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Review

Impact of historical legacy pesticides on achieving legislative goals in Europe

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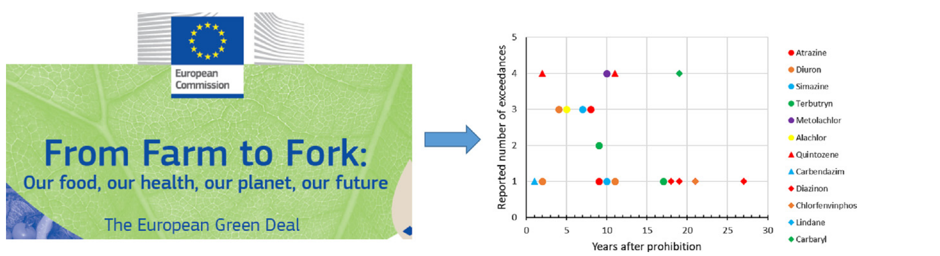
HIGHLIGHTS

- 2030 targets for pesticide reduction may be missed due to static pesticide use.
- Detection of legacy pesticides will compromise achievement of EU targets.
- MOFs and VBSs are promising methods of legacy pesticide remediation.
- Improvement of future EU strategies required for targeting legacy pesticides.

GRAPHICAL ABSTRACT



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ABSTRACT

Pesticides are widely used in agriculture to optimise food production. However, the movement of pesticides into water bodies negatively impacts aquatic environments. The European Union (EU) aims to make food systems fair, healthy and environmentally friendly through its current Farm to Fork strategy. As part of this strategy, the EU plans to reduce the overall use and risk of chemical pesticides by 50 % by 2030. The attainment of this target may be compromised by the prevalence of legacy pesticides arising from historical applications to land, which can persist in the environment for several decades. The current EU Farm to Fork policy overlooks the potential challenges of legacy pesticides and requirements for their remediation. In this review, the current knowledge regarding pesticide use in Europe, as well as pathways of pesticide movement to waterways, are investigated. The issues of legacy pesticides, including exceedances, are examined, and existing and emerging methods of pesticide remediation, particularly of legacy pesticides, are discussed. The fact that some legacy pesticides can be detected in water samples, more than twenty-five years after they were prohibited, highlights the need for improved EU strategies and policies aimed at targeting legacy pesticides in order to meet future targets.

Contents

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1. Introduction

Pesticides are defined as substances that are used to suppress, eradicate or prevent organisms which are considered harmful to crops or nuisance, including biocidal products and plant protection products (EU, 2021a). Pesticide use is not only associated with the mass production of foodstuffs to cater for the global demand, but also their unintended release from both agricultural and urban sectors into non-target ecosystems (Schreiner et al., 2016; Chow et al., 2020; Mojiri et al., 2020). Once released into the environment, pesticides can move through soil or surface water to streams and groundwater, where they can have unintended ecological effects such as accumulation in aquatic organisms and loss of ecosystem biodiversity (Beketov et al., 2013; Stehle and Schulz, 2015; Arisekar et al., 2019). Pesticides also may have carcinogenic, mutagenic, neurotoxic and/or teratogenic effects on human health (Pereira et al., 2015; Harmon O'Driscoll et al., 2022).

Pesticide residues are widespread in soils where crops have been planted and grown (Li and Niu, 2021; Shahid and Khan, 2022; Yang et al., 2022a). The persistence of pesticide residues in soil has been categorised using pesticide half-life (DT_{50}), which is defined as the time required for the chemical concentration under defined conditions to decline to 50 % of the amount at application (Lewis et al., 2016). Non-persistent pesticides have a $DT_{50} < 30$ days, moderately persistent have a DT_{50} of 30–100 days, persistent have a DT_{50} of 100–365 days, and very persistent have a $DT_{50} > 365$ days (Silva et al., 2019). “Persistent” and “very persistent” pesticides can remain in the environment for several decades after their use has been prohibited, giving rise to so-called “legacy” pesticides.

The detection of legacy pesticides in water samples has been mainly attributed to their desorption from soils or sediments, where they may have accumulated during previous pesticide applications (Postigo et al., 2021; Pizzini et al., 2021). Legacy pesticides in the environment arise from a four-step process: (1) application of pesticides to the land, (2) run-off to streams and rivers, (3) partition to sediments, and (4) desorption/resuspension from sediments. Depending on their properties (e.g. polarity, octanol-water partition coefficient), pesticides can be adsorbed onto soil or sediment particles, with hydrophobic pesticides being particularly affected (Khanzada et al., 2020). High pollutant levels in sediments can give rise to further pollution of the waterway due to the possible resuspension of the pollutants in the water during handling, dredging, or disposal of the contaminated sediment (Pizzini et al., 2021; Mishra et al., 2022). Ivanova et al. (2021) demonstrated that the intensive usage of dichlorodiphenyltrichloroethanes (DDT-related pesticides) in the past was observed in river sediments taken from all rivers in Moldova. They suggested that the contamination was from agricultural deposition that had undergone degradation under either aerobic or anaerobic conditions. In a similar study, Qu et al. (2018) found high concentrations (0.6–99.6 $ng \cdot g^{-1}$) of organochlorine pesticides in marine sediments from the Gulfs of Naples and Salerno, which were attributed to historical applications. Pesticide residues can bioaccumulate in soils, soil microorganisms, aquatic microorganisms, air and food chains (Silva et al., 2019; Li, 2022). Urseler et al. (2022) reported on the detection of atrazine in groundwater and bovine milk samples in Argentina. They recorded atrazine concentrations of 1.40 $\mu g \cdot l^{-1}$ in groundwater and 20.97 $\mu g \cdot l^{-1}$ in the milk samples. The latter value is over the limit value for human consumption of 20 $\mu g \cdot l^{-1}$ established by the US EPA (2018). They also concluded that the detection of atrazine in the milk samples indicated that the quality of milk was affected by the groundwater that the cattle consumed. While studies have focused on the relationship between sediment adsorption/desorption and legacy pesticides, there is a deficiency of articles contemplating potential soil legacy issues regarding the role of soil adsorption during the process of pesticide movement to waterways, despite the ongoing Farm to Fork strategy (EU, 2020).

Many international organisations have established regulations regarding pesticides and their permissible detectable concentration limits in the environment (WHO, 2017; US EPA, 2019; EU, 2021b; Australian Government, 2022). Within the European Union (EU), the Regulation on Plant Protection Products (Regulation (EC) No. 1107/2009) on placement of pesticides on the market ensures a high level of protection of both human and animal health and the environment (EU, 2009a). Council Directive 98/83/EC (EU, 1998) on the quality of water intended for human consumption sets the maximum allowable concentration for pesticides, either individually or total, as 0.1 $\mu g \cdot l^{-1}$ or 0.5 $\mu g \cdot l^{-1}$, respectively. At EU level, the monitoring of pesticide residues in soil is not required, in contrast to the monitoring of pesticides in water, which is regulated by the EU Water Framework Directive (EU, 1998).

Sustainable food production in the EU aims to make food systems fair, healthy and environmentally friendly (EU, 2020). As part of this Farm to Fork strategy, the EU plans to reduce the overall use and risk of chemical pesticides by 50 % by 2030. The EU also plans to revise the Sustainable Use of Pesticides Directive (Directive 2009/128/EC), as well as promoting greater use of safe alternative methods of protecting harvests from pests and diseases (EU, 2009b). This will be achieved by making the best use of nature-based, technological and digital solutions to deliver better climatic and environmental results, and reduce and optimise the use of pesticides (EU, 2020). One such solution is the common European agricultural data space which will enhance the competitive sustainability of EU agriculture through the analysis of production, land use, environmental and other data. This will allow a precise and tailored application of production methods at farm level (EU, 2020). The EU's current sustainable food production policy leaves the issues of legacy pesticides unaddressed (EU, 2020). Furthermore, any policy regarding future use of pesticides needs to be linked with remediation of existing problems, including legacy pesticides.

