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Review

Interactions of Microplastics with Pesticides in Soils and Their Ecotoxicological Implications

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Highlights:

1. Soil pollution by microplastics (MPs) has steadily grown in recent years.
2. MPs may interact with pesticides that reach the soil during pest control.
3. MPs increase adsorption and reduce transport and degradation of pesticides.
4. No major effects of soil properties on MP–pesticide interactions.
5. Joint MPs–pesticides exhibit variable toxic effects on soil organisms.

Abstract: In the middle of the 20th century, the production of plastics exploded worldwide because of their low cost and the versatility of their applications. However, since plastic debris is highly resistant to environmental degradation, a growing presence of plastics in all the ecosystems has been confirmed. Among them, plastic particles < 5 mm, also known as microplastics (MPs), are of special concern because they are dispersed in aerial, terrestrial and aquatic environments, being the soil the main environmental sink of these contaminants. Due to their large specific surface area and hydrophobicity, MPs are considered good adsorbents for other environmental organic pollutants also present in terrestrial ecosystems, such as pharmaceuticals, personal-care products or pesticides with which they can interact and thus modify their environmental fate. In this review article, we examine the recent literature (from 2017 to 2022) to get a better understanding of the environmental fate of pesticides in soil (adsorption, mobility and/or degradation) when they are simultaneously present with MPs and the ecological risks on living organisms of the interactions between MPs and pesticides in soil. More studies are needed to fully understand the toxicological impact of the copresence in soil of pesticides and MPs.

Keywords: soil plastisphere; pesticides; transport; uptake; ecological risk

Citation: Peña, A.; Rodríguez-Liébana, J.A.; Delgado-Moreno, L. Interactions of Microplastics with Pesticides in Soils and Their Ecotoxicological Implications. *Agronomy* **2023**, *13*, 701. https://doi.org/10.3390/agronomy13030701

Academic Editors: María Sonia Rodríguez-Cruz and Jesús M. Marín-Benito

Received: 31 January 2023
Revised: 23 February 2023
Accepted: 23 February 2023
Published: 27 February 2023

1. Introduction

The industrial production of plastics exploded in the mid-20th century. Since then, plastics have directly influenced the global economy, and have been mass-produced in a large number of industrial sectors due to their low cost, and great durability and versatility for varied applications [1]. Before and during the COVID crisis, plastic production increased worldwide from 359 t in 2018 to 369 t in 2020, with the highest production in Asia (49%) and specifically in China (32%). The European demand of plastics, mainly for packaging (ca. 40%), represented a total of 49.1 $\times$ 10^6 t in 2020, with Germany (23.3%) and Italy (14.1%) at the head, among the different European countries [2].

Despite their excellent properties and cost effectiveness, conventional plastics produced from non-renewable resources have a major drawback: they are extremely resistant to natural degradation processes. In other words, they persist in the environment for

long periods of time, with half-lives between 0.035 and 9000 years [3]. At present, a great effort is being made to reduce the impact of plastics in the environment through the establishment of different measures such as more stringent regulations on their use and disposal in landfills, the improvement of their reusability and recyclability, or their total or partial replacement by novel materials with similar properties and less impact (for instance, bioplastics and/or biodegradable and compostable polymers) [4,5]. Nevertheless, plastic debris is frequently pointed out as the protagonist of serious pollution episodes of natural ecosystems. Of special concern are plastic particles smaller than 5 mm, commonly referred to as microplastics (MPs), and even smaller (less than 0.1 μm or than 1 μm, depending on the authors), defined as nanoplastics (NPs) [6,7], which have emerged in recent years as main contributors of pollution since they are dispersed in aerial, terrestrial and aquatic environments. Hence, these emerging pollutants may potentially accumulate in the trophic chain and cause detrimental effects on plants, animals and human beings [7].

Monitoring studies have shown worldwide the presence of MPs in aquatic sources, with polypropylene (PP) and polyethylene (PE) as the most frequently found [8,9]. Already in the 1970s, Carpenter and Smith [10] alerted about the risks associated with the increasing production of plastics and their uncontrolled disposal. Although the concentration of MPs in the aquatic environments is continuously increasing and raising public concern, MPs are usually more abundant in soil than in water. In fact, their content in terrestrial ecosystems has been estimated to be between 4 and 23 times higher than in the oceans [11]. Furthermore, the presence of MPs in freshwater environments has been reported to be a direct consequence of land transference or runoff [12,13]. However, when Xu et al. [14] studied a large watershed estuarine area of Bohai Sea, they found double as much MP in the soil (40–980/kg) than in the adjacent sediment (6.7–320/kg). The authors were unable to establish relationships between the two compartments, which suggests low transfer between them, acting the soil as a sink for MPs. In addition, MP vertical and horizontal transport will depend on the type and density of the vegetation covering its surface, on the topography and on the rainfall amount [15]. However, the zones heavily polluted with MPs are mainly placed in densely populated areas and their abundance diminishes with altitude [16].

Apart from the impact that MPs produce by themselves when released into soil environments, they may also interact and play a crucial role in the fate of other contaminants. MPs and NPs have large specific surface area and hydrophobicity which makes them good adsorbents for environmental organic pollutants [7,9,17], and consequently capable to act as vectors of contaminants in different ecosystems. In addition, MPs might alter soil microbiota structure and metabolic status [18], which directly affects the degradation of organic pollutants in soils and their persistence [19]. Therefore, the risk assessment for environmental organic pollution should consider the presence and composition of MPs in soil and water to accurately establish environmental risk levels and propose management practices to minimize their environmental and human health impact. In this sense, environmental legislations should consider the future inputs in soil of potentially harmful plastics, including precaution measures and providing clear guidelines [20,21].

Among organic pollutants, pesticides deserve special attention since they are used extensively and continuously in modern agriculture and cause environmental contamination and public health problems [22]. Pesticides represent a broad class of chemicals with different properties. Their occurrence and behaviors in the environment have been comprehensively studied but there is still little information about the impact of MPs on the transport, exposition routes and toxicity of pesticides. This review is a compilation of recent scientific literature dealing with the interactions between MPs and pesticides to better understand their impact on the pesticide environmental distribution and their ecotoxicological risk. The information found was organized into four sections: (i) entry routes of MPs to agricultural soils; (ii) effects of MPs on soil health and functioning; (iii) role of MPs on the adsorption, degradation and mobility of pesticides; and (iv) effect of

MPs–pesticide interactions on living organisms. Knowledge gaps for future research are subsequently outlined.

2. Sources of Plastics in Agricultural Soils

Monitoring studies in the last decades has shown worldwide the presence of MPs in aquatic sources, both in marine and freshwater environments [23,24], even in remote high mountains lakes [25]. Although previously a few works had considered the presence of plastics in terrestrial environments, it was not until 2018 when several articles [26,27] and reviews [6,28,29] alerted about the presence of plastics in agricultural soils, and since then, the related scientific literature has grown exponentially. However, one of the main challenges for establishing the actual level of MP pollution in soil is the development of robust and reliable measurement methods. This, together with the renewed general interest for MPs, has led to the development of novel analytical technologies [30–32] aimed to simplify and standardize the existing laborious protocols.

According to recent review reports, landfills, beaches, urban areas and agricultural lands are the soil ecosystem areas most largely affected by MPs [28,33]. In general, MPs reach soils by either direct addition of plastics manufactured from varied industrial sectors (for instance personal care and hygiene products, paints, adhesives, pharmaceuticals or synthetic agrochemicals), or indirectly after embrittlement and subsequent fragmentation of plastic parts from varied sources such as landfills, household items, or agricultural practices [6,11,34]. Among all the entry routes, municipal solid waste, wastewater treatment plants (WWTPs) and, even, atmospheric deposition after wind and rain events have been identified as major contributors to soil pollution by MPs [35–39].

