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Review

Review: Presence, distribution and current pesticides used in Spanish agricultural practices

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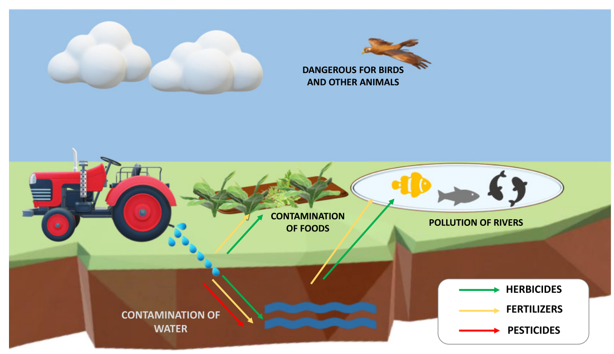
HIGHLIGHTS

- Factors influencing sustainable use of pesticides in Spanish agriculture.
- Relationships between the uses of pesticides and their regional prevalence.
- Current pesticide uses and prevalence relative to geographic area in Spain.
- Sustainable pesticides usage to reduce the risks on human health and the environment.
- Climatic changes and pesticide fluctuations association.

GRAPHICAL ABSTRACT



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ABSTRACT

To guarantee an adequate food supply for the world's growing population, intensive agriculture is necessary to ensure efficient food production. The use of pesticides helps maintain maximum productivity in intensive agriculture by minimizing crop losses due to pests. However, pesticide contamination of surface waters constitutes a major problem as they are resistant to degradation and soluble enough to be transported in water. In recent years, all groups of pesticides defined by the World Health Organization have increased their use and, therefore, their prevalence in the different environmental compartments that can have harmful effects. Despite this effort, there is no rigorous monitoring program that quantifies and controls the toxic effects of each pesticide. However, multiple scientific studies have been published by specialized research groups in which this information is disseminated. Therefore, any attempt to systematize this information is relevant. This review offers a current overview of the presence and distribution of the most widely-used pesticides (insecticides, herbicides, and fungicides) by crop type and an evaluation of the relationships between their uses and environmental implications in Spain. The data demonstrated that there are correlations between the presence of specific pesticides used in the main crops and their presence in the environmental compartments. We have found preliminary data pointing to existing associations between specific pesticides used in the main crops and their presence in environmental compartments within different geographical areas of Spain; this should be the subject of further investigation.

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Contents

1. Introduction

Pesticides are chemicals substances used in agriculture to reduce crop pests and ensure agricultural production. According to the World Health Organization, the pesticides can be classified based on their purpose (OMS, 2020): acaricide, aphicide, bacteriostat (soil), fumigant, fungicide, herbicide, insecticide, insect growth regulator, ixodicide, larvicide, molluscicide, miticide, nematocide, plant growth regulator, rodenticide, and repellent. The use of pesticides around the world has increased in recent decades due to changes in agricultural practices and increasingly intensive agriculture. This widespread use of pesticides has led to the presence of residues and contaminants in various environments. These substances can be present in water, sediments and biota depending on their physicochemical properties, and can present dangers to the environment, living organisms and human health (Campo et al., 2013; Damásio et al., 2011; Masiá et al., 2015).

The contamination of surface waters by pesticides has been studied extensively and constitutes a major problem that raises many concerns (Cerejeira et al., 2003; Huber et al., 2000). Pesticide residues can reach the aquatic environment through runoff, leaching, agricultural returns, and adsorption as well as plant uptake, groundwater intrusions, and vaporization into the atmosphere thereby affecting water quality and aquatic organisms. (Kafilzadeh, 2015; Rajmohan et al., 2020). Pesticides move from agricultural fields to surface waters in surface runoff; the amount transported to surface waters depends on several factors: topography, climate, agricultural practices, and the chemical and environmental properties of the pesticides (Kapsi et al., 2019). These chemicals, which are sufficiently resistant to degradation and sufficiently soluble to be transported in water, can reach bodies of water in significant quantities (González García et al., 2019).

Contamination caused by the use of pesticides in agricultural activities is a source of soil and water pollution in some countries of the European Union (EU) (Kovač et al., 2021; Qu et al., 2019; Serra et al., 2020; Zambito Marsala et al., 2020). Further, degradation products from pesticides, caused by biological, chemical, and physical processes, frequently give rise to more persistent and toxic byproducts, with important impacts on biota (Bruzzoniti et al., 2014; Martínez-Domínguez et al., 2015; Roig et al., 2015). The Mediterranean area is affected by climatic changes that alter hydrological conditions and cause large fluctuations in the concentrations of the pesticide residue mixtures present in the water (Batalla et al., 2004). It is important to analyze and study the different existing pesticides and their use in different crops and thus be able to make environmental decisions to coordinate and implement adequate environmental policies to better protect the environment.

Various bibliographic reviews have previously been published addressing aspects related to the use and prevalence of pesticides in Spain. Among them, the most recent publications highlight human exposure, such as the work of Yusà et al. (2022), who analyzed previous data on the population exposure in relation to non-persistent pesticides in Spain through biomonitoring. Although this work presented a unique perspective concerning exposure and risk, particularly for children and mothers, it is not necessarily representative of the use and prevalence of these pesticides in the natural environment within different compartments (water, soil, etc.). Additionally, Knapke et al. (2022) reviewed the relationship between the environmental and occupational exposure of humans to pesticides and the influence on sperm parameters in a study that is not geographically limited to Spain; this study was not representative of the use nor the prevalence of these pesticides in the natural environment.

On the other hand, even though some relatively recent works have reviewed the occurrence and distribution of different pollutants in the natural environment in Spain, none of them cover the entire Spanish geography nor are they focused exclusively on pesticides or agriculture. For example, Merhaby et al. (2019) analyzed 194 studies in the Mediterranean basin (including Spain but also Italy, France, and Egypt, to name a few) concerning PAHs and PCBs and highlighting the critical situation in the Mediterranean Sea. Additionally, Jurado et al. (2019), reviewed the existing data concerning the occurrence, fate, and environmental risk assessment in Spanish groundwater (GW) of emerging organic contaminants (EOCs), including 9 pesticides, but also a number of pharmaceuticals, oestrogens, UV filters, and antioxidants (2,6-di-tert-butyl-4-methylphenol, BHT); on the other hand, the analysis of Porta et al. (2014) was focused on a variety of endocrine disrupters, including pesticides, on a general, representative sample of Catalonia's population (Spain).

Others focused on the prevalence of different environmental pollutants, including some pesticides in foods, but not including the analysis of their origin from different environmental compartments, such as González et al. (2019), who carried out a comparative review of the occurrence in organic vs. conventional food as well as González-Martín et al. (2018), who focused on analyzing the data in different commercially processed propolis products in relation to the presence of heavy mineral elements (Cr, Ni, Cu, Zn and Pb), and pesticide residues (fungicides, herbicides and acaricides), in a variety of countries including Spain. Other reviews that slightly address the topics reviewed here are also outdated, such as the work of Jurado et al. (2012) which covers emerging organic contaminants in the groundwater compartment, and the work of González et al. (2012) which is focused on emerging contaminants in the region of the Llobregat River basin, among others (Domingo et al., 2008; García-Fernández et al., 2008; Mañosa et al., 2001; Porta et al., 2008). Therefore, this review attempts to fill the current gap by reviewing the occurrence of pesticides throughout the Spanish geography in different environmental compartments.

The toxicity caused by pesticides, which affects both ecosystems and human health, is recognized by authorities at global, European, and national levels (de Castro Lima et al., 2020; Deknock et al., 2019; Kadlikova et al., 2021; Kafaei et al., 2020; Si et al., 2021). For this reason, a regulatory framework was built in the European Union that allows a regulated and safe commercialization. In 2009, the European Parliament and the Council approved two legal texts that significantly modified the regulations previously enforced regarding the marketing and usage of phytosanitary products, incorporating the postulates of the strategy for the sustainable use of pesticides and considering the provisions of the VI Community Environmental Action Program. On the one hand, the DIRECTIVE 2009/128/EC (European Commission, 2009a) and subsequent modifications, established a framework for community action to achieve sustainable pesticide usage, according to which the member states are obliged to publish the relevant risk data. This framework contains the basic provisions necessary to permit a rational usage of pesticides while reducing risks and harmful effects on human health and the environment. Previously, Regulation (EC) No. 1185/2009 (European Commission, 2009b) had already been established. Relating to pesticide statistics, this common framework was developed to ensure the systematic production of community statistics relating to the marketing and use of plant protection products, thus facilitating compliance with the directive on sustainable pesticide usage.

