Science of the Total Environment 1009 (2025) 181074

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Assessing the impact of viticulture plant protection products in the pollution of surface and ground waters

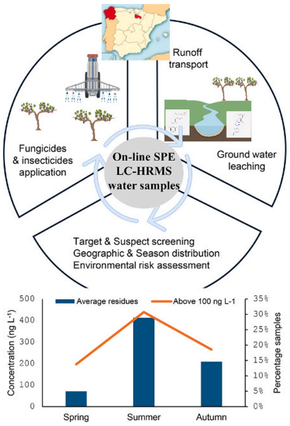
V. Fernández-Fernández [a], M. Ramil [a], E. Díaz-Losada [b], M.D. Loureiro-Rodríguez [b], E. Trigo-Córdoba [b], M.S. Andrades [c], J.M. Marín-Benito [d], M.S. Rodríguez-Cruz [d], I. Rodríguez [a,*]

[a] *Department of Analytical Chemistry, Nutrition and Food Sciences, ARCUS – Aquatic One Health Research Centre, Universidade de Santiago de Compostela, R/ Constantino Candeira, 5, 15782 Santiago de Compostela, Spain*
[b] *Estación de Viticultura e Enoloxía de Galicia-AGACAL, Ponte San Clodio s/n, 32428 Leiro-Ourense, Spain*
[c] *Department of Agriculture and Food, Science and Technology Complex, University of La Rioja, Madre de Dios 51, 26006 Logroño, Spain*
[d] *Institute of Natural Resources and Agrobiology of Salamanca (IRNASA-CSIC), Cordel de Merinas 40-52, 37008 Salamanca, Spain*

HIGHLIGHTS

- Prevalence of fungicides in the aquatic environment of investigated vineyards.
- Different distribution of individual pesticides between geographical areas
- Significant variations as function of sampling season
- Moderate to high environmental risks recorded for five fungicides.
- Phased-out herbicides and their transformation products detected in ground water.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Fungicides
Insecticides
Liquid chromatography accurate mass spectrometry
Vineyards
Environmental risk assessment

ABSTRACT

Plant protection products, particularly fungicides and insecticides, are intensively used in viticulture. Washing from leaves of vines, runoff transport, and soil penetration might lead to pollution of surface and ground waters. Herein, we present a systematic study on the occurrence and evolution of fungicides and insecticides in samples from two major wine production areas in Spain (La Rioja and Galicia). Above 400 water samples, corresponding to eight sub-zones, from two regions with different pedoclimatic conditions, were analyzed by liquid chromatography accurate mass spectrometry. Total residues of target compounds followed a homogeneous distribution in all sub-zones except one; nevertheless, their average values were slightly lower in La Rioja than in Galicia (181.1 ng L^{-1} and 260.8 ng L^{-1}, respectively). The highest pollution levels in the complete set of samples were measured in summer campaigns, corresponding to the most intensive application season of fungicides and insecticides. Nonetheless, in some wells, residues increased from summer to autumn, confirming their leaching to

---

* Corresponding author.
E-mail address: isaac.rodriguez@usc.es (I. Rodríguez).

https://doi.org/10.1016/j.scitotenv.2025.181074
Received 7 August 2025; Received in revised form 24 November 2025; Accepted 25 November 2025

ground water. Fungicides were prevalent versus insecticides with distribution patterns varying between regions. Tetraconazole, fluopyram and boscalid recorded higher detection frequencies in waters from La Rioja (from 16 % to 24 %) than in Galicia (between 4 % and 10 %). The opposite trend was observed for azoxystrobin (11 % vs 35 %), zoxamide (3 % vs 34 %), mandipropamide (1 % vs 27 %) and fluopicolide (1 % vs 23 %), with lower detection rates in La Rioja compared to Galicia. Attending to detection frequencies and ratios between measured and predicted non-effect concentrations, azoxystrobin, carbendazim, fluopicolid, tebuconazole and zoxamide were rated as the most environmental concerning pollutants. Suspect screening of accurate MS data revealed the presence of additional pesticides, including herbicides and their transformation products, in the monitored aquatic environments.

---

1. Introduction

Viticulture is the agricultural activity generating the major profit through transformation of grapes to wine and wine related drinks. Also, it permits the use of low fertility soils, which are not suitable for the growth of other crops. On the other hand, viticulture is a pesticide-intensive use sector. The high susceptibility of vines to fungal pests, and the role of different insects as vectors of diseases affecting vineyards, require their regular spraying with different combinations of fungicides and insecticides (Calliera et al., 2025; Oliveira et al., 2019; Pinheiro et al., 2025). Depending on the pressure of pests, up to 12–14 treatments are sprayed on the canopy of vines each campaign (Fouillet et al., 2022). Winegrowers also apply herbicides to manage weeds and vegetation competing with vines for nutrients and water (Silva et al., 2011).

The repeated application of plant protection products in viticulture has led to the contamination of vineyard soils (Imfeld et al., 2024; Pérez-Mayán et al., 2020; Vallejo et al., 2019). In this regard, results obtained in LUCAS (*Land Use and Coverage Area frame Survey*) project of the European Union pointed out to vineyards as the most polluted agricultural soils, according to number and total pesticide residues (Silva et al., 2019). The transport of these compounds from topsoil to surface water (SW, including streams, rivers and ponds in the vicinity of vineyards) depends on their physicochemical properties and those of soils, the slope of vineyards, the frequency and the intensity of rain events (Imfeld et al., 2020; Maillard et al., 2011; Marin et al., 2022). Their leaching to ground water (GW) is controlled by the stability and mobility of each compound in soil, which are affected by the soil pH, organic matter (OM), and texture. Moreover, the position of aquifers versus vine growing areas also determines the likelihood of GW pollution (Suciu et al., 2020; Zambito Marsala et al., 2020).

The determination of pesticides in the aquatic environment of agricultural areas is a recurrent topic (Chow et al., 2023; Curchod et al., 2020; Fernández-García et al., 2024); however, studies focussed in viticulture areas are still scarce. Pollution of GW has been reported in intensive viticulture areas in the North of Italy (Suciu et al., 2020; Zambito Marsala et al., 2020), with residues of several fungicides above 100 ng L^{-1}. In Spain, vineyards cover more than 900,000 ha, distributed among 103 Denominations of Origin (D.O.) (MAPA. Summary of Wine Producing D.O. in Spain, 2024). To the best of our knowledge, systematic studies of the impact of pesticides on the nearby aquatic compartment have been conducted only in two of them, D.O. La Rioja (Manjarres-López et al., 2021) and D.O. Jumilla (Murcia) (Herrero-Hernández et al., 2020). Galicia, in the Northwest of Spain, gathers five different D.O., with a total surface devoted to vineyards of 27,000 ha. They are distributed in hilly areas, around natural water courses and/or reservoirs. They are exposed to a remarkably higher pressure of fungal infections than in other areas of the country due to the frequency and intensity of rainfall events. Thus, they require intensive treatments with different combinations of fungicides to prevent the main diseases impacting the sustainability of vines, particularly downy and powdery mildew, oidium, black rot and botrytis. These practices are reflected in the presence of fungicides in soil and wine (Fernández-Fernández et al., 2025b; Pérez-Mayán et al., 2020). Recently, in some D.O. of this region, the application of insecticides to vineyards has become mandatory to control the spread of *Flavescence dorée* (Xunta de Galicia. Pest Affecting Vineyards, 2024).

This research conducts a systematic, updated study of the occurrence, distribution and evolution of pesticides in SW and GW from two major wine production regions in the North of Spain (La Rioja and Galicia), with different pedoclimatic conditions, representing around 8 % of total vineyard surface in Spain. The determinations conducted provide seasonally and geographically resolved data on pesticide residues, enabling a better understanding of the impact of viticulture on the aquatic environments of production areas with varying pest pressures (both in type and severity) as well as differing pedoclimatic conditions. Furthermore, the use of accurate mass detection aims to address the limitations of conventional target methods based on triple quadrupole instruments, employed in most of previous studies (Herrero-Hernández et al., 2020; Manjarres-López et al., 2021; Suciu et al., 2020), which are unable to detect non-preselected pollutants. The specific aims of the study were to identify those compounds showing the highest prevalence and concentrations in SW and GW, to assess their potential risks derived from observed residues versus toxicological thresholds and/or regulated levels, and to pinpoint additional pesticides to be quantified in further studies. Six sampling campaigns were conducted from the beginning of spring to autumn, over two consecutive years (2023–2024). Liquid chromatography (LC), combined with quadrupole time-of-flight mass spectrometry (QTOF-MS), was used for the quantitative determination of 44 pre-selected fungicides and insecticides, as well as for suspect screening of additional pesticides.

2. Material and methods

2.1. Standards and solvents

Standards of 44 pesticides and 14 isotopically labelled analogues were obtained from Sigma-Aldrich (Milwaukee, WI, USA), Cymit (Barcelona, Spain) and Toronto Research Chemicals (Ontario, Canada). Choice of target compounds was made considering their occurrence in wines produced in both regions where samples were taken (Esteve-Turrillas et al., 2016; Fernández-Fernández et al., 2025b), and data on pesticide consumption available from the Spanish Ministry of Agriculture, Fisheries and Food (MAPA. Statistics of Phytosanitary Compounds per Crop in Spain, 2025). Table S1 summarizes the selection of compounds including data of polarity (Log D values at pH 7), persistence in soil based on degradation half-lives (DT_{50}) in field studies, and their Groundwater Ubiquity Score (GUS) index (Lewis et al., 2016). Native compounds were acquired as pure standards (purity >98 %). Individual stocks (ca. 1000 ng mL^{-1}) and further dilutions were prepared in methanol (MeOH). Their labelled analogues were purchased either as pure substances, or as solutions in MeOH (usually at 100 μg mL^{-1}). Two independent mixtures of native pesticides and labelled compounds were made in MeOH. They were used to prepare calibration solutions (prepared in ultrapure water) and to spike samples of SW and GW during assessment of the accuracy of the procedure. Isotopically labelled compounds were used as surrogate standards (SS), added to calibration standards and water samples at the same concentration level (200 ng L^{-1}).