Focusing on agricultural soils, the sources of pollution by MPs have been recently reviewed and consider direct (plastic mulching, plastic pipes, plastics used to cover plants and, in general, plastic materials used in agriculture) or indirect inputs (sewage sludge, compost, irrigation, etc) [40–42]. In agricultural soils, Huerta Lwanga et al. [42] found >3000 MP/kg soil, increasing to >5000 MP/kg soil for some agricultural practices, such as sewage sludge amendment or plastic mulching (mostly PE). Wang et al. [41] reported higher values (>42,000 MP/kg) in Chinese agricultural soil, while very high values were found in suburban soil (4.1×10^5 MP/kg) [40]. From the above results, mulching (mulch films and greenhouse materials) has been identified as a major contributor of MP entry in agricultural soils [33,43]. Meng et al. [43] also point to high-intensity machine tillage as responsible for higher fragmentation of macro-plastics and more severe MP pollution. In areas with extensive mulching, the combined effect of light exposure and mechanical forces like tillage favors the formation of MPs [44].

Indirect plastic input routes are irrigation (polluted water, wastewater) and use of amendments rich in organic matter, such as urban sewage sludge or compost, which are agricultural practices that are very usually employed in OC-poor soils or in arid/semiarid environments [45–47]. The WWTPs are usually very efficient in removing MPs, being able to induce a decrease of >90% and up to >98% in some cases [48–51]. Apart from the specific wastewater treatment, the efficiency of MP removal depends greatly on the nature, shape and size of MPs, with fibers generally being less retained. Despite the high removal efficiency and due to the large volumes processed, the small fractions of MPs released from WWTPs result in significant amounts of MPs entering the environment when agricultural soils are irrigated with wastewater.

The second main indirect way of MP entry to the soil is the use of organic amendments, both fresh and after biological treatment. Tan et al. [52] reported that, among different organic materials including food waste, livestock manure and sludge, the latter has greater capability to accumulate MPs followed by food wastes and manure. The major fraction of MPs included PE, PP and polyethylene terephtalate (PET), both as fibers and films. The presence of cracks, holes and other defects in MPs after biological treatment (for example composting) indicated that MPs could be further fragmented during the process, which implies greater ecological risks. To avoid this, the authors recommended the minimization

of MPs input into the waste before the treatments. Regarding this, Yang et al. [53] demonstrated that the removal of plastic packages reduced the amount of MPs and the variability of polymer types in a digestate produced through anaerobic digestion of biogenic wastes.

Due to their effective removal from wastewaters in WWTPs, MPs concentrate in sewage sludge, passing to the agricultural lands when it is applied as soil amendment [54–58]. It has been estimated that application of sludges can provide up to 430,000 t of MPs to the agricultural lands in Europe [59]. The type of treatment in the WWTP affects the ability to reduce MPs in the effluents. Bayo et al. [60] found that fibers were less efficiently retained in WWTPs than particulate MPs (56.2 vs. 90.0%) suggesting that some purification treatments clearly discriminate between MP forms. Similarly, in a study in China, the dominance in effluents of fibers (76.7–90.0%) and small particle sizes (<2.0 mm, 62.5–81.5%) suggested that they escaped easily from WWTPs [61]. Recently, van den Berg et al. [57] studied the accumulation of MPs in 16 agricultural fields located in the east of Spain with 0–8 sewage sludge applications at a rate of 20–22 t ha^{-1} per application. Soils without addition of sewage sludge had an average load of 930 ± 740 and 1100 ± 570 for low- (<1 g cm^{-3}) and high-density (>1 g cm^{-3}) MPs, respectively. After soil amendment, these amounts increased to 2130 ± 950 for light density plastics and to 3060 ± 1680 for high-density plastics. On average, each consecutive application of sewage sludge enhanced the concentration of MPs by 280 MPs kg^{-1} for low-density plastics and 430 MPs kg^{-1} for high-density plastics. In other words, consecutive application of sewage sludges led to the accumulation of MPs in soils.

Rough estimates point to an annual deposit on European farmlands of 63,000–430,000 t of MPs through sewage sludge application [62]. This situation creates a pathway for the entrance of MPs in the soil environment with unknown consequences. For instance, although Hernández-Arenas et al. [63] found that sewage sludge containing MPs fostered the growth of tomato plants, it also delayed and reduced fruit production, but it was not completely clear whether other factors were simultaneously occurring. It has also been reported that the application of MP-containing sewage sludge widened MPs contamination to nearby land with no history of direct sewage application [64]. On the other hand, neither soil erosion nor surface runoff have been identified as relevant mechanisms of MPs transport/export processes, pointing to the fact that agricultural soils can be considered as long-term accumulators of MPs in arid and semi-arid regions [65,66].

Compost represents another major carrier of MPs into agroecosystems [67,68]. Irrespective of the origin of the materials to be composted, fragmentation processes of plastics into MPs accelerate under composting conditions, thus posing a threat of agricultural soil pollution when composts are used as organic amendments. Composting of the organic fraction of municipal solid wastes has been recently reported to produce a total of 10–30 plastic particles g^{-1} dry compost, from which MPs accounted for 5–20 particles [69]. These authors conducted a comprehensive analysis focusing on the shapes and types of the MPs present in the compost, and highlighted the dominance of fibers. Moreover, they found that PE, polystyrene (PS), polyester, PP, polyvinyl chloride (PVC) and acrylic polymers (in order of abundance) represented 94% of the MPs items. In a prior study, van Schothorst et al. [70] urged for the need to establish threshold levels for MPs in composts in order to effectively regulate the total influx of plastic pollution to agricultural soils. They demonstrated that a compost produced from municipal organic waste had major potential to accumulate MPs (PE and PP in the size range 0.03–2 mm) than that obtained after the composting of gardening waste. When used as organic fertilizers in two Dutch farmlands with an annual compost application of 10 t ha^{-1}, the composts led to MPs accumulation in soil samples, averaging 888 ± 500 MPs kg^{-1} soil. After the composting of biowaste and sewage sludge, Scopetani et al. [71] detected a concentration of MPs in compost of 6.6 ± 1.5 pieces kg^{-1}. They estimated that 4–23 × 10^7 MP pieces ha^{-1} $year^{-1}$ could reach agricultural soils fertilized with such compost by following common recommendations for compost application. The addition of composted household organic waste has been also reported to release MPs on agricultural soils. In this sense, Gui et al. [72] concluded that the composting of rural

domestic waste was a significant source of MPs in soils, since MPs amount in compost related to both the quantity and type of plastic before the production of the compost. They found 2400 ± 358 MPs items kg^{-1} dry compost, with polyester, PP and PE in the form of fibers and films as the most common MP types. An interesting observation from this study is that, under the influence of composting conditions, a piece of either expanded PS, PP and PE could release 4–63 MP particles at the end of the process.

3. Effect of MPs on Soil Health and Functioning

As indicated before, soil is the main sink of MPs in the environment [11]. The presence of MPs in the soil profile may alter some relevant soil properties related to the behavior of pesticides in soil. In this context, a comprehensive revision of the impact of MPs on soil properties and functions, especially those affecting the environmental fate of pesticides, is fundamental to accomplishing the ultimate aim of this review paper.

MPs adsorb on soil by surface sorption, electrostatic or hydrophobic interactions, and this sorption increases with soil organic carbon (OC) and Fe/Al oxide contents but decreases with clay content and increasing values of pH and ionic strength [73–75]. MPs will be mainly concentrated in top soil layers, because infiltration capacity is very low [65,66], or because plants' root growth will accumulate them in the top soil [76].

The presence of plastics in soil has been reported to affect some relevant physicochemical soil properties, although contradictory results about the trends observed are often found. In general, the studies analyzed agree that MPs, especially fibers, reduce the soil bulk density and modify the size distribution and stability of soil aggregates altering soil pore structure and water transport [77]. Therefore, MPs may potentially play a crucial role in the leaching of pollutants to deeper soil layers.