Several physical and chemical treatment approaches, including adsorption, membrane filtration and advanced oxidation processes, as well as biological approaches, such as bioremediation, activated sludge processes and phytoremediation, have been employed to remove pesticides from aqueous solutions (Mojiri et al., 2020). Each method provides its own benefits and drawbacks in terms of both technical and economical aspects (Saleh et al., 2020). Chemical adsorption is more economical, more efficient and faster than biological approaches (Uddin, 2017). While the ease of operation and the flexability of the design are the main advantages of an adsorption method, the main disadvantage is the requirement for a regeneration process (Mojiri et al., 2020). It is therefore important for the future quality of both water and soil that more efficient and effective mitigation methods for the removal of pesticides are developed. One of the most extensively used remediation methods of pesticides is adsorption onto low-cost materials (Mojiri et al., 2020). This is simple and cost-effective. However, the issues of incomplete removal of pesticides and the generation of toxic side products are the main disadvantages of this method (Mojiri et al., 2020; Shahid et al., 2021).

In the context of the above discussion of legacy pesticides and their remediation being beyond the scope of the Farm to Fork strategy, this review will address these knowledge gaps in order to better facilitate achievement of the 2030 targets. To do this, the current knowledge regarding pesticide use in Europe, as well as pathways of loss of pesticides, will be examined. The specific issue of legacy pesticides, including exceedance and persistence in the environment, will be examined in detail. Finally, existing and emerging methods of pesticide mitigation, particularly of legacy pesticides, will be discussed.

2. Methodology

The methodology followed during this review is outlined in Fig. 1. The main steps that were followed were, first, a literature search on legacy pesticides, their mitigation and current regulations; second, refining of papers obtained, and finally, extraction of relevant information from those papers and websites, where appropriate. A detailed literature search was undertaken by searching key words including: pesticide, soil, surface water, groundwater, adsorption, legislation, legacy, and mitigation. The search was limited to peer-reviewed papers published, in English, between 2011 and 2020. A geographical limitation of the twenty-seven countries of the EU was employed for the search. The twenty-seven countries of the EU will be referred to as the "EU-27" throughout this article. Search engines used included databases such as Scopus, as well as publisher-specific search engines including ScienceDirect, the American Chemical Society, and the Royal Society of Chemistry. References from several papers found in these searches were also examined for relevant information. Research papers were selected based on the relevance to the review. A total of 628 articles and a small number of book chapters and reports were reviewed.

Pesticides can be categorised not only by type of use, but also by target organism, the origin of their active substances, or their hazard category. The EU and the Pesticide Properties Database (PPDB) classify pesticides into the categories of herbicide, fungicide, insecticide, and others, while the PPDB also includes physicochemical, human health and ecotoxicological data (Lewis et al., 2016; EU, 2021c). The classification of pesticide used herein is based on pesticidal activity, that is, fungicide, herbicide, insecticide, etc., not on hazard.

The information on pesticide usage required for this review is not readily available. The Eurostat pesticide sales website contains information on pesticide sales across the EU-27, for each individual country, covering the years 2011–2020 (Eurostat – Pesticide Sales, 2022). This information is divided into six pesticide categories (fungicides, herbicides, insecticides, molluscicides, plant growth regulators and other protection products), which are further subdivided in various groupings based on class of compounds to give 157 pages of data. The appropriate herbicide, fungicide and insecticide data for each EU member state were mined from the online data and correlated for use. Land use data were also downloaded from the Eurostat website (Eurostat – Land use, 2022) and the relevant land use data for each EU member state were extracted for use. The kilogram of pesticide used per hectare of land data was calculated for each EU member state by dividing the appropriate herbicide, fungicide and insecticide data by the relevant land use data.

3. Pesticide usage and pathways of loss

3.1. Usage of pesticides in the EU-27

The sale of pesticides used within the EU-27 over the ten-year period (2011–2020) has fluctuated from 356 kt in 2011 to 350 kt in 2020, with the highest sales of 368 kt recorded in 2018 (Fig. 2). The largest year-on-year increase was between 2019 and 2020, when the sales of pesticides increased by 21 kt, while the biggest year-on-year decrease of 33 kt was between 2018 and 2019. In 2019, the weather was the most significant influence on the pesticide market with dry conditions and drought across major areas of Europe, leading to reduced disease pressure and lower demand for both herbicides and fungicides (IHS Markit, n.d.). The top five pesticide consumers across the EU-27 were Spain, France, Italy, Germany and Poland, with average annual sales over the ten-year period of 74, 68,

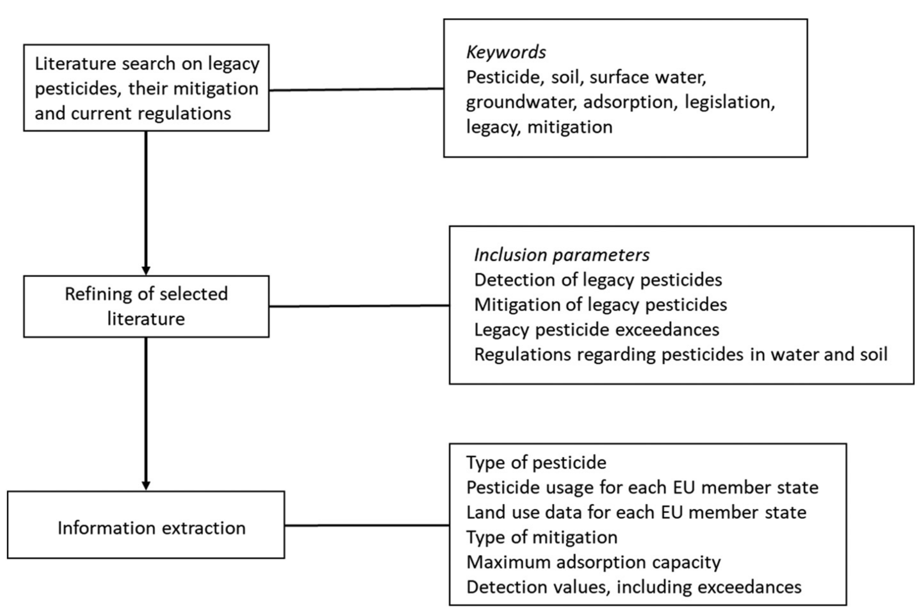

Fig. 1. Methodology flowchart.

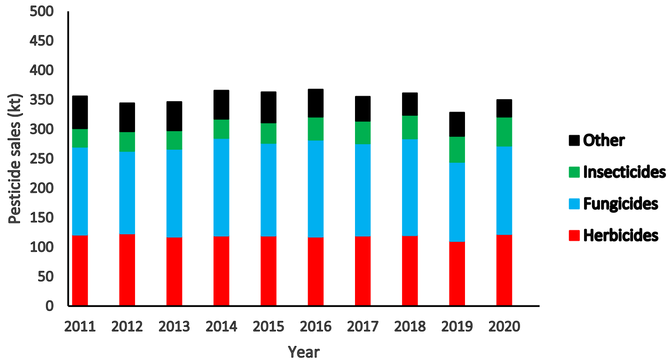

Fig. 2. Pesticide usage, given as classes of pesticides, in the study area, for the years 2011–2020 (Eurostat – Pesticide sales, 2022).

58, 46, and 24 kt, respectively. In contrast, the five countries with the lowest average annual pesticides sales were Malta, Luxembourg, Estonia, Slovenia, and Cyprus with 108, 150, 621, 1046, and 1139 t, respectively. Despite the introduction of the regulations, Regulation No 1107/2009 on Plant Protection Products, Regulation No 396/2005 on Maximum Residue Levels in Food, Directive 2009/128/EC on Sustainable Use of Pesticides, and Regulation No 528/2012 on Biocidal Products (EU, 2005; EU, 2009a; EU, 2009b; EU, 2012), no decline in overall pesticide use has been observed over the past ten years. One reason for this could be the rapid replacement of unapproved pesticides with alternatives by manufacturers.