Ultrapure water was produced in the laboratory using a Geni U system (Rephile, Shanghai, China). Formic acid (FA), MeOH and acetonitrile (ACN), for LC-MS analysis, were provided by Merck (Darmstadt, Germany). The on-line solid-phase extraction (SPE) cartridges (Agilent PLRP-S, 12.5 mm × 2.1 mm, containing styrene-divinylbenzene packed in a stainless-steel holder) were purchased from Proquinorte (Bilbao, Spain).

2.2. *Water samples*

Samples included in this study correspond to GW, obtained from wells and springs, and SW from permanent streams and rivers. They were collected in two reputed viticulture geographical areas in the North of Spain, La Rioja and Galicia. The first region is characterized by continental weather and calcareous soils. It includes three main wine production sub-zones (Rioja Alavesa, ALA; Rioja Alta, ALT; and Rioja Oriental; ORI). Galicia comprises five major wine production areas, hereafter referred as D.O. (Rías Baixas, RB; Ribeiro, R; Valdeorras, VAL; Monterrei, MO; and Ribeira Sacra, RS). Climate conditions in these D.O. varied from continental to Atlantic depending on their distance to the coast and/or the influence of major rivers. Monthly values of total rainfall (L m^{-2}) and average temperature (°C) during years 2023 and 2024, in the sub-zones of La Rioja and the D.O. of Galicia, are shown as supplementary information, Fig. S1. Regarding soil characteristics, vineyards from Galicia present lower pH values, and higher OM contents than those from La Rioja (data not shown).

Six sampling campaigns were conducted in spring (between middle March and 1st week April), beginning of summer (between middle June and 1st week July), and autumn (between middle October and 1st week November), during years 2023 and 2024. The number of sampling points in La Rioja was 27 (6–11 points per sub-zone). All of them corresponded to GW from wells and springs. In Galicia, 44 sampling points, involving SW from streams and rivers surrounding vineyards (20 sites), and GW from wells within the boundary of vineyards (23 sites) and one spring, were selected. Fig. S2 shows the position of sampling sites at both geographical areas. In a few cases, springs dried up in autumn; also, three wells in Galicia were sampled in the campaigns of 2024, but not in the previous one. Finally, sampling was repeated in some wells showing high concentration of residues, either in the same season, or even in winter. Globally, 425 samples were analyzed, 171 GW from La Rioja, 144 GW and 110 SW from Galicia. Samples of well water were taken with authorization of grape growers, despite neither they participated in the sampling process nor were informed of the exact sampling dates.

Samples were taken in high density, 500 mL volume, polyethylene (HDPE) vessels. They were frozen (−20 °C) in the next few hours and maintained at this temperature until analysis. Sample preparation included filtration, using 0.22 μm hydrophilic PTFE syringe filters, addition of a 15 % of MeOH and acidification with FA (0.4 %, v:v). For convenience, 5 mL volume aliquots were spiked with SS and used for analysis.

2.3. *Analytical equipment*

Quantification of selected compounds, and suspect screening of additional pesticides were conducted using a liquid chromatography quadrupole time-of-flight mass spectrometry (LC-QTOF-MS) instrument, model 6550, acquired from Agilent (Santa Clara, CA, USA). An auxiliary quaternary pump and a two-position, multiport valve were used for loading, washing and desorption of compounds from the on-line SPE sorbent. Compounds were separated using a C_{18}-type LC column (100 mm, 2.1 mm, 3.5 μm) acquired from Agilent. Data acquisition, and operational conditions of SPE, LC, ESI source and MS modules were controlled using a *Mass Hunter* software package from Agilent. On-line SPE and LC parameters are available in a previous publication describing the coupling between SPE and LC-QqQ-MS determination of pharmaceuticals and pesticides in water samples (Fernández-Fernández et al., 2023). The ESI source was used in positive ionization (ESI+), and the hybrid MS analyser operated in the data independent acquisition (DIA) mode. In addition to the MS channel (herein, MS^1 function), two different collision energies (20 eV and 40 eV) were alternated to obtain information of fragment ions for every compound eluting from the LC column, amenable to ESI+ ionization. Both pseudo-MS/MS channels and the MS^1 function were recorded at a frequency of 3 Hz. Details regarding optimization of DIA parameters to maximize the response of target compounds are available elsewhere (Fernández-Fernández et al., 2025a).

2.4. *Quantification of target compounds and risk assessment*

Quantification of target compounds was carried out with responses obtained for a selected ion, recorded in the MS^1 function. Except in case of methoxyfenozide and tebufenozide, the $[M + H]^+$ ion was considered as quantifier. For confirmatory purposes, a second ion was used. Preferably, it corresponded to a characteristic fragment recorded in one of the pseudo-MS/MS functions. Alternatively, for certain chlorinated and brominated compounds, producing low intensity fragments (i.e. fenhexamide and pyriofenone), the $[M + H + 2]^+$ was used as qualifier, Table S2. Identification of compounds in non-spiked samples was made considering retention times and *m/z* values for quantifier and qualifier ions, obtained for calibration standards, with maximum differences of ±0.1 min, and absolute mass errors lower than 10 ppm (± 5 ppm), respectively. Furthermore, the coelution between quantifier and qualifier ions should stay above 90 %. Minimum S/N ratios for quantifier and qualifier were set at 10. Responses (peak areas) for each compound were corrected with those measured for the assigned SS, Table S2. The obtained ratios were compared with those obtained for calibration solutions, prepared in ultrapure water, containing the same level of SSs (200 ng L^{-1}). Detection frequencies, mean, median and maximum concentration residues were calculated using Excel package for Microsoft Office. Same software was employed to build the different graphs shown in this research.

The environmental risk of pesticides found in water samples was evaluated using risk quotients (RQs). RQs were calculated dividing the measured levels of each compound between its predicted non-effect concentration (PNEC), for the most sensitive freshwater organism (Norman Ecotoxicological Database, 2025). RQ values below 0.1 correspond to a low environmental risk, those from 0.1 to 1 represent a moderate risk. Compounds with RQs above 1 constitute an environmental hazard.

2.5. *Screening studies*

Suspect screening was conducted using information associated to DIA LC-QTOF-MS data. The *Find by Formula* algorithm, included in *Mass Hunter* software, identifies clusters of ions in the MS^1 function matching the empirical formula of pesticides included in a spectral database of 740 compounds, integrated also in *Mass Hunter* software package, attending to mass accuracy and isotopic profiles for their pseudo-molecular ions (i.e. protonated form, and adducts with ammonium, sodium and potassium in ESI+). When the normalized match between experimental MS spectra and the theoretical ones stayed above 80 %, the product ions of candidates, obtained from the spectral database, were mined in the two simultaneously recorded pseudo MS/MS functions. Tentatively confirmed species might present at least one fragment ion at the same retention time (coelution score above 90 % with the chromatographic peak of the pseudo-molecular ion), and mass errors lower than ±5 ppm. Thereafter, in a further injection, a target MS/MS experiment was conducted using *m/z* values of precursor ions and retention times for the tentatively identified species. This authentic MS/MS (product ion) spectrum was compared again with those existing in the database. At least, 50 % of product ions need to be confirmed for a level 2 of confidence identification following the scale proposed by

Schymanski and co-workers (Schymanski et al., 2014). Finally, when a standard was available, match of retention times was used to achieve a level 1 of confidence.

2.6. Quality control

Samples were grouped in batches (ca. 20 samples per batch) and processed in duplicate, together with the set of calibration standards, at eight different levels, in the range of concentrations comprised between their LOQs (from 2 ng L^{-1} to 25 ng L^{-1}) and 500 ng L^{-1}. Each batch included the analysis of a spiked sample (50 ng L^{-1}) processed in triplicate. A procedural blank (ultrapure water with addition of only SSs) was analyzed every 10 samples. The stability of calibration was verified with the same frequency, by injection of a medium concentration (between 25 ng L^{-1} and 100 ng L^{-1}) standard. For screening studies, only those compounds highlighted by the data mining algorithm in the duplicate analyses of each sample, and absent in procedural blanks, were pre-selected as tentative identifications.

3. Results and discussion

3.1. Performance of the quantitative method

The performance of the SPE on-line LC-QTOF-MS procedure for the quantitative determination of target compounds was assessed in terms of limits of quantification (LOQs), linear response range, and accuracy. LOQs varied in the range from 2 ng L^{-1} to 25 ng L^{-1}, Table 1. The achieved values depended on the intensity of responses for quantifying and qualifying ions of each compound. The upper limit of the linear response range was also compound dependent. For most pesticides, linearity was maintained up to concentrations of 2000 ng L^{-1}. However, for highly efficiently ionized compounds linearity was lost at concentrations above 500 ng L^{-1}. The reason was the negative impact of very intense ions in the mass accuracy of the QTOF-MS instrument. Consequently, some highly polluted samples required re-analysis after dilution to quantify the levels of higher concentration pollutants. Accuracy of the procedure was assessed with samples spiked at three different concentration levels, from 25 ng L^{-1} to 100 ng L^{-1}. Differences in concentrations found in spiked and non-spiked fractions ($n = 3$ replicates) of each sample were divided by the added value and multiplied by 100. In general, recoveries remained in the range from 70 % to 120 %, with

Table 1
Recoveries of the analytical procedure for spiked environmental samples ($n = 3$ replicates) and procedural limits of quantification (LOQs, ng L^{-1}).