These effects in soils have been proven in alterations in the performance of some crops, such as in the water-use efficiency of maize [78] or in the blockage of root growth of garden cress [79]. De Souza Machado et al. [80,81] found that a wide variety of plastics differing in length and diameter reduced, in general, soil bulk density because plastics are usually less dense than soil. Moreover, some MPs affected the soil water holding capacity or induced a decrease in the water-stable aggregates. In line with this, the presence of large-sized PE in soil (2–10 mm) has been reported to significantly accelerate the water evaporation process from soil, forming surface cracks, because they destroy the integrity of the soil surface structure and reduce the tensile strength of the soil surface at their interface [82]. However, Zhang et al. [83] found no obvious changes in the soil density or saturated hydraulic conductivity in clay-like soil in both pot and field trials. The same authors found, only in the pot experiment, an increase in the contents of water stable large macroaggregates. This divergence was explained because of differences in the physical and chemical characteristics of the soils. The results of a meta-analysis [84] confirmed most of the reported changes in soil properties, such as making the soil more porous or increasing its water retention, but without relevant changes in soil microbial diversity, suggesting that MPs would occupy physical soil space but would not be integrated into the soil biophysical matrix.

The presence of MPs has also led to increased [85], decreased [86] or not changed [87] soil pH, depending on MPs type, shape, dosage and exposure time [88]. MPs increase the dissolved organic carbon (DOC) content [88,89] depending on the degree of MPs degradability. However, since MPs tend to slowly degrade in the environment because plastics are relatively inert [3], DOC from this source could not be generated in a large amount [89]. MPs will also indirectly affect organic matter and DOC contents due to their influence on soil microbial biomass and activity [88,90], changing the decomposition and transformation of organic materials. However, Steinmetz et al. [44] alerted that application of plastic mulches would potentially favor soil organic matter degradation because of increased soil temperatures. No significant influence of MPs on the amounts of available phosphate, nitrate, and ammonium, and on crop growth was either observed in a meta-analysis based on 32 works [89]. In contrast, De Souza Machado et al. [81] found an enrichment of soil N

and N content in onion leaves when polyamide (PA) fibers were added to the soil because this plastic contains N in its molecule that could be released to the environment. In a soil containing six different plastic types, the authors also found a generally positive effect on the growth of onions and their colonization by arbuscular mycorrhizal fungi, which in turn, would contribute to an improvement in nutrient availability and plant nutrient content. The positive effect of MPs on the development of arbuscular mycorrhizal fungi might be attributed to the changes caused in the soil structure, which have a direct impact on the habitat space and conditions for these fungi. Qi et al. [91] have also reported an increase in the C:N ratio due to the presence in the soil of low-density PE and biodegradable plastic mulch films.

MPs have been also shown to affect microbial activity in the soil environment [86]. For instance, various meta-analyses have recently concluded that MPs would not or only slightly reduce soil microbial diversity but would significantly enhance soil microorganism amounts and activity [84,89]. In contrast, Awet et al. [92] reported a negative effect of PS on microbial biomass and enzyme activities in soils, with an increase in basal respiration rate and metabolic quotient due to increased cell death. Likewise, Yi et al. [93] indicated a decrease in urease, dehydrogenase and alkaline phosphatase activities after the addition of three types of MPs (membranous PE, fibrous PP and microsphere PP). The effects of microsphere PP were different from the other two, probably owing to the different sizes and lower concentrations. Fei et al. [94] added PVC and PE to acid soil (pH 5.5) and found that both MPs inhibited fluorescein diacetate hydrolase activity, stimulated urease and acid phosphatase activities, and declined the richness and diversity of the bacterial communities. The effects were, in general, more severe in the PE-treated soils. On the contrary, Brown et al. [95] reported no changes in soil bacterial community diversity or in the size and structure of the PLFA-derived soil microbial community, Liu et al. [96] measured a stimulation of FDAse activity in soil driven by PP, while Zang et al. [18] found that PE and PVC increased the soil microbial biomass and changed the structure and metabolic status of the microbial community. These changes would significantly influence key pools and fluxes of the soil C cycle with the response being both dose-dependent and MP-specific.

The soil properties and functions discussed in this section include those that have been reported as directly modified by the presence of MPs in soils. However, other soil properties can be indirectly affected by changes caused by the aforementioned ones. Apart from soil organic matter, soil electrical conductivity has shown unclear trends (increases, decreases or no modifications) under MP addition [86,87,91]. In general, as suggested by Qi et al. [87,91], the effects of plastic debris on soil parameters are highly variable because they are present in different types, sizes and contents, factors that may additionally interact among them in complex and sometimes little understood ways.

4. Plastics and Pesticide Fate/Behavior

4.1. Mechanisms and Factors Governing the Interactions of Pesticides and MPs

MPs may combine with other organic pollutants present in soil environments, including pesticides, and affect their distribution and bioavailability. Therefore, understanding the interactions between pesticides and MPs in aqueous systems becomes essential to address the final behavior when they coexist in soils.

The mechanisms that govern pesticide−MP interactions in aqueous phases represent a novel field of research. Recent studies have assessed the mechanisms controlling the adsorption behavior of pesticides on MPs, using kinetic and isotherm data. In general, the adsorption kinetics of pesticides to MPs fit the pseudo-second-order and intraparticle diffusion models well, meaning that the process would mainly occur via surface adsorption and subsequent pore filling by diffusion [97–102]. In general, it can be said from the available literature that pesticides adsorb rapidly to MP surfaces, and afterwards pore diffusion proceeds at different rates depending on the characteristics of both pesticide and MP. Sorption of triazole fungicides to PS microparticles increased rapidly in the first 6 h

and was practically unchanged after 24 h [98]. A similar rapid adsorption was found for the low-density PE/α-endosulfan system, though in this case, a longer time (48 h) was needed to reach equilibrium [103]. In contrast, the adsorption equilibrium of carbendazim, trichlorfon, malathion, diflubenzuron and difenoconazole on PE, formed after embrittlement of agricultural films, reached equilibrium after only 2 h of contact [99,104,105]. When aged PE was used, the equilibrium time shortened for some pesticides [104,105]. Similarly, rapid adsorption of carbendazim on PE and PP was found, although carbofuran presented a slower adsorption rate [100]. Concerning different types of MPs, Gong et al. [97] found that fipronil sorption rates were faster for biodegradable MPs (equilibrium within 12 h contact) than for traditional MPs (within 48 h contact). Furthermore, thiacloprid adsorption reached equilibrium at 34 h, 4 h or 1 h depending on the type of MP studied [102].

The adsorption isotherms of a wide variety of pesticide−MP systems were mainly fitted to the Freundlich equation [98–101,104–107], a model that explains better the adsorption onto non-homogeneous adsorbents, such as MPs, by forming mono- or multilayers. Since the slopes of the Freundlich model are, in general, close to linearity, especially for neutral pesticides, adsorption should occur through hydrophobic partition on the plastic surface and, consequently, it has been frequently correlated with octanol/water partition coefficients (log K_{ow}) of pesticides [98,99,105,108]. In this sense, adsorption of the fungicides triadimefon and difenoconazole on polybutylene succinate (PBS), PE and PVC conformed also to the linear model [109]. On the other hand, when ionic or ionizable pesticides are considered, log K_{ow} fails to predict adsorption [110]. For these types of compounds (e.g., glyphosate, MCPA or mecoprop), electrostatic interactions appear to be preferred [100,110–113].