The other important legal reference provision on plant protection products is Regulation (EC) No. 1107/2009 (European Commission, 2009c) concerning the placement of plant protection products on the market and challenging Council Directives 79/117/EEC and 91/414/EEC. This regulation establishes the procedure and the requirements for active substances to be approved within the European Union. It also includes the procedure for the national authorization of commercialization and use of phytosanitary products, establishing for the first time, the concept of zonal evaluation. Thus, this regulation harmonizes the evaluation and authorization procedures in all countries when placing plant protection products on the market in such a way that active substances are authorized at the community level whilst plant protection products containing these active substances require authorization at member state level. From this regulation several regulations have been generated for its application. (European Commission, 2013a; European Commission, 2013b; European Commission, 2011a; European Commission, 2011b).

In Spain, Directive 2009/128/EC (European Commission, 2019) was transposed into the national system based on Real Decreto 1702/2011 (Ministerio de Medio Ambiente y Medio Rural y Marino, 2011) which instituted periodic inspections of plant protection product application equipment, and Real Decreto 1311/2012 (Ministerio de la Presidencia, 2012) which established the framework of action to achieve a sustainable use of phytosanitary products. In addition, to achieve the objectives of the directive, national action plans were established. The duration of Spain's current national action plan is 2018–2022; this plan was prepared by taking into consideration the results of the previous 2013–2017 plan, annual reports, indicators, and recommendations of the European Commission.

In addition to these two Reales Decretos, there are other legal texts that, while being older, are still valid as they provide security in the use and marketing of these products.(Jefatura del Estado, 2002; Ministerio de la Presidencia, 2014; Ministerio de Medio Ambiente y Medio Rural y Marino, 2011; Presidencia del Gobierno, 1983).

The legislative framework that accompanies these products is extensive and denotes the efforts made to harmonize the evaluation procedures while being able to keep them on the market so that people can continue to take advantage of their use while minimizing potential risks for humans and the environment.

1.1. Objective and methodology

The objective of this review is to investigate the relationship between the uses of pesticides and the contamination they generate within different environments of Spain while accounting for seasonal patterns.

In 2021, The Ministry of Agriculture, Fisheries and Food of the Government of Spain published a survey on the use of phytosanitary products in 2019 (MAPA, 2019), which collects the quantities of active substances contained in pesticides applied to crops throughout Spain considering the crop (Table 1). Statistical data is limited from September 2018 to October 2019. All pesticides applied in more than five tons per year were individually searched for in all collections of the Web of Science database as keywords. Subsequently, inclusion and exclusion criteria were taken into consideration, excluding studies prior to 2000, as well as academic theses; reports; abstracts of published events, books or chapters; review articles, as well as articles published in languages other than English. Potentially eligible articles were reviewed and refined; the inclusion criterion applied was the quantitative description of the presence of pesticides in air, soil, water, and plants in the Spanish geography. They were published between 2000 and 2022. This review has been structured considering the most common crops and depending on the scope of application of insecticides, herbicides or fungicides used in Spain in recent years. The structuring process diagram is shown in Fig. 1.

2. Classification of pesticides based on use

2.1. Insecticides

The use of phytosanitary products in agriculture has increased in recent decades due to the advantages it brings to agricultural production. Among these products, insecticides are used by humans in a wide variety of fields such as agriculture, horticulture, forestry and gardening as well as home and office maintenance. Its uses include controlling vectors that transmit human and animal diseases, such as mosquitoes and ticks, as well as deterring pests that destroy crops as these pests present the danger of great economic losses (Gupta et al., 2019).

Table 1
Statistics on the use of pesticides in Spain in 2019.

(Ton)	Barley	Citrus	Sunflower	Vegetables	Olive	Wheat	Vineyard	TOTAL	%
Fungicide	235.2	370.7	0.8	4290.3	2062.2	377.5	22,867.2	30,203.9	80.2
Herbicide	1105.4	197.3	442.2	252.5	1813.3	1131.1	437.4	5379.3	14.3
Insecticide	8.0	1058.9	24.8	241.4	431.0	126.7	183.9	2074.6	5.5

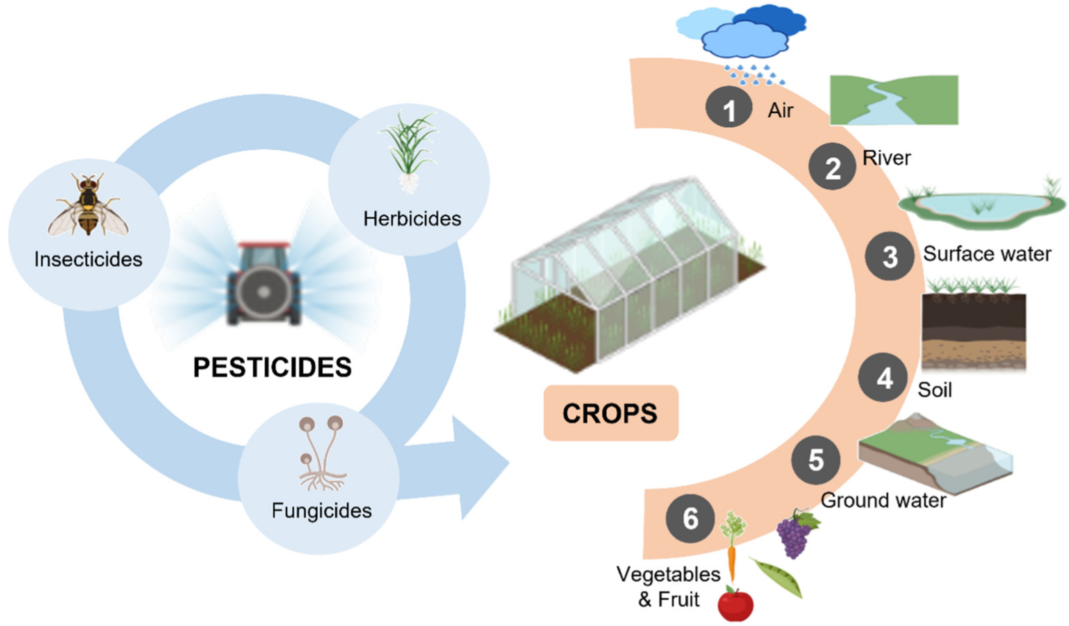

Fig. 1. Process review scheme by geographical areas in Spain.

At the same time, there is growing pressure to reduce insecticide usage given that the data indicates these phytosanitary products may later be found as residues in plant foods which will limit their commercialization in international markets since they pose a risk to the health of consumers (Sousa et al., 2020; Thompson et al., 2020). Moreover, exposure to non-persistent pesticides in the Spanish population has been shown to be practically ubiquitous, with examples such as Chlorpyrifos, which reaches detection frequencies between 74 % and 100 % of analyzed, or some pyrethroids, which is detected in >65 % of the samples studied (Yusà et al., 2022).

In relation to the most common practices that use insecticides, there is clear evidence that low-intensity farming systems and the implementation of environmentally-friendly management practices (e.g.; the ban of synthetic pesticides and fertilizers) presents the advantage of allowing a higher biodiversity than conventional systems (Froidevaux et al., 2017). However, the option of completely eliminating the use of synthetic chemical insecticides does not appear to be a viable alternative to support the global food system. Instead, the adoption of integrated pest management (IPM) is frequently the best approach; this approach permits the integration of selective chemical insecticides with biological control agents such as mirid predators and egg parasitoids, microbial insecticides (i.e., *Bacillus thuringiensis*) and sex pheromone-based control (Giorgini et al., 2019).

However, as reflected in Fig. 2 "Uses of insecticides on crops in Spain (MAPA, 2019)", using pest control solutions of natural origin, such as the

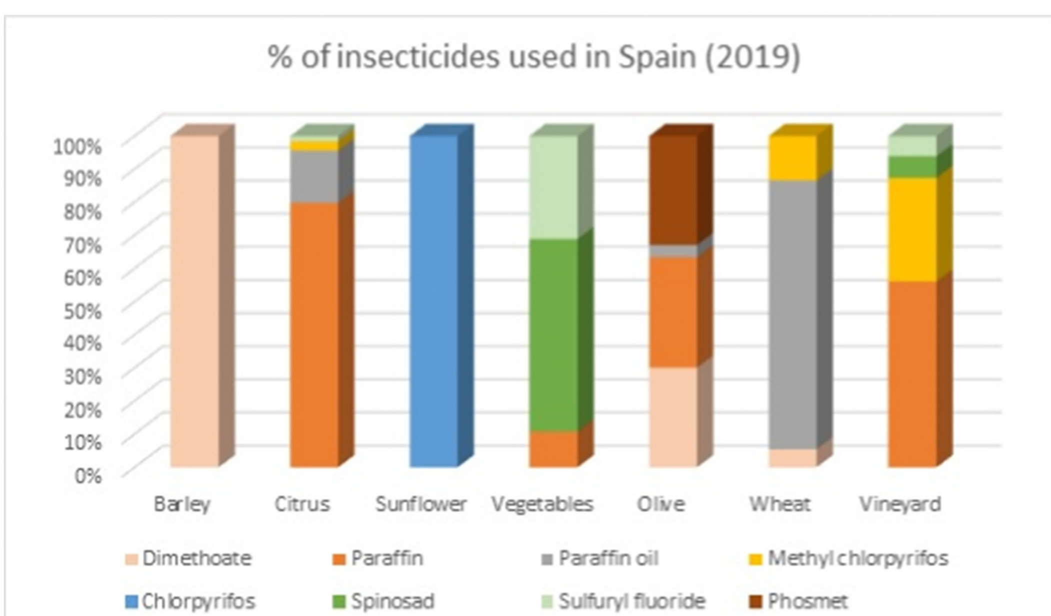

Fig. 2. Uses of insecticides on crops in Spain in 2019.

chemical compound *Spinosad*, biological agent *Bacillus thuringiensis kurstaki*, Paraffin, and Paraffin oils, is becoming increasingly important (Nile et al., 2019). Therefore, authorities encourage to moderate the use of synthetic chemical insecticides, in favor of other, less aggressive to the environment, ecological pest-control techniques.