Compound	Added concentration						LOQs (ng L^{-1})
	25 ng L^{-1}		50 ng L^{-1}		100 ng L^{-1}		
	Mean	SD	Mean	SD	Mean	SD	
Acetamiprid	116 %	4 %	109 %	2 %	110 %	1 %	2
Ametoctradin	81 %	1 %	89 %	4 %	108 %	7 %	2
Azoxystrobin	110 %	1 %	93 %	2 %	114 %	3 %	2
Benalaxyl	105 %	2 %	108 %	3 %	96 %	5 %	5
Boscalid	121 %	4 %	85 %	6 %	105 %	3 %	5
Bupirimate	85 %	2 %	105 %	2 %	114 %	12 %	2
Carbendazim	155 %	2 %	89 %	5 %	108 %	2 %	10
Cyflufenamid	93 %	8 %	83 %	2 %	102 %	3 %	5
Cyproconazole	112 %	3 %	92 %	5 %	103 %	3 %	5
Cyprodinil	94 %	2 %	100 %	2 %	108 %	6 %	25
Difenoconazole	96 %	2 %	102 %	1 %	97 %	3 %	5
Dimethomorph	131 %	3 %	83 %	1 %	120 %	5 %	5
Fenamidone	131 %	2 %	87 %	1 %	108 %	3 %	5
Fenhexamide	106 %	16 %	98 %	19 %	105 %	3 %	25
Fenpyrazamine	95 %	1 %	112 %	2 %	107 %	2 %	2
Fluopicolide	106 %	7 %	86 %	3 %	101 %	4 %	2
Fluopyram	101 %	1 %	101 %	1 %	103 %	2 %	2
Imazalil	96 %	1 %	127 %	2 %	105 %	2 %	2
Imidacloprid	119 %	6 %	97 %	6 %	115 %	4 %	10
Iprovalicarb	91 %	10 %	92 %	1 %	117 %	11 %	5
Isofetamid	107 %	2 %	109 %	1 %	114 %	6 %	5
Mandipropamide	103 %	3 %	85 %	2 %	105 %	4 %	2
Metalaxyl	108 %	1 %	106 %	1 %	98 %	6 %	2
CGA 62826	104 %	6 %	107 %	4 %	107 %	8 %	25
Methoxyfenozide	121 %	10 %	94 %	5 %	114 %	10 %	5
Metrafenone	88 %	5 %	91 %	1 %	102 %	2 %	2
Myclobutanil	107 %	3 %	101 %	2 %	104 %	2 %	5
Penconazole	98 %	1 %	98 %	7 %	107 %	1 %	2
Prochloraz	101 %	4 %	71 %	7 %	115 %	6 %	2
Propiconazole	108 %	3 %	98 %	2 %	108 %	3 %	10
Proquinazid	77 %	2 %	90 %	2 %	101 %	9 %	2
Pyraclostrobin	98 %	1 %	88 %	2 %	104 %	4 %	5
Pyrimethanil	104 %	2 %	103 %	2 %	106 %	1 %	10
Pyriofenone	74 %	7 %	86 %	9 %	84 %	40 %	10
Quinoxyfen	102 %	1 %	86 %	3 %	106 %	1 %	10
Spiroxamine	62 %	2 %	70 %	16 %	134 %	10 %	2
Tebuconazole	105 %	2 %	105 %	4 %	104 %	2 %	5
Tebufenozide	98 %	9 %	119 %	2 %	117 %	3 %	2
Tetraconazole	98 %	4 %	97 %	3 %	102 %	3 %	2
Thiabendazole	86 %	1 %	107 %	4 %	96 %	4 %	2
Thiamethoxam	111 %	6 %	101 %	9 %	95 %	17 %	5
Triadimefon	104 %	1 %	83 %	4 %	96 %	2 %	10
Trifloxystrobin	79 %	3 %	79 %	3 %	93 %	2 %	2
Zoxamide	108 %	4 %	98 %	2 %	110 %	6 %	2

standard deviations below 10 %, Table 1. In a few cases, recoveries were overestimated in the study at the lowest addition level (carbendazim, dimethomorph and fenamidone), but not at 50 ng L^{-1} and 100 ng L^{-1}. Spiroxamine showed recoveries in the range from 62 % to 134 %. This large variability was the consequence of the coelution of this fungicide with the organic matrix of environmental samples, and the lack of an isotopically labelled analogue of spiroxamine to be used as SS. Thus, concentrations determined for this compound are considered as semi-quantitative values.

3.2. Occurrence and distribution of pesticides in water samples

Concentrations of compounds above their procedural LOQs, in samples from both geographical areas, are included in Tables S3 and S4, compiling data for La Rioja and Galicia, respectively. The Box-Whisker plot of total residues reflects similar median and interquartile values in both areas, Fig. 1A. As regards average residues, slightly lower levels were observed in La Rioja (181.1 ng L^{-1}) compared to Galicia (260.8 ng L^{-1}), Fig. 1A. In the same vein, the percentage of samples containing total residues above the environmental quality standard (500 ng L^{-1}) accounted for 3.7 % and 9.8 % in La Rioja and Galicia, respectively. The mean number of pesticides per sample, and the percentage of sampling sites containing residues of at least one pesticide in all campaigns were 2.2. and 7 % in La Rioja, versus 3.2 and 32 % in Galicia. Fig. 1B and C show the Box-Whisker plots corresponding to the distribution of total residues at the level of the three sub-zones within La Rioja geographic area (Fig. 1B), and the five D.O. within Galicia region (Fig. 1C). In La Rioja region, slightly higher median and mean values were found in water samples from ALA versus the other two sub-zones, Fig. 1B. As regards Galicia, the highest total residues corresponded to D.O. RB, Fig. 1C.

Fig. S1 summarizes monthly precipitations (L m^{-2}) and average temperatures (°C) collected from representative meteorological stations in the different sub-zones (or D.O.). During summer months, all sub-zones in La Rioja recorded higher temperatures and less rain that the different D.O. of Galicia, Fig. S1. In the latter region, vineyards from RB received 2230 L m^{-2} $year^{-1}$ of rainfall, with 619 L m^{-2} accumulated in the period from April to September. These values are 2–3 times higher than those recorded for the other D.O. in Galicia and the three sub-zones in La Rioja, Fig. S1. Furthermore, in RB, the mean temperatures from June to August were 2 °C lower than those recorded in the rest of sub-zones from both regions, Fig. S1. Thus, the combination of frequent rainfalls and mild temperatures boost fungi infections in vines of RB. Consequently, they are fumigated with a higher frequency than those from other areas. This situation is reflected in the pollution of water samples from RB, with median and mean values of 65 ng L^{-1} and 587 ng L^{-1}, respectively, Fig. 1C. These figures stay above those found in the sub-zones of La Rioja and the rest of D.O in Galicia, Fig. 1B and Fig. 1C.

Apart from their severity, the type of pests affecting vines varies depending on climate conditions and on the susceptibility of plant varieties to different kinds of fungal infections. Thus, they may modulate the selection of pesticides used by winegrowers in different regions. Furthermore, the physicochemical properties of soils could affect the stability of pesticides and their exchange ratios between upper soil layers and GW, as well as their release to SW (Carpio et al., 2022). Consequently, in addition to their total residues, the distribution of pesticides may differ among regions and sub-zones. Detection frequencies, maximum, median and average concentrations of individual pesticides are summarized in Table S5. The number of compounds above the procedural LOQs of the method was similar in both regions, with 32 and 35 substances, out of 44 pesticides involved in the target procedure, identified in water samples from La Rioja and Galicia, respectively.

Fig. 2A shows a radial plot with detection frequencies of those compounds found in more than 10 % of the samples from, at least, one of the two regions. Thirteen active ingredients (all of them used as fungicides), and the environmental transformation product of metalaxyl (CGA 62826), stayed above this threshold. Benalaxyl, tetraconazole, fluopyram, boscalid and CGA 62826 displayed a higher occurrence in water samples from La Rioja than in those from Galicia. Conversely, azoxystrobin, zoxamide, mandipropamide, fluopicolide and iprovalicarb were more often detected in samples from Galicia. Finally, metalaxyl, carbendazim and tebuconazole present similar detection rates (from 13 % to 32 %, depending on the compound) in waters from both regions. Globally, the most often detected fungicides in water samples from La Rioja are consistent with those reported in a previous study from year 2019 in the same area (Manjarres-López et al., 2021). The three fungicides showing high, similar detection frequencies in both intensive viticulture areas (carbendazim, metalaxyl and tebuconazole) were also rated as some of the most prevalent pollutants in surface and ground water samples from intensive agriculture areas from different countries (Chow et al., 2023; Curchod et al., 2020; Zambito Marsala et al., 2020).

Occurrence of individual compounds in the aquatic environment is obviously related to their application rates. Furthermore, differences in soil permeability and pH might contribute to the higher or lower persistence of certain species, such as the transformation product of metalaxyl. Whilst the detection frequencies of the parent fungicide (metalaxyl) were similar in both regions (32 % in La Rioja and 30 % in Galicia), those of CGA62826 were higher in water samples from La Rioja (17 %) than in those collected in Galicia (10 %), Fig. 2A. The maximum residues of the latter compound followed a similar trend, with values of 1363 ng L^{-1} and 566 ng L^{-1} in La Rioja and Galicia, respectively. Considering that CGA62826 is generated through hydrolysis of an ester moiety, existing in the structure of metalaxyl, to render a carboxylic acid function, its leaching potential might be higher in basic, karstic soils from La Rioja (Iñigo, 2022), than in the acidic, OM-rich ones of Galicia (Blanco et al., 2024). The normalized plot of maximum residues for compounds included in Fig. 2A confirms the existence of significant differences between both regions. More specifically, maximum residues of fluopyram were 409 ng L^{-1} in La Rioja versus 8.5 ng L^{-1} in Galicia. Top levels of zoxamide, mandipropamide and fluopicolide in water samples from Galicia accounted for 13,000 ng L^{-1}, 410 ng L^{-1} and 1692 ng L^{-1}. These figures are clearly above their maximum levels found in La Rioja (9.7 ng L^{-1}, 21 ng L^{-1} and 4.0 ng L^{-1}), Fig. 2B.