Other proposed adsorption mechanisms are van der Waals interactions, π–π interactions or H bonds, which may coexist to different extents depending on the molecular structure of the pesticide and on the surface chemistry of the MP. For instance, it has been recently postulated that the partitioning of thiacloprid between the aqueous phase and cellulose acetate is probably dominated by van der Waals forces, though H-bonding between the N atom of the insecticide and the –OH groups in the polymer backbone might also participate [102]. The latter mechanism is mainly proposed in aged MPs because the aging process accelerates oxidation and favors the appearance of O-containing functional groups and microcracks in the MP surface [99,105,107,110,114–116]. Thus, although MPs are, in general, resistant to decomposition, sterilization processes taking place in WWTPs (such as chlorination or UV disinfection) or natural weathering in soil environments due to the action of mechanical abrasion, sunlight irradiation or even soil microorganisms, may cause alterations in MPs' specific surface area and surface chemistry [115,117,118], usually leading to an increase in pesticide adsorption. For instance, atrazine adsorption increased on aged PE, PS and PP [119] and that of carbendazim, diflubenzuron, malathion, difenoconazole or trichlorfon on aged PE was also enhanced, especially for the more hydrophobic diflubenzuron and difenoconazol [99,105]. For atrazine adsorption in pristine MPs, partitioning and electrostatic attraction were proposed as the governing mechanisms, whereas in aged MPs the adsorption would occur mainly via surface diffusion and H-bonding [119]. This is in line with Lan et al. [105] who proposed hydrophobic partitioning to be pivotal in the adsorption of pesticides to PE, but also H-bonding should be considered in aged PE due to the appearance of polar O-containing functionalities in the oxidized MP surface. In the same way, Miranda et al. [116] reported stronger adsorption of four pesticides after different aging treatments of low-density PE and unplasticized PVC, although the sorption capacity of PET was not significantly modified after aging. The authors highlighted that pentachlorophenol, with the highest hydrophobicity, exhibited a stronger affinity for both pristine and aged MPs. Similarly, higher adsorption was stated for endosulfan and endrin on aged PE, PA, PS and PVC, being the highest that of the more hydrophobic endrin [120]. However, Concha Graña et al. [121] found no differences in the adsorption of chlorpyrifos and α-endosulfan on pristine and aged (UV–Vis radiation) PA and a biopolymer. Similarly, Bele et al. [122] studied the adsorption of the insecticides chlorpyrifos and dichlorvos on PE,

PP and PS before and after treatment with O_3 and O_3/H_2O_2, a process that is commonly used in WWTPS with advanced oxidation systems. They found that the adsorption of the hydrophobic chlorpyrifos was higher on virgin MPs, and probably occurred due to π–π interactions, while that of dichlorvos, more polar, was higher in treated MPs and the proposed mechanisms were weak electrostatic interactions and H-bonds. The authors concluded that treated MPs underwent an increase in polarity that would lead to enhanced adsorption, especially of polar pesticides. Finally, variable adsorption of the polar imidacloprid on polar MPs (PA and polylactic acid (PLA)) after UV irradiation was measured with increases (PLA) or decreases (PA), depending on the capacity of the MP to absorb UV light [113].

Several studies have also evaluated the impact of environmental properties (pH, ionic strength, dissolved organic matter (DOM)) or MPs properties (dosage, size) on pesticide adsorption. Jiang et al. [109] indicated that changes in pH did not significantly influence the adsorption of two triazole fungicides (triadimefon and difenoconazole) onto PBS, PE and PVC. In line with this, pH was found to negligibly affect the adsorption of metolachlor on PP, PE and PVC [123]. However, although pH has been the environmental factor more deeply investigated, contrasting results have been assessed. Therefore, the adsorption on PS of the triazole fungicides myclobutanil and hexaconazole, of intermediate hydrophobicity, was affected by the pH of the background solution with the highest rate at pH 5.5. However, pH did not modify the adsorption of triadimenol [98]. While carbendazim and trichlorfon adsorption decreased with a pH increase in the range 3–6, that of diflubenzuron and difenoconazole initially increased and then kept stable. In addition, malathion exhibited higher adsorption at pH 4 [99]. This behavior was not significantly changed when aged PE was used as a sorbent [104,105]. On the other hand, the adsorption of epoxiconazole and flusilazole gradually increased when the pH was raised from 6 to 9 [114]. Finally, the maximum adsorption on PE of difenoconazole, buprofezin and imidacloprid, pesticides showing a wide range of polarity, was reached at basic pH [106], while the adsorption of 19 pollutants, including eight pesticides, on PS and PE was generally higher at neutral (7) or acid (4) pH values [110]. Results differ largely because they depend on the MP type and size and on the pesticides' properties, since pH will affect the degree of ionization of pesticides, as well as MP surface charge and chemistry.

The presence of ions in the aqueous phase may also induce modifications in the adsorption of pesticides to MPs. Difenoconazole, buprofezin and imidacloprid adsorption on PE seemed to be favored at low-salinity conditions [106]. In agreement with this, α-endosulfan adsorption on different MPs was greater when distilled water was used as a liquid phase, followed by the river and tap waters with higher ionic strengths [103]. In a similar study, Fatema and Farenhorst [124] assessed the adsorption of 2,4-D, atrazine, glyphosate and DDT on four MP types by using deionized or river water as the aqueous phase. They found that the hydrophobic DDT was substantially adsorbed by MPs, but MPs were unlikely to accumulate the more polar 2,4-D, atrazine and glyphosate. In addition, they suggested that the higher ion concentration in river water interfered in the adsorption of glyphosate to PVC, probably by competition for sorption sites. In contrast, other studies reported increased adsorption of triazole fungicides with the increase in salinity up to a certain concentration from which a plateau was reached. On pristine PE, aged PE and PS adsorption initially increased with increasing concentration of NaCl, and then it was inhibited with a continued increase in NaCl concentration [99,104,105,113,114]. In accordance with the foregoing, the adsorption of endrin and endosulfan was the highest when using saline water (35% NaCl) [120], while Cui et al. [107] found that salinity promoted the adsorption of tebuconazole on PA, but diminished it on PP and PS, pointing to the essential role of the different MPs and the interaction mechanisms with pesticides. Moreover, these works suggest that Cl^- anions may hinder the adsorption of Cl−containing compounds such as diflubenzuron and difenoconazole on the MP surface. From all these reports, it stands out that, despite competition between pesticides and ions for MP sorption sites may occur in some cases, most studies reveal increased adsorption

with increasing salt concentration likely due to a salting out effect that reduces the water solubility of pesticides, thus strengthening their affinity for MP surfaces. From a certain ionic strength, this adsorption increase appears to be inhibited.

Similarly, the effect of DOM differed among the studies. A reduced adsorption of the relatively polar pesticides, carbendazim and carbofuran on PE and PP was reported in the presence of oxalic acid and glycine used as DOM sources, more for carbofuran probably because of its weaker binding strength on MPs [100]. The authors also postulated that stronger hydration of carbofuran molecules in the presence of DOM could have inhibited its adsorption. Similar behavior was observed by other works using oxalic and/or humic acids for flusilazole, epoxiconazole and thiacloprid on different MPs [102,114]. Pan et al. [102] demonstrated that humic acids were able to form van der Waals forces and H bonds with both thiacloprid and MPs, and the reduction in thiacloprid adsorption was the result of the combined effect of two processes: (a) competition for sorption sites that prevails at low-DOM concentrations (0–10 mg L^{-1}), and (b) bridging that is preferred at higher DOM concentrations (25–50 mg L^{-1}). This bridging effect led to a gradual increase in thiacloprid adsorption with the increase in humic acid concentration in the solution. In a study by Ateia et al. [111], the adsorption of atrazine on various plastic types was found to increase in the presence of natural DOM and the authors proposed the formation of a DOM–pesticide complex in the solution, which was then retained on the MPs by co-sorption or cumulative sorption as the main mechanism. Finally, increasing concentrations of humic and fulvic acids, used as DOM sources, significantly decreased the adsorption of the fungicides triadimefon and difenoconazole on PE and PVC [109]. It was also reported that adsorption on PBS surface was not altered, suggesting that the response of biodegradable MPs to environmental factors are different from that of conventional plastics.

Considering plastic types and forms, adsorption capacity of clothing and filter microfibers for the insecticide thiacloprid was higher than that found for commercial cellulose acetate microparticles [102]. In a different work, a broad range of MPs originating from different sources and suppliers was evaluated and large differences in their adsorption capacities were found, even for the same plastic type [111]. In this sense, Martín et al. [125] and Fajardo et al. [126] considered blue, fluorescent blue and white PE microbeads for the retention of the herbicide simazine and several pharmaceuticals. Adsorption depended on the type of PE, with simazine showing variable results, while the adsorption of other contaminants, namely sertraline and amoxicillin, was the highest on blue PE.