Part of the current problem with synthetic chemical insecticides is their persistence in the environment. For example, Maia et al. (2016) worked with IPM programs in Madrid to carry out persistence studies with six pesticides currently used in corn crops: Pendimethalin, Lambda-Cyhalothrin, Abamectin, Hexythiazox, Deltamethrin, and Chlorpyrifos. The primary objective of this study was to determine the factors that affect the existence of these pesticides after application and the duration of their harmful effects to predators. Deltamethrin and Chlorpyrifos, the two most toxic pesticides in the lab, were aged under greenhouse conditions in the presence and absence of artificial rainfall; Deltamethrin was classified as short lived in both cases. On the other hand, Chlorpyrifos was graded accelerated in the presence of rainfall, thus contributing to its classification as slightly persistent. However, it behaved as persistent in the absence of rainfall. Based on these results, Deltamertherin was recommended for inclusion in corn IPM programs where predators are present, while Chlorpyrifos was not as it exhibited high direct toxicity in the lab and prolonged residual action, even in presence of rainfall.

With this in mind, there is a growing interest in the development of new formulas for the chemical pesticides used in order to make them more effective and in such a way that their dose can be reduced as to lessen their environmental impact while achieving the same beneficial effect. Thus, Machekano et al. (2019) demonstrated an enhanced effect of low doses of certain pesticides such as Deltamethrin or Spinosad, when combined with diatomaceous earths (DEs). The combination of pesticides with key natural enemies (NE) as well as controlling the vectors of certain virus transmissions to provide a second line of defense under IPM has been evaluated (Dáder et al., 2020; Ruiz Garcia and Janssen, 2020), Moreover, investigating synergistic effects of certain viruses with insecticides for IPM is of interest (Dáder et al., 2020), and comparing conventional vs. ecological practices such as those carried out by Carpio et al. (2019) against the olive fly in Andalusia which was comprised of treatments using 40 % Dimethoate plus hydrolyzed protein (conventional olive grove) or 0.024 % Spinosad. One more example of this trend change can be found in Rodríguez et al. (2019), who evaluated three different whitefly control strategies (biological, chemical, and integrated) in commercial zucchini greenhouses. The study concluded that the most effective strategy for virus suppression was integrated management (73 %), followed by biological control (58 %), whilst chemical control provided only limited success (44 %). Another noteworthy investigation was the bioassays in Andalusia with Cry1Ab crystals (81 % purity) which is a toxin from a bacterial culture of *B. thuringiensis ssp* (Castañera et al., 2016). This analysis was carried out in the three main maize growing areas in Spain: the northeast (Catalonia and Aragón), central Spain (Madrid and Castilla-La Mancha) and the southwest (Extremadura and Andalusia). Also, Miñarro and García (2018) carried out a comparative study distributed over a 600 km^2 area in Asturias, to determine the factors driving pest infestation, in which three of the orchards were organic, one applied the broad-spectrum insecticide Lambda-cyhalothrin and the rest followed IPM guidelines. Additionally, Sánchez-Moreno et al. (2018), assessed the effects of organic farming with *Bacillus thuringiensis* on pest control, soil diversity and functioning in Castilla La Mancha. Moreover, Happe et al. (2019) studied the influence of local factors such as orchard management and integrated production (IP) in various regions including Catalonia. The principal objective of this study was to establish the relationship between these factors and the abundant, communal composition of predatory arthropods in apple orchards by providing only reduced targeted quantities of synthetic agrochemicals, including insecticides containing Chlorpyrifos, Deltamethrin and Phosmet (Happe et al., 2019). Additionally, García-Martínez et al. (2019) studied different factors affecting persimmon cultivation, a crop experiencing an important increase in recent years in the Valencia region, for which chemical treatments are the principal strategy to date to lessen the impact of pests. They compared conventionally vs organically managed persimmon orchards. Growers in conventional orchards conducted Chlorpyrifos-methyl treatments (García-Martínez et al., 2019). More recently, Rosas-Ramos et al. (2020a, 2020b), explored the response of spider assemblages to the farming system (organic and conventional) and the hillside aspect (sunny or shady) from a taxonomical, behavioral, and morphological perspective in Extremadura. Treatments in conventional orchards included the application of synthetic insecticides such as Lambda-cyhalothrin, Acetamiprid, Tiacloprid, Spinosad, Cihalotrin, and Piroproxifen). Another outstanding alternative to the use of these pesticides is the use of genetically modified (GM) insect-resistant maize. There is only one GM maize currently authorized in the European Union (EU); García-Ruiz et al. (2020) studied this particular maize and its possible impacts on nontarget arthropods (García-Ruiz et al., 2020).

Considering the growing interest that exists in having reliable data on the use and prevalence of chemical synthetic insecticides, the following lines are focused on these in particular in order to provide a precise idea about the degree and nature of their exposure. This will be accomplished by reviewing and classifying the scientific literature pertaining to main chemical insecticides and different media for the varying regions in Spain.

2.1.1. Aquatic environment

In regards to the aquatic environment, Moreno-González and León (2017) found a high presence of Chlorpyrifos in the Mar Menor lagoon surface marine sediments (Table 2) (Moreno-González and León, 2017). Moreover, in the surrounding environment of the Mar Menor lagoon, Carratalá et al. (2017), studied the prevalence and distribution of pesticides in the air; Chlorpyrifos were found to be the most predominant. In addition, Sánchez-González et al. (2013), assessed the ecological impact of pesticides, including insecticides, used in the agriculture near the Águeda river basin which is located between Spain and Portugal. The study included samples of groundwater as well as soil and found Chlorpyrifos in >50 % of the Spanish samples and over 40 % of the Portuguese samples, respectively.

Even though it is far more difficult to measure the prevalence of this type of pesticide in the sea than in river waters due to its dilution ability, among other factors, some researchers have carried out detailed studies of its prevalence. For instance, Köck-Schulmeyer et al. (2019) found significant quantities of Diazinon and the EU-banned pesticides, Terbutryn and Terbuthylazine, within seawater samples along the coastline of Catalonia (NE Spain); these samples were collected inside and outside of marinas. While the pollutant concentrations were very low, it has been shown that a synergistic effect with other pollutants can boost their harmful effects. Similarly, the ecological risk of Chlorpyrifos was found to be potentially accentuated by plastic debris acting as pollution vectors in South-eastern Spanish Mediterranean coastal areas (León et al., 2019).

Cruzeiro et al. (2017) carried out a one-year case study investigation at the estuary of the international Douro River in the Iberian Peninsula, sampling at six sites to determine the presence of a large number of pesticides (> 50). They found significant quantities in the category of insecticides including Deltametrin, Lambda-cyhalothrin, Chlorpyrifos, Cyfluthrin, Cypermethrin, Beta-Cyfluthrin, Phosmet, Terbutryn, Dichlorvos, Terbuthylazine, and Diazinon. On the other hand, León et al. (2019) studied the prevalence of >100 contaminants of emerging concern (CECs), including a large number of pesticides, in 59 fish samples from the Spanish rivers Guadalquivir, Júcar, Ebro, and Llobregat, where they found notable quantities of more than ten insecticides including Deltametrin, Esfenvalerate, Lambda-cyhalothrin and Chlorpyrifos.

Arenas-Sánchez et al. (2019) carried out an investigative and toxicological risk assessment about the water quality status in the tributaries of the upper Tagus River in central Spain. The potential acute risks to invertebrates and fish due to Chlorpyrifos contamination as well as the threat to invertebrate species because of the hazardous compound Imidacloprid was established.

Not only are these types of insecticides found in large bodies of water and the surrounding environments, but also in water sediments. This

Table 2
Scientific publications on main insecticides in Spain.

Insecticide	CP	HE	PY	AC	CYF	FLU	CA	DI	SP	SPI	ETO
Found in honeybee samples	(García-Valcárcel et al., 2019)	(García-Valcárcel et al., 2019)	(García-Valcárcel et al., 2019)	(García-Valcárcel et al., 2019)							
Found in vegetables and derived foods	(Quijano et al., 2016)						(Aliste et al., 2022)				(Martínez-Domínguez et al., 2016)
Found in agro-wastewater				(Vela et al., 2019)			(Vela et al., 2019)		(Vela et al., 2019)		
Found in river sediments	(Ccanccapa et al., 2016)				(Feo et al., 2013)	(Feo et al., 2013)	(Aliste et al., 2022)				(Ccanccapa-Cartagena et al., 2017)
Found in river Superficial Water (SW)	(Cruzeiro et al., 2017)			(Fonseca et al., 2019)	(Cruzeiro et al., 2017)			(Quintana et al., 2019)			
Found in river Ground Water (GW)	(Sánchez-González et al., 2013)										
Found in river Water (not specified if SW or GW)	(Aguilar et al., 2017; Arenas-Sánchez et al., 2019; Ccanccapa et al., 2016)	(Aguilar et al., 2017)						(Aguilar et al., 2017)			(Ccanccapa-Cartagena et al., 2017)
Found in river biota samples	(Ccanccapa et al., 2016; Pico et al., 2019)	(Pico et al., 2019)			(Pico et al., 2019)			(Pico et al., 2019)			
Found in Surface Marine Sediments (SMS)	(Moreno-González and León, 2017)										
Found in Sea Water (SW)	(León et al., 2019)										
Found in soils	(Sánchez-González et al., 2013)						(Aliste et al., 2022)			(Pastor-Belda et al., 2015)	
Found in Air	(Carratalá et al., 2017)										

Chlorpyrifos (CP), Hexythiazox (HE), Pyriproxyfen (PY), Acetamiprid (AC), Cyfluthrin/Betacyfluthrin (CYF), Fluvalinate (Flu), Chlorantraniliprole (CA), Dimethoate (DI), Spinosad (SP), Spirodiclofen (SPI), Etofenprox (ETO).

finding was revealed by Feo et al. (2013) who evaluated the presence of a number of pyrethroid insecticides in sediment samples collected along the Ebro River (north-east of Spain) which is far away from agricultural, industrial, and highly urbanized areas. Cyfluthrin, Cypermethrin, and Fluvalinate were found; however, the bioavailability was dependent on the organic carbon content of the sediments, which was generally very low with Cyfluthrin appearing to be the more bioavailable. Also, Barbieri et al. (2019) developed a reliable LC-MS/MS-based method for determining if there is a high number of polar pesticides in sediments at trace levels. This method is based on pressurized liquid extraction (PLE), extract clean-up by solid phase extraction (SPE), and analyte determination by liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS). This method was applied to the analysis of the target pesticides in sediments from the Llobregat River (NE Spain) which showed the presence of Terbutryn, Dichlorvos, Terbuthylazine, Diazinon, and Irgarol; all of these pesticides demonstrate high potential for bioaccumulation and risk to aquatic organisms.

Additionally, Ccanccapa et al. (2016) evaluated the prevalence of 50 pesticides in the Ebro River basin in water, sediment, and biota which demonstrated high ecotoxicological risks of Chlorpyrifos and Diazinon. Further, Aguilar et al. (2017) developed a methodology based on liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) to quantify farming chemicals in the Júcar River basin; the methodology was applied to >50 target pesticides and concluded the regular presence of Chlorpyrifos and Terbuthylazine at high concentrations, among other pesticides. In addition, Ccanccapa-Cartagena et al. (2017) found Etofenprox in sediment samples taken from the mouth of the Turia River, near the Albufera wetland, a natural park located in the eastern coast of Spain. Water samples were also analyzed, but no pyrethroids or pyrethrin insecticides were found; a possible explanation for this could be the hydrophobicity of pyrethroids that tend to accumulate in sediment compartments (Ccanccapa-Cartagena et al., 2017).

Moreover, Fonseca et al. (2019) investigated the occurrence of a large number of insecticides in groundwater (GW) and surface water (SW) samples in the Eastern part of the Iberian Peninsula (Castilla La Mancha and Valencian Region) through a means of wide-scope screening by liquid chromatography coupled with high-resolution mass spectrometry (LC-QTOF MS). 17 compounds were confirmed; among them was Imidacloprid (frequency of 9 % of the samples), Acetamiprid (25 %), and Diazinon (25 %). In correspondence with this investigation, Jurado et al. (2019) reviewed the existing occurrence data in regards to Spanish groundwater (GW) and the emerging organic contaminants (EOCs) defined in the Surface Water Watch Lists of Decisions 2015/495/EU and 2018/840/EU; some of the EOCs listed included Imidacloprid, Methiocarb, Acetamiprid, Oxadiazon, and Thiacloprid. From the 9 pesticides included in the Watch Lists, only Imidacloprid, and Methiocarb were detected in the GW of Spain. Four other pesticides (Oxadiazon, Neonicotinoids, Thiacloprid, and Acetamiprid) were also investigated, but not detected in any sample.

On the other hand, Herrero-Hernández et al. (2017) investigated the occurrence of Imidacloprid in SW and GW of the vineyard region of La Rioja (north-central of Spain) by analyzing 90 sampling points (78 from GW and 12 from SW) monitored over the course of four periods (September 2010, March 2011, June 2011, and September 2011). Thus, Imidacloprid was detected in all the sampling campaigns with an average detection frequency of 9 % (ranged from 7 % to 18 %) and a maximum concentration of 656 ng/L observed in June 2011 after the pesticide application period. Moreover, high concentrations of Imidacloprid were also found in GW in the surroundings of a solid waste treatment plant of Castellón (eastern Spain) that was monitored between 2011 and 2013.

Remarkably, Borrull et al. (2019) studied the incidence of a varied group of contaminants of emerging concern (CEC), including pesticides, in water samples taken from the lower course of the Ebro River in Spain. While this region is not densely inhabited, it receives discharges from several agro-industries where notable quantities of Imidacloprid were found. Furthermore, Quintana et al. (2019) monitored the complex occurrence of pesticides in natural and drinking waters in the Barcelona metropolitan area (Catalonia, NE Spain). Thus, a monitoring campaign was carried out during 2016–2017 and determined that pesticide contamination at the bottom stretch of Llobregat River and within its aquifer is severe; maximum concentrations for carbendazim, DEET, diuron and propiconazole were in the range of a few μg/L, and in the range 0.1–0.5 μg/L for Bentazone, Imidacloprid, Isoproturon, Simazine, Metazachlor, Methomyl, Terbutryn, and Tebuconazole. However, the advanced treatments involved in drinking water production allows for the complete removal of pesticides and potable drinking water for consumers.

2.1.2. Food

Regarding the prevalence of these insecticides in food, Aliste et al. (2022) carried out a prevalence study in the Region of Murcia (SE of Spain), where Chlorantraniliprole, Imidacloprid, Pirimicarb, and Thiamethoxamon were found in soil and lettuce at the end of cultivation when the crops were irrigated with non-reclaimed, contaminated water. Fortunately, these insecticide residues disappeared when irrigation was done with reclaimed water through solar photocatalytic technologies (Aliste et al., 2022). Moreover, a number of insecticides, such as Acetamiprid, Chlorantraniliprole, and Spinosad, were found in agro-wastewater in the area of Torre Pacheco (Murcia, SE of Spain) (Vela et al., 2019). In addition, Quijano et al. (2016) evaluated the exposure to certain pesticides through fruit and vegetable consumption in the region of Valencia (Spain) where they found that Deltametrin, Lambda-cyhalothrin, Chlorpyrifos, Cypermethrin, and Phosmet were the most frequently detected insecticides. Moreover, Martínez-Domínguez et al. (2016) found Etofenprox in diverse nutraceutical supplements obtained from local supermarkets in Almería (Spain).

Additionally, Pastor-Belda et al. (2016) carried out a study in fruits and vegetables (tomatoes, peppers, lemons, oranges and grapefruit) obtained from local supermarkets in the region of Murcia, where they analyzed the prevalence of some spirocyclic tetronic/tetramic acid derivatives, such as Spirodiclofen, and some neonicotinoids, such as Acetamiprid. The results indicated that only Spirotetramat and Spiromesifen were detected and the distribution was well below the corresponding maximum residue levels.

2.1.3. Soils

In regard to the prevalence of these insecticides in soils, there are not many studies focused specifically on soils, but rather those that demonstrate their mobility from soil to other media. These studies tend to be more in line with the impact on living organisms, such as the studies already mentioned from Aliste et al. (2021, 2022) that was performed in the region of Murcia (SE of Spain) and focused on soil and lettuce and the mobility of these insecticides. Another examples is that of Sánchez-González et al. (2013) that concentrated on groundwaters and soils. Also, we can highlight the study of Pastor-Belda et al. (2015) who detected a number of new generation pesticides, including Chlorantraniliprole and Spirodiclofen, in soil samples taken from greenhouses that had been previously used throughout the crop cycle cultivation in Campo de Cartagena, Murcia (south-eastern, Spain).

2.1.4. Biota

In relation to the mobility of these insecticides on the biota, the studies carried out in the region of Catalonia stand out the most in which García-Valcárcel et al. (2019) developed a simple analytical method to evaluate pesticide residue levels in honeybees and corbicular pollen with the intention of determining the exposure of honeybees to plant protection products (PPPs). Clofentezine and Etoxazole were found in a pollen sample, but not in honeybees. Hexythiazox was found in honeybees throughout the entire flowering period and specifically during mid-flowering. Pyriproxyfen was found at the end of the flowering period in both pollen and honeybees, and Corcellas et al. (2017), detected the presence of pyrethroid insecticides in 93 % of the hundred unhatched eggs sampled among 16 different species of wild birds from Doñana (nature reserve in southwestern Spain) and surrounding areas. This reflects the variety of pyrethroids in the environment as Cypermethrin, Cyhalothrin and Bifentrhin were the most ubiquitous pyrethroids and present in >77 % of samples.

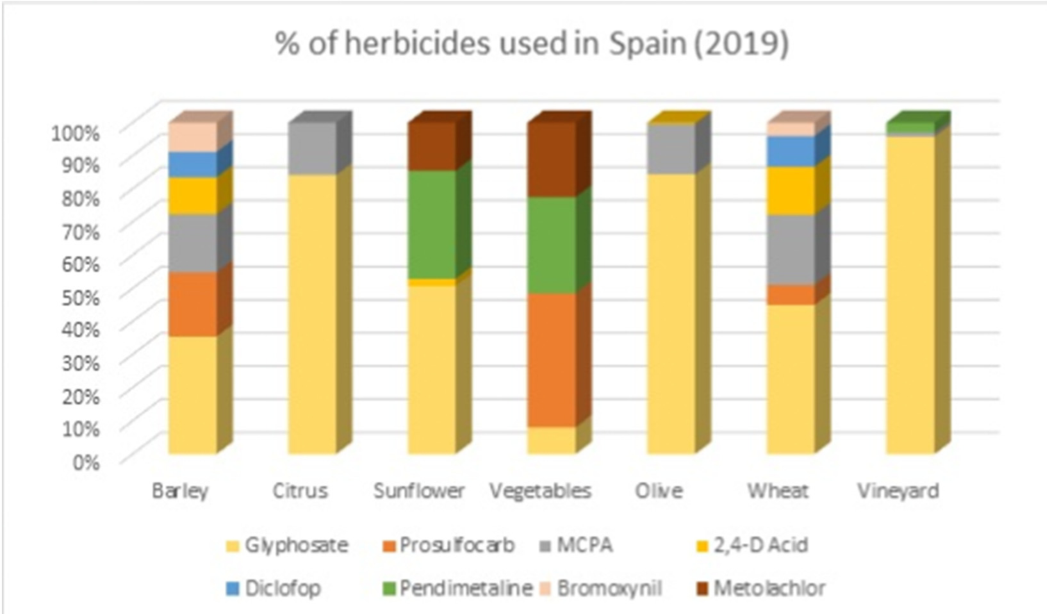

Fig. 3. Uses of herbicides used on crops in Spain in 2019.

2.2. Herbicides

Herbicides are the pesticides most widely used on Spanish crops representing 80.9 % of the total kilograms of pesticides used in Spain. The crops in which the greatest amounts of herbicides are used include olives, composing 34.20 % of the total tons of herbicides used in Spain, wheat (21.13 %) and barley (20.67 %). Considering that these three crops account for the majority of cultivated surface area in Spain, herbicides could generate a significant quantity of residues in soil and water. The total of herbicides used by each crop, measured in tons, is shown in Fig. 3.

The Glyphosate is the most widely used herbicide compound in Spain making up 51.87 % of the all herbicides used, followed by 2-methyl-4-chlorophenoxyacetic acid (MCPA) (11.40 %) and 2,4-D acid (4.42 %). In Spain, Glyphosate is mostly used for olives, barley, citrus, sunflower, wheat, and grapes. MCPA, on the other hand, is most commonly used on barley, sunflower, olives, and wheat while 2,4-D acid is used on grains such as barley and wheat. Other compounds are used to a lesser extent. The usage of Glyphosate is important for olive crops even though the cultivation surface area for olives in Spain is less than barley. In 2019, 1286.4 tons of this compound was used in olives crops in comparison to barley crops, which was responsible for the usage of only 319 tons.

On the other hand, MCPA is widely used in grains (barley and wheat), which averages about 100 tons per crop. As for 2,4-D acid, this herbicide is largely used for olive and vineyard crops with a total combined average of approximately 57 tons; 2,4-D acid, however, is used in a higher proportion in olive crops (46.3 ton). An analysis of these statistics suggest that it is easy to find a high presence of the residues of Glyphosate (GPS), MCPA, and 2,4-D acid (2,4-D) in Spanish soil and water. Nevertheless, an overall bibliographic review shows several data for the high presence of GPS and 2,4-D acid while MCPA residue is not as widely reported in water and soil. This could be due to the fact that MCPA use was not significant until 2013; however, its usage has increased considerably in the last 6 years (MAPA, 2019).

2.2.1. Glyphosate and AMPA

Several literature reports show the presence of Glyphosate (GPS) in soil and water throughout Spain (Table 3) (Ibáñez et al., 2006; Puértolas et al., 2010; Sanchís et al., 2012; Veiga et al., 2001). In these studies, the concentrations of GPS include its primary metabolite aminomethylphosphonic acid (AMPA). The presence of GPS in soil is attributed to its strong adsorption and limited mobility (Candela et al., 2007); however, according to laboratory experiments, it is suggested that GPS poses a low risk for groundwater pollution due to its phosphonate functional group and strong adsorption to clay minerals, iron and aluminum-oxides (Candela et al., 2010). Despite this research, residues of GPS and AMPA have been found in different aquifer mediums (Ibáñez et al., 2006; Sanchís et al., 2012).

Candela et al. (2007) demonstrated the presence of GPS and AMPA in Catalonia through modeling the existence of a relative mobile pool of Glyphosate adsorption in soil from the Barcelona Maresme area; the absorption was concluded to be irreversible. Despite these findings, there is not a quantitative determination of its presence in soil and water. However, this is a remarkable explanation for describing Glyphosate behavior and its permanence in Spanish soils and waters. Yet, regarding this issue, Candela et al. (2010) found a clear potential risk of GPS transport to groundwater due to its deep-leaching ability which was detected in a weathered granite soil profile under natural field conditions; there appeared to be no association with irrigation conditions or the climatic season. Presence of GPS residues were detected at depths of 1.10 and 1.9 m in both irrigated and non-irrigated soil samples; this suggests that the pesticide may have the capacity to migrate into deep soil layers and, eventually, to groundwater.

Evidence of this migration can be confirmed with the studies conducted by Sanchís et al. (2012), where 47 % of samples of groundwater from Catalonia demonstrated quantifiable levels of GPS; between 0.097 and 0.409 μg/L of this compound were present. Taking in to account that the limit in Europe for singular pesticides in groundwater is 0.1 μg/L and for a combination of pesticides, 0.5 μg/L (European Commission, 1998), this finding demonstrates a clear contamination problem with this compound in groundwater. As can be expected, more samples of contamination were found in regions with thriving agricultural activity. While Glyphosate tends to be immobilized in soils, it has been determined that Glyphosate contamination of aquifers is attributed to its intensive use.

In the case of surface water, studies performed in the Llobregat River (Barcelona, Spain) show that GPS levels in river water following herbicide application were quite high (20–60 μg/L) (Puértolas et al., 2010). Furthermore, 12 days after the initial application, leaching of Glyphosate from sprayed riverbanks was quite high in the pore water (20–85 μg/L), but not in the river water. These samples taken from the Llobregat River suggest a relevant problem regarding GPS application of riverbanks (for the control

Table 3
Scientific publications on main herbicides in Spain.

Herbicide	GPS	2,4D	OXI	ISO	PRO	DIC	MCPA	PE	LI	MET
Found in soils	(Candela et al., 2010, Candela et al., 2007; Geissen et al., 2021; Panettieri et al., 2013; Veiga et al., 2001)	(Díez and Barrado, 2010; Dorado et al., 2003)								
Found in Surface Water (SW)	(Ibáñez et al., 2006; Maqueda et al., 2017; Puértolas et al., 2010)	(Herrero-Hernández et al., 2013a; Köck-Schulmeyer et al., 2019)	(Carratalá et al., 2017; González-Martín et al., 2017)	(Borrull et al., 2019; Fraile et al., 2009)			(Köck-Schulmeyer et al., 2019; Sánchez-González et al., 2013)	(Carratalá et al., 2017; Fraile et al., 2009)		(Carratalá et al., 2017; Fraile et al., 2009)
Found in Ground Water (GW)	(Ibáñez et al., 2006; Sanchís et al., 2012)	(Herrero-Hernández et al., 2013a; Moral et al., 2012)								

Glyphosate (GPS), 2,4-D Acid (2,4D) Oxifluorfen (OXI), Isoproturón (ISO), Prosulfocarb (PRO), Diclofop (DIC), 2-methyl-4-chlorophenoxyacetic acid (MCPA), Pendimetaline (PE), Linurón (LI), Metribuzine (MET).

of giant reeds) because it is possible for this herbicide to reach higher concentrations during the first three days post-application. Nevertheless, this study did not detect any signs of AMPA; one explanation for this could be that GPS does not have enough time to decompose in this environment. This hypothesis is in accord with recent studies conducted in France (Carles et al., 2019) where it was found that GPS concentration in surface water has a kinetic profile. Therefore, as the concentration of GPS decreases each day, the kinetic growth of AMPA concentration is not detectable until the 4th or 5th day.

In Andalusia, results of the studies carried out in the Vibora riverbed (Jaen) show a high and irreversible GPS adsorption in the soils and reservoir sediments. Nevertheless, GPS shows a quick dissipation in water samples in which it only takes between 6 and 11 days to reduce approximately 70 % of the initial GPS content (Maqueda et al., 2017). This behavior seems to show a relatively low toxicity risk in this particular zone where GPS is widely used for olives crops. However, investigations carried out in Seville soils (Panettieri et al., 2013) confirmed that GPS presence could affect soil biochemical parameters (dehydrogenase and β-glucosidase activities).

In Galicia, residues of GPS and AMPA were detected in forest soils (solid and liquid phase) previously treated with 5–8 L/ha (Veiga et al., 2001). In the solid phase, an average of 0,85 μg/g of GPS was found. On the other hand, in the liquid phase, concentrations of approximately 0,14 μg/L of GPS and 0,11 μg/L of AMPA were detected. However, GPS and AMPA concentrations show a trend in which their concentrations decrease over time. For instance, dissipation rates lasted between 29 and 40 days and began to demonstrate lower concentrations only 1 month after the initial treatment. In this sense, the properties of Galicia forest soils (moderately deep, acidic, rich in organic matter, and poor in nutrients) appear to promote Glyphosate degradation, thereby reducing the risk of off-site movements.

Other studies were carried out in Murcia and Valencia where GPS and AMPA residues were found as main compounds in soils from conventional farms; these results demonstrated a pesticide residue content between 0.8 mg/kg and 2 mg/kg (Geissen et al., 2021). Organic soils, however, presented lower residue concentrations by 70–90 % in comparison with the corresponding conventional soils. This means that although soils from organic farms have significantly fewer residues, there is a severe lack of knowledge concerning the effects of the accumulated, complex mixtures of pesticide residues found in soils. As a result, when thinking about the process of transitioning to organic farming, the residue mixtures at the conversion time and their residence time in soil should be taken into heavy consideration.

Ground and surface water from this region were also analyzed from an agricultural area where GPS is widely used in the Spanish Mediterranean region (Valencia). Concentrations between 0.11 and 0.84 μg/L of GPS were found by Ibáñez et al. (2006). Similar to the studies carried out in Catalonia (Sanchís et al., 2012), the results revealed concentrations of GPS over the limit established by the EU for single pesticides in water (European Commission, 1998; Risica and Grande, 2000). This discovery brings to light two challenges: the first being the investigation and detection of different herbicides in soil and water using analytical technologies, and the second, carrying out exhaustive analyses of soil and water where there is a possibility that these herbicides are present, since, as observed throughout this bibliographic study, there are relatively few studies in this regard.

2.2.2. 2,4-D acid

In relation to 2,4-D residues, some studies reported its presence in Spain, specifically in surface and ground water of Andalusia (Córdoba and Jaén) (Moral et al., 2012). Concentrations between 0.1 and 0.4 μg/L of 2,4-D were found, analogous to other publications (Ibáñez et al., 2006; Sanchís et al., 2012). These amounts are still above the limits allowed by the EU, which from a legal and environmental perspective, present a substantial problem for the conventional agricultural sector-particularly for barley and wheat crops were 2,4-D is widely used. Nevertheless, López-Roldán et al. (2013) hypothesized that a concentration of 500 μg/L of 2,4-D would have no effect on aquatic organisms; this value is higher than other previous studies.

On the other hand, 2,4-D was detected in sea water in Catalonian coastal areas with a median concentration of 0.01 μg/L; in comparison with another regions, this is not significant (Köck-Schulmeyer et al., 2019). However, in La Rioja, 2,4-D was found in surface and ground water with concentrations between 0.02 and 0.17 μg/L (Herrero-Hernández et al., 2013a). The fact that concentrations of 2,4-D exceeding the established limit were found in water samples from La Rioja is really remarkable because this zone is widely known as a vineyard region where the use of this herbicide is rare.

In Castilla y León, a kinetic study of 2,4-D residues were carried out in typic xerofluvent soil (Díez and Barrado, 2010). This kind of soil is widely used to cultivate barley. The results show a full dissipation of 2,4-D in the soil during summer conditions. Nevertheless, studies in the region of Madrid (Dorado et al., 2003) show that the 2,4-D sorption and permanence in the soil largely depends of the quality of the humic organic matter accumulated in the soil. This suggests that the retention of this compound in the soil will always depend on of the type of soil that is treated with the herbicide. Therefore, a total dissipation in some types of soil is entirely plausible, as was shown by Díez and Barrado (2010), but residues of this herbicide in soils with humic acids of larger maturity degree is also a possibility.

2.2.3. Other herbicides

Despite MCPA being used frequently throughout Spain, its existence has only been reported by Köck-Schulmeyer et al. (2019) in water samples from coastal areas of Catalonia with concentrations of 0.2 μg/L. As expected, herbicides used in smaller quantities in Spain have not been widely reported as residues in water and soil. Only Linuron was detected in water samples from river areas in Castilla y León, with concentrations around 0.2 μg/L (Sánchez-González et al., 2013). Nevertheless, this is an exceptional case given that an infrequently used herbicide was reported to have a concentration above the established limits for water. This presents another limitation of knowledge and requires that the use of these herbicides is quantified and their permanence and effect in water mediums is studied, in addition to agricultural areas in this region.

In the case of Prosulfocarb and Diclofop, there are not many studies avaible concerning their concentrations in water and soil in Spain. In regards to Oxifluorfen, its presence was studied in water samples from the coastal area of Mar Menor, but this compound was not detected (Carratalá et al., 2017; Moreno-González and León, 2017). On the other hand, Isoproturon was found in water samples from Navarra (Fraile et al., 2009) and the Ebro River in Catalonia (Borrull et al., 2019), but with insignificant concentrations, exhibiting a maximum of 50 ng/L. The same situation occurred with Pendimetalin and Metribuzine; these two herbicides were detected in water samples from Mar Menor and Navarra, but in nonsignificant amounts (Carratalá et al., 2017; Fraile et al., 2009). Nevertheless, there is one study that reported Metribuzine and other herbicides compounds such as Diuron, Simazine and Terbuthylazine in concentrations around 0.1 μg/L in the Tagus River in Madrid (Rico et al., 2019). This last investigation reveals an important issue concerning the usage of herbicides and concentrations of residues identified because, as previously observed, Diuron, Simazine and Terbuthylazine are not widely used in Spain, but various studies discovered quantities of these herbicides above the specified limit in different water samples. This could be attributed to the versatility of these compounds to be applied to a variety of crops as well as their increasing usage as a substitute for GPS.

2.3. Fungicides

Fungicides are substances that are used to prevent the growth of or eliminate fungi and molds that are harmful to plants or animals; they are applied via spraying, dusting or fumigation. The presence of fungicides is related to their agricultural use as they are used to treat a wide variety of vegetables, olives, vineyards, fruits, and cereal crops. Fig. 4 shows the different fungicides as it pertains to crop in Spain. According to the data, Sulfur is the most used fungicide with a total usage of about 22,288.4 tons, of which 21,007.7 tons are used to treat vineyards. Fosetil-Al ranks second among the most used fungicides with an overall usage of 2167.4 tons; vegetables account for 1629.5 tons. Among the various other fungicides showned in Fig. 4, only Benalaxyl, Cyprodinil, Folpet, Maneb, Metalaxyl, Myclobutanil, and Tebuconazole were relevant to consider given their use in specific crops including citrus fruits, sunflowers, vegetables, olives, wheat and grapes.

A wide range of scientific publications concerning fungicides contamination were found and analyzed as can be seen in the following Table 4:

2.3.1. Benalaxyl

Benalaxyl is a systemic phenylamide with preventive, curative, and eradicative fungicidal ability. It is characterized by its capability to selectively act on peronosporales (mildew-producing fungi), such as saprophytes and obligate parasites as well as alternariosis or black leaves (Alternaria sp., black-producing fungi of numerous horticultural plants). This fungicide stops the mycelial growth of the saprophytic peronosporales and acts on the obligate parasites in various ways including preventing the development of the mycelium in the tissues of the host plant, inhibting the release of zoospores by the zoosporangia, and impeding germination. It is often used on citrus fruits and vegetables as well as in vineyards. Benalaxyl was detected both in 2009 and 2010 in in surface marine sediments from a Mediterranean coastal lagoon located in Murcia, Spain. The levels found were higher in 2010 than in 2009 with values of 0.5 ng/g in the spring of 2009 and 6.6 ng/g in the fall of 2010 In a 2013 study carried out in La Rioja, Spain where viticultural is the main agricultural, Benalaxyl were detected in groundwaters (Herrero-Hernández et al., 2013b).

2.3.2. Cyprodinil

Cyprodinil is quite versatile and is used to treat a broad spectrum of fungi including ascomycetes, basidiomycetes, deuteromycetes and oomycetes. Its method of operation is different from that of other fungicides as it inhibits spore germination, germ tube growth and penetration into the plant. Applied directly to the leaves, Cyprodinil is absorbed and immediately distributed by a translaminar route and acropetic system into the xylem. The active substance is immobile in the soil and it degrades rapidly, its half-life being 60 days. This particular fungicide retains more organic carbon in non-sterile soils than in sterile soils and under anaerobic conditions. As a result, retention of organic carbon is stronger when there is a higher soil pH, a higher ion exchange capacity, and a higher nitrogen. Cyprodinil is used to treat vegetables and vineyards as well as to obstruct the growth of monilinia in stone fruit production in Spain. Cyprodinil was

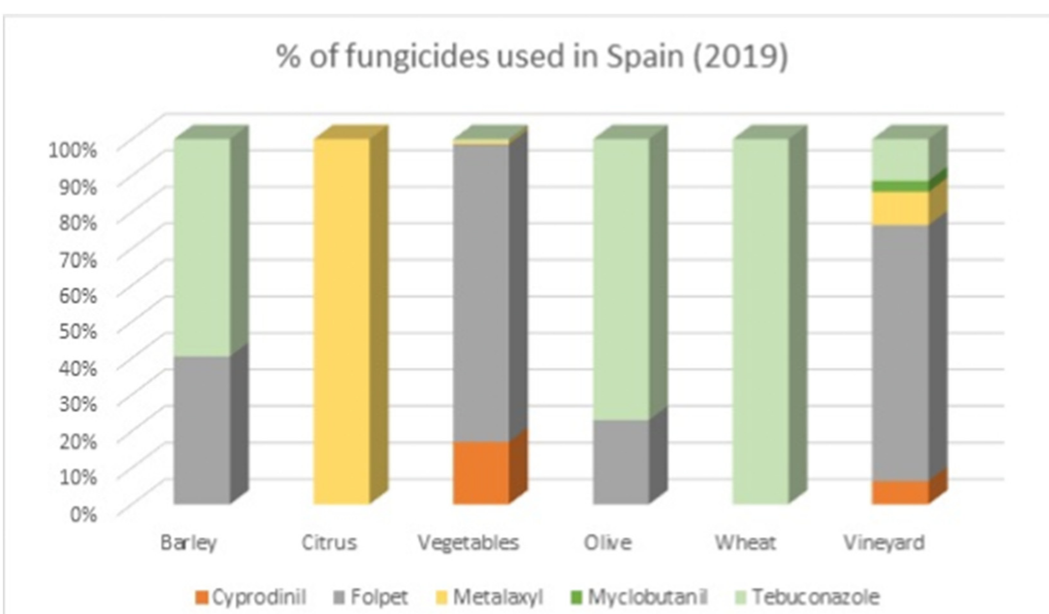

Fig. 4. Uses of fungicides on crops in Spain in 2019.

Table 4
Scientific publications of main fungicides used in Spain.

FUNGICIDE	BENA	CYP	FOL	MB	MT	MY	TE
Found in Propolis and fruits			(González-Martín et al., 2017)			(Obi et al., 2018)	
Found in air			(López et al., 2017)				
Found in soils		(Arias et al., 2005; López-Periago et al., 2006)					
Found in Surface Water (SW)	(Moreno-González and León, 2017)			(Mañosa et al., 2001)		(Moreno-González and León, 2017)	(Herrero-Hernández et al., 2013a)
Found in Ground Water (GW)	(Herrero-Hernández et al., 2013a)				(Sánchez-González et al., 2013)		(Sánchez-González et al., 2013)

Benalaxyl (BENA), Cyprodinil (CYP), Folpet (FOL), Maneb (MB), Metalaxyl (MT), Myclobutanil (MY), Tebuconazole (TE).

one of the most frequently detected pesticides in the groundwater and soils in the agricultural areas of the Águeda River Basin (Sánchez-González et al., 2013). The fungicide, Cyprodinil, was detected in 96 % of the samples. In a sampling carried out in the winter of 2012, the presence of Cyprodinil was detected in groundwater collected from the Agueda River with concentrations of ≥ 0.5 μg/L, detected in 96 % of the Spanish samples. According to the GUS index, the sorption process of fungicides depends on the organic matter (OM) and clay content of the soil which may explain the frequent presence of Cyprodinil in groundwater despite Cyprodinil being very hydrophobic (Kow = 4) and non-leaching. In a study carried out in the reigon of Murcia (southeast of Spain), the dissipation of Cyprodinil in lettuce and table grapes in both the field as well as cold storage was investigated (Marín et al., 2003). Cyprodinil dissipation was similar for both crops (lettuce and table grapes) with residual levels of 7 days in lettuce and 21 days in table grapes. The greater persistence in grapes than in lettuce is likely due to the "dilution effect" caused by the rapid growth of lettuce since the residue is expressed in proportion to weight (mg/kg). As the weight of the plant material increases, the proportion of residue decreases. This is known as "apparent kill" and is important in fast growing crops such as lettuce, which can easily double in weight within a few days (Coscollá, 1996). The study confirms the influence of temperature and sunlight on the dissipation rates of Cyprodinil. The presence of residues at harvest time (especially table grapes) can be problematic if the harvest is stored or transported in cold conditions for long periods of time. This behavior is due to the fact that the most important factor in the dissipation of pesticides is chemical degradation, especially that caused by high temperatures and solar radiation (Coscollá, 1996).

In another work carried out in Pontevedra (Galicia) the adsorption-desorption dynamics of Cyprodinil in vineyard soils was studied (Arias et al., 2005). The fungicide exhibited linear adsorption isotherms and the Kd values for Cyprodinil were significantly correlated with the organic matter content of the soil ($r^2 = 0.675, p < 0.01$). A linear adsorption model involving non-equilibrium conditions and an irreversible adsorption term reproduces prior results concerning the impact of transport. In a study carried out in an agricultural field near Ourense, Spain, the influence of methanol on the dynamics of Cyprodinil retention and release was studied through an analysis of agricultural soil (López-Periago et al., 2006). The results of the influence of methanol on the adsorption of Cyprodinil concluded that the effective partition coefficient of Cyprodinil between the soil and the solution, Kdc, decreases linearly as the concentration of methanol in the solution increases until a percentage of 20 % is reached.

2.3.3. Folpet

Folpet, a fungicide from the phthalimide group, has a foliar fungicidal and preventative ability and is presented in the form of a concentrated suspension to be applied as a foliar spray. It is effective in the preventive control of numerous diseases caused by endoparasitic fungi such as dent and canker of fruit trees, alternaria, anthracnose of the rose bush, and other anthracnose including botrytis, heterosporium, mildew, monilia, and black rot of the vine. In Spain, it is used to control diseases in the following crops: citrus, vegetables, olive trees and grapes. The presence of Folpet was analyzed in a study of 106 samples of crude propolis from Castile & Leon and Galicia (González-Martín et al., 2017). The results unveiled the presence of Folpet in the samples of crude with a concentration of 3.74 mg/kg. In another study carried out in the Valencian Community (Spain), pesticide levels (including that of Folpet) were monitored in natural waters and revealed a concentration of 6525 μg/mL (Pico et al., 2019). Similarly, a risk assessment of airborne pesticides in the Mediterranean region of Spain carried out in Valencia detected Folpet in the air at concentrations of 38 (pg/m^3) with a detection frequency of 16 % (López et al., 2017).

2.3.4. Maneb

Maneb is another foliar fungicide with the capacity to treat diseases caused by endoparasitic fungi. This fungicide works by degrading rapidly in the soil when diluted in water under anaerobic conditions. Its degradation in the soil is not stimulated by solar radiation and can contaminate groundwater. Maneb is used on barley, wheat, citrus, vegetables and olives. In the Ebro Delta, the presence and accumulation of pesticides such as Maneb have been detected, which are considered potentially harmful to the estuarine and coastal environment (Mañosa et al., 2001).

2.3.5. Metalaxyl

Metalaxyl is an active ingredient that belongs to the group of phenylamides (acylalanines) in which it provides specific, preventive and curative treatment against oomycete fungi. This fungicide has translaminar properties and is absorbed by the leaves, stems, and roots. Its movements are defined as acropeto apoplastic and its antifungal activity is based on preventing protein biosynthesis in sensitive fungi by interfering with the synthesis of ribosomal RNA. Metalaxyl is used on citrus fruits, vegetables, olive, and grapes. Samples carried out in the Águeda River detected levels of Metalaxyl in the groundwater sampled at concentrations of 0.1 μg/L. The presence of this fungicide was also found in soils. Soils containing dissolved organic matter do not help absorb pesticides, but rather increase their mobility in the soil. As a result, the groundwater contamination could be due to the presence of dissolved organic matter as it increases the mobility of these compounds (Sánchez-González et al., 2013).

2.3.6. Myclobutanil

Myclobutanil is a systemic fungicide with protective and healing properties. The compound is absorbed by the leaves and stems and then transported in the plant to growth areas via xylem. Myclobutanil belongs to the chemical group of triazoles and acts by inhibiting the biosynthesis of ergosterol from fungi (critical sites in the formation of cell membranes) and mainly inhibits the C14 demethylation stage in the ergosterol biosynthetic pathway. Myclobutanil is used on citrus, vegetables and grapes as well as against monilinia in the production of stone fruit in Spain (Obi et al., 2018). Dissolved Myclobutanil was detected through the El Albujón watercourse to the Mar Menor lagoon during two flash floods in September 2016 (Moreno-González and León, 2017).

2.3.7. Tebuconazole

Tebuconazole is a systemic, triazole fungicide with preventive, curative and eradicative ability in that comes in the form of an oil-in-water emulsion. It can be applied as a foliar spray or directly to the ground and is effective in the preventive and curative control of botrytis, cladosporium, sclerotinia, stenfilium, powdery mildew, rusts, and other diseases of fungal origin. Tebuconazole is most commonly used on barley, wheat, citrus, vegetables, olives and grapes. Tebuconazole was detected in water samples from La Rioja vineyards in 2013. It was also detected in in 72 % of the samples of groundwater and soils taken from agricultural areas in the Águeda River Basin with concentrations of up to 0.804 μg/L in some of the samples (Sánchez-González et al., 2013). Lastly, the fungicide was detected in a large number of samples at a concentration of 3.236 μg/L in natural waters throughout the winegrowing region of La Rioja (Rioja DOCa) (Herrero-Hernández et al., 2013a).

3. Outlook and conclusions

The use of pesticides has improved crop yields and has played a key role in large-scale food production. However, this practice has generated some controversy since the massive use of pesticides can pose various problems for the environment and human health. For this reason, sustainability has become the principal factor in the European agricultural model regarding the use of pesticides. As a result, one of the fundamental pillars within agricultural production is now based on the sustainable use of pesticides in order to reduce the risks and negative effects of pesticides on human health and the environment.

In this review, we have studied the use of pesticides as pertaining to geographical area and the crops associated with these specific areas, which is largely based on climate and water availability. The crops discussed are often associated with a specific pesticide to control weeds, insects, and fungi as these things can reduce the quality of the agricultural products harvested. According to the overall ranking, Paraffin is the most used insecticide accounting for about 1012.6 tons. Then, in second place, we find Paraffin oil with a use of 171.2 tons and, in third place, Phosmet with a use of 133.6 tons. In the rest of the insecticides studied, the total tons used were below that of Phosmet, but have been considered concerning their use in specific crops. Regarding the use of insecticides in crops, citrus fruits used the largest amount of pesticides with 1058.9 tons, followed by olive with 431.0 tons, vegetables with 241.4 tons, vineyards with 183.9 tons, and cereals (barley and wheat) with 134.7 tons. The total amount used by sunflowers does not even account for 25 tons. Based on which crops used which insecticides, residues and traces of insecticides were observed and detected in different areas throughout Spain. Thus, concentrations of Dimethoate were detected in Andalusia as they are used to treat whiteflies in olive trees and in horticultural crops, such as zucchini, in greenhouses. In the area of Catalonia, levels of Chlorpyrifos, Deltamethrin and Fosmet used in orchards and apple plantations were detected. In addition, concentrations of Clofentezine, Etoxazol, Hexitiazox and Piriproxyfen were detected in the pollen and in the bees themselves which affects the quality of the beekeeping fauna. Chlorpyrifos levels have also been detected in the Mar Menor and in rivers such as the Duero, Ebro, Guadalquivir, Jucar, and Llobregat. Terbutryn and Terbuthylazine levels were detected on the coast of Catalonia. Finally, in the vineyards of La Rioja and the Ebro, concentrations of Imidacloprid were detected due to the use of insecticides in agro-industries. These detected concentrations of insecticides in the different areas of Spain serve as an indicator of the different effects of insecticides and provide support to regulate their used and concentration in order to be more environmentally considerate.

The most widely used herbicides in Spain are Glyphosate with 2716.9 tons, MCPA with 597.1 tons, Prosulfocarb with 289.1 tons. The other herbicides such as Diclofop, Pendimetaline, Linuron, and Metribuzine all exhibit less usage than those previously listed. Among all crops that utilize herbicides for weed control, olives made up 34 % of usage, wheat consisted of 21 %, barley was responsible for 20 %, grapes and sunflowers each accounted for 8 %, and vegetables and citrus made up 4 %. Relating the uses of herbicides with the crops and the detected concentrations in the different environments, we can see that GPS has been detected in a large proportion of underground and surface waters in Catalonia and the Llobregat River. GPS concentrations have also been detected in olive trees in Andalusia, Galicia, Murcia, and Valencia. With respect to 2,4D, it has been detected in surface and groundwater in Córdoba and Jaén (Andalusia), the coast of Catalonia, and in the groundwater and surface waters of La Rioja and Madrid. Concentration of MCPA and Linuron have been detected in Catalonia and Castilla y León.

Regarding fungicides, Sulfur is the most used fungicide with a value of 22,288.41 tons. The second most-used fungicide is Fosetil-Al with a use of 21,007.7 tons. In the rest of the fungicides studied, the uses were lower than that of Sulfur and Fosetil-Al,but were taken into account given their use in specific crops. Pertaining to the use of fungicides in different crops, vineyard stand out with a usage of 22,867.2 tons; this extreme number is attributed to the various treatments necessary for this crop to avoid diseases, such as mildew and powdery mildew. The next crop known to use the most fungicides is vegetables which were found to have a use of 4290.3 tons, followed by olives which were reported to be using 2062.2 tons. The crops with the lowest usage of fungicides include barley, wheat, citrus, and sunflowers. The regions of La Rioja, Galicia, Catalonia, and Castilla y León stand out when considering the usage of fungicides as higher concentrations have been detected given that these agricultural areas are primarily dedicated to vineyards. This has caused fungicides to be detected at different concentrations in surface and groundwater. In the Mar Menor, other types of fungicides, such as Myclobutanil, have also been detected.

By interpreting this data and evaluating the relationship between the different crops, regions of Spain, and concentrations of pesticides detected in different environmental ecosystems, researchers are better equipped to establish controls for levels of contamination by pesticides and adopt the necessary measures to avoid contamination, reduce the use of pesticides, or attempt to replace pesticides with other products that pose less of a risk to the environment and human health. This study should assist public and private environmental safety organizations in making decisions to avoid an accumulation of pesticides and prevent damage to different environmental ecosystems. More research is needed in different countries and geographical regions of Europe in order to prevent pesticide contamination brought on by heavy pesticide usage in agriculture.

CRediT authorship contribution statement

All co-authors have contributed equally to this work; MGG, JILS, KASB, MDCC and EPS: Methodology, Writing – original draft, Writing – review & editing. JILS: Funding acquisition. EPS: Supervision, Project administration.

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.

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Appendix A. Supplementary data

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