The distribution of pesticides as function of water type (GW versus SW) was investigated in samples from Galicia. Median values of total residues were higher in GW (39.4 ng L^{-1}, $n = 144$ samples) than in SW (15.8 ng L^{-1}, $n = 110$ samples). Same trend was observed for the average number of compounds, above their procedural LOQs, in both types of water (3.7 in GW vs 2.7 in SW). Fig. 3 shows the median concentrations of a selection of pesticides with detection frequencies above 10 %, and median concentrations above 10 ng L^{-1}, in any of both types of water. Twelve out of fifteen compounds showed higher median residues in GW than in SW. Tebuconazole and zoxamide were found at similar values in both waters and only the transformation product of metalaxyl (CGA 62826) was reported at higher concentration in SW than in GW. The shorter distance between vineyards and GW sampling points (particularly wells) compared to that existing with streams and rivers justifies the above trend. Nevertheless, the presence of pesticide residues in GW highlights the potential of viticulture used pesticides to leach from topsoil to underground aquifers. A thorough assessment of the relative importance of runoff-erosion, aerial drifts and leaching processes to explain the transfer of pesticides from application sites, at vineyards, to surface water reservoirs (runoff and drifts) and groundwaters (leaching) requires dedicated field experiments, i.e. using lysimeters and analysis of storm waters, conducted in soils with different features as regards texture and OC, selecting vineyards with different slopes.

The target compounds most often detected in this study are currently approved fungicides and insecticides, Table S5. Among substances whose authorization of use has expired, the fungicide myclobutanil was quantified in 1 % and 8 % of samples from La Rioja and Galicia, respectively. The neonicotinoid insecticide imidacloprid and tridiamefon (degradation product of the banned fungicide triadimenol) were still

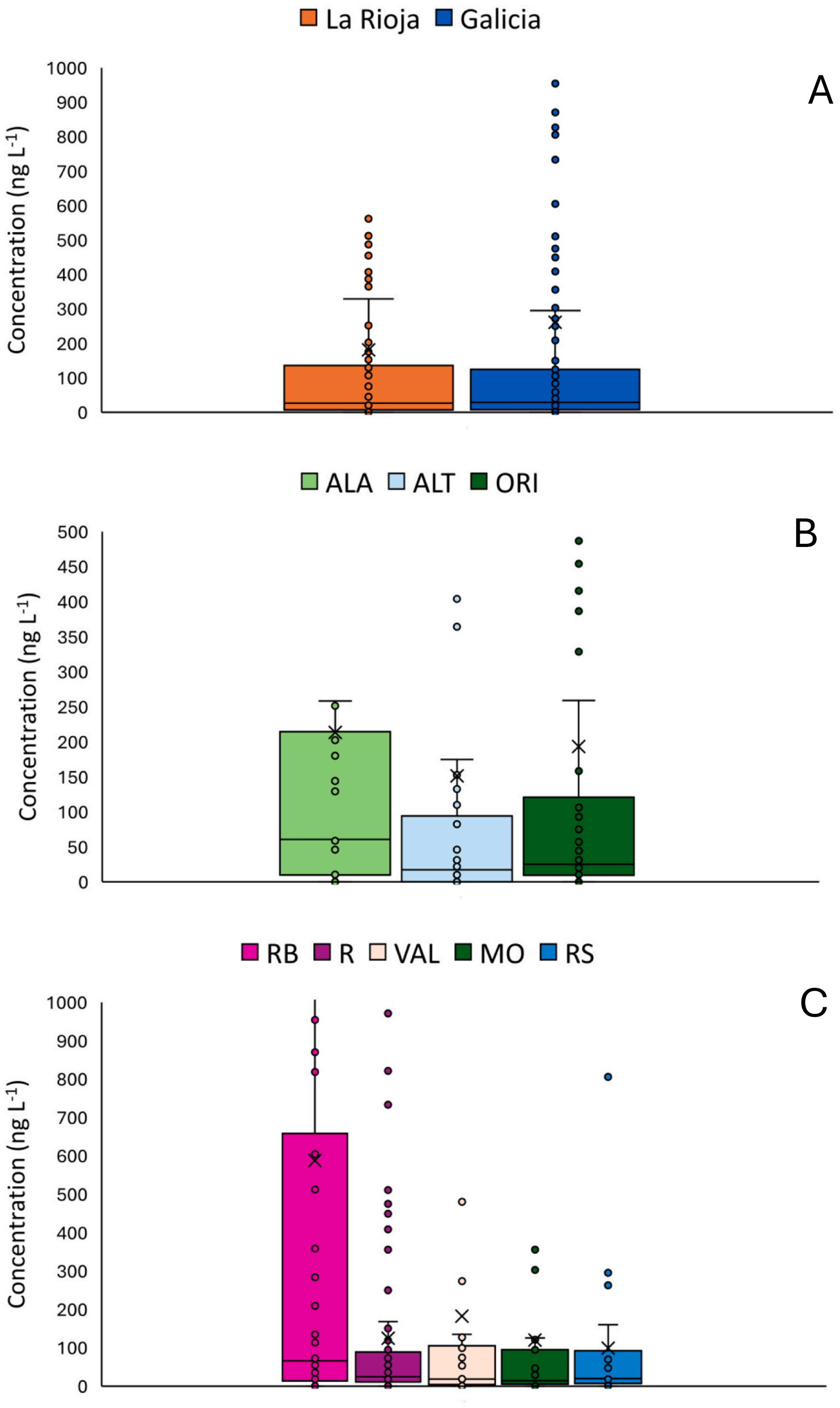


Fig. 1. Box-Wisker plots with total residues over the six different campaigns as function of geographical area (A), and among the three sub-zones of La Rioja (B), and the five D.O. recognized within Galicia (C). Abbreviations: ALA (Rioja Alavesa), ALT (Rioja Alta), ORI (Rioja Oriental), RB (Rías Baixas), R (Ribeiro), VAL (Valdeorras), MO (Monterrei), RS (Ribeira Sacra).

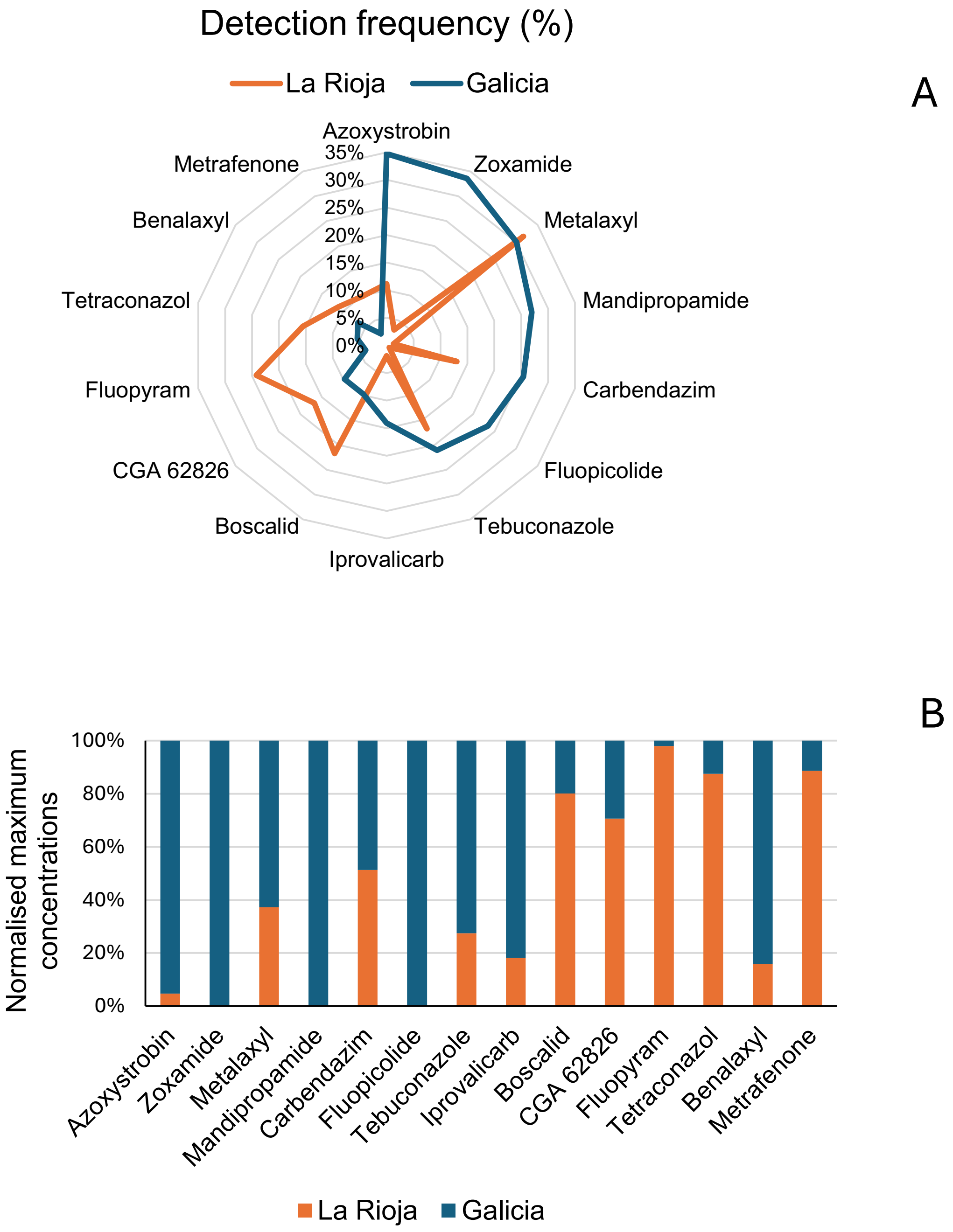


Fig. 2. Radial plot with detection frequencies in all sampling campaigns (A) and normalized maximum concentrations (B). Data limited to compounds with detection frequencies above 10 % of water samples from at least one of the two geographical areas.

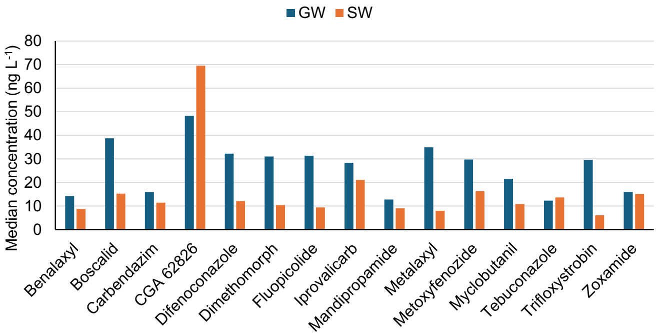


Fig. 3. Median concentrations (ng L^{-1}) of selected pesticides in GW ($n = 144$) and SW ($n = 110$) samples collected in vineyards from Galicia region.

present in 1 % of water samples collected in Galicia. Carbendazim, showed a high prevalence in both regions, Fig. 2A. Despite being also a non-authorized compound, its presence in water samples may be a consequence of degradation of other environmentally labile compounds, not covered by this study, such as methyl thiophanate.

The application of fungicides and insecticides to vineyards is concentrated in the period from middle April to the end of August. Thus, it seems likely that residues in aquatic environment would differ depending on the sampling season. Fig. 4A depicts the average of total concentrations (bar graph), and the percentage of samples containing residues above 100 ng L^{-1} (line plot), as function of sampling season, in years 2023 and 2024. In both regions, the lowest values for both variables were noticed in water samples collected at the beginning of spring, before application of fungicides and insecticides on the canopy of vines. Their maximum levels were measured in the summer campaign. While

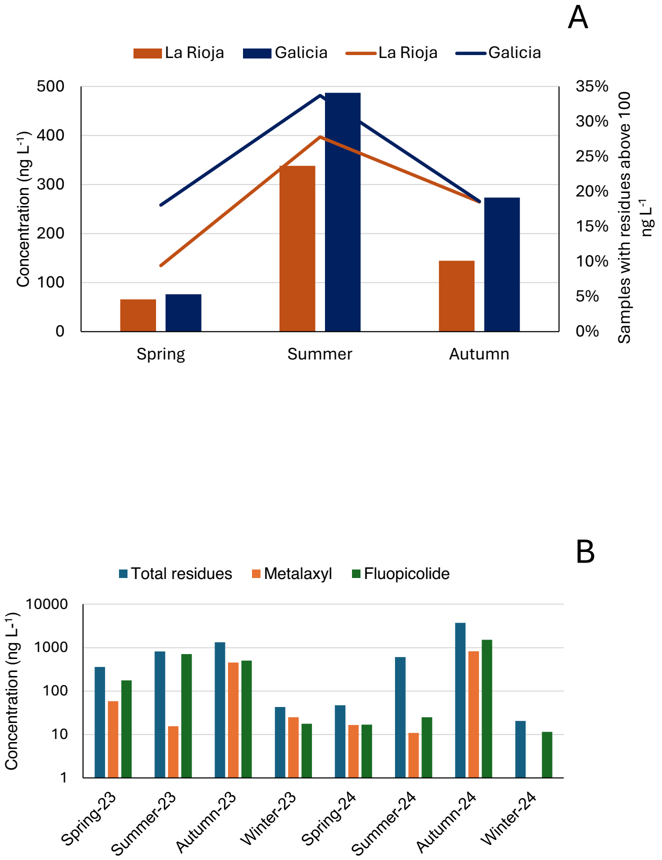


Fig. 4. A, seasonal evolution of pesticide residues in all samples, as average values (bars) and percentage of samples with residues above 100 ng L^{-1} (lines). B, seasonal residues in a highly polluted groundwater site (well code RB-6).

the trend depicted in Fig. 4A is representative of the global set of samples, it does not reflect the situation of some GW samples. This statement is illustrated with data corresponding to well code RB-6, located at D.O. RB, Galicia. At this point, the maximum residues in two consecutive years were detected in autumn, Fig. 4B. Also, the levels of the medium and high leachable compounds metalaxyl and fluopicolide (GUS index 2.06 and 3.20, respectively) (Lewis et al., 2016) in autumn were higher than (or similar to) those found in summer, Fig. 4B. Autumn rainfall may contribute to the leaching of pesticides from top soil to deeper layers, resulting in the pollution of GW (Willkommen et al., 2019). In another severely polluted well from the same D.O. (code RB-3), residues of metalaxyl and fluopicolid in winter campaigns (end of December) were even higher than those found in autumn and summer, Fig. S3A. In well code R-1, located in La Rioja, levels of four fungicides, ubiquitous at this point, also increased slightly from spring to autumn, Fig. S3B. Levels of pesticides in wells are expected to depend on several parameters, such as depth, distribution of rainfall and hydrogeological variables; thus, their seasonal variations are more difficult to predict than those observed in SW samples.

3.3. *Environmental and toxicological implications*

Fig. 5 summarizes risk quotients (RQs) for compounds with detection frequencies above 10 %. The left axis represents the RQs calculated for the maximum concentration of each compound, while the right axis corresponds to the percentage of samples where moderate to high risks were identified based on RQ values above 0.1.

Carbendazim was the only compound with a maximum RQ value above the unit in water samples from La Rioja. Moreover, only this compound and tebuconazole represented a moderate hazard (RQ values between 0.1 and 1) in 2 % and 5 % of the samples from this area, respectively, Fig. 5A. In Galicia, high environmental risks (RQs $>$ 1) were estimated from maximum concentrations measured for azoxystrobin, carbendazim, fluopicolide, tebuconazole and zoxamide. The percentage of samples where moderate to high risks were noticed (RQs above 0.1) ranged from 2 % in case of carbendazim to 9 % for zoxamide, Fig. 5B. The above fungicides showed minimum PNEC thresholds below 0.5 ng mL^{-1} for freshwater organisms. Thus, they present a significant higher environmental risk than other fungicides quantified in this study (i.e., metalaxyl, boscalid, mandipropamid and fluopyram) with one order of magnitude higher PNEC values (Norman Ecotoxicological Database, 2025). Recent ecotoxicological studies have reflected a range of deleterious effects for above compounds in different aquatic organisms, from alterations in the microbiome of biofilms growing in polluted freshwater environments (Gómez-Martínez et al., 2024) to genotoxicity to fish (Ray et al., 2024) at higher concentrations. In vitro studies have pointed out to carbendazim as a disrupter of the antioxidant system in mammalian tissues (Sharma et al., 2022).

In addition to environmental concerns, the presence of fungicides and insecticides in the aquatic environment might represent a toxicological risk when streams, or ground water aquifers, are used either as a source of tap water, or even consumed directly, without any further treatment. This was the case of wells codes RB-2 and RB-9, located in RB, Galicia. This D.O. presents a moderate density, dispersed population, with detached houses usually surrounded by vines. At well code RB-2, in two out of six sampling campaigns, the sum of pesticide residues stayed above the 500 ng L^{-1} threshold established for drinking water production. Moreover, the individual concentrations of benalaxyl, dimethomorph, fluopicolide, iprovalicarb and metalaxyl remained above 100 ng L^{-1}, in at least one of the campaigns. At site RB-9, total residues did never surpass the 500 ng L^{-1} value. However, individual concentrations of boscalid, carbendazim, CGA62826, tebufenozide and zoxamide were higher than 100 ng L^{-1}, Table S4.

3.4. *Screening studies*

LC-QTOF-MS data were also used for screening purposes with the aim to detect additional pesticides, which should be included in further monitoring campaigns. Fig. 6 illustrates the steps involved in the identification of the non-authorized herbicide diphenamid ($C_{16}H_{17}NO$). The extracted ion chromatogram (EIC) for the pseudo-molecular ($[M + H]^{+}$) ion of the compound, mined by the suspect screening workflow in a sample of GW, is shown in Fig. 6A. The match between the experimental (lines) and the calculated MS spectra (boxes) of the compound is presented in Fig. 6B, being the normalized score (accounting for mass accuracy isotopic abundance and ion spacing) equal to 99.2 %. The clean pseudo-MS/MS spectra at the retention time of the suspect compound is included in Fig. 6C. In a further analysis, the MS/MS spectra of the suspect chromatographic peak was recorded using collision energies of 20 and 40 eV, Fig. 6D. The product ions at *m/z* 72.0444, 91.0546, 134.0963, and 167.0851 matched those in the database spectra, Fig. 6E, with differences below 1 mDa. Since no standard was available, diphenamid was identified at confidence level 2.

Table 2 summarizes identifications derived from suspect screening. The experimental product ion spectra of those compounds identified at confidence level 2 are provided as supplementary information in Fig. S4. Out of 15 substances, 11 were either herbicides, or herbicide degradation products. Among them, atrazine, diphenamid and the parent compound of terbumeton desethyl are non-authorized pesticides. Particularly, the application of atrazine as herbicide in the EU was banned in year 2004 (Lewis et al., 2016). However, recent studies confirmed the presence of the parent pesticide and its metabolites in water samples from intensive agriculture areas in the Southeast of Spain (Bijlsma et al., 2021; Fernández-García et al., 2024). Other authors reported the ubiquity of hydroxylated and dealkylated forms of triazine-like herbicides in the aquatic environment of intensive agriculture

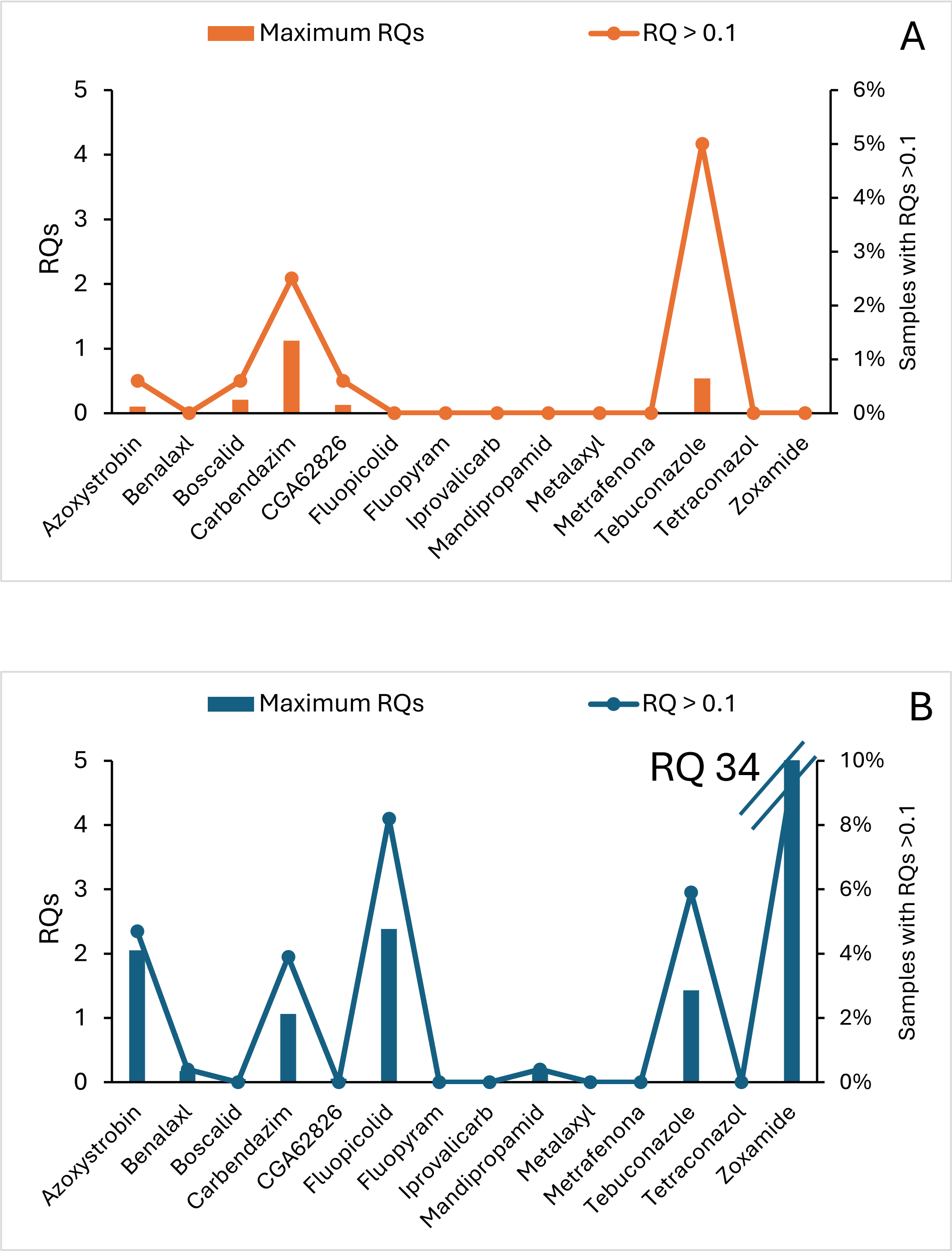


Fig. 5. RQ values derived from maximum residues for the most frequently detected pesticides (bar chart) and percentage of samples with RQs above 0.1 (line plot), in La Rioja (A), and Galicia (B).

areas where parent compounds were applied (Chow et al., 2023). Overall, the prevalence of compounds compiled in Table 2 was higher in samples collected in La Rioja than in Galicia, particularly for the authorized herbicides and the desethyl form of terbumeton identified in more than 40 % of water samples from the first geographical area. In summary, most of compounds identified following the suspect screening methodology corresponded either to approved or phase-out herbicides. At difference to Galicia, vineyards areas in La Rioja are surrounded by other crops, such as wheat, corn and sugar beet fields. Thus, the prevalence of atrazine-type compounds in GW from this region might be also related to their former use as selective herbicides (against broad leaf weeds) in these rotational crops. Whatever their origin, detection of phased-out triazine-like compounds agrees with their categorization as persistent and mobile pollutants in the aquatic environment (Berger et al., 2017).

3.5. *Limitations*

The use of accurate MS detection, in our case based on a QTOF-MS instrument, offers the possibility to identify additional pollutants to those considered during method development and validation for pre-selected compounds. Nevertheless, QTOF mass analysers show a lower sensitivity than triple quadrupole systems when operated in the multiple reaction monitoring (MRM) mode. Thus, in this research the occurrence

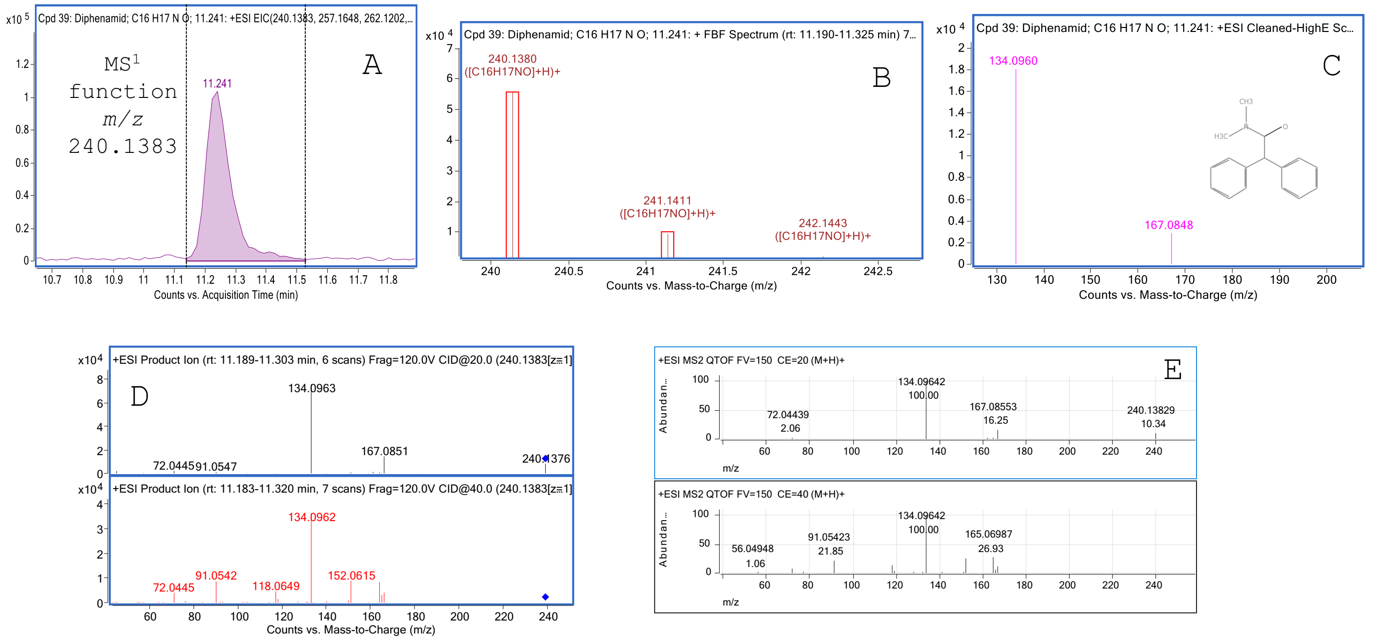


Fig. 6. Plots corresponding to the identification of diphenamid using SPE on-line DIA LC-QTOF-MS data. A, extracted ion chromatogram for the $[M + H]^+$ ion in the MS1 function obtained using the *Find by Formula* function. B, match between experimental (lines) and predicted (boxes) MS spectra. C, fragment ions from the pseudo-MS/MS functions compatible with the database spectra of diphenamid. D, experimental MS/MS spectra of the peak assigned to diphenamid recorded at 20 eV (upper) and 40 eV (lower). E, database MS/MS spectra at same collision energies.

Table 2
Summary of identified compounds from DIA, on-line SPE LC-QTOF-MS records.

Compound	Confidence level	Use	CAS number	Retention time (min)	m/z values				Detection frequency	
					$[M + H]^+$	Q1	Q2	Q3	La Rioja	Galicia
2-hydroxy-terbuthylazine	1	Herbicide	66,753–07-9	6.20	212.1506	158.0879	128.0566	114.0662	1.86 %	_
Atrazine	1	Herbicide	1912-24-9	10.15	216.1010	174.0504	146.0228	104.001	2.48 %	3.52 %
Desethyl terbuthylazine	1	Herbicide	30,125–63-4	9.20	202.0854	146.0228	104.001	79.0057	9.94 %	1.95 %
Desethyl atrazine	1	Herbicide	6190-65-4	7.15	188.0698	146.0228	104.001	79.0057	0.62 %	6.64 %
Diflufenican	1	Herbicide	83,164–33-4	14.95	395.0813	266.0412	375.0751	238.0462	4.35 %	_
Flazasulfuron	1	Herbicide	104,040–78-0	11.19	408.0584	182.0558	156.0767	227.0087	6.83 %	_
Isoxaben	1	Herbicide	82,558–50-7	12.77	333.1809	165.0546	150.0311	57.0698	1.24 %	0.39 %
Metolachlor	1	Herbicide	51,218–45-2	13.153	284.1412	252.1149	176.1433	134.0964	13.04 %	3.52 %
Terbuthylazine	1	Herbicide	5915-41-3	11.74	230.1167	174.054	104.001	146.0228	11.18 %	1.56 %
Terbumeton desethyl	1	Herbicide	33,124–62-8	6.30	198.1349	142.0723	86.0348	100.0505	47.20 %	1.17 %
Pirimicarb	1	Insecticide	23,103–98-2	6.40	239.1502	182.1287	72.04439	195.1604	11.18 %	4.69 %
Empenthrin	2	Insecticide	54,406–48-3	9.19	275.2006	187.1481	173.1325	159.1168	_	0.80 %
8-Hydroxyquinoline	2	Fungicide	148–24-3	6.40	146.0604	128.0494	118.06451	101.0385	0.62 %	1.56 %
Diphenamid	2	Herbicide	957–51-7	11.21	240.1382	167.0855	134.0962	91.0542	1.24 %	1.17 %
Pirimicarb desmethyl	2	Insecticide	30,614–22-3	5.60	225.1346	180.0767	168.1131	72.0444	0.62 %	0.39 %

frequency of pre-defined target compounds is likely underestimated. Another limitation is that the employed concentration and determination conditions do not cover the analysis of zwitterionic pesticides of importance in viticulture, such as the fungicide fosetyl, the herbicide glyphosate and its major environmental transformation product. Detection and quantification of these compounds require specifically designed approaches, beyond the scope of the current research.

3.6. Future perspectives

Assessing the impact of viticulture in the pollution of the aquatic environment requires the multiresidue determination of currently authorized pesticides, phase-out compounds and their known, or suspect, transformation products. Some of the most often detected compounds in this study, posing from moderate to high environmental risks in a relevant percentage of samples, have known transformation products, whose determination should be addressed in further studies. Some examples are 1,2,4 triazole, recognized as a relevant metabolite of the fungicide tebuconazole; the 3,5-dichloro-4-methyl benzoic acid resulting from the hydrolysis of zoxamide; 2,6-dichlorobenzamide arising from fluopicolide; and the acidic form of azoxystrobin (Lewis et al., 2016). In case of small, polar molecules, i.e. 1,2,4-triazole, reversed-phase mechanisms, used for sample concentration and LC analysis, do not grant their sensitive analysis; thus, alternative analytical approaches (i.e. supercritical fluid chromatography) are required.

Pollution of GW in viticulture areas represents a concerning issue, particularly in high density population areas (within this study the D.O. RB, in Galicia), where GW is either directly consumed, or used for production of drinking water. Understanding the leaching of pesticides from topsoil to underground aquifers would require a multidisciplinary approach, combining the analysis of pesticides in soil columns with a thorough characterization of soil properties, and the study of hydrogeological features in the investigated regions.

4. Conclusions

Average and median values of total pesticides were similar in water samples from the different sub-zones, or D.O., from both geographical areas (La Rioja and Galicia), except in D.O. Rías Baixas, where higher values were found. Fungicides showed a higher prevalence than insecticides with important differences in their distribution between both geographical areas. Fluopyram, CGA 62826, boscalid, tetraconazole and metrafenone were prevalent in water samples from La Rioja, whilst azoxystrobin, zoxamide, mandipropamide and fluopicolide were more often found in Galicia. Maximum residues were usually measured during the summer sampling campaign. However, the levels of moderate and highly leachable compounds increased from summer to autumn in some wells. This trend points out to leaching from topsoil layers to groundwater. Residues of carbendazim, azoxystrobin, fluopicolide, tebuconazole and zoxamide represented a relevant hazard in a few samples containing concentrations above their PNEC values. Moreover, they posed a moderate risk (RQ values between 0.1 and 1) in more than 5 % of the analyzed samples. Occurrence data obtained for these compounds grant further research to investigate the presence of their known transformation products in the aquatic environment. Legacy triazine herbicides need to be included in further selections of target pesticides to determine their concentrations in ground waters.

CRediT authorship contribution statement

V. Fernández-Fernández: Validation, Methodology, Investigation, Formal analysis, Data curation, Writing – review & editing, Writing – original draft. **M. Ramil:** Supervision, Methodology, Funding acquisition, Writing – review & editing. **E. Díaz-Losada:** Funding acquisition, Conceptualization, Writing – review & editing. **M.D. Loureiro-Rodríguez:** Methodology, Conceptualization, Writing – review & editing. **E. Trigo-Córdoba:** Methodology, Conceptualization, Writing – review & editing. **M.S. Andrades:** Methodology, Conceptualization, Writing – review & editing. **J.M. Marín-Benito:** Supervision, Project administration, Methodology, Funding acquisition, Conceptualization, Writing – review & editing. **M.S. Rodríguez-Cruz:** Supervision, Project administration, Funding acquisition, Formal analysis, Conceptualization, Writing – review & editing, Writing – original draft. **I. Rodríguez:** Supervision, Project administration, Funding acquisition, Formal analysis, Conceptualization, Writing – review & editing, Writing – original draft.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Economic support from projects TED2021-129962B-C42, funded by the "Spanish Ministry of Science and Innovation (MCIN/AEI/10.13039/501100011033)" and by the "European Union NextGeneration EU/PRTR"; and ED431C 2025/21, from Xunta de Galicia, co-funded by "ERDF A way of making Europe", is acknowledged. M.D.L.R. acknowledges a Senior Talent Programme contract funded by Xunta de Galicia. The authors thank J.M. Ordax for his technical assistance in the water samplings.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2025.181074.

Data availability

Data will be made available on request.

References

Berger, U., Ost, N., Kühne, R., Schüürmann, G., Neumann, M., Reemtsma, T., 2017. Assessment of persistence, mobility and toxicity (PMT) of 167 REACH registered substances. http://www.umweltbundesamt.de/publikationen.

Bijlsma, L., Pitarch, E., Hernández, F., Fonseca, E., Marín, J.M., Ibáñez, M., Portolés, T., Rico, A., 2021. Ecological risk assessment of pesticides in the Mijares River (eastern Spain) impacted by citrus production using wide-scope screening and target quantitative analysis. J. Hazard. Mater. 412, 125277. https://doi.org/10.1016/j.jhazmat.2021.125277.

Blanco, P., Rodríguez, I., Fernández-Fernández, V., Ramil, M., Castrillo, D., Acín-Albiac, M., Adamo, I., Fernández-Trujillo, C., García-Jiménez, B., Acedo, A., Calvo-Portela, N., Parente-Sendín, A., Acemel-Míguez, L., Alonso-Vega, F., 2024. Physicochemical Properties and Microbiome of Vineyard Soils from DOP Ribeiro (NW Spain) Are Influenced by Agricultural Management. Microorganisms 12, 12030595. https://doi.org/10.3390/microorganisms12030595.

Calliera, M., Capri, E., Lomadze, A., Bertuzzi, T., Beone, G.M., Delpero, E., Varotto, A., Bergaglio, S., Anselmetti, E., Suciu, N.A., 2025. Evaluating point source pesticide contamination via sprayer washing water dispersal: A northern Italian vineyard area case study. Sci. Total Environ. 964, 178551. https://doi.org/10.1016/j.scitotenv.2025.178551.

Carpio, M.J., Rodríguez-Cruz, M.S., Sánchez-Martín, M.J., Marín-Benito, J.M., 2022. Pesticide fate in soils under different agricultural management practices. In: Rodríguez-Cruz, M.S., Sánchez-Martín, M.J. (Eds.), Pesticides in Soils. The Handbook of Environmental Chemistry, vol. 113. Springer, pp. 251–286.

Chow, R., Curchod, L., Davies, E., Veludo, A.F., Oltramare, C., Dalvie, M.A., Stamm, C., Röösli, M., Fuhrimann, S., 2023. Seasonal drivers and risks of aquatic pesticide pollution in drought and post-drought conditions in three Mediterranean watersheds. Sci. Total Environ. 858. https://doi.org/10.1016/j.scitotenv.2022.159784.

Curchod, L., Oltramare, C., Junghans, M., Stamm, C., Dalvie, M.A., Röösli, M., Fuhrimann, S., 2020. Temporal variation of pesticide mixtures in rivers of three agricultural watersheds during a major drought in the Western Cape. South Africa. Water Res. X 6. https://doi.org/10.1016/j.wroa.2019.100039.

Esteve-Turrillas, F.A., Agulló, C., Abad-Somovilla, A., Mercader, J.V., Abad-Fuentes, A., 2016. Fungicide multiresidue monitoring in international wines by immunoassays. Food Chem. 196, 1279–1286. https://doi.org/10.1016/j.foodchem.2015.10.102.

Fernández-Fernández, V., Ramil, M., Cela, R., Rodríguez, I., 2023. Occurrence and risk assessment of pesticides and pharmaceuticals in viticulture impacted watersheds from Northwest Spain. Chemosphere 341, 140098. https://doi.org/10.1016/j.chemosphere.2023.140098.

Fernández-Fernández, V., Castro, G., Ramil, M., Rodríguez, I., 2025a. Assessment of LC-QTOF-MS data independent acquisition for quantification and suspect screening of pesticides in agriculture impacted water samples. J. Chromatogr. A 465957. https://doi.org/10.1016/j.chroma.2025.465957.

Fernández-Fernández, V., Ramil, M., Blanco, P., Andradres, M.S., Rodríguez, I., 2025b. Pesticides in wines from two major production regions in the North of Spain. J. Food Compos. Anal. 142. https://doi.org/10.1016/j.jfca.2025.107525.

Fernández-García, A., Martínez-Piernas, A.B., Moreno-González, D., Gilbert-López, B., Molina-Díaz, A., García-Reyes, J.F., 2024. Occurrence and risk assessment of pesticides and their transformation products related to olive groves in surface waters of the Guadalquivir river basin. Chemosphere 357, 142075. https://doi.org/10.1016/j.chemosphere.2024.142075.

Fouillet, E., Delière, L., Chartier, N., Munier-Jolain, N., Cortel, S., Rapidel, B., Merot, A., 2022. Reducing pesticide use in vineyards. Evidence from the analysis of the French DEPHY network. Eur. J. Agron. 136, 126503. https://doi.org/10.1016/j.eja.2022.126503.

Gómez-Martínez, D., Selvin, M.A., Nilsson, A.K., Carmona, E., Ngou, J.S., Kristiansson, E., Nilsson, R.H., Corcoll, N., 2024. Environmental concentrations of the fungicide tebuconazole alter microbial biodiversity and trigger biofilm-released transformation products. Chemosphere 369. https://doi.org/10.1016/j.chemosphere.2024.143854.

Herrero-Hernández, E., Simón-Egea, A.B., Sánchez-Martín, M.J., Rodríguez-Cruz, M.S., Andrades, M.S., 2020. Monitoring and environmental risk assessment of pesticide residues and some of their degradation products in natural waters of the Spanish vineyard region included in the Denomination of Origin Jumilla. Environ. Pollut. 264, 114666. https://doi.org/10.1016/j.envpol.2020.114666.

Imfeld, G., Meite, F., Wiegert, C., Guyot, B., Masbou, J., Payraudeau, S., 2020. Do rainfall characteristics affect the export of copper, zinc and synthetic pesticides in surface runoff from headwater catchments? Sci. Total Environ. 741, 140437. https://doi.org/10.1016/j.scitotenv.2020.140437.

Imfeld, G., Meite, F., Ehrhart, L., Fournier, B., Heger, T.J., 2024. Dissipation of pesticides and responses of bacterial, fungal and protistan communities in a multi-contaminated vineyard soil. Ecotoxicol. Environ. Saf. 284, 116994. https://doi.org/10.1016/j.ecoenv.2024.116994.

Iñigo, V., Marín, A., Andrades, M.S., Jiménez-Ballesta, R., 2022. Soil spatial variability in the vineyards of La Rioja PDOC (Spain). Int. J. Environ. Stud. 79 (3), 502–512. https://doi.org/10.1080/00207233.2021.1929385.

Lewis, K.A., Tzilivakis, J., Warner, D.J., Green, A., 2016. An international database for pesticide risk assessments and managemen. Hum. Ecol. Risk Assess. Int. J. 22 (4), 1050–1064.

Maillard, E., Payraudeau, S., Faivre, E., Grégoire, C., Gangloff, S., Imfeld, G., 2011. Removal of pesticide mixtures in a stormwater wetland collecting runoff from a vineyard catchment. Sci. Total Environ. 409 (11), 2317–2324. https://doi.org/10.1016/j.scitotenv.2011.01.057.

Manjarres-López, D.P., Andrades, M.S., Sánchez-González, S., Rodríguez-Cruz, M.S., Sánchez-Martín, M.J., Herrero-Hernández, E., 2021. Assessment of pesticide residues in waters and soils of a vineyard region and its temporal evolution. Environ. Pollut. 284, 117463. https://doi.org/10.1016/j.envpol.2021.117463.

MAPA. Statistics of phytosanitary compounds per crop in Spain, 2025. Spanish Ministry of Agriculture, Fisheries and Food. https://www.mapa.gob.es/es/estadistica/temas/estadisticas-agrarias/agricultura/estadisticas-medios-produccion/fitosanitarios.aspx.

MAPA. Summary of wine producing D.O. in Spain, 2024. Spanish Ministry of Agriculture, Fisheries and Food. https://www.mapa.gob.es/es/alimentacion/temas/calidad-diferenciada/dop-igp/.

Marin, B., Dousset, S., Caner-Chabran, A., Guillaneuf, A., Billet, D., 2022. Pesticide sorption and mitigation efficiency of a detention pond in a Champagne vineyard catchment. Heliyon 8, 11475. https://doi.org/10.1016/j.heliyon.2022.e11475.

Norman Ecotoxicological Database, 2025. https://www.norman-network.com/nds/ecotox/.

Oliveira, M.J.R.A., Roriz, M., Vasconcelos, M.W., Bertaccini, A., Carvalho, S.M.P., 2019. Conventional and novel approaches for managing "flavescence dorée" in grapevine: knowledge gaps and future prospects. In: Plant Pathology. Blackwell Publishing Ltd., pp. 3–17. https://doi.org/10.1111/ppa.12938. Vol. 68, Issue 1.

Pérez-Mayán, L., Ramil, M., Cela, R., Rodríguez, I., 2020. Multiresidue procedure to assess the occurrence and dissipation of fungicides and insecticides in vineyard soils from Northwest Spain. Chemosphere 261, 127696. https://doi.org/10.1016/j.chemosphere.2020.127696.

Pinheiro, D.F., Maciel, G.M., Lima, N.P., Liviz, C. do A.M., Lima, N.F., Haminiuk, C.W.I., 2025. Assessment of pesticides concentration in South American wines by liquid chromatography-tandem mass spectrometry. J. Food Compos. Anal. 140, 107225. https://doi.org/10.1016/j.jfca.2025.107225.

Ray, A., Dutta, D., Ghosh, B., Bahadur, M., 2024. Azoxystrobin induced genotoxicity in Pethia conchonius, a freshwater fish of river Teesta. India. Aquat. Toxicol. 277. https://doi.org/10.1016/j.aquatox.2024.107135.

Schymanski, E.L., Jeon, J., Gulde, R., Fenner, K., Ruff, M., Singer, H.P., Hollender, J., 2014. Identifying small molecules via high resolution mass spectrometry: Communicating confidence. Environ. Sci. Technol. 48 (4), 2097–2098. https://doi.org/10.1021/es5002105.

Sharma, M., Maheshwari, N., Khan, F.H., Mahmood, R., 2022. Carbendazim toxicity in different cell lines and mammalian tissues. In Journal of Biochemical and Molecular Toxicology (Vol. 36, Issue 12). John Wiley and Sons Inc. https://doi.org/10.1002/jbt.23194.

Silva, E., Batista, S., Caetano, L., Cerejeira, M.J., Chaves, M., Jacobsen, S.E., 2011. Integrated approach for the quality assessment of freshwater resources in a vineyard area (South Portugal). Environ. Monit. Assess. 176 (1–4), 331–341. https://doi.org/10.1007/s10661-010-1586-1.

Silva, V., Mol, H.G.J., Zomer, P., Tienstra, M., Ritsema, C.J., Geissen, V., 2019. Pesticide residues in European agricultural soils – A hidden reality unfolded. Sci. Total Environ. 653, 1532–1545. https://doi.org/10.1016/j.scitotenv.2018.10.441.

Suciu, N., Farolfi, C., Zambito Marsala, R., Russo, E., De Crema, M., Peroncini, E., Tomei, F., Antolini, G., Marcaccio, M., Marletto, V., Colla, R., Gallo, A., Capri, E., 2020. Evaluation of groundwater contamination sources by plant protection products in hilly vineyards of Northern Italy. Sci. Total Environ. 749, 141495. https://doi.org/10.1016/j.scitotenv.2020.141495.

Vallejo, A., Millán, L., Abrego, Z., Sampedro, M.C., Sánchez-Ortega, A., Unceta, N., Gómez-Caballero, A., Goicolea, M.A., Diez-Navajas, A.M., Barrio, R.J., 2019. Fungicide distribution in vitiviniculture ecosystems according to different application strategies to reduce environmental impact. Sci. Total Environ. 687, 319–329. https://doi.org/10.1016/j.scitotenv.2019.06.112.

Willkommen, S., Pfannerstill, M., Ulrich, U., Guse, B., Fohrer, N., 2019. How weather conditions and physico-chemical properties control the leaching of flufenacet, diflufenican, and pendimethalin in a tile-drained landscape. Agric. Ecosyst. Environ. 278, 107–116. https://doi.org/10.1016/j.agee.2019.03.017.

Xunta de Galicia, 2024. Pest affecting vineyards. https://mediorural.xunta.gal/gl/temas/agricultura/sanidade-vexetal/organismos-nocivos-de-corentena.

Zambito Marsala, R., Capri, E., Russo, E., Bisagni, M., Colla, R., Lucini, L., Gallo, A., Suciu, N.A., 2020. First evaluation of pesticides occurrence in groundwater of Tidone Valley, an area with intensive viticulture. Sci. Total Environ. 736, 139730. https://doi.org/10.1016/j.scitotenv.2020.139730.