When comparing different plastic types, PE usually exhibits a higher ability for pesticide adsorption than other conventional polymers [98,111,122,127]. A suggested explanation is that polymers such as PE and PP are in a rubbery state at room temperature, in which polymer structure is expanded and flexible with higher free volume and thus higher accessibility for organic contaminants. In contrast, other studied MPs, such as PS or PVC, are in a glassy state, with more condensed and cross-linked chains that limit pesticide diffusion [97,98]. Accordingly, the rubbery/glassy character of the polymer seems to play a crucial role in the adsorption of fipronil on MPs [97] or in that of various organochlorine pesticides and polychlorinated biphenyls on six different polymers [127]. On the other hand, biodegradable MPs usually have a higher specific surface area, a higher number of pores and/or different chemical properties that favor the formation of bonds with pesticides [97,108,109]. Hence, they have shown higher adsorption capacity for different compounds such as triadimefon, difenoconazole or fipronil [97,109]. When degradable (e.g., PLA or PBS) and non-degradable (e.g., PE, PS, PVC or PP) MPs were evaluated for their ability to retain various pesticides [97], a larger contribution of external mass transport was verified for non-degradable MPs, while intraparticle diffusion played a major role as a rate-controlling mechanism for biodegradable MPs due to their higher porosity.

Additionally, higher pesticide adsorption is usually reported for smaller plastic particles, probably because of an increment of available adsorbent surface and effective sorption sites [98,100]. However, Fatema and Farenhorst [124] unexpectedly found higher adsorption of DDT on MPs of higher size. Another parameter that can affect pesticide adsorption

is MP dosage. More sorption sites are available at higher MP dosages, but the number of non-effective sorption sites is also multiplied [99]. Therefore, the whole impact of MP dosage on the effective adsorption of pesticides would be a balance between these two effects. Although this will be dependent on the specific MP/pesticide system, it can be generally said that increasing MP dosage affects negatively pesticide adsorption, as reported recently by different authors [99,100,114].

Finally, higher adsorption will contribute to reduced availability for degradation. Thus, the decay of 38 pesticides, with a wide range of chemical properties, sorbed on various plastics was on average 30% lower than in the absence of plastics [108]. This decay was correlated with the percentage of pesticide sorption onto the plastics. A study with chiral imidazolinone herbicides [101] reported that the half-lives of imazapic, imazamox and imazethapyr in water increased from 87–231 d (control) to 347–886 d with PP, possibly due to adsorption on the MP and gradual desorption. They interestingly proved that PP favors stereoselective degradation of imazapic but not that of the other two herbicides. Likewise, Ramos et al. [128] found that PE protected deltamethrin from chemical degradation, but not from photodegradation.

4.2. Adsorption/Desorption and Transport Behavior of Pesticides in Soils Contaminated with MPs

Due to the relatively high concentration of MPs in soil ecosystems, their interaction with pesticides, also present at relatively high concentrations, is a relevant phenomenon to be taken into consideration, especially in lands with intensive agriculture. In comparison to studies without soil, the number of articles dealing with the effects of MPs on pesticide dynamics in the soil is rather small. However, as MPs may act as carriers for pesticides, it is essential to evaluate whether the presence of MPs in the soil may alter the adsorption/desorption and transport behavior in soil and, if so, to what extent. As previously stated, MPs are mainly concentrated in top soil layers, because of their low infiltration capacity [65,66]. Moreover, Castan et al. [129] have suggested that the desorption of organic contaminants from MP surfaces is too fast to act as transport facilitators in soils. Nevertheless, other works postulated that the residual vertical movement could increase the hazard of pesticide co-transport to deeper soil layers, and even groundwater [130,131], depending on the MP−pesticide−soil system. Earthworms and soil arthropods could also facilitate pesticide dispersion through the soil profile [42,132–135].

The interactions between MPs and pesticides in agricultural soils have aroused scientific interest in recent years. In 2015, Ramos et al. [128] concluded that, in a horticultural system, plastic residues from PE mulch films may act as pesticide collectors (Table 1). They demonstrated that chorpyrifos, trifluralin and procymidone can migrate from the plastic surface to its interior matrix without the assistance of a solvent, and that the retained pesticides can then be transferred to the surrounding soil either in desorption or in soil column experiments. The balance between these two contrasting processes was dependent on the chemical properties of the pesticides, as well as on the thickness and size of film pieces. In this regard, chlorpyrifos was confirmed to be released from contaminated low-density PE to the soil at rates that were dependent on particle size [136].

Table 1. A summary of the effect of microplastics (MPs) on the environmental fate of pesticides in soil.

Pesticide	Log K_{ow}	Soil Properties	MPs Employed (Size and Concentration)	Experimental Design	Results	Refs
Endosulfan Procymidone Chlorpyrifos Trifluralin Deltamethrin	4.75 3.3 4.7 5.27 4.6	Horticultural soil	■ PE (low density) ■ Meso and macroplastic (0.60–2850 cm2)	■ Laboratory and field assays ■ Adsorption on/desorption from plastic ■ Column transport ■ Chemical and photodegradation	Pesticides applied on the plastic mulches reached the soil after 24 h. Pesticides migrate to the interior of the plastic, more for thicker plastics, and were then partially released to the soil and the atmosphere (especially trifluralin, with high vapor pressure). Plastic mulches protected from chemical degradation but not from photodegradation	[128]
Chlorpyrifos	4.7	OECD artificial soil: Kaolin clay 20%, quartz sand 70%, peat 10%	■ PE (low density) ■ 5 mm, and 250 µm–1 mm	■ Microcosm ■ MPs sprayed with the pesticide	PE released chlorpyrifos into soil. Desorption rate depended on MP size, being much higher (≈ 135 times) for smaller (1 mm) than bigger (5 mm) PE sizes	[136]
Atrazine 2,4-DB	2.7 1.22	OC 1% Sandy loam texture	■ PE ■ 125–250 µm ■ 10%	Adsorption	The MP reduced the adsorption of both herbicides, because of a weak molecular interaction with the aliphatic PE. Likely reduced mobility of both compounds, due to a diminished soil retention capacity	[137]
Acetamiprid Chlorantraniliprol Flubendiamide	0.8 2.86 4.14	pH 7.67 soil OC 2.30% Alluvial soil	■ Black PP particles ■ White PE fibers	■ Soil with 1 and 5% MP ■ Batch adsorption	In joint conditions, reduced pesticide adsorption to soil, especially for the more hydrophobic flubendiamide. No effect on acetamiprid adsorption. MPs could act as carriers for apolar pesticides, increasing their risk of mobility in the soil ecosystem	[62]
Thiacloprid	1.26	pH 7.73 OM 3.61% Clay 9.2%, silt 83.4%, sand 7.4%	■ PS-50 (2–110 µm), PVC-42000 (100–290 µm) and PVC-10 (0.5–1.4 µm) ■ 0.2 and 1% soil	■ Batch adsorption ■ Soil incubation (10 d) ■ Soil enzyme activities	Negligible effect of a variety of MP composition and size on the adsorption or dissipation of the relatively polar thiacloprid at the concentrations explored, which are environmentally relevant.	[138]
Imidacloprid Flumioxazin	0.57 2.55	Soil from a cotton field	■ Pristine and aged PE and PBAT (bio-MP) ■ 0, 0.2 and 2%	■ Batch kinetics and adsorption isotherms ■ Degradation (incubation for 90 d)	MPs slowed down the adsorption rate and the time to reach adsorption equilibrium. Adsorption data were better fitted to the Freundlich equation. The effect depended on the pesticide and MP properties. MPs reduced the adsorption capacity of the soil for the polar imidacloprid, especially for aged and bio-MPs with more functional groups and larger surfaces. For flumioxazin, PBAT increased the sorption capacity and the aged MP reduced it. The degradation of both pesticides was accelerated with pristine MP and delayed with aged and bio-MPs, more at higher MP concentrations.	[139]