Fungicides and herbicides were the dominant pesticides used in the EU-27 from 2011 to 2020, as per Fig. 2, accounting for 40–44 % and 30–36 % respectively, of total pesticide sales. A smaller proportion (9–16 %) of pesticides used were insecticides, with the remainder represented by a mixture of plant growth regulators, anti-sprouting agents, and molluscicides. The use of herbicides and fungicides increased from 2011 to 2019, at which point usage decreased by up to 17 % for fungicides. Two possible causes for this decrease were: (1) the increasing strict regulatory environment (IHS Markit, n.d.), and (2) weather conditions. The use of insecticides has increased over the ten-year period, with increases ranging from 35 kt in 2011 to 64 kt in 2020. This increase can be accounted for by such factors as economic growth, the emergence of new pests and diseases, as well as increased insecticide resistance (Sparks et al., 2020).

The variation in pesticide usage per hectare ($kg{\cdot}ha^{-1}$) of agricultural land was considerable between countries within the EU-27, from Ireland with 0.6 $kg{\cdot}ha^{-1}$ up to >11 $kg{\cdot}ha^{-1}$ for Malta (Fig. 3, Table S1). Most countries reported fluctuating usage over the ten-year period (2011–2020). Comparing the amount used per ha in 2011 to that used in 2020, eleven countries, Belgium, Czechia, Denmark, Ireland, Lithuania, Luxembourg, Netherlands, Portugal, Romania, Slovenia, and Sweden, reported decreasing usage of pesticides per hectare (Fig. 3 and Tables S2–4). Sixteen countries in 2020 applied <2 $kg{\cdot}ha^{-1}$, compared to eighteen countries in 2014 (EU, 2017). However, as reported by López-Ballesteros et al. (2022), the available pesticide usage data across the EU-27 in terms of area of application is sparse, with only Spanish and Irish databases including values of both basic and treated/sprayed areas. Focussing on the weight of pesticide applied per unit area can be problematic. While the quantity of pesticide applied can be related to its toxicity, the toxicity of pesticides differs from one pesticide to the next. As a result of these differences, the environmental pollution risk might not be proportional to the quantity of pesticide applied (López-Ballesteros et al., 2022). Jess et al. (2018) reported that, while there was a 34 % reduction in the area of arable crops grown in Northern Ireland since 1992, there was an increase of 37 % in the area treated by pesticides, which was attributed to intensification of agriculture.

Although sixteen countries in the EU-27 applied <2 $kg{\cdot}ha^{-1}$ of pesticides, the overall amount of pesticides being applied across the EU-27 continues to rise. The recent EU strategy on sustainable food production, implemented in 2020, proposes to cut the overall pesticide use in the EU-27 by 50 % by 2030, as well as reducing nutrient losses (especially nitrogen and phosphorus) by 50 % and fertilisers by 20 % (EU, 2020). One possible way of achieving this would be to transition from a grassland-dominated system to a more arable crop-based system. While this could achieve the required reduction in nutrient loss, it could also lead to an increase in pesticide usage, particularly herbicides, required for arable and vegetable crops.

3.2. Pathways of pesticide loss

A significant percentage of pesticides applied in agricultural practices never reach their target organism (Ali et al., 2019), with Schulz (2004) estimating that 10 % of applied pesticides reach non-target areas. As a result, and due to the widespread use of pesticides in agricultural and urban areas, they can migrate to various surface water resources by several pathways, including surface run-off (Chen et al., 2019; Cosgrove et al., 2022), leaching (Cosgrove et al., 2019), spray-drift (Ravier et al., 2005), groundwater inflow (Gzyl et al., 2014) and sub-surface drainage systems (Halbach et al., 2021) (Fig. 4). Surface run-off is the predominant pathway, mainly through heavy rainfall events and snowmelt, particularly in saturated fields, or fields with hilly slopes or fields with shallow level of water table (Jing et al., 2021). The input of pesticides to surface water is particularly high during the main application period of spring and summer, and also increases during rainfall events (Szöcs et al., 2017).

The main factors influencing the transport of pesticides to receptors are adsorption and desorption to and from soil particles (Paszko and Jankowska, 2018), DT_{50} (Fankte et al., 2014), and physico-chemical properties of soil (Boivin et al., 2005). Adsorption is predominantly influenced by the properties and chemical composition of the soil, which is a complex mixture of inorganic materials and organic matter (Leovac et al., 2015), and the physicochemical properties of the pesticide (Kodešová et al., 2011). The adsorption of pesticides on the soil surface determines how pesticides are either transported or degraded, which will, ultimately, determine the concentration of pesticides in both soil and soil solution (Gondar et al., 2013; McGinley et al., 2022). The relationship between the organic content of the soil and pesticide adsorption has been well examined in the literature (Rojas et al., 2013; Wei et al., 2015; Wu et al., 2018). Many soil characteristics have been investigated with regard to pesticide adsorption, including pH (Kodešová et al., 2011; Gondar et al., 2013), organic content (Boivin et al., 2005; Conde-Cid et al., 2019), pore size (Siek and Paszko, 2019), cation exchange capacity (Kodešová et al., 2011), and soil texture (McGinley et al., 2022). McGinley et al. (2022) showed that there is a high potential pesticide transmission risk from soils containing either <20 % clay or >45 % sand.

Mixtures of pesticides are commonly detected in agricultural soils (Schaeffer and Wijntjes, 2022). Silva et al. (2019) analysed 76 target pesticides in 311 agricultural topsoils across the EU and observed that almost 60 % of the soils contained mixtures of two or more residues in various combinations. There are several reasons for this, including pesticides being applied as tank mixtures, repeated pesticide applications during the season, and the binding of pesticides to the soil matrix leading to a reduction in bioavailability, which in turn may lead to significantly reduced degradation. Mixtures of two or more pesticides can form a complex substance that may express properties unique to that combination (de Souza et al., 2020). Research on the impact of such mixtures on soil biota has shown that the threshold value of a pesticide for certain organisms, as defined in the risk assessment, can be exceeded (Sybertz et al., 2020). Mixtures of pesticides can elicit synergistic effects on biota, even if compounds within the mixture are contained in concentrations below the individual level effects (Sybertz et al., 2020). The annual repetition of pesticide spraying can result in high exposure of soil organism to pesticides for long periods of time, since some pesticides can remain in the soil for long periods of time depending on their specific degradation or DT_{50}, as discussed in detail in the next sub-section (Sybertz et al., 2020).

