0.002	0.005
Triadimenol	5	16.4	112 128 (906)/168 (745)	77	15	0.993	0.005	0.021
Flutriafol	5	20.6	123 164 (552)/219 (255)	80	17	0.997	0.005	0.013
Myclobutanil	5	21.4	179 82 (451)/150 (449)	83	15	0.999	0.003	0.013
Kresoxim-methyl	5	22.2	116 131 (533)/206 (516)	91	14	0.989	0.016	0.041
Tebuconazole	6	24.6	125 250 (847)/70 (492)	84	17	0.997	0.006	0.022
Nuarimol	6	25.3	107 139 (765)/235 (744)	83	14	0.994	0.124	0.284

[a] Calculated from the replicated analysis (n = 5) of spiked (0.1 μg L^{-1}) groundwater samples; [b] Linear calibration range. [b] Lineal 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

References

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