Table 1. *Cont.*

Pesticide	Log K_{ow}	Soil Properties	MPs Employed (Size and Concentration)	Experimental Design	Results	Refs
2,4-D Atrazine Glyphosate DDT	−0.82 2.7 −6.28 6.91	River sediment	■ PE fibers (<5 mm), PE beads (250–300 µm), PVC (<5 mm) and tire fragments (<5 mm)	■ Batch adsorption ■ Deionized and river water	The mixed treatment (MPs+ pesticides) with sediments, did not modify pesticide adsorption, neither in deionized nor in river water, in comparison with the sediment alone.	[124]
Epoxiconazole Tebuconazole Myclobutanil Azoxystrobin Simazine Terbutylazine Atrazine Metolachlor	3.3 3.7 2.89 2.5 2.3 3.4 2.7 3.4	Sediment	■ PE powder ■ 40–48 µm ■ 0.01–50 g/L	■ Batch adsorption/desorption ■ Effect of MP aging (wet/dry heat or mechanical abrasion) and sunlight irradiation ■ Residues in sediment microcosm ■ MP characterization (ATR-FTIR, SEM) ■ Fitting to models	No effect of aging or sunlight irradiation on pesticide adsorption. Good fitting to Freundlich with linear adsorption, pointing to partitioning (correlation of hydrophobicity and adsorption) rather than surface interaction, probably by van der Waals forces. In the liquid phase, pesticide half-lives increased with MPs. However, since PE powder floats in water, its interaction with the sediment is scarce and does not alter the half-lives of the pesticides retained in the sediment.	[140]
p,p′-DDT *o,p′*-DDT *p,p′*-DDE *p,p′*-DDD α-HCH β-HCH γ-HCH δ-HCH	6.2–6.9 6.8 5.7–7.0 6.02 3.8 3.8 3.6–3.7 4.1	pH 7.93 OM 1.37%	■ PE ■ 120 and 180 µm (powder) ■ 2000 and 3000 µm (pellets)	■ Batch adsorption ■ MP characterization (SEM) ■ Fitting to equations	Linear pesticide adsorption, better fitted to the Freundlich equation, with partition as the possible sorption mechanism. Small particle MPs were able to adsorb more pesticides. This MP (rubbery with low crystallinity and high internal area) could enrich the concentration of apolar pesticides in soil	[141]
Imazamox Imazapic Imazethapyr	5.36 2.47 1.49	Sediment	PP	■ Adsorption kinetics and isotherm in water ■ Incubation in a microcosm sediment/water (60 d) ■ Analysis of herbicide enantiomers	Kinetic and isotherm data fitted to pseudo-second-order and Freundlich models, respectively. Higher half-lives of the pesticides in the presence of MPs (after pesticide addition either to the water or to the sediment). Enantioselective dissipation was found for imazapic, but not for the other two herbicides, when they were added to the liquid phase in the microcosm.	[101]
Glyphosate	−6.28	Model minerals: Calcite and iron hydroxides	■ PS with different functional groups ■ PS, PS-COOH, PS-HCO3, PS-NH2	■ Adsorption ■ AFM and Raman spectroscopy	Glyphosate, possessing + and–charged groups, interacts more with the functionalized PSs, occluding in calcite and Fe hydroxides, by hillock growth and aggregation, respectively.	[112]
Glyphosate	−6.28	OM 0.2% Sandy soil	■ PE (light density) ■ <150 µm ■ 0–60%	■ Soil microcosm ■ *Lumbricus terrestris*	Glyphosate and its metabolite remained almost completely at the upper soil layers (1–2 cm). Due to limited water availability in the microcosm, *L. terrestris* would have been responsible for the transport of pesticides to deeper soil layers.	[142]

Table 1. *Cont.*

Pesticide	Log K_{ow}	Soil Properties	MPs Employed (Size and Concentration)	Experimental Design	Results	Refs
Chlorpyrifos	4.7	OM 0.2% pH 6.4 Artificial sandy soil: 50% sand, 50% loamy silt	■ Low-density PE and bio-MP (85% PBAT) ■ 50–150 µm ■ 0, 7 and 28% in litter	■ Mesocosm with the insecticide at three different concentrations ■ Analysis of two metabolites of chlorpyrifos	Both MPs decreased the concentration of one of the insecticide metabolites (TCP) in soil, pointing to an inhibition of insecticide degradation, probably retained on the MPs	[143]
Simazine	2.3	pH 5.7 OC 0.5% Sandy clay loam texture	■ PE and PVC ■ <125 µm ■ 1, 45, 10 and 20%	■ Incubation in pots (35 d), planted with *Triticum aestivum* ■ Phospholipid fatty acid ■ Enzymes involved in C and N cycling	Simultaneous application of MPs resulted in slower simazine degradation, releasing less $^{14}CO_2$ and producing higher residues in soil, especially at the 20% MP level. MPs induced a reduction in soil density and led to a shift in soil microbial composition towards fungi, thus potentially affecting pesticide degradation.	[19]
Glyphosate	−6.28	pH 8.6 OM 0.51% Clay 18.5%, silt 25%, sand 55.9%	PP powder	■ Pesticide degradation ■ Incubation in pots ■ Enzyme activities ■ Fitting to equations	Similar decay rates for individual or joint additions. Soil respiration and enzyme activities related to C, N and P cycling changed during the incubation. PP size diminished during the incubation period	[144]
Glyphosate	−6.28	pH 8.45 OC 0.87% Clay 18.4%, silt 24.9%, sand 55.85%	■ Homopolymer PP ■ <250 µm ■ 7 and 28%	■ Incubation (30 d) ■ EEM fluorescence spectroscopy and specific UV absorbance ■ Soil enzymes (FDAse and phenol oxidase) ■ DOM evolution	The doses of MPs affected differently glyphosate behavior. Joint application of the herbicide and high PP dose increased soil enzyme activities, DOC, DOP, tryptophan-like material and decreased humic-like material and fulvic acid, but not DON. Overall, the joint addition resulted in positive effects on soil microbial activity and nutrient availability in DOM	[145]
Prothioconazole	2.0	C 9.9%	■ PE (low density) and biodegradable PBAT ■ 0.85–2.0 mm ■ 1%	■ Effect of the pesticide on MP degradation ■ Incubation (6 wk) ■ MP characterization (ATR-FTIR, SEM, ICP-MS)	Significant changes in MP functional groups. The addition of the fungicide led to accelerated irregularities in MPs and promoted their degradation, more in PBAT than in PE. Prothioconazole also affected the adsorption/desorption of heavy metals on both MPs	[146]
Propiconazole	3.72	pH 5.5 OM 0.74%	■ PE (low density) and PBAT ■ 2–4 mm	■ Effect of the pesticide on MP degradation ■ Effect of pH (5.5, 7 and 8.5) ■ MP characterization (ATR-FTIR, SEM, ICP-MS)	Propiconazole accelerated the degradation of MPs at low concentrations (< 40 mg/kg), by enhancing microbial activity, due to the production of carbonyl groups on MPs. PE and PBAT were more easily degraded in alkaline soil and degradation accelerated under UV radiation + pesticide. More heavy metals were adsorbed on the MPs during the degradation process	[147]

Pollutant properties from PPDB (https://sitem.herts.ac.uk/aeru/ppdb/en/atoz.htm (accessed on 24 February 2023)). Log K_{ow}, octanol/water partition coefficient. OC/OM, content in organic carbon/matter. DOC/DOP/DON, dissolved organic carbon/phosphorus/nitrogen. SEM, Scanning electron microscopy. AFM, Atomic force microscopy. ATR-FTIR, Attenuated total reflectance Fourier transform infrared spectroscopy. ICP-MS, Inductively coupled plasma mass-spectrometry. PP, polypropylene. PE, polyethylene. PS, polystyrene. PVC, polyvinylchloride. PBAT, polybutylene adipate terephthalate.