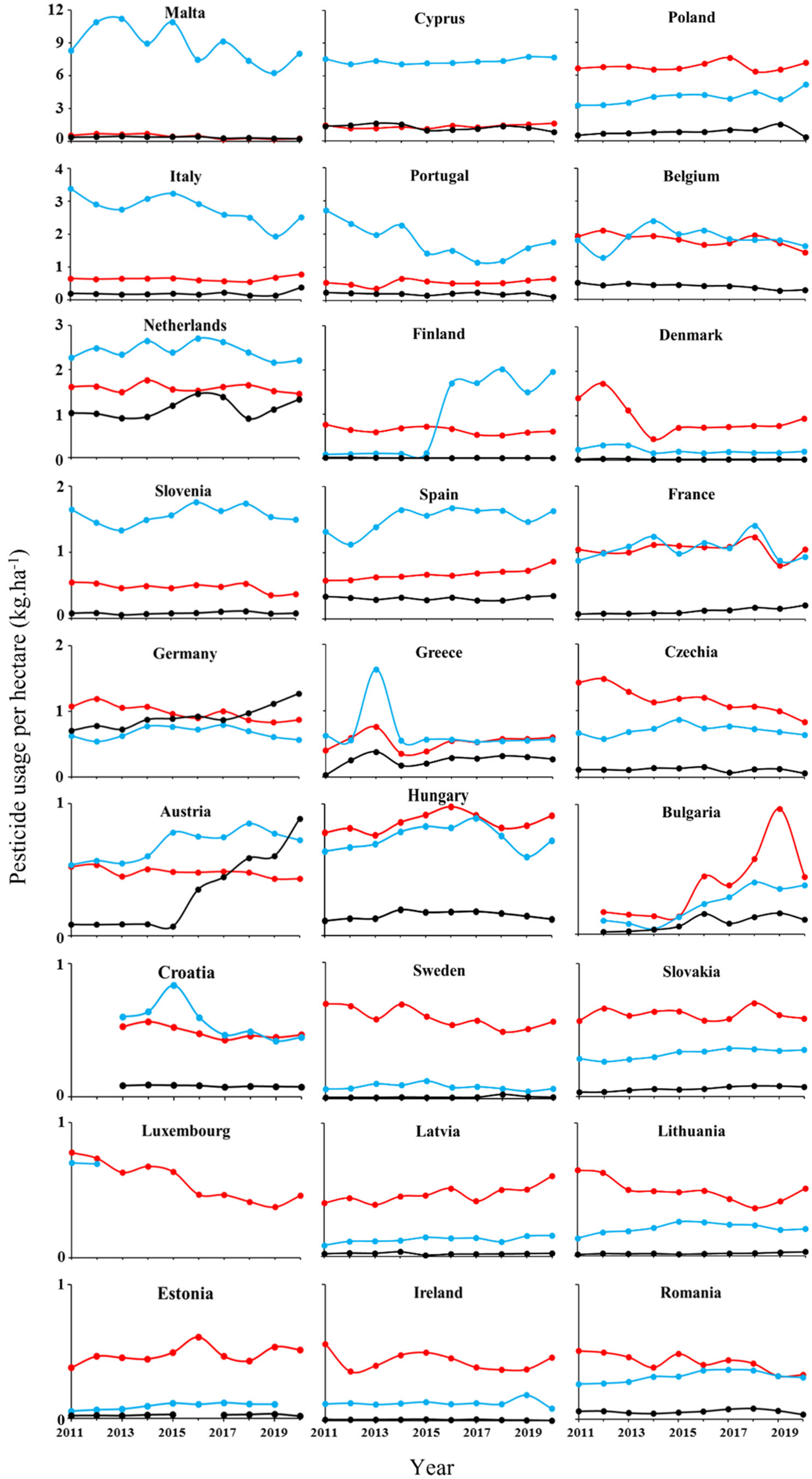

Fig. 3. Tonnes of pesticide used per hectare agricultural land across EU for the years 2011–2020 (Data sources: Eurostat – Pesticide Sales, 2022; Eurostat – Land use, 2022). Herbicides are shown in red, fungicides in blue and insecticides in black. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

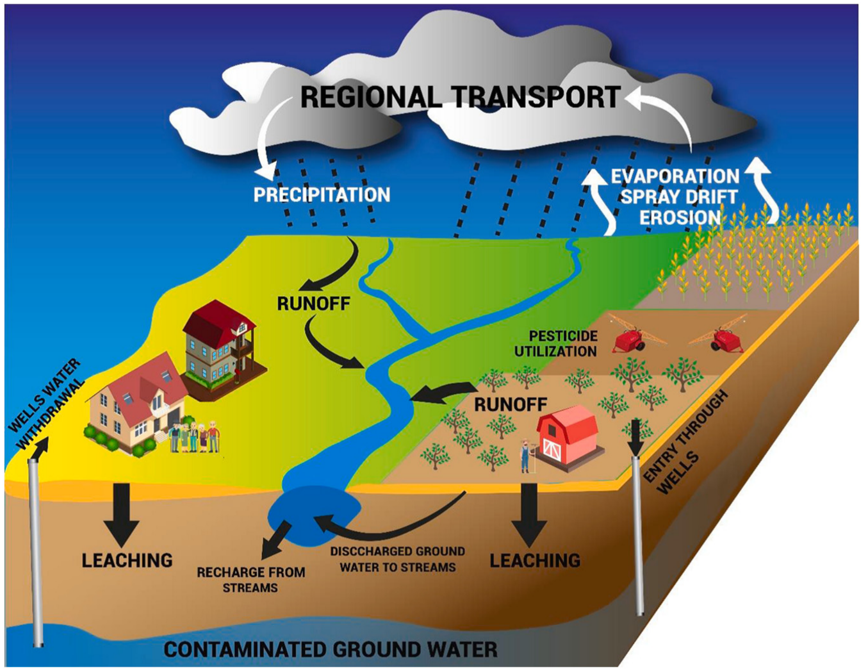

Fig. 4. Pesticide transfer routes to surface and ground water (Lunardi et al., 2022; Reproduced with permission).

4. Legacy issues

Soil microorganisms play an essential role in soil dynamics and nutrient cycling, and have been used as soil quality indicators (Ashworth et al., 2017). They are responsible for regulating gas exchange, inducing microaggregation and altering the biochemical soil environment (White and Rice, 2009). The implementation of a no-tillage process increases a soil's total organic carbon and decreases its pH, thereby affecting the potential adsorption and long-term leaching of pesticides (López-Piñeiro et al., 2019). While a soil's microbial activity may increase under reduced tillage conditions, this does not necessarily imply faster degradation of pesticides (Jørgensen and Spliid, 2016). Increased crop rotations may increase the functions performed by soil microbial communities, which would benefit plant growth. However, because of the increase in crop rotation, extensive pesticide applications may adversely affect the soil richness and microbial diversity. Groundwater makes up the largest reservoir of freshwater in the world (EU, 2008). Approximately 75 % of EU residents rely on groundwater for their drinking water supply (EU, 2008). Agricultural practices can deliver high quantities of pesticides into aquifers, which can make groundwater unsuitable for domestic use (Hakoun et al., 2017; McManus et al., 2017; Aguiar et al., 2017).

Many toxic pesticides have been banned by the EU, although some can persist in the environment for decades (Ccanccapa-Cartagena et al., 2019). In 2022, 452 active substances were approved for use as plant protection products (PPP) in the EU-27, while 937 had been prohibited (EU Pesticides Database, 2022). Of the active substances that were on the market before 1993, 70 % have since been withdrawn (EU, 2017). McKnight et al. (2015) found that several banned pesticides, such as dinitro-*ortho*-cresol (prohibited in 1998) and simazine (prohibited in 2004), were found in either streams, sediments or groundwater in Denmark between 2010 and 2012, either at or above the EU maximum allowed concentration for pesticides of 0.1 $\mu g \cdot l^{-1}$. The number of reported detections of unapproved pesticides that were detected in water sources across Europe for the time period 2011–2020 are shown in Table S5, with several pesticides being detected on numerous occasions in the same year. Fig. 5 shows the top 12 herbicides, fungicides and insecticides, from Table S5, that were detected across the EU-27 after they were not approved by the EU, with several being detected many years after being unapproved for use.

The legislation that defines the maximum allowable concentration of pesticides in drinking water in the EU has been described as the most stringent in the world (Knauer, 2016; Climent et al., 2019). Because of this stringency, many unapproved pesticides continue to be detected in Europe at levels exceeding legal limits in both surface and ground water (Table S4). In total, 233 pesticide detections have been observed in EU waterways after they were prohibited for use in the EU, including some that were banned in the last century, although not all were above the maximum permissible concentration (Table S4). This includes 121 herbicide detections from 29 different herbicides, 27 fungicide detections from 15 different fungicides, and 85 insecticide detections from 27 different insecticides. Soil half-life expresses the potential for degradation of a pesticide in soil (Melin et al., 2020). Given the short DT_{50} of some of these pesticides, they should no longer be detected in surface waters during the time period of 2011 and 2020. Papadakis et al. (2018) suggested that the detection of prometryn, several years after it has been "not approved", was due to the ongoing, illegal use of the herbicide, groundwater inflows into streams, or long-range transport and atmospheric deposition. A further possible

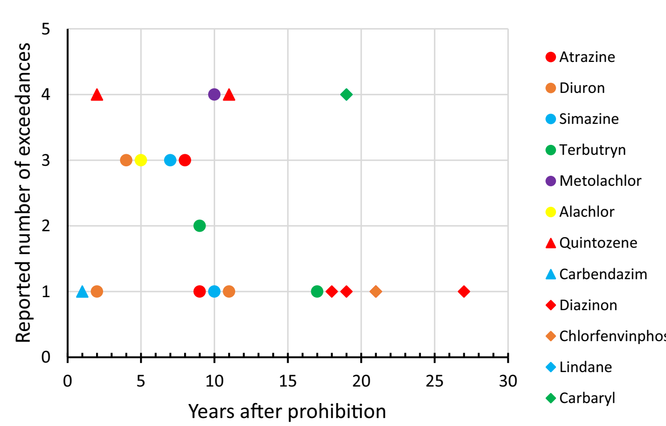

Fig. 5. Timeline of reported exceedances of some selected prohibited pesticides. Herbicides are denoted by circles, fungicides by triangles and insecticides by diamonds (citations are in Table S5).

scenario that could explain their presence is that the pesticides have been bound to soil particles and had only been disturbed prior to the sampling period during which they were detected (Postigo et al., 2021).

The most commonly detected unapproved herbicides in surface waters, for the period 2011–2020, were atrazine (17), diuron (13), simazine (12), terbutryn (11), metolachlor (9) and alachlor (9) (Table S4). Atrazine is strongly hydrophobic, meaning it has a low solubility in water (de Souza et al., 2020). Furthermore, it breaks down slowly in water, having negligible breakdown in neutral or slightly basic solution, with an aqueous DT_{50} of >2 years, which categorises it as "very persistent". In slightly acidic solutions, the aqueous DT_{50} decreases to approximately 84 days (de Souza et al., 2020). According to Fig. 5, atrazine was detected multiple times up to nine years after approval was removed, which is well beyond the DT_{50} value of two years. This highlights how persistent pesticides can be in the soil.

The most commonly detected unapproved fungicides in surface waters, for the period 2011–2020, were hexachlorobenzene (6), quintozene (5), and carbendazim (2) (Table S4). Twelve different fungicides were detected for the period 2011–2020. The range of concentrations found for hexachlorobenzene (0.029–0.048 $\mu g \cdot l^{-1}$) were all below the maximum allowed concentration. Twenty seven different unapproved insecticides were detected in surface waters over the ten year period 2011–2020 (Table S4). The most commonly detected insecticides were diazinon (12), chlorfenvinphos (8), lindane (7) and carbaryl (5) (Table S4). From Fig. 5, diazinon was detected 27 years after approval was removed. The fact that the DT_{50} value for diazinon is 18 days (Lewis et al., 2016) indicates how long these pesticides can remain in the environment. If the pesticide is adsorbed by either soil or sediment, then the DT_{50} tail of the pesticide can obviously be extended indefinitely.

5. Mitigation options

Conventional methods to remove pollutants, including pesticides, from the environment include adsorption, sedimentation, advanced oxidation processes and membrane technologies (Mojiri et al., 2020; Jatoi et al., 2021; Shahid et al., 2021). Although these methods are commonly used, they can involve high operating costs, can generate toxic side products and do not completely remove the pollutants (Mon et al., 2018). The development of a more efficient and safer removal systems is necessary. A complete survey of mitigation systems is beyond this review. A list of these systems, along with relevant references, is given in Table S6. Some new, or emerging, systems are now discussed.

5.1. Metal-organic frameworks

With the development of nanotechnology, Metal Organic Frameworks (MOFs) have emerged as powerful functional materials for the remediation of contaminated water (Mon et al., 2018; Mondol and Jhung, 2021; Wagner et al., 2021; Lunardi et al., 2022). MOFs are arrays of inorganic nodes, either single ions or clusters of ions, connected by organic linkers. The resulting 3D network has a well-built pore structure, and structure tunability, which provides high selectivity for pesticide adsorption. Furthermore, these materials can have a high surface area, typically 3000–4000 $m^2\ g^{-1}$ (Lunardi et al., 2022).

MOFs can be divided into four groups: (1) pristine MOFs, (2) functionalisation of MOFs, (3) MOF-based composites and (4) MOF-derived materials. Pristine MOFs are composed of the inorganic-organic hybrid porous materials without any functionalisation. In the functionalisation of MOFs group, functional groups are incorporated into the MOFs via traditional synthesis conditions using organic linkers identical to the pristine ligand but with attached functional groups, thereby increasing the number of adsorption sites and selectivity (Lunardi et al., 2022). In MOF-based composites, the MOF has been integrated with other functional materials, such as graphene oxide, to increase their adsorption capacity (Lunardi et al., 2022). MOF-derived materials, which are highly porous nano- or mesoporous-materials, are obtained by pyrolysing MOFs under a protective atmosphere, to give a material with improved diffusivity (Lunardi et al., 2022). Table 1 shows some of the recent published research in this area on the adsorption of unapproved pesticides.

Akpinar and Yazaydin (2018) studied the performance of three pristine MOFs (ZIF-8, UiO-66 and UiO-67) for the adsorption of the unapproved herbicide atrazine. Because of their larger pore apertures and large pore size, UiO-67 adsorbed significantly more atrazine than either of the other MOFs. In a further study, Akpinar et al. (2019) showed that the MOF NU-1000 had a maximum adsorption capacity of 36 $mg \cdot g^{-1}$ for atrazine, which was three times larger than that of UiO-67. This increase was due to the increased pore size of NU-1000, which facilitates easier diffusion of the herbicide.

The functionalisation of pristine MOFs is an effective way of enhancing adsorption performances. Yang et al. (2019) modified Cr-MIL-101 with substituted furan and thiophene groups and used them in the detection of four unapproved herbicides, alachlor, diuron, gramoxone (paraquat) and tebuthiuron. They observed that all the functionalised MOFs showed efficient adsorption capacities towards the herbicides, which were preferable to that of the pristine MOF. The adsorption of the unapproved insecticide dimethoate onto amine-modified MOFs was investigated by Abdelhameed et al. (2021a). Different amino ratios were synthesised using aluminium as the metal centre and two different ligands, BDC and $BDC\text{-}NH_2$. Their results showed that a 1:1 ratio of ligands gave an $Al\text{-}(BDC)_{0.5}(BDC\text{-}NH_2)_{0.5}$ MOF which had the highest surface area and the highest adsorption capacity for dimethoate. The 1:1 MOF had a maximum adsorption capacity of 513.4 $mg \cdot g^{-1}$, which was higher than the pristine MOF Al-BDC (154.8 $mg \cdot g^{-1}$) or the amino MOF $Al\text{-}BDC\text{-}NH_2$ (266.9 $mg \cdot g^{-1}$).

MOF-based composites, which are MOFs coupled with other functional materials, have been shown to improve adsorption performance compared to individual substances (Lunardi et al., 2022). Abdelhameed and Emam (2022) synthesised MOF@cotton hybrids by inclusion of MOFs (based on Al, Fe, Ti and Zr) within cotton fibres. These were used in the adsorption of the unapproved pesticides, diazinon and chlorpyrifos. Maximum adsorption capacities were in the range 296.8–464.7 $mg \cdot g^{-1}$, with Zr-MOF@cotton exhibiting the highest adsorption capacity for both pesticides. Nikou et al. (2021) prepared a MOF composite ZIF-8/GO, based on graphene oxide, which was also used as an adsorbent for diazinon and chlorpyrifos. The maximum adsorption capacity for both diazinon and chlorpyrifos, in this case, was found to be 54.3 $mg \cdot g^{-1}$ and 47.2 $mg \cdot g^{-1}$ respectively, which are significantly lower than the values observed by Abdelhameed and Emam (2022) for their composite cotton material. Abdelhameed et al. (2021b) synthesised a porous MOF composite based on cellulose acetate (Cu-BTC@CA). The surface area of the porous CA membrane was significantly increased by incorporation of Cu-BTC within the membrane from 347.2 $m^2 \cdot g^{-1}$ to 965.8 $m^2 \cdot g^{-1}$, while the maximum adsorption capacity for dimethoate increased from 207.8 $mg \cdot g^{-1}$ to 321.9 $m^2 \cdot g^{-1}$ on using the MOF composite rather than the CA membrane itself. Liang et al. (2021) constructed two MOF composites using multi-walled carbon nanotubes as the template to give two MOF-modified aerogel, ZIF8@MPCA and $UiO66\text{-}NH_2$@MPCA. The $UiO66\text{-}NH_2$@MPCA was better at the adsorption of the herbicides, chipton and alachlor, with maximum adsorption capacity values of 246.8 $m^2 \cdot g^{-1}$ and 232.8 $m^2 \cdot g^{-1}$, respectively. The authors ascribed the improved adsorption performance to be due to the large pore at the micron level of MPCA which enabled the fast adsorption of the herbicides.

MOF-derived nanoporous carbon (NPC) and carbon hybrid materials have received much attention recently for pollutant removal, because of their high surface area, versatile porous structure and ease of production (Yu et al., 2021). Zhao et al. (2022) synthesised a hollow MOF-derived NiO/Co@C magnetic nanocomposite using cobalt ions as inducers without the conventional preparation of Fe_3O_4. This nanocomposite was successfully used for the adsorption removal of six organic nitrogen pesticides from waste water. In a comparison with commercial materials (activated carbon, single walled carbon nanotube and multi-walled carbon nanotube),

Table 1
Summary of pesticide adsorption over metal-organic frameworks.

MOF type	Adsorbent	Pesticide	BET surface area ($m^2 \cdot g^{-1}$)	Total pore volume ($cm^3 \cdot g^{-1}$)	Max. capacity ($mg \cdot g^{-1}$)	Reference
Pristine	UiO-67 (Zr)	Atrazine	2345	1.249	11.9	Akpinar and Yazaydin, 2018
	NU-1000 (Zr)	Atrazine	2210	n.d.	36	Akpinar et al., 2019
	CaFu	Imidacloprid	2308	0.11567	467.2	Singh et al., 2021
	MIL-53 (Al)	Dimethoate	866	n.d.	154.8	Abdelhameed et al., 2021a
	Al-TCPP	Chlorantraniliprole	1359	0.8	371.9	Xiao et al., 2021
	UiO-66 (Zr)	Ciprofloxacin	730.6	0.046	111.7	Bayazit and Şahin, 2020
		Naproxen	730.6	0.046	43.9	
	NU-1000 (Zr)	Fenamiphos	1980	n.d.	212.3	González et al., 2021
	Zr-LMOF	Parathion-methyl	1453.2	n.d.	n.d.	He et al., 2019
Modified	MIL-101-C1 (Cr)	Diuron	951.3	0.554	148.97	Yang et al., 2019
		Alachlor	951.3	0.554	122.72	
		Tebuthiuron	951.3	0.554	79.47	
		Gramoxone	951.3	0.554	49.05	
	MIL-101-C2 (Cr)	Diuron	502.6	0.302	135.87	
		Alachlor	502.6	0.302	107.67	
		Tebuthiuron	502.6	0.302	73.35	
		Gramoxone	502.6	0.302	45.41	
	MIL-101-C3 (Cr)	Diuron	490.6	0.282	141.42	
		Alachlor	490.6	0.282	104.02	
		Tebuthiuron	490.6	0.282	69.71	
		Gramoxone	490.6	0.282	50.18	
	MIL-101-C4 (Cr)	Diuron	492.4	0.285	161.25	
		Alachlor	492.4	0.285	105.15	
		Tebuthiuron	492.4	0.285	81.73	
		Gramoxone	492.4	0.285	64.11	
	MIL-101-C5 (Cr)	Diuron	543.2	0.319	186	
		Alachlor	543.2	0.319	149.79	
		Tebuthiuron	543.2	0.319	94.57	
		Gramoxone	543.2	0.319	57.99	
	MIL-53-NH_2 (Al)	Dimethoate	1060	n.d.	266.9	Abdelhameed et al., 2021a
	Al-$(BDC)_{0.5}(BDC\text{-}NH_2)_{0.5}$	Dimethoate	1260	n.d.	513.4	
Composites	Al-MOF@cotton	Diazinon	–	n.d.	367.62	Abdelhameed and Emam, 2022
		Chlorpyrifos	–	n.d.	296.77	
	Fe-MOF@cotton	Diazinon	–	n.d.	402.02	
		Chlorpyrifos	–	n.d.	340.33	
	Ti-MOF@cotton	Diazinon	–	n.d.	459.73	
		Chlorpyrifos	–	n.d.	372.01	
	Zr-MOF@cotton	Diazinon	–	n.d.	464.69	
		Chlorpyrifos	–	n.d.	389.69	
	ZIF8@MPCA	Chipton	–	0.029	160.9	Liang et al., 2021
		Alachlor	–	0.029	196.2	
	UiO66-NH_2@MPCA	Chipton	6.42	0.035	246.8	
		Alachlor	8.87	0.035	232.8	
	Cu-BTC@cellulose acetate	Dimethoate	965.8	n.d.	321.9	Abdelhameed et al., 2021b
	M-ZIF-8@ZIF-67	Fipronil	219	0.07	n.d.	Li et al., 2020
	BSA/PCN-222 (Fe)	Methyl parathion	1015	n.d.	370.4	Sheikhi et al., 2021
		Diazinon	1015	n.d.	400	
	ZIF-8/GO (Zn)	Chlorpyrifos	720.6	0.80	54.3	Nikou et al., 2021
		Diazinon	720.6	0.80	47.2	
	Fe_3O_4@C@UiO-66 (Zr)	Triticonazole	552	0.18	148.81	Wang et al., 2022
		Epoxiconazole	552	0.18	150.15	
		Prothioconazole	552	0.18	188.32	
		Imazaquin	552	0.18	173.31	
		Metalaxyl	552	0.18	135.14	
		Myclobutanil	552	0.18	145.99	
		Hexaconazole	552	0.18	169.49	
		Diniconazole	552	0.18	141.84	
	Fe_3O_4/MIL-101 (Fe)	Fenitrothion	957.48	0.78	209.71	Samadi-Maybodi and Nikou, 2021
Derived	NiO/Co@C	Chlorothalonil	n.d.	n.d.	110.6	Zhao et al., 2022
		Tebuconazole	n.d.	n.d.	43.69	
		Chlorpyrifos	n.d.	n.d.	113.3	
		Butralin	n.d.	n.d.	47.57	
		Deltamethrin	n.d.	n.d.	50.0	
		Pyridaben	n.d.	n.d.	78.8	
	CDM-74 (Zn)	DEET	1395	1.75	340	Bhadra et al., 2020

the extraction efficiency of the MOF-nanocomposite was significantly higher than those of the commercial materials, particularly for the pesticide chlorothalonil.

Although MOFs show promise in pesticide remediation from water, their competitiveness, in terms of cost, selectivity and reusability against other adsorbents, has to be taken into consideration.

5.2. Nanoparticles

Nanotechnology emerged as the scientific innovation of the twenty-first century (Jadoun et al., 2021). The use of nanoparticles for the removal of pesticides from water have been reviewed in many articles (Ighalo et al., 2021; Nguyen et al., 2022; Shan et al., 2022; Kajitvichyanukul et al.,

Table 2
Summary of pesticide adsorption over nanoparticle materials.

NP type	Adsorbent	Pesticide	BET surface area ($m^2 \cdot g^{-1}$)	Total pore volume ($cm^3 \cdot g^{-1}$)	Max. capacity ($mg \cdot g^{-1}$)	Photocatalytic efficiency (%)	Reference
Adsorption	Biochar-alginate	Chlorpyrifos	131.09	0.165	6.25	–	Jacob et al., 2022
	Fe_3O_4@SiO_2@SBA-3-SO_3H MMNP	Paraquat	67.15	0.141	14.7	–	Kouchakinejad et al., 2022
	AG-g-PAO/$CuFe_2O_4$	Chlorpyrifos	1.03	–	769.2	–	Hassanzadeh-Afruzi et al., 2022
	Alum nWTR	Thiamethoxam	129	0.051	50.0	–	El-Kammah et al., 2022
	rGO@ZnO	Chlorpyrifos	79.51	0.065		–	Gulati et al., 2020
Degradation	Co-Fe_3O_4@UiO-66	Fenitrothion	202	0.385	23.6	96.6	Zheng et al., 2022
	Co_3O_4/MCM-41	Methyl parathion	623	0.53	175.2	100	Salam et al., 2020
	Ag@ZnONSt	Methyl parathion	39.72	0.398	–	100	Veerakumar et al., 2021
		Trifluralin	39.72	0.398	–	–	
	Pd@ZnONSt	Methyl parathion	32.34	0.375	–	100	
		Trifluralin	32.34	0.375	–	–	
	PANI/ZnO-$CoMoO_4$	Imidacloprid	142.6	–	–	97.4	Adabavazeh et al., 2021
	FGD-20	Simazine	75.8	–	–	97	Boruah et al., 2021

2022; Mehta et al., 2022; Intisar et al., 2022). Nanoparticles (NPs) are characterised by a large surface area, typically up to 2500 $m^2 \cdot g^{-1}$, which gives them an adsorption rate considerably higher than that of conventional adsorbents. They are more active and faster in the removal and eradication of both inorganic contaminants and organic pollutants, such as pesticides. They have been used to either adsorb or degrade pesticides. Table 2 shows the most recently published material on the adsorption and degradation of prohibited pesticides by NPs.

While adsorption is a scalable and cost-effective method of eliminating pesticides, it has a major disadvantage of creating secondary waste as a result of the adsorption of the pesticides. Photocatalytic degradation is a more ecologically friendly technique, as the degradation process results in the transformation of the pesticides into less hazardous intermediates, which then degrade further to produce H_2O and CO_2 (Qumar et al., 2022). The photodegradation process is governed by the adsorption capability of the organic contaminants of the photocatalyst surface. However, to achieve a high photodegradation rate, the pesticide adsorption must also be effective. A further disadvantage of the degradation process is that degradation efficiency was found to be negligible in the absence of the photocatalyst, indicating that light intensity is an important factor influencing the efficiency process of the photocatalytic degradation of pesticides (Veerakumar et al., 2021; Adabavazeh et al., 2021).

5.3. Membrane removal of pesticides

Membrane processes, such as nanofiltration, reverse osmosis and forward osmosis are very efficient in the removal of microcontaminants, such as pesticides, from water sources (Fujioka et al., 2020; Khanzada et al., 2020). Vitola et al. (2021) developed a phosphotriesterase-loaded membrane which was capable of degrading the pesticide paraoxon-ethyl in vegetative water containing biomolecules similar in size and structure to the pesticide. The stability of the phosphotriesterase-loaded membrane was four times higher in vegetative waters than the free enzyme. The immobilised enzyme also showed activity towards the pesticide degradation in vegetative water after four months, whereas the free enzyme showed activity for three weeks only.

Yang et al. (2022b) developed an NH_2-MIL-125 (Ti)-based filter paper membrane, which was used to remove organophosphorus pesticides, including fenitrothion, from aqueous solutions. The combination of the Ti-based MOF with the filter paper created a low-cost membrane which resulted in the rapid separation of samples and the removal of organophosphorus pesticides. When compared with the MOF itself, the filter paper membrane demonstrated the same removal efficiency of organophosphorus pesticides.

Khairkar et al. (2020) fabricated hydrophobic membranes for pesticide removal using polyamide-polydimethylsiloxane chemistries. These reverse osmosis membranes exhibited increased pesticide adsorption from the feed waters compared to commercial reverse osmosis membranes (95 % removal of imidacloprid compared to 89 % for the commercial membrane). The procedure for the synthesis of the membranes is cost effective and easy to incorporate into membrane manufacturing processes.

Lopes et al. (2020) evaluated the potential of a membrane bioreactor to treat effluents from a fruit processing factory for the removal of pesticides. The removal efficiency of atrazine by the reactor was only partial (45 %), which highlighted the requirement of other treatment technologies to get complete removal of the pesticide. When combining the membrane reactor with a post-treatment of activated carbon, the removal efficiency increased to >99.9 %, indicating that the membrane reactor in combination with an activated carbon post-treatment system was very successful.

Mohammed and Jaber (2022) synthesised a Pickering emulsion liquid membrane, using Fe_3O_4 nanoparticles and oleic acid, for the extraction of Abamectin from aqueous solutions. Extraction percentages of 99 % were obtained in 10 min, with minimal breakage percentage. The membrane could be recycled for three cycles with no loss of extraction capability. Krishnan et al. (2022) modified a polyvinylidene fluoride (PVDF) membrane with either an amine or a bismuth tungstate (BWO) modified MOF for the reduction and photodegradation of pirimicarb. The BWO-modified MOF membrane showed the best removal of the pesticide (84 %) and also the best photocatalytic degradation of the pesticide (86 %).

5.4. Semiconductors

Semiconductor-assisted photocatalysis, based on the use of TiO_2, is a well-studied, advanced oxidation process for the degradation of pollutants, including pesticides (Luna-Sanguino et al., 2020; Shafiee et al., 2022). Some of the advantages of this semiconductor are its cheap price, stability and chemical and biological inertness. Zeshan et al. (2022) discuss the basic mechanism of TiO_2-based photocatalysis, types of reactors used for photocatalysis, and conditions for pesticide demineralisation into non-hazardous compounds, such as CO_2 and H_2O. They demonstrated that advancements in the characteristics of TiO_2-based photocatalysts by doping or composites enhanced the efficiency of minaralisation. They also showed that TiO_2-based photocatalysts mineralised the pesticides more efficiently in natural sunlight, thereby promoting their potential use in pilot-scale experiments.

5.5. Vegetated buffers

Vegetated buffer strips (VBS) can protect streams and other wetland habitats, as well as improving water quality (Lovell and Sullivan, 2006). A vegetated buffer strip is defined as an area of land located between land used for agriculture and land not in agricultural production (e.g., forest, stream, river, pond). A VBS can decrease the amount of pesticide transported to surface water from fields during rainfall (Wang et al., 2018).

Villamizar et al. (2020) reported a study of mitigation approaches to compare the efficacy of propyzamide removal in a 900-ha headwater catchment. They observed that increasing the VBS to 20-m-width would be the most effective mitigation intervention. Prosser et al. (2020) reviewed the efficacy of VBS to reduce pesticide transport into surface waters from agricultural fields, and found that it varied widely, ranging from 10 to 100 %. They also observed that the majority of studies investigating the ability of VBS to limit pesticide transport had studied herbicides (89 %). While the study of the transport of fungicides and insecticides is limited, the authors believed that the buffers would be as effective at mitigating the transport of fungicides and insecticides as they were at limiting the transport of herbicides (Prosser et al., 2020). Lorenz et al. (2022) showed that the presence of VBS contributed to a reduction in pesticide risk compared to when no VBS were present. Furthermore, they demonstrated, through the use of modeling, that the risk to freshwaters was reduced by 29 %, if a 5-m buffer strip was used, and 47 %, if a 10-m buffer strip was used. Andrade et al. (2021) demonstrated that the pesticide concentration found in run-off water depended on the pesticide solubility, the slope of the streams and the percentage of woody riparian vegetation cover, and that all of these factors should be taken into account when designing mitigation measures for the run-off of pesticides. Butkovskyi et al. (2021) evaluated the use of novel bed mixtures, consisting of pumice, vermiculite and water superabsorbent polymer (SAP), for the retention of ionic and water soluble pesticides in unplanted and planted pot experiments. They observed that mixtures of all three materials resulted in high retention of both hydrophobic and hydrophilic pesticides, but with lower leaching potential compared to systems without SAP. They suggested that mixtures of such materials would provide treatment options in VBS.

Le Cor et al. (2021) demonstrated the buffering effect of a pond, as a VBS. Upstream of the pond, ecotoxicological standards were exceeded with pesticide concentrations of up to 23.9 $\mu g \cdot l^{-1}$, while downstream of the pond, the concentration of the pesticides reduced by 90 % with few exceedances and a maximum concentration of 0.5 $\mu g \cdot l^{-1}$, reflecting significant water quality improvement. Chaumet et al. (2022) also demonstrated the buffering effect of a pond, which reduced between 29 and 56 % of the targeted pesticide molecules (metolachlor, boscalid, epoxiconazole, tebuconazole, aclonifen, and pendimethalin). They argued that riparian wetlands should be among the beneficial suggestions for agricultural land management, which could be further enhanced by promoting vegetation as an alternative route to pesticide retention or degradation.

6. Management implications across Europe

Following the introduction of the EU Directive on Sustainable Use of Pesticides in 2009 (EU, 2009b), many papers have been published regarding measures for reducing pesticide use. A recent review focussed on the effectiveness of public policy instruments in reducing pesticide use by farmers in Europe (Lee et al., 2019). Bans, zoning, monitoring and penalties were placed in the regulatory domain, while those of the certification, training, and advisory services were in the informative domain. While the review determined that no specific instrument was guaranteed to reduce pesticide use, they suggested that measures were frequently identified as ineffective if based on the sole use of regulatory-based instruments, namely bans and prescriptions (maximum doses or pesticide levels). On the other hand, prescriptions and subsidies, prescriptions and advisory services, or prescriptions, taxes, training, monitoring and advisory services, were seen as most beneficial to pesticide reduction.

In a separate review of pesticide monitoring to assess surface water quality, Chow et al. (2020) attributed a reduction in pesticide use as the main factor linked to reductions in aquatic pesticide concentration. The reduction in pesticide use included bans and use restrictions. While the restriction or banning of a pesticide is a powerful mitigation measure, directly affecting the quantity of pesticide available for transport to surface waters, the benefits can be obscured if a banned pesticide is simply replaced by another pesticide. Furthermore, the effectiveness of a pesticide use regulation depends on the quantity of pesticide that a farmer uses, which is influenced by both the weather conditions and pest pressure.

As previously mentioned, the latest Farm to Fork strategy (EU, 2020) aims to cut chemical pesticide use across the EU-27 by 50 % in 2030. To achieve this, the Commission intends to "revise the Sustainable Use of Pesticides Directive (SUD; EU, 2009b), enhance provisions on integrated pest management (IPM) and promote greater use of safe alternative ways of protecting harvests from pests and diseases" (EU, 2020). The IPM will be one of the main tools in reducing the use and dependence on chemical pesticides. One approach, that is intended to achieve this goal, is the placing of pesticides containing biologically-active substances on the market. In a recent EU factsheet, it was noted that, although member states had made progress implementing the SUD, fewer than one in three states had completed the review of their National Action Plan within the five-year legal deadline (EU, 2021a).

The target of reducing chemical pesticide use by 50 % by 2030 has come under attack from pesticide and agribusiness lobbyists, who claim that the target is overly ambitious and unrealistic for EU farmers to achieve (Save bees and farmers, 2020). The pesticide industry also called for an impact assessment to be made that would look at possible negative effects of the legislation on EU agriculture. The call for an impact assessment has been supported by a large number of EU member states. In response, the EU Commission has said that not enough was being done to reduce the level of pesticide usage across the EU by member states, resulting in the proposed strategy (Save bees and farmers, 2020).

Farm Europe is a think tank that focuses on all EU policy areas that impact on rural business. They have reported that the impact of the Farm to Fork strategy (EU, 2020) on the agricultural sector across Europe will cause revenues of farmers to plummet by up to € 5000 on average per holding (FarmEurope, 2021). They also believe that the EU net trade position will worsen, and that there will be an increase in producer prices that would cost consumer prices to rise across the EU (FarmEurope, 2021). They believe that, as a result of this strategy, agricultural sectors will face massive restructuring, with the abandonment of the least productive lands and a huge reduction in the number of farm holdings. A report from the Economic Research Service of the United States Department of Agriculture reported that, if the Farm to Fork Strategy was implemented by the EU, the impacts would include a decline in agricultural production by up to 12 %, an increase in food costs, and a significant reduction in the EU's gross domestic product (GDP: ERS USDA, 2020).

There has been considerable media coverage regarding the 50 % chemical pesticide reduction by the year 2030. However, the positive messaging, as proposed by the EU Commission, has largely been lost. This would suggest that the informative instrument, discussed by Lee et al. (2019), has not worked properly and now it appears as if the EU Commission is trying to force this strategy through by means of regulation instruments.

7. Conclusions

The EU strategy to make food production environmentally friendly by reducing the overall use of chemical pesticides by 50 % by 2030 may be too ambitious, given that usage has remained relatively constant since 2011. Non-attainment of this target may be further attributed to legacy pesticides, which have been detected in water bodies across the EU-27. The omission of legacy pesticides from the current EU Farm to Fork strategy, and the requirement of a maximum allowable concentration of pesticides in soils or sediments, may be a serious omission.

Among several emerging mitigation methods for the removal of pesticides from water, MOFs are among the most promising, due to their well-defined pore structure and high surface areas. One disadvantage that all adsorbent materials have is the removal of the pesticides from the adsorbents, and the interactions of the cleaning materials with the pesticides requires further exploration. The most cost-effective method is the use of VBS to protect streams and other wetland habitats as well as improving water quality. Buffer strips of at least 5 m width are appropriate to substantially reduce the risk to freshwaters posed by pesticide use. Further research is required to investigate the applicability and cost-effectiveness of potential remediation processes of pesticides on larger scales.

CRediT authorship contribution statement

J. McGinley: Methodology, Investigation, Formal analysis, Writing – original draft, Writing – review & editing. **M.G. Healy:** Conceptualization, Funding acquisition, Project administration, Supervision, Writing – review & editing. **P.C. Ryan:** Writing – review & editing. **Harmon O'Driscoll:** Writing – review & editing. **P.-E. Mellander:** Writing – review & editing. **L. Morrison:** Writing – review & editing. **A. Siggins:** Conceptualization, Funding acquisition, Project administration, Supervision, Writing – review & editing.

Data availability

All data is included, or cited, in the manuscript.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Dr. Alma Siggins reports financial support was provided by Environmental Protection Agency. Dr. Alma Siggins reports financial support was provided by Government of Ireland Department of Agriculture Food and the Marine.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.162312.

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