Environmental Pollution 284 (2021) 117463

Contents lists available at ScienceDirect

Environmental Pollution

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

Assessment of pesticide residues in waters and soils of a vineyard region and its temporal evolution☆

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ARTICLE INFO

Keywords:
Pesticide residues
Seasonal and temporal change
Environmental pollution
Vineyard area

ABSTRACT

Sustainable agriculture practices and integrated pest management for avoiding environmental pollution are necessary to maintain a high yield in vineyard areas. Pesticide residues in groundwater in a vineyard area of La Rioja (Spain) have been evaluated in previous years, and they could now have varied after farmers have adopted the different measures recommended. Accordingly, this research's objectives were (i) to evaluate the occurrence and seasonal distribution (spring, summer, and autumn samplings) of pesticides (36) plus their degradation products (DP) (11) in water and soil samples (23 + 15) in La Rioja (Northern Spain), and (ii) to compare the current water quality (2019) with that determined previously (2011). A multi-residue method based on solid phase extraction (for water samples) or solid liquid extraction (for soil samples) and high-performance liquid chromatography coupled to mass spectrometry (HPLC-MS) was used to determine and quantify pesticides. The results reveal the presence in waters of 30 compounds from those selected (15 fungicides + 2 DP, 7 insecticides + 1 DP, and 3 herbicides +2 DP), with 14 of them at concentrations > 0.1 μg L^{-1} (water quality threshold for human consumption). The highest number of compounds was detected in summer (waters) and spring (soils). The pesticides most frequently detected in water samples were the fungicides metalaxyl, tebuconazole, and boscalid, with the last one being the compound found in the highest number of soil samples. The comparison of water pollution in 2011 and 2019 indicates a significant decrease in the total concentration of herbicides, fungicides and insecticides in 95–100%, 76–90%, and 42–85% of samples in the three campaigns, respectively. The results indicate that an optimized and sustainable use of pesticides in intensive and high-yield agricultural areas could reduce environmental pollution.

1. Introduction

The growing concern to ensure economic progress compatible with the environment prompted the United Nations in 2015 to adopt the 2030 Agenda for Sustainable Development to promote prosperity while protecting the planet (UN, 2019). One of the 17 goals proposed includes the protection of aquatic ecosystems and the reduction of aquifer pollution.

Pesticides are used to protect and improve crop yields, with the average world consumption being 2.68 kg per ha of cultivated land (FAOSTAT, 2019). The marketing of these products in the European Union (EU) was 362,626 t in 2017, with Spain accounting for the highest percentage of sales (72,118 t), followed by France, Italy, and Germany (MAPAMA, 2017). The use of pesticides is widespread and affects almost all crops (vineyards, orchards, cereals, olive groves, vegetables, etc.) in different forms and times, where they can migrate into the soil and surface and ground waters and contaminate these systems (Close et al., 2021; Tauchnitz et al., 2020). The fact that pesticide residues may remain in the environment after their application has been widely reported and studied in the world (de Souza et al., 2020).

Pesticides are considered of special environmental interest because of their potential toxicity and the physicochemical properties that some active substances have to interact with the environment, leading to a

☆ This paper has been recommended for acceptance by Da Chen.
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https://doi.org/10.1016/j.envpol.2021.117463
Received 8 February 2021; Received in revised form 21 May 2021; Accepted 22 May 2021
Available online 28 May 2021

high mobility and/or persistence. The mobility of pesticides by leaching due to rain or irrigation (Chaplain et al., 2011) could lead to the contamination of water for human consumption and to the ban on their use when the environmental quality standard is not met (Barbieri et al., 2020). The Groundwater Ubiquity Score (GUS) index, based on the organic-carbon adsorption constant (K_{oc}) and degradation rate (DT_{50}) of pesticides in soils, classifies these compounds as likely to leach (GUS > 2.8), unlikely to leach (GUS < 1.8), and marginal leaching potential (1.8 < GUS < 2.8), and has been implemented as a very simple indicator of the chemical potential for leaching into groundwater (PPDB, 2020). Soil contamination is non-point during the application of pesticides in crops, but may also be point due to the improper management of storage containers. This contamination could alter its microbiota and modify its functionality and ecosystem services (Vašíčková et al., 2019) or contaminate surface and ground waters. The highest persistence of these compounds is frequently found in soils with high organic matter (OM) content, which are the most vulnerable due to their high adsorption capacity (Pose-Juan et al., 2015).

As a control tool to prevent diffuse pollution associated with the use of this type of agricultural inputs, Directives 98/83/EC (EC, 1998) and 2006/118/EC (EC, 2006) on the protection of water against pesticide contamination, in both cases used in agriculture, were established at European level. They set the value of 0.1 μg L^{-1} as the maximum concentration for each pesticide detected in a water sample, and 0.5 μg L^{-1} for the sum of all individual pesticides detected and quantified in the monitoring procedure, including their relevant metabolites, degradation, and reaction products in water for human consumption. Pesticides, such as atrazine and some of its degradation products, terbutryn and alachlor, are part of the list of the 45 priority substances to be controlled in the field of water policy and established the parameters of environmental quality standard (EQS) expressed as the maximum allowable concentration (MAC-EQS), updated through Directive 2013/39/EU (EC, 2013). Within the regulations for the prevention of soil contamination, potentially polluting activities are defined, and the methodology for the declaration of contaminated soils is established in Spain under Royal Decree (RD) September 2005 (BOE, 2005). However, there is currently no legislation that establishes admissible thresholds for pesticides detected in soils equivalent to those previously cited for waters and that may pose a risk for aquifer contamination (Silva et al., 2019). The only EU legislation related to this subject is the Regulation No. 1107/2009 (EC, 2009a) that makes reference to maximum concentrations/contents of approved pesticides in soils through the estimation of the Predicted Environmental Concentrations (PEC) for each approved active substance in the review process previous to the authorization and commercialization of the plant protection products.

Due to the interest in developing sustainable agriculture, studies are required to identify chemical products that may be affecting aquatic ecosystems and soils. These studies have been carried out worldwide for some time now, although they have increased in recent years in countries such as China (Zheng et al., 2016; Wang et al., 2018), India (Mondal et al., 2018), Costa Rica (Carazo-Rojas et al., 2018), Hungary (Székács et al., 2015), France (Cotton et al., 2016), Croatia (Fingler et al., 2017), Greece (Kapsi et al., 2019; Papadakis et al., 2018) and Italy (Zambito Zambito et al., 2020), along with studies involving different countries (Schreiner et al., 2016). In Spain, this issue has also been addressed in different coastal areas of Catalonia (Köck-Schulmeyer et al., 2019), in the river basins of the Guadalquivir (Masiá et al., 2013), Ebro (Ccanccapa et al., 2016a; Barbieri et al., 2020), Jucar and Turia (Ccanccapa et al., 2016b), and Tagus (Rico et al., 2019; Arenas Sánchez et al., 2019), and in different surface and ground waters in vineyard areas, such as La Rioja and Jumilla (Herrero-Hernández et al., 2013, 2020) and in northern Spain (Hildebrandt et al., 2008).

The studies on pesticide residues in soil samples or sediments have been less frequent, although they can also be adsorbed by these environmental matrixes, being retained over time and becoming a non-point source of pesticide pollution of surface and ground waters (Hvězdová et al., 2018). Most of these studies report the presence of organochlorine pesticides in soils from Uganda (Ssebugere et al., 2010), India (Khuman et al., 2020; Mishra et al., 2012), or China (Shi et al., 2013). These studies now include other herbicides, fungicides, and insecticide residues in European agricultural soils (Hvězdová et al., 2018; Kosubová et al., 2020; Silva et al., 2019). In the case of Spain, some studies have reported the presence of pesticides in vineyard soils (Bermúdez-Couso et al., 2007; Pérez-Mayán et al., 2020; Pose-Juan et al., 2015). However, the simultaneous presence of pesticides in soils and waters has rarely been studied, although persistent pesticides in soils could contaminate surface waters for a long time (Tauchnitz et al., 2020), or the shallow topsoil in certain areas could even facilitate the leaching of these compounds into groundwater (Sánchez-González et al., 2013).

Pollution due to the use of pesticides in agriculture deserves special attention in some Spanish regions, such as La Rioja, with intensive agriculture dedicated mainly to vineyards (34.6%), especially across a wide area classified as Rioja Qualified Designation of Origen (DOCa Rioja). The economy based on this activity is very important to this region, and a high consumption of pesticides per hectare is usual in this wine-growing area to guarantee production (MAPAMA, 2017). The authors of this paper have reported the presence of herbicides, insecticides, and fungicides in surface and ground waters (Herrero-Hernández et al., 2016, 2017), and in soils (Pose-Juan et al., 2015) in the DOCa Rioja area in a high percentage of the samples analyzed, even at levels higher than permitted by EU legislation for drinking water. In this sense EU regulations have been established concerning the placing of plant protection products on the market (Regulation No 1107/2009/EC) (EC, 2009a) and on the sustainable use of pesticides (Directive, 2009/128/EC) (EC, 2009b) (Calliera et al., 2021). After these regulations have been adopted by Member States as the Spanish legislation included in RD 1311/2012 (BOE, 2012) and an action framework including different objectives and measurements for the sustainable use of pesticides in agriculture have been developed to avoid environmental pollution. In consequence it is possible to wait that pest management practices by farmers may have changed in recent years. An assessment of this regulation's effect could be tested by analyzing those pesticide residues in water that have been recorded in previous studies (Herrero-Hernández et al., 2016, 2017).

Accordingly, this study's objectives were (i) to evaluate the seasonal changes in pesticide residues in surface and ground waters from the eastern part of La Rioja as representative area of DOCa Rioja, ii) to compare the water contamination in this area based on the current pesticide residues detected and those recorded in previous years for the same water samples to evaluate whether temporal sustainability improved, and iii) to evaluate the seasonal changes in the residues of pesticides in soils around the wells, and where possible, find a relationships between water-soil contamination that has been previously detected in the area.

2. Materials and methods

2.1. Area of study

The area of study is La Rioja Oriental (also referred to as Rioja Baja) is a sub-area in the east of the DOCa Rioja vineyard region (Northern Spain) (Fig. S1 and Supplementary Material). Its hydrography is conditioned by the dynamics of the basins of the Iregua, Leza, Cidacos, Alhama, Linares, Ega, Arga and Ebro rivers. The soils are generally clay-calcareous, which means slightly alkaline, poor in OM (<2%), and with moderate-to-low water availability during the summer (CR DOCa Rioja, 2020). Wine growing is one of the main economic activities in this area, with a high consumption of pesticides, as in the whole Rioja region (MAPAMA, 2017). In addition, La Rioja Oriental or Baja has a different climate to the other sub-areas (Rioja Alta and Rioja Alavesa), with a Mediterranean influence and drier and warmer weather.

2.2. Analysis of pesticide residues in water and soil samples

Forty-seven pesticides (insecticides (12), herbicides (14), and fungicides (21)), and eleven of their degradation products were selected for this study (Table S1). They belong to different chemical families and include the most widely used pesticides in the vineyards, as detected by Herrero-Hernández et al. (2013) in previous studies, and some of new use in the area according to the data provided by farmers through different cooperatives, wineries as Vivanco SL and companies that market the products. Pesticide standards were supplied by Sigma Aldrich Química S.A. (Madrid, Spain) and used at 98% purity. Stock standard solutions (1000 or 500 μg mL^{-1}) were prepared for each of the selected analytes in methanol and stored in the dark at 4 °C together with a lower standard solution at a concentration of 10 μg mL^{-1} of all the target analytes. The lower standard solution was used for spiking the aqueous calibration standards. The organic solvents (acetonitrile, methanol, and acetone) were of HPLC grade, and supplied by Scharlab S. L. (Barcelona, Spain). Ultra-high quality (UHQ) water was obtained with a Milli-Q water purification system (Millipore, Milford, MA, USA).

The compounds were separated in a 150 mm × 4.60 mm Luna PFP2 analytical column, packed with 3.0 μm particles (Phenomenex, Torrance, CA, USA) with a C-18 Waters Sentry pre-column (Waters, Milford, MA, USA). All the pesticides were quantified by HPLC–MS using a Waters (Milford, MA, USA) system coupled with a Micromass ZQ single quadrupole mass spectrometer with an ESI interface as it is indicated in **Supplementary Material** and in Tables S2 and S3.

2.3. Water sampling

Three water sampling campaigns were carried out in three different seasons in 2019. Twenty-three water samples were collected at different points in La Rioja Oriental vineyards (inside the cropped field or next to crops) in spring (prior to pesticide application to detect the oldest pesticide residues), summer, and autumn (Fig. S1A). The sampling points were selected from among those previously analyzed by Herrero-Hernández et al. (2013) to compare the evolution of pesticide residues, with 18 samples corresponding to groundwater from springs and private wells with depths between one and 10 m, and five samples of surface water from the Ebro, Leza, Iregua and Ega rivers and the Lodosa canal (Table S4). The wells of monitoring network were distributed along the vineyard area described (Fig. S1A).

Water samples were collected and processed as previously reported by Herrero-Hernández et al. (2013, 2020) and indicated in **Supplementary Material**. Specific physicochemical parameters of water quality, such as pH and electrical conductivity, were determined in situ with Crison specific portable devices (Crison Instruments S.A., Barcelona, Spain). The inorganic anions (Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) were analyzed with an ionic chromatograph (Metrohm USA Inc) (Table S4). Nitrate concentrations indicated that fewer than 35% of the samples exceeded the limit set by the EU (50 mg L^{-1}).

2.4. Soil sampling

Fifteen soil samples were simultaneously collected with water samples in spring (prior to pesticide application to detect the oldest pesticide residues), summer, and autumn in 2019 from the surface layer (0–15 cm) in cultivated areas around the wells (distance < 10 m) (Fig. S1B). They were sampled after the soil surface was cleaned to ensure that the sample did not contain stones, roots, or remnants of previous crops. The samples were gathered with a stainless-steel scoop, stored in labeled plastic bags, and transported to the laboratory in iceboxes. The soils were air-dried, sieved (<2 mm), and stored at 4 °C until extraction.

Pesticides were extracted from the soil samples in triplicate using the optimized multi-residue method described by Pose-Juan et al. (2014) and indicated in **Supplementary Material**. The physicochemical characteristics (pH, electrical conductivity, carbonates, OM, and granulometry) were determined following the standard methods of soil analysis (Sparks, 1996) (Table S5). The soil texture was generally sandy clay loam or sandy loam; the soil pH was in the 7.73 to 8.91 range, and the OM content was between 0.37% and 2.94%.

2.5. Data analysis

Single and multiple linear regression models were used to relate at different sampling times: 1) the concentrations of pesticides detected in waters or soils with their properties (water solubility, K_{ow}, GUS index and DT_{50}), 2) the total concentrations of pesticides or that of different groups (herbicides, insecticides and fungicides) detected in different sites with properties of water (including water depth) and soils, and 3) the total concentrations of pesticides or that of different groups (herbicides, insecticides and fungicides) detected in soils and waters. Pearson correlation coefficients were determined using the IBM SPSS Statistics v26 software package (IBM, NY, USA).

3. Results and discussion

3.1. Seasonal evolution of pesticides in water samples

The evaluation of pesticide residues in water samples indicated that 35% of the pesticides included in this study were not detected in any sample during the three seasonal sampling campaigns carried out in 2019 (Table 1). The fungicides cyprodinil, azoxystrobin, pyrimethanil, and penconazole; the herbicides ethofumesate, pendimethalin, oxyfluorfen, atrazine and their degradation products DEHA, DIA, DIHA, HA and DEA, and the insecticides acephate, diazinon, dimethoate and the degradation product chlorpyrifos-oxon were not detected, although some of them had been found in previous water samplings in La Rioja region (Herrero-Hernandez et al., 2013, 2016, 2017) and in other Spanish agricultural areas (Herrero-Hernandez et al., 2020) or in surface water ecosystems (Ccanccapa et al., 2016; Rico et al., 2019). This suggests that several pesticides were substituted by other compounds with a similar activity or they were banned. However, some compounds detected correspond to substances banned in Spain (PPDB , 2020), such as nuarimol, azinphos-methyl, methidathion and carbendazim (also metabolite of the fungicides thiophanate and thiophanate-methyl applied in grapes but non-evaluated here). It is noteworthy that several pesticides, such as the fungicides nuarimol, fenbuconazole, trifloxystrobin, flutriafol, and cyproconazole, and the insecticides azinphos-methyl and hexythiazox were only detected in the spring sampling campaign, and at very low concentrations (Table 1). These residues may correspond to compounds applied in previous years, but now no longer.

Only four of the pesticides analyzed were detected individually at concentrations over 0.1 μg L^{-1} in the three sampling periods (Table 1). They corresponded to some of the most ubiquitous fungicides, such as metalaxyl and its degradation product CGA-62826, with maximum concentrations (C_{max}) detected for the parent compound of 0.932 μg L^{-1} (summer) and 0.540 μg L^{-1} (spring), and tebuconazole with C_{max} 0.917 μg L^{-1} in autumn. These compounds have been widely used in different crops for some time, and they have been widely detected in surface and ground waters in different agricultural areas (Rico et al., 2019; Schreiner et al., 2016; Tauchnitz et al., 2020). Residues of these fungicides were found here at higher concentrations in groundwaters than in surface waters, which could not be explained by their properties because they have a different GUS index related to their mobility in the soil and very different water solubility. Another compound widely detected is the fungicide boscalid (C_{max} 0.207 μg L^{-1} in autumn). Boscalid is active against a broad range of fungal pathogens in a wide array of crops, with low water solubility (PPDB, 2020). It is a fungicide that has only recently been approved for its use, and its residues have rarely been included in water monitoring programs, although it has been detected in surface waters by Papadakis et al. (2018) and Tauchnitz et al. (2020) at

Table 1
Positive water samples (%) with concentrations (C) over and below 0.1 μg L^{-1} and concentrations of pesticides detected (mean and maximum) in the three sampling campaigns.

Pesticides		Spring (n = 23)				Summer (n = 23)				Autumn (n = 23)			
		Positive samples (%)		Concentration (μg L^{-1})		Positive samples (%)		Concentration (μg L^{-1})		Positive samples (%)		Concentration (μg L^{-1})	
		C<0.1	C>0.1	Mean	Maximum	C<0.1	C>0.1	Mean	Maximum	C<0.1	C>0.1	Mean	Maximum
Fungicides	Nuarimol	52	–	0.011	0.026	–	–	–	–	–	–	–	–
	Metalaxyl	52	9	0.060	0.540	39	22	0.178	0.932	9	13	0.177	0.312
	Tebuconazole	52	9	0.048	0.271	30	13	0.065	0.149	26	22	0.161	0.917
	Fenbuconazole	17	–	0.006	0.007	–	–	–	–	–	–	–	–
	Boscalid	26	4	0.057	0.168	4	4	0.119	0.179	39	9	0.063	0.207
	Trifloxystrobin	22	–	0.004	0.007	–	–	–	–	–	–	–	–
	Myclobutanil	22	–	0.012	0.021	4	4	0.099	0.157	9	–	0.021	0.023
	CGA-62826	13	4	0.056	0.187	4	4	0.099	0.136	22	9	0.059	0.121
	Benalaxyl	17	–	0.041	0.090	22	0	0.023	0.032	4	–	0.018	0.018
	Dimethomorph	9	4	0.117	0.318	13	4	0.126	0.265	17	–	0.029	0.073
	Flutriafol	4	–	0.020	0.020	–	–	–	–	–	–	–	–
	Cyproconazole	4	–	0.016	0.016	–	–	–	–	–	–	–	–
	Kresoxim-methyl	9	–	0.022	0.038	17	–	0.011	0.016	–	–	–	–
	Fluopyram	4	–	0.072	0.072	43	9	0.082	0.541	9	4	0.094	0.265
	CGA-92370	–	–	–	–	17	–	0.022	0.031	4	–	0.013	0.013
	Carbendazim	–	–	–	–	4	–	0.025	0.025	26	9	0.126	0.423
	Iprovalicarb	–	–	–	–	9	–	0.038	0.057	–	–	–	–
Herbicides	Terbuthylazine	35	–	0.023	0.066	9	–	0.049	0.087	9	–	0.023	0.038
	HT	13	4	0.049	0.132	26	–	0.029	0.061	17	–	0.041	0.068
	Fluometuron	13	4	0.069	0.177	4	–	0.028	0.028	4	–	0.026	0.026
	Metolachlor	4	–	0.030	0.030	26	–	0.019	0.034	–	–	–	–
	DET	–	–	–	–	13	–	0.050	0.078	4	–	0.013	0.013
Insecticides	Hexythiazox	35	4	0.039	0.181	–	–	–	–	–	–	–	–
	Imidacloprid	13	–	0.046	0.070	13	–	0.030	0.053	4	–	0.004	0.004
	Methoxyfenozide	9	–	0.021	0.023	–	4	0.184	0.184	13	4	0.108	0.367
	Chlorpyrifos	9	–	0.034	0.035	4	–	0.021	0.021	–	–	–	–
	Pirimicarb	4	4	0.071	0.140	22	–	0.020	0.045	–	–	–	–
	Azinphos-methyl	4	–	0.018	0.018	–	–	–	–	–	–	–	–
	Pyrimidinol	–	9	0.261	0.357	17	4	0.140	0.518	4	–	0.064	0.064
	Methidathion	–	–	–	–	4	–	0.014	0.014	–	–	–	–

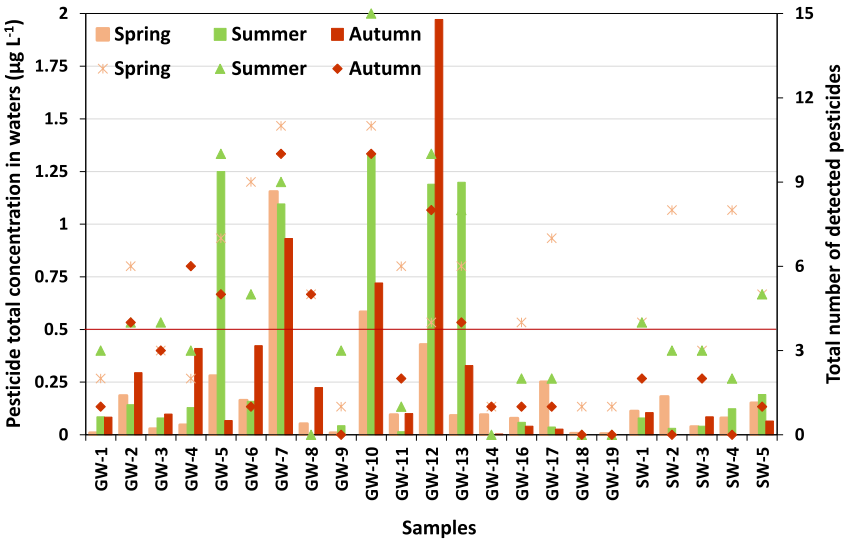

Fig. 1. Total concentrations of pesticides for each water sample (bars) in principal axis and the total number of pesticides detected in each sample in spring (stars), summer (triangles) and autumn (diamonds) in secondary axis during each sampling period. The quality limit of total concentration of pesticides in water as defined by the EU (0.5 µg L^{-1}) is indicated.

concentrations below 0.1 µg L^{-1} and with a low detection frequency.

Other pesticides were detected during one or more of the three sampling campaigns at concentrations over 0.1 µg L^{-1}, such as the fungicides fluopyram (0.541 µg L^{-1} in summer and 0.265 µg L^{-1} in autumn), dimethomorph (0.318 µg L^{-1} in spring and 0.265 µg L^{-1} in summer), and myclobutanil (0.157 µg L^{-1} in summer), the herbicide fluometuron and the degradation product HT, which only exceeded the limit in spring (0.177 and 0.132 µg L^{-1}, respectively), the insecticide methoxyfenozide in autumn (0.367 µg L^{-1}) and in summer (0.184 µg L^{-1}), and the degradation product pyrimidinol in spring (0.357 µg L^{-1}) and in summer (0.518 µg L^{-1}). Other pesticides detected in all the sampling campaigns, although at concentrations below 0.1 µg L^{-1}, were the fungicide benalaxyl, the herbicide terbuthylazine, and the insecticide imidacloprid (Table 1).

The highest number of pesticides was detected in the spring sampling campaign, with a total of 115 positive detections, and at least one pesticide in all the water samples (Fig. 1 and Table S6). This number decreased in the following sampling periods, with 96 and 67 positive detections in the summer and autumn campaigns, respectively, where no pesticide was detected in four and five samples, although positive detections with concentrations over 0.1 µg L^{-1} were higher in these last sampling periods.

It is noteworthy that ten or more pesticides were detected in several samples (GW-10 with 11, 15 and 10 or GW-7 with 11, 9 and 10 pesticides) respectively, in the three sampling campaigns or in just one (GW-5 and GW-12). Some of the pesticides present in waters were found at concentrations over 0.1 µg L^{-1} in GW-7 and GW-12 (five pesticides in both spring and autumn), and in GW-5, GW-12 and GW-7 (four pesticides in summer or autumn). Only two of the surface samples contained one pesticide with concentrations over 0.1 µg L^{-1}, SW-4 and SW-5 in summer. The highest number of compounds detected in some water samples could be explained by the management of different pesticides used to control crop/vineyard pests around waters or by the shorter distance from the field to the water source (Schreiner et al., 2016). Nonetheless different processes which affect the fate of pesticides in soils when applied in crops such adsorption, volatilization, degradation which could affect the transport of these compounds into surface and ground waters (Hvězdová et al., 2018; Suciu et al., 2020).

The presence of several pesticides in the water samples exceeded the threshold value (>0.5 µg L^{-1}) established by EU legislation for the concentration of these compounds in water for human consumption (Fig. 1). This was found in two samples (8.7%), GW-7 and GW-10, during the three sampling periods, with concentrations up to 1.155 µg L^{-1} in spring and 1.327 µg L^{-1} in summer, respectively (Table S6). Other sampling points also recorded concentrations over the established limit in one or two sampling campaigns (GW-5, GW-12, and GW-13) or recorded the highest total concentration of pesticides (1.972 µg L^{-1}) in the autumn campaign (GW-12). By contrast, none of the surface water samples exceeded the limit of 0.5 µg L^{-1} of total pesticide concentration. The correlation study carried out between total concentration of pesticides in groundwater samples with more than 5 compounds detected and the properties of these compounds showed a significant positive correlation with the water solubility in GW4, GW5, GW12, GW13 and GW17 ($p < 0.01$–0.001), GUS index in GW10 and GW12 ($p < 0.05$) or DT50 of pesticides in GW7, GW13 and GW14 ($p < 0.05$) while a negative correlation was observed with Kow of pesticides in GW10 ($p < 0.05$). However, no significant correlations were determined between total concentration of pesticides and nitrate content or other characteristics of waters and/or the water depth (Table S4 in Supplementary Material).

All the groundwater evaluated corresponded to wells with relatively low depths located in extensive vineyard areas, signaling the influence of intensive agricultural activities in groundwater pollution, as reported for different areas around the world (Schreiner et al., 2016). Agricultural activities require the use of pesticides with herbicide, fungicide, and insecticide applications in the different seasons throughout the year (spring and summer, mainly) according to crop preparation and/or growth. In general, farmers are advised to undertake the necessary seasonal application of these compounds without harmful effects. However, the high concentration of these compounds detected in some water samples suggests that they may have reached the water due to their repeated applications in the different seasons (Fig. S1A and Fig. 1). Contamination by point-sources could also explain these high concentrations as indicated by other authors (Suciu et al., 2020) although this could not be verified here. A decrease in the total concentrations of herbicides and insecticides was recorded over time, while a seasonal increase in total concentration of fungicides was observed (Fig. S2A), which is consistent with the usual application patterns also reported for other contaminants in river waters (Arenas-Sanchez et al., 2019). The presence of pesticides with different uses could be the result of the amounts applied in different areas and crops as recommended by the

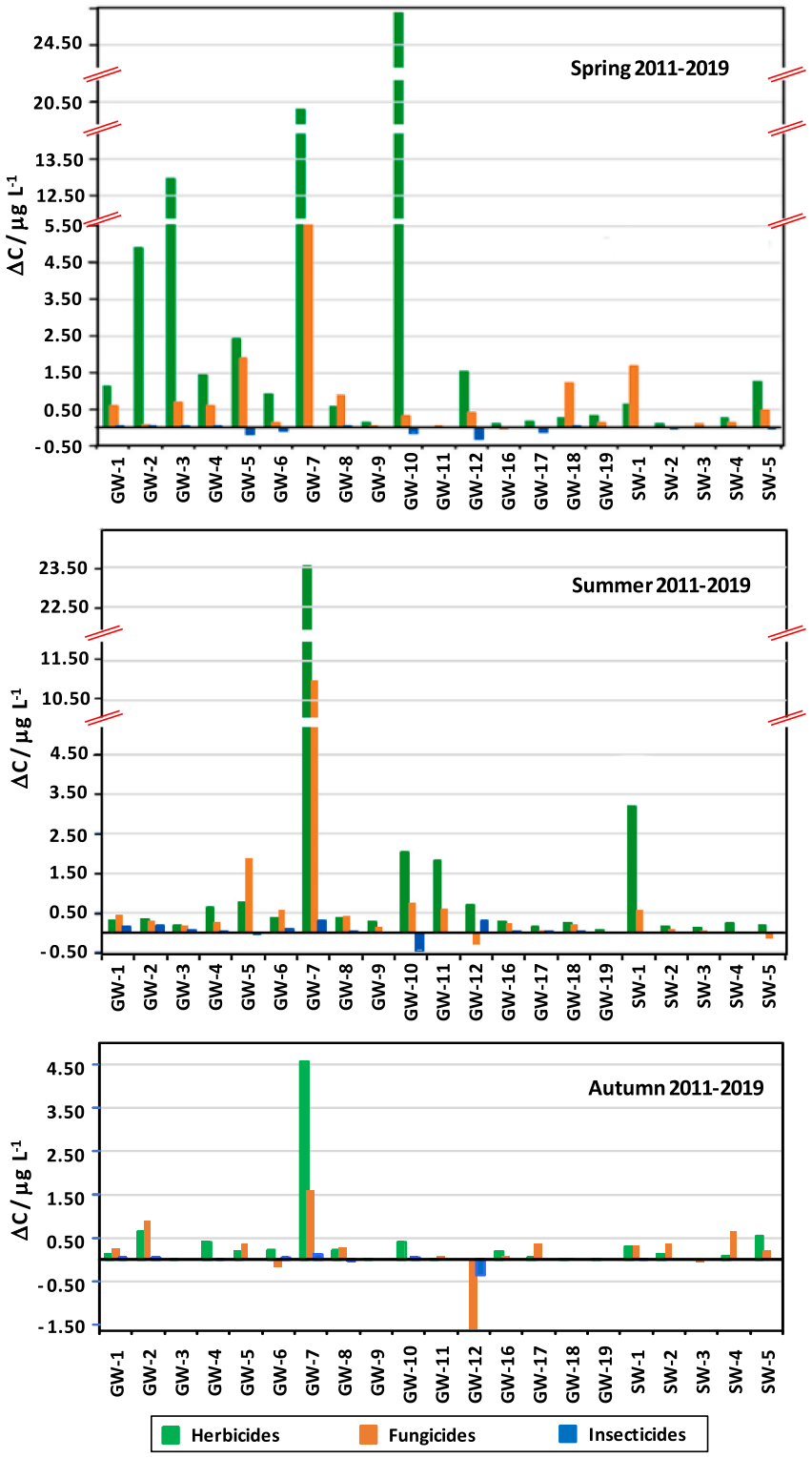

Fig. 2. Difference of concentrations for each group of pesticides in each water sample and campaign evaluated in 2011 and 2019.

authorities and experts for tackling ad hoc diseases in the different areas through the Department of Agriculture, Livestock and Environment (Gobierno de La Rioja, 2021).

Therefore, herbicides were the least detected substances in the vineyard areas evaluated here (Fig. S2A) with these results refuting the data reported in other agricultural areas in different countries (Schreiner et al., 2016; Tauchnitz et al., 2020). Insecticides were detected more than herbicides, albeit less so than fungicides, possibly due to their use in specific and timely circumstances in vineyards. Fungicides were detected at the highest concentrations because they are applied more frequently depending on vineyard needs and weather conditions throughout the growth period. This pattern is usually observed in other aquatic environments, and some authors have indicated that fungicides have become a dominant group of pesticide residues in the environment (Zheng et al., 2016; de Souza et al., 2020). Fungicides could also have adverse effects, although their toxicity is lower than that of insecticides.

3.2. Comparison of current pesticide residues in waters with past data from the 2011 monitoring campaign

The surface and ground waters selected in this work had been previously analyzed in 2011 (Herrero-Hernández et al., 2013, 2016 and 2017), and the pesticide residues detected before and now have been compared to evaluate the temporal sustainability of waters in the selected vineyard area. The common compounds were analyzed by similar methodology and experimental conditions in both periods and include 12 herbicides (atrazine and its five degradation products -DIHA, DEHA, DIA, HA and DEA-, fluometuron, terbuthylazine and its two degradation products -HT and DET-, ethofumesate and metolachlor), six insecticides (imidacloprid, methoxyfenozide, chlorpyrifos, pirimicarb, acephate, and dimethoate), and 16 fungicides (metalaxyl and its degradation product -CGA-92371-, flutriafol, nuarimol, azoxystrobin, iprovalicarb, myclobutanil, dimethomorph, penconazole, tebuconazole, kresoxim-methyl, benalaxyl, cyprodinil, trifloxystrobin, cyproconazole, and pyrimethanil).

The total concentrations of herbicides, fungicides, and insecticides were compared in the corresponding water samples taken during the three sampling campaigns in 2011 and 2019 (Fig. 2). The results indicated a significant decrease in water pollution, confirmed by the decrease in the total concentrations of herbicides, fungicides and insecticides in 95–100%, 76–90% and 42–85% of samples, respectively, in the three sampling campaigns. The decrease in the concentration of herbicide and fungicide residues was the most relevant, as the presence of herbicides only increased in one of the spring samples, and the presence of fungicides was only higher in 2–5 samples in the three campaigns. However, the concentration of insecticides increased in 3–12 of the total samples evaluated.

The decrease in the total concentrations of herbicides, fungicides and insecticides was explained by the number of compounds detected in 2011 and 2019. Fig. S3 includes results corresponding to the summers of 2011 (a) and 2019 (b) sampling campaign. As regards herbicides, atrazine, its degradation products (DIA and DEA), and ethofumesate were detected in 52%–74% of the samples at concentrations over 0.1 μg L^{-1} in 2011, but they were not detected at all in 2019. Likewise, the concentrations of fluometuron and terbuthylazine decreased in all the samples in 2019, while they were found at concentrations over 0.1 μg L^{-1} in 48%–52% of the samples in 2011 (Fig. S3). The dramatic decrease in herbicide concentrations in 2019 could be explained by the protracted absence of banned compounds, such as atrazine (Flinger et al., 2017), or by the replacement of some compounds by others with similar herbicidal activity. The decrease in terbuthylazine and fluometuron concentrations could therefore be explained considering their possible substitution by the herbicide glyphosate, a compound commonly used in recent years and widely detected in waters in different countries (Székács et al., 2015; Schreiner et al., 2016; Tauchnitz et al., 2020), although it was not included in this study.

A decrease in some fungicide concentrations (iprovalicarb, CGA-92370, myclobutanil, and kresoxim-methyl) was also observed in all the samples taken in 2019 compared to those in 2011, or there was an absence of other fungicides (cyprodinil, cyproconazole, azoxystrobin, penconazole, trifloxystrobin, flutriafol, and pyrimethanil) in 2019 or in some sampling periods. Only the fungicide nuarimol increased significantly the number of samples in which it was detected, from 7% in 2011 to 20% in 2019. Metalaxyl and dimethomorph concentrations increased in a lower percentage of sample number than those detected for nuarimol (40–49% and 7–16%, respectively). In addition, new fungicides included in 2019, such as boscalid and fluopyram, were found in several samples. Regarding insecticides, the most significant decrease was found for pirimicarb and dimethoate, being present in 43% and 13% of the 2011 samples, respectively, and 10% and 0% in 2019. However, imidacloprid increased from 9% in 2011 to 13% in 2019, although at concentrations below 0.1 μg L^{-1}. Some compounds undetected in 2011 such as pyrimidinol (degradation product of insecticide diazinon) or non-analyzed in 2011 as methidathion were found in 2019, in a number of samples (<10%) with concentrations below 0.1 μg L^{-1}. On the whole, the use of insecticides and fungicides was maintained, although different compounds were possibly used in response to the incidence of specific diseases or pests.

The largest decrease in the concentrations of herbicide and fungicide residues was recorded in sample GW-7 in the three sampling campaigns, although this sample also recorded the highest total concentration of pesticide residues in 2019. The results in GW-7 are possibly related to the higher incidence of diseases and pests in vineyards that forced winegrowers to the widespread application of pesticides or other factors not considered here such as the slope of soil surrounding the well or its location as it has been reported (Suciu et al., 2020; Zambito Zambito et al., 2020). Nevertheless, the results could be related to changes in the agricultural practices toward more sustainable management. A reduction in the use of pesticides together with a substantial increase in

Table 2
Positive soil samples (%) with concentrations (C) over and below 100 μg kg^{-1} and concentrations of pesticides detected (mean and maximum) in the three sampling campaigns.

Pesticides		Spring (n = 15)				Summer (n = 15)				Autumn (n = 15)			
		Positive samples (%)		Concentration (μg kg^{-1})		Positive samples (%)		Concentration (μg kg^{-1})		Positive samples (%)		Concentration (μg kg^{-1})	
		C <100	C >100	Mean	Maximum	C <100	C >100	Mean	Maximum	C <100	C >100	Mean	Maximum
Fungicides	Metalaxyl	13	7	89	206	–	47	336	670	40	–	46	93
	Tebuconazole	27	27	212	626	20	20	285	596	13	20	287	673
	Boscalid	20	73	369	1143	33	47	245	763	20	53	266	614
	Myclobutanil	53	13	52	208	13	7	44	102	20	7	53	111
	Benalaxyl	53	–	23	74	13	7	106	260	13	–	44	46
	Dimethomorph	27	13	193	822	13	20	153	348	13	7	99	212
	Flutriafol	33	–	19	47	–	–	–	–	–	–	–	–
	Cyproconazole	20	–	26	47	–	–	–	–	–	–	–	–
	Kresoxim-methyl	20	–	19	33	–	–	–	–	–	–	–	–
	Fluopyram	27	33	206	805	27	20	241	916	20	20	249	936
	Iprovalicarb	33	–	19	37	7	–	20	20	–	–	–	–
	Cyprodinil	20	–	8	11	–	–	–	–	–	–	–	–
	Penconazole	–	–	–	–	7	–	14	14	20	–	17	20
Herbicides	Terbuthylazine	7	–	21	21	–	–	–	–	–	–	–	–
	Pendimethalin	33	7	64	100	–	–	–	–	–	–	–	–
Insecticides	Imidacloprid	–	–	–	–	20	–	46	88	20	7	42	550
	Methoxyfenozide	20	27	117	270	27	7	75	265	20	–	28	42
	Azinphos-methyl	20	–	17	35	–	–	–	–	–	–	–	–
	Chlorpyrifos	–	–	–	–	–	–	–	–	13	–	18	21

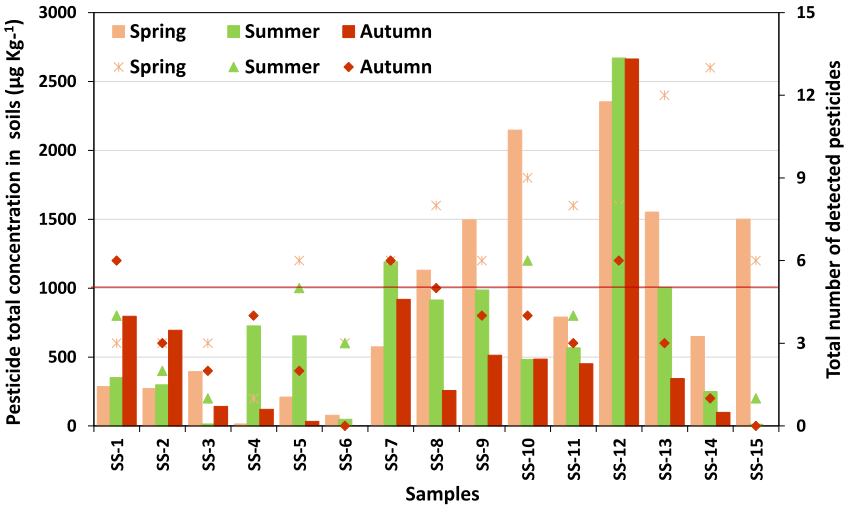

Fig. 3. Total concentrations of pesticides for each soil sample (bars) in principal axis and the total number of pesticides detected in each sample in spring (stars), summer (triangles) and autumn (diamonds) in secondary axis during each sampling period. An arbitrary indicator for comparison samples is indicated at 1000 µg kg^{-1}.

organic farming or in the washing of the containers and tools for the pesticide application in the warehouses of vine growers are recommendations of La Rioja Government and advisers of farmer cooperatives and wineries of DOCa Rioja (personal communication). A significant reduction in pesticide concentrations in groundwater over the past 16 years has also been found in New Zealand's agricultural, horticultural, viticultural, and cropping sectors compared to previous surveys (Close et al., 2021), despite pesticide use increasing over the past 25 years. This has been attributed partly to the implementation of integrated pesticide and disease management strategies.

3.3. Seasonal evaluation of pesticides in soil samples

More than half of the pesticides studied (56%) were not detected in soils in any of the sampling periods (Table 2). Moreover, some compounds detected in the water samples, such as the fungicides carbendazim, nuarimol, fenbuconazole, trifloxystrobin, and CGA-62826, the herbicides fluometuron and metolachlor, and the insecticides, pyrimidinol, pirimicarb, methidathion and hexythiazox, were not found in soil samples. However, other compounds, such as cyprodinil and penconazole (fungicides) and the herbicide pendimethalin were detected in soils, but not in waters. Only 19% of the pesticides analyzed (including seven fungicides and an insecticide) were detected in the three sampling campaigns (Table 2).

The most ubiquitous compounds were the fungicides observed in water samples, mainly boscalid and tebuconazole. They were present up to 70% and 25% of soil samples, respectively, reaching a C_{max} > 600 µg kg^{-1} in all the periods, although for boscalid the C_{max} decreased from 1143 µg kg^{-1} to 614 µg kg^{-1} from spring to autumn. The other fungicides detected were fluopyram and dimethomorph up to 30% of the samples, respectively, in the three sampling campaigns, reaching a C_{max} > 800 µg kg^{-1} in some of these periods. Boscalid and dimethomorph were also detected in other vineyard soils in Spain (Pérez-Mayán et al., 2020). Silva et al. (2019) have also reported that fungicide residues are common in EU agricultural soils (i.e., boscalid, epoxiconazole, tebuconazole, and phthalimide (>10% of soils). These authors have reported that the presence of fungicides is not unexpected, as they are approved, broad spectrum, and moderately-persistent or persistent compounds.

Pendimethalin and terbuthylazine were the only herbicides detected; they were present in 33% and 7% of the spring samples at a C_{max} of 100 µg kg^{-1} and 21 µg kg^{-1}, respectively, but they were not detected in the other sampling periods. The insecticide methoxyfenozide was present in a number of samples in all the campaigns, decreasing from 27% in spring to 7%–20% in summer and autumn, and with a C_{max} of 270 µg kg^{-1}, 265 µg kg^{-1}, and 42 µg kg^{-1}, respectively, in successive samplings. Imidacloprid was also detected in 20% of samples in the summer and autumn campaigns with a C_{max} > 80 µg kg^{-1}. This insecticide has also been found in 7% of EU topsoil samples analyzed by Silva et al. (2019), albeit at lower concentrations.

Fewer pesticides were detected in soils than in water samples, with 94 positive detections being recorded in spring, and 54 and 48 in the other sampling campaigns, respectively, and, in general, at least one pesticide detected in all the soil samples in some of the three sampling periods (Fig. 3 and Table S7). The presence of several compounds in the soil samples recorded a higher total concentration than that detected by Pose-Juan et al. (2015) in the DOCa Rioja region, or those recorded in other European arable soils (Hvězdová et al., 2018), although they are within the same range as those found by Pérez-Mayán et al. (2020) in vineyard soils in Spain. It is noteworthy that pesticide residues in soils decreased over time, as also reported in other studies (Pose-Juan et al., 2015). However, the total pesticide concentration could not be considered for evaluating the level of soil contamination because there is no EU legislation establishing thresholds or quality standards for total or individual pesticide residues in the soil, even though this subject should be addressed in the characterization of overall soil quality (Silva et al., 2019).

A value of 1000 µg kg^{-1} for total pesticide concentration in soils was considered as a yardstick for comparing soil contamination levels. The SS7, SS8, SS9, SS10, SS12, SS13 and SS15 soils exceed this reference value in one or more sampling campaigns, and in some cases high pesticide concentrations were also found in the water samples collected around the soils (Fig. 3). The fungicides recorded the highest concentrations in soils (Fig. S2B), followed by insecticides and herbicides, similar to the results found in the water samples. However, the highest concentrations in the soils corresponded to the spring sampling, while in the waters they corresponded to the summer sampling (Fig. S2). A significant positive correlation ($r = 0.857$, $p < 0.001$) was observed between the total pesticide content in waters and soils in samples corresponding to the autumn campaign. Furthermore, a significant correlation was also observed between the total content of fungicides in waters and soils in samples taken in summer ($r = 0.558$, $p < 0.05$) and autumn ($r = 0.816$, $p < 0.001$).

Metalaxyl is one of the compounds detected in most of the water samples in both spring and summer (up to 52%). However, this

fungicide is less ubiquitous in soil samples, appearing in 13%, 47%, and 40% of the samples from spring, summer, and autumn, respectively. This could be attributed to its high water solubility (8400 mg L^{-1}) and GUS index (3.02), being classified as leachable, and more likely to be found in water than in soil. A different behavior was observed for the fungicide boscalid, which was detected in all the sampling periods, both in water and soil samples. However, the highest percentage of positive samples was found in soils, with values of 93%, 80% and 73% in spring, summer and autumn, respectively. This result is attributed to its low water solubility (4.6 mg L^{-1}) and its classification as a transient leacher according to its GUS index (2.66), so the probability of finding it in soils is greater than in waters. Additionally, its degradation half-life is over six months, which explains its detection over the three sampling periods.

The influence soil characteristics have on the residual amount of pesticide is to be expected, as the process of adsorption by the organic and inorganic components of the soil could enhance the persistence of these compounds. In fact, some studies in the literature report the influence of OM and/or clay content on the adsorption, degradation and/or persistence of some of the compounds detected in soils (Andrades et al., 2001; Chaplain et al., 2011; Marin-Benito et al., 2009). However significant correlations between total pesticide concentrations and physicochemical properties of soils (Table S5 in Supplementary Material) were not found in any sampling time.

Significant correlations were only observed between pesticide concentrations and the OM content of soils (when more than five soils with pesticide residues were considered) for methoxyfenozide ($r = 0.954$, $p < 0.001$) and myclobutanil ($r = 0.832$, $p < 0.05$), both being hydrophobic compounds with high degradation half-lives (Table S1). A significant correlation ($p < 0.05$) with clay or silt content was also observed for compounds with very different properties (flutriafol, cyproconazole, and kresoxim-methyl) in spring samples. No more single or multiple correlations were found between pesticide concentrations and soil properties. However, there was a significant correlation ($r = 0.717$, $p < 0.01$) between the total residual concentrations determined in summer and autumn samples. There were no significant correlations between the total residual concentrations determined in spring and summer or spring and autumn, indicating that the presence of residues in the months of highest incidence is not related to soil properties, but to other application processes and/or mechanisms, for example. It is noteworthy that the OM content of these soils (<2% in 70% of the soils) was very low for facilitating adsorption, and the content of clay/silt (>45% in 50% of soils) was insufficient to facilitate the adsorption of a greater number of compounds (Andrades et al., 2001). The pathway, frequency, and rate of application could determine the formation of pesticide residues in the soil (Damalas and Eleftherohorinos, 2011). A uniform application may reduce pesticide losses through volatilization and runoff, while the repeated application of pesticides in agricultural practices could affect the half-life of pesticides in soils.

4. Conclusions

The results have revealed that 65% of the pesticides included in the study were detected in one or more water samples during the three seasonal sampling campaigns, and 30% were detected at concentrations of over 0.1 μg L^{-1}. However, only 45% of pesticides were detected in soil samples around the wells. Fungicides were the most detected compounds in waters and in soils according to the characteristics of vineyard cultivation in DOCa Rioja. Metalaxyl, tebuconazole, and boscalid were the most significant compounds in water samples, with the last one being the main one in soil samples. The highest total concentration of pesticides in waters occurred in summer, while in soils this corresponded to spring. However, the properties of the pesticides detected and soil properties did not explain the presence of certain compounds. The results clearly indicate the influence on water quality of agricultural practices in vineyard areas. Nevertheless, a comparison between the results obtained in 2019 and 2011 reveals a significant decrease in water contamination, confirmed by the decrease in the total concentration of herbicides, fungicides, and insecticides. This effect could be explained by the absence of banned compounds or by the replacement of some compounds with others with a similar purpose that were not included in the monitoring study. Additionally, it may be also attributed to the effect of measures conducted for best management practices for the sustainable use of pesticides. However, a deeper analysis of territorial and hydrological context around the wells or on detailed handling of pesticides would be necessary to explain the changes observed in the concentrations without reducing crop protection.

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.

Acknowledgments

The authors thank project 25P/18-VITIREG funded by FEADER, Regional Government of La Rioja and MAPAMA. Diana P. Manjarres-López thanks the University of La Rioja the financial support to perform this research.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2021.117463.

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References

Andrades, M.S., Sánchez-Martín, M.J., Sánchez-Camazano, M., 2001. Significance of soil properties in the adsorption and mobility of the fungicide metalaxyl in vineyard soils. J. Agric. Food Chem. 49, 2363–2369.

Arenas-Sánchez, A., Rico, A., Rivas-Tabares, D., Blanco, A., Garcia-Doncel, P., Romero-Salas, A., Nozal, L., Vighi, M., 2019. Identification of contaminants of concern in the upper Tagus river basin (central Spain). Part 2: spatio-temporal analysis and ecological risk assessment. Sci. Total Environ. 667, 222–233.

Barbieri, M.V., Monllor-Alcaraz, L.S., Postigo, C., López de Alda, M., 2020. Improved fully automated method for the determination of medium to highly polar pesticides in surface and groundwater and application in two distinct agriculture-impacted areas. Sci. Total Environ. 745, 140650.

Bermúdez-Couso, A., Arias-Estévez, M., Nóvoa-Muñoz, J.C., López-Periago, E., Soto-González, B., Simal-Gándara, J., 2007. Seasonal distributions of fungicides in soils and sedimentsof a small river basin partially devoted to vineyards. Water Res. 41, 4515–4525.

BOE, 2005. (BOE-A-2005-8959). Real Decreto 9/2005, de 14 de enero, por el que se establece la relación de actividades potencialmente contaminantes del suelo y los criterios y estándares para la declaración de suelos contaminados. Boletin Oficial del Estado. https://www.boe.es/eli/es/rd/2005/01/14/9/con.

BOE-A-2012-11605, 2012. Real Decreto 1311/2012, de 14 de septiembre, por el que se establece el marco de actuación para conseguir un uso sostenible de los productos fitosanitarios. https://www.boe.es/eli/es/rd/2012/09/14/1311/con.

Calliera, M., Capri, E., Zambito Marsala, R., Russo, E., Bisagni, M., Colla, R., Marchis, A., Suciu, N., 2021. Multi-actor approach and engagement strategy to promote the adoption of best management practices and a sustainable use of pesticides for groundwater quality improvement in hilly vineyards. Sci. Total Environ. 752, 142251.

Carazo-Rojas, E., Pérez-Rojas, G., Pérez-Villanueva, M., Chinchilla-Soto, C., Chin-Pampillo, J.S., Aguilar-Mora, P., Alpízar-Marín, M., Masís-Mora, M., Rodríguez-Rodríguez, C.E., Vryzas, Z., 2018. Pesticide monitoring and ecotoxicological risk assessment in Surface water bodies and sediments of a tropical agro-ecosystem. Environ. Pollut. 241, 800–809.

Ccanccapa, A., Masia, A., Navarro-Ortega, A., Pico, Y., Barcelo, D., 2016a. Pesticides in the Ebro River basin: occurrence and risk assessment. Environ. Pollut. 211, 414–424.

Ccanccapa, A., Masia, A., Andreu, V., Pico, Y., 2016b. Spatio-temporal patterns of pesticide residues in the Turia and Júcar Rivers (Spain). Sci. Total Environ. 540, 200–210.

Chaplain, V., Mamy, L., Vieublé-Gonod, L., Mougin, C., Benoit, P., Barriuso, E., Nélieu, S., 2011. Fate of pesticides in soils: toward an integrated approach of influential factors, pesticides in the modern world - risks and benefits. In: Stoytcheva, M. (Ed.). ISBN: 978-953-307-458-0. http://www.intechopen.com/.

Close, M.E., Humphries, B., Northcott, G., 2021. Outcomes of the first combined national survey of pesticides and emerging organic contaminants (EOCs) in groundwater in New Zealand 2018. Sci. Total Environ. 754, 142005.

Cotton, J., Leroux, F., Broudin, S., Poirel, M., Corman, B., Junot, C., Ducruix, C., 2016. Development and validation of a multiresidue method for the analysisof more than 500 pesticides and drugs in water based on on-line and liquid chromatography coupled to high resolution mass spectrometry. Water Res. 104, 20–27.

DOCa Rioja, C.R.. (Consejo regulador de la Denominación de Origen calificada Rioja). http://es.riojawine.com/es/home.html.

Damalas, C.A., Eleftherohorinos, I.G., 2011. Pesticide exposure, safety issues, and risk assessment indicators. Int. J. Environ. Res. Publ. Health 8, 1402–1419.

de Souza, R.M., Seibert, D., Quesada, H.B., Bassetti, F.J., Fagundes-Klenc, M.R., Bergamasco, R., 2020. Occurrence, impacts and general aspects of pesticides in surfacewater: a review. Process Safety Environ. Protection 135, 22–37.

EC (European Commission), 2009a. Regulation (EC) No 1107, 2009 of the European Parliament and of the Council of 21 October 2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC (European Commission). Off. J. Eur. Union L 309, 1.

EC (European Commission) 2009b. Directive, 2009/128/EC of the European Parliament and of the Council of 21 October 2009, establishing a framework for Community action to achieve the sustainable use of pesticides. Off. J. Eur. Union, L 309, 71–86.

EC (European Commission), 1998. Directive 98/83/EC of the Council of 3 November 1998 on the quality of water intended for human consumption. Off. J. Eur. Union L330, 32–54.

EC (European Commission) 2006. Directive 2006/118/EC of the European Parliament and of the Council of 12 December 2006 on the protection of groundwater against pollution and deterioration. Off. J. Eur. Commun L 372, 19–31.

EC (European Commission), 2013. Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. Off. J. Eur. Union 226, 1–17.

FAOSTAT, 2020. Food and agriculture organization of the united Nations. on October 2020. http://faostat3.fao.org.

Fingler, S., Mendaš, G., Dvoršćak, M., Stipičević, S., Vasilić, Z., Drevenkar, V., 2017. Herbicide micropollutants in surface, ground and drinking waters within and near the area of Zagreb, Croatia. Environ. Sci. Pollut. Res. 24, 11017–11030.

Rioja, Gobierno de La, 2021. Boletín de Avisos fitosanitarios. Consejería de Agricultura, ganadería y medio ambiente, gobierno de La Rioja. http://www.larioja.org/agricultura/es/publicaciones/boletinavisos-fitosanitarios.

Herrero-Hernández, E., Andrades, M.S., Álvarez-Martín, A., Pose-Juan, E., Rodríguez-Cruz, M.S., Sánchez-Martín, M.J., 2013. Occurrence of pesticides and some of their degradation products in waters in a Spanish wine region. J. Hydrol 486, 234–245.

Herrero-Hernández, E., Pose-Juan, E., Sánchez-Martín, M.J., Andrades, M.S., Rodríguez-Cruz, M.S., 2016. Intra-annual trends of fungicide residues in waters from vineyard areas in La Rioja region of northern Spain. Environ. Sci. Pollut. Res. 23, 22924–22936.

Herrero-Hernández, Rodríguez-Cruz, Pose-Juan, M.S., Sánchez-González, E., S., Andrades, M.S. Sánchez-Martín, M.J, 2017. Seasonal distribution of herbicide and insecticide residues in the water resources of the vineyard region of La Rioja (Spain). Sci. Total Environ. 609, 161–171.

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.

Hildebrandt, A., Guillamón, M., Lacorte, S., Tauler, R., Barceló, D., 2008. Impact of pesticides used in agriculture and vineyards to surface and groundwater quality (North Spain). Water Res. 42, 3315–3326.

Hvězdová, M., Kosubová, P., Košíková, M., Scherr, K.E., Šimek, Z., Brodský, L., Šudoma, M., Škulcová, L., Sáňka, M., Svobodová, M., Krkošková, L., Vašíčková, J., Neuwirthová, N., Bielská, L., Hofman, J., 2018. Currently and recently used pesticides in Central European arable soils. Sci. Total Environ. 613, 361–370, 614.

Kapsi, M., Tsoutsi, C., Paschalidou, A., Albanis, T., 2019. Environmental monitoring and risk assessment of pesticide residues in surface waters of the Louros River (N.W. Greece). Sci. Total Environ. 650, 2188–2198.

Khuman, S.N., Vinod, P.G., Bharat, G., Mohana Kumar, Y.S., Chakraborty, P., 2020. Spatial distribution and compositional profiles of organochlorine pesticides in the surface soil from the agricultural, coastal and backwater transects along the south-west coast of India. Chemosphere 254, 126699.

Köck-Schulmeyer, M., Postigo, C., Farré, M., Barceló, D., López de Alda, M., 2019. Medium to highly polar pesticides in seawater: analysis and fate in coastal areas of Catalonia (NE Spain). Chemosphere 215, 515–523.

Kosubová, P., Skulcová, L., Poláková, S., Hofman, J., Bielská, L., 2020. Spatial and temporal distribution of the currently-used and recently banned pesticides in arable soils of the Czech Republic. Chemosphere 254, 126902.

MAPAMA, 2017. Estadística anual de consumo de productos fitosanitarios y Estadística quinquenal de utilización de productos fitosanitarios en la Agricultura. April 2020. https://www.mapa.gob.es.

Marín-Benito, J.M., Sánchez-Martín, M.J., Andrades, M.S., Pérez-Clavijo, M., Rodríguez-Cruz, M.S., 2009. Effect of spent mushroom substrate amendment of vineyard soils on the behavior of fungicides: 1. Adsorption-desorption of penconazole and metalaxyl by soils and subsoils. J. Agric. Food Chem. 57, 9634–9642.

Masiá, A., Campo, J., Vázquez-Roig, P., Blasco, C., Picó, Y., 2013. Screening of currently used pesticides in water, sediments and biota of the Guadalquivir River Basin (Spain). J. Hazard Mater. 263, 95–104.

Mishra, K., Sharma, R.C., Kumar, S., 2012. Contamination levels and spatial distribution of organochlorine pesticides in soils from India. Ecotoxicol. Environ. Saf. 76, 215–225.

Mondal, R., Mukherjee, A., Biswas, S., Kole, R.K., 2018. GC-MS/MS determination and ecological risk assessment of pesticides in aquatic system: a case study in Hooghly River basin in West Bengal, India. Chemosphere 206, 217–230.

Papadakis, E.-N., Tsaboula, A., Vryzas, Z., Kotopoulou, A., Kintzikoglou, K., Papadopoulou-Mourkidou, E., 2018. Pesticides in the rivers and streams of two river basins in northern. Greece. Sci. Total Environ 624, 732–743.

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.

Pose-Juan, E., Herrero-Hernández, E., Álvarez-Martín, A., Sánchez-Martín, M.J., Rodríguez-Cruz, M.S., 2014. Development of a procedure for multiresidue analysis of pesticides in vineyard soils and its application to real samples. J. Separ. Sci. 37, 2215–2224.

Pose-Juan, E., Sánchez-Martín, M.J., Andrades, M.S., Rodríguez-Cruz, M.S., Herrero-Hernández, E., 2015. Pesticide residues in vineyard soils from Spain: spatial and temporal distributions. Sci. Total Environ. 514, 351–358.

PPDB (Pesticide Properties Data Base), November 2020. 2020. Agriculture and Environment Research Unit (AERU). University of Hertfordshire. https://sitem.herts.ac.uk/aeru/ppdb/en/.

Rico, A., Arenas-Sánchez, A., Alonso, C., López-Heras, I., Nozal, L., Rivas, D., Vighi, M., 2019. Identification of contaminants of concern in the upper Tagus river basin (central Spain). Part 1: screening, quantitative analysis and comparison of sampling methods. Sci. Total Environ. 666, 1058–1070.

Sánchez-González, S., Pose-Juan, E., Herrero-Hernández, E., Álvarez-Martin, A., Sánchez-Martín, M.J., Rodríguez-Cruz, S., 2013. Pesticide residues in groundwaters and soils of agricultural areas in the Agueda River Basin from Spain and Portugal. Int. J. Environ. Anal. Chem. 93, 1585–1601.

Schreiner, V.C., Szöcs, E., Bhowmik, A.K., Vijver, M.G., Schäfer, R.B., 2016. Pesticide mixtures in streams of several European countries and the USA. Sci. Total Environ. 573, 680–689.

Shi, Y., Lu, Y., Meng, F., Guo, F., Zheng, X., 2013. Occurrence of organic chlorinated pesticides and their ecological effects on soil protozoa in the agricultural soils of North Western Beijing, China. Ecotoxicol. Environ. Saf. 92, 123–128.

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.

Sparks, D.L., 1996. Methods of soil analysis. Part 3-chemical methods. Soil Science Society of America, Inc. (Madison, WI).

Ssebugere, P., Wasswa, J., Mbabazi, J., Nyanzi, S.A., Kiremire, B.T., Marco, J.A.M., 2010. Organochlorine pesticides in soils from south-western Uganda. Chemosphere 78, 1250–1255.

Suciu, N.A., Farolfi, C., ZambitoMarsala, 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.

Székács, A., Mörtl, M., Darvas, B., 2015. Monitoring pesticide residues in surface and ground water in Hungary: surveys in 1990-2015. J. Chem. 1–15. https://doi.org/10.1155/2015/717948, 717948.

Tauchnitz, N., Kurzius, F., Rupp, H., Schmidt, G., Hauser, B., Schrodter, M., Meissner, R., 2020. Assessment of pesticide inputs into surface waters by agricultural and urban sources - a case study in the Querne/Weida catchment, central Germany. Environ. Pollut 267, 115186.

UN. Sustainable Development Goals. 2019. https://www.un.org/sustainabledevelopment/es/(Accessed, December 2019).

Vašíčková, J., Hvězdová, M., Kosubová, P., Hofman, J., 2019. Ecological risk assessment of pesticide residues in arable soils of the Czech Republic. Chemosphere 216, 479–487.

Wang, Y., Zhang, S., Cui, W., Meng, X., Tang, X., 2018. Polycyclic aromatic hydrocarbons and organochlorine pesticides in surface water from the Yongding River basin, China: seasonal distribution, source apportionment, and potential risk assessment. Sci. Total Environ. 618, 419–429.

Zambito, Marsala, Capri, R.Z., Russo, E., Bisagni, E., Colla, M., Lucini, R., Gallo, L., Suciu, A., N.A, 2020. First evaluation of pesticides occurrence in groundwater of Tidone Valley, an area with intensive viticulture. Sci. Total Environ. 736, 139730.

Zheng, S., Chen, B., Qiu, X., Chen, M., Ma, Z., Yu, X., 2016. Distribution and risk assessment of 82 pesticides in Jiulong River and estuary in South China. Chemosphere 144, 1177–1192.