Recent research has corroborated that, in soil ecosystems, MPs could act as carriers of pesticides, thus increasing the risk of their mobility through the soil matrix or to other environmental compartments. For instance, Hüffer et al. [137] found that soil adsorption of atrazine and 2,4-DB was reduced by the presence of PE particles. This was explained by the weaker bonds that the pesticides formed with the aliphatic chains of PE as compared with those with soil organic matter. Therefore, PE diluted the overall adsorption ability of soil for both herbicides. In another study, the presence of polyester fibers and PP particles (0.5–1 mm size) at 1% and 5% also decreased the capability of alluvial soil to retain three pesticides widely differing in polarity (acetamiprid, chlorantraniliprole and flubendiamide) [62]. In this case, the decreased sorption was correlated with the polarity of the pesticides, being more pronounced for the more hydrophobic flubendiamide and practically negligible for the more polar acetamiprid. In line with this, Xu et al. [138] informed of comparable thiacloprid (another relatively polar neonicotinoid insecticide) adsorption on loamy sand soil with and without the presence of PS and PVC particles with different sizes. In contrast, Wu et al. [139] found that the presence of MPs released from conventional low-density PE and biodegradable mulch films enhanced the adsorption of flumioxazin in soil collected from a cotton cropland. On the other hand, the same work reported that adsorption of imidacloprid was decreased by both types of MPs, and postulated these differences to be related to the Log K_{ow} of the pesticides. Finally, the adsorption on sediment of highly differing pesticides on various MPs (PE fibers and beads, PVC and tire fragments) did not differ from the adsorption on the sediment alone [124].

However, not only pesticide properties, but also those of MPs may influence pesticide adsorption to soils. In this sense, an important parameter of polymers is the glass transition temperature (T_g). When a polymer is below its T_g the structure is rigid or in a glassy state. Above the T_g, the polymer is in the rubbery state and the molecular chains increase their flexibility and mobility, thus facilitating the diffusion of organic contaminants. This has been recognized as the main reason for the differences observed in the adsorption of polycyclic aromatic hydrocarbons on soils contaminated with conventional and biodegradable polyurethane foams [148]. In addition, as PE is in a rubbery state under environmental conditions, the flexibility of its structure may be identified as a main contributor of higher pesticide adsorption by comparison with other conventional MPs present in agricultural soils, such as PS or PVC that are in a glassy state. Since PE is the major plastic used in agriculture, agricultural fields are mostly contaminated with PE residues. Hence, PE MPs may serve as potential carriers for pesticides, thus having a significant influence on their fate in soils.

The aging that plastic residues undergo during their stay in the soil is another aspect to consider, since it leads to significant changes in the morphology and chemical properties of plastic surfaces [99,105,107,110,114–117,144]. Different aging treatments of PE (wet/dry heat, mechanical abrasion or sunlight irradiation) were evaluated in sediment by Wang et al. [140], who found no effect of the different treatments on the adsorption of eight pesticides. Finally, the reduction in PE size from 3000 to 120 μm led to an increase in pesticide adsorption in soil suspensions [141].

The mechanisms of adsorption have also been investigated in different research articles. The presence of MPs has been reported to hinder the rapid adsorption of pesticides on soil surfaces, thus inducing a delay in the time to reach sorption equilibrium [139]. As in the prior subsection, the good fitting to the Freundlich equation confirmed that pesticide interactions with soil in the presence of MPs are affected by chemical and physical mechanisms in a multilayer adsorption process. This has been reported for varied pesticide–MP–soil systems such as organochlorine DDTs and HCHs on PE (powder and pellets) in a soil suspension [141]; eight pesticides of varied families on PE powder in sediment [140]; three chiral imidazolinone herbicides in another sediment [101]; and imidacloprid and flumioxazin in a soil devoted to cotton crops added with a PE mulch film, a biodegradable mulch film and another mulch film that was naturally aged in the cotton fields for three years [139]. Although in some cases no comparison with soil alone was reported, it can be generally said

that MPs do not significantly alter the mechanisms that govern pesticide interactions with soil particles and, therefore, a correlation between pesticide hydrophobicity and adsorption on the soil is recurrently observed.

Organic matter is the major fraction that participates in pesticide dynamics in soils. Nonetheless, soil minerals may play an important role in the adsorption of ionic or ionizable pesticides, especially in soils with low or very low OC content [149]. In this sense, the adsorption of glyphosate, a widely used ionic herbicide, was evaluated with model soil minerals (calcite and iron hydroxides) in the presence of functionalized PS (PS–COOH, PS–HCO_3 and PS–NH_2) [112]. Results show that the ionic herbicide interacted more with the functionalized MPs than with virgin PS, forming glyphosate–MP complexes that were occluded in calcite and Fe hydroxides particles. Therefore, the inorganic fraction of soil may help to immobilize simultaneously MPs and glyphosate within the soil matrix, and may have implications in the transport of the herbicide.

An alternative pathway for pesticides to reach deeper soil layers is co-transport with MPs by the action of soil organisms such as earthworms, although contradictory results have been published. On one hand, Rodríguez-Seijo et al. [136] could not demonstrate if low-density PE can be an efficient carrier of chlorpyrifos to earthworms. However, this MP increased the total amounts of glyphosate [142] and chlorpyrifos [143] transported by earthworms. The latter stated that biodegradable MPs also increased the contents and biogenic transport ratios of chlorpyrifos at 0–10 cm and 10–20 cm soil depths, likely due to an increase in chlorpyrifos concentrations in earthworm casts and decreased bioaccumulation in bodies.

4.3. Dissipation Behavior of Pesticides in Soils Contaminated with MPs

Since in most cases a part of the pesticides remains adsorbed on the different MPs, reduced degradation of pesticides has been generally noted due to a reduced pollutant availability to soil microorganisms or non-biotic degradation processes. Hu et al. [101] reported higher half-lives of imazamox, imazapic and imazethapyr in sediment in the presence of PP, regardless of whether the pesticides were added to the water or to the sediment. Similarly, Wang et al. [140] found that the half-lives of eight pesticides increased in another sediment in the presence of PE powder and pellets when added to the water. However, when pesticides were added to the sediment they found no modification of pesticide dissipation and they attributed this behavior to the fact that PE floats in water and, therefore, scarce interaction takes place between the MP and the sediment. In another study, the dissipation of the herbicide simazine in a sandy clay loam soil was also slowed down when PE and PVC were present, resulting in higher residues in soil, especially at high MP doses (20%), which are not environmentally meaningful [19]. The addition of both MPs to the soil led to a shift in microbial composition towards fungi, which could potentially slow down pesticide degradation, mainly driven by bacteria. Finally, the presence of both low-density PE and biodegradable MPs inhibited the degradation of chlorpyrifos in an artificial sandy soil with 0.2% organic matter content due to lower bioavailability because of the adsorption of the insecticide on the MP surface [143].

In soil contaminated with PS fragments and PVC beads of different sizes, Xu et al. [138] did not find differences in the dissipation of thiacloprid as well as in urease, acid phosphatase, invertase and catalase activities of soil. The authors ascribed this behavior to similar adsorption of the pesticide before and after plastic co-presence. In addition, thiacloprid exhibits rapid degradation in soils [150], which may have also overlapped the role of MPs in the process. Glyphosate, a herbicide that possesses positive and negative charges depending on pH, has presented variable results. On one hand, in sandy loam in the presence of PP powder, similar decay rates of glyphosate were found for individual or joint additions [144]. On the contrary, homopolymer PP increased glyphosate dissipation in the same soil [145]. In the former study, respiration and enzyme activities related to the C, N and P cycling changed during incubation, while high doses of PP in the latter (28%,

largely exceeding environmental concentration) induced increased soil enzyme activities, and DOC, dissolved organic phosphorus and tryptophan-like material concentrations.

The opposite, that is modification of MP degradation by pesticides, may also occur. Thus, pesticide residues may also trigger the degradation of plastics in soils. Two studies [146,147] evaluated the effect of two pesticides, prothioconazole and propiconazole, respectively, on the degradation of PE and biodegradable polybutylene adipate terephthalate (PBAT). In both cases, the presence of pesticides in the soil accelerated the degradation of the MPs, thus increasing the formation of irregularities in their surfaces. While Li et al. [146] found no changes in MP functional groups, Liu et al. [147] reported the production of carbonyl moieties, evidence of plastic oxidation. The presence of propiconazole at low concentration (<40 mg/kg) would have enhanced the microbial activity and triggered the MP attack by microorganisms, more in PBAT than in PE. The plastic degradation would occur more easily in alkaline soil and be accelerated by a simultaneous effect of UV radiation and pesticides.

5. Effect of Microplastics and Pesticides Interactions on Living Organisms

5.1. Aquatic Ecosystems

Figure 1 shows a compilation of the interactive effects of MPs and pesticides on aquatic and terrestrial living organisms that will be highlighted in this section. Several studies have been conducted in recent years with the aim of establishing whether the co-occurrence of MPs and pesticides has an effect on living organisms. However, most of them deal with aquatic organisms because MPs have been long recognized as contaminants in aquatic ecosystems. As a common result, these studies generally state that the effects of MPs alone on different organisms are low or negligible, independently of the target living organism [151–157]. However, some studies have indicated the toxic effects of MPs on various aquatic organisms, such as alterations of the metabolic profiles, genotoxicity or neurotoxicity [158–161].

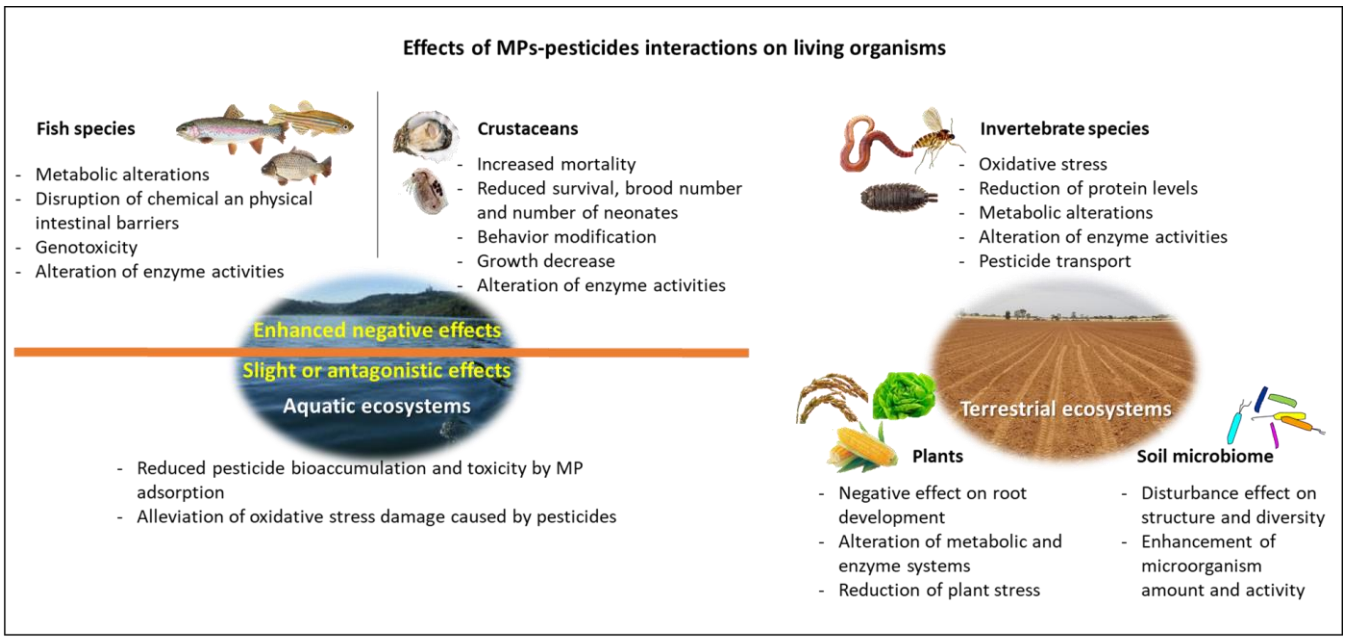

Figure 1. Effects of MPs–pesticides interactions on living organisms.

The combination of MPs and pesticides increases in general the toxicity of either individual stressor. This occurs in several fish species, such as the rainbow trout, *Oncorhynchus mykiss*, for which alterations were measured in amino acid and fatty acid composition and protein contents, as well as in histopathological and histomorphometrical biomarkers, after the simultaneous addition of PE and the insecticide chlorpyrifos [153,162]. For the

carp, *Cyprinus carpio*, the disruption of chemical and physical intestinal barriers, changes in the abundance and diversity of gut microbiota and metabolic alterations were assessed when the herbicide glyphosate and PE were present [156]. Likewise, Hanachi et al. [163], studying the responses of juvenile zebra fish exposed to the insecticide abamectin and PET, found a higher effect of the combined treatment in the expression of various genes and several enzyme activities.

Not only fishes have been investigated, but also crustaceans. Thus, an enhanced negative effect of MPs and pyrethroids was found concerning survival, brood number and number of neonates per surviving females of *Daphnia magna* [152]. Another crustacean, *Minuca ecuadioriensis*, also experienced increased mortality in the presence of MPs and the organophosphorus insecticide chlorpyrifos [155]. In a similar way, the Pacific oyster suffered from the combined application of high-density PE and the herbicide chlortoluron at high environmental concentrations, which affected its behavior (valve microclosure, valve opening amplitude and duration) as well as its growth [164]. The enzyme activities (glutathione–S–transferase, acetyl cholinesterase or carboxylesterase) of the tadpole *Scinax squalirostris* were, in general, more affected when exposed to a mixture of PE and the herbicides glyphosate and glufosinate ammonium, than to the individual pollutants [165]. The herbicides interacted with PE leading to the formation of PE–herbicides bonds. Fernández et al. [166] found that, when the mussel *Mytilus galloprovincialis* was exposed to microalgae and MP (PE, 22 µm), both carrying the insecticide chlorpyrifos, the effects were very similar. Thus, PE could act as a vehicle of the insecticide as efficiently or even more than microalgae. All of these results suggest a promoted effect by the joint application of both stressors, MPs and pesticides.

However, slight or antagonist effects between MPs and the pesticides have been sometimes reported. This is the case in the study by Li et al. [167] who found that MP reduced the bioaccumulation of the triazole fungicide difenoconazole on zebra fish, alleviating the oxidative stress damage inflicted by the pesticide. Likewise, the reduced bioavailability of chlorpyrifos for zebra fish, *Danio rerio* [157], or glyphosate for blue-green algae, *Microcystis aeruginosa* [151] has been attributed to strong sorption of the pesticides on different MPs. In the latter study, a secondary effect of glyphosate was that this herbicide enhanced the stability of the MP dispersion, favoring higher adsorption of the MP on the algae and presumably inducing an enrichment of MPs in the food chain. Similarly, the reproduction rate and DNA integrity of *Ceriodaphnia dubia* was not modified by the combination of PS and imidacloprid in comparison with PS alone [161], whereas the acute toxicity exerted by dimethoate and deltamehrin in *D. magna* remained unchanged when PE was present [168], even though deltamethrin was much more hydrophobic than dimethoate and, therefore, more prone to adsorption on the MP. Thus, the type of MP, the pesticide and its mode of action, and the animal species determine the specific interactions between MPs and the environmental pollutant.

A few studies have proposed alternative approaches, which help shed light on different aspects of the interactions considered. For instance, Ziajahromi et al. [169] evaluated the effect of PE and pyrethroid bifenthrin on midge larvae (*Chironomus tepperi*) in both synthetic and river waters. In synthetic water, the toxicity of bifenthrin was alleviated, because >92% of this highly hydrophobic compound was adsorbed on the MP. On the contrary, mitigation of bifenthrin toxicity did not occur in river water, which contained 9.6 mg/L DOM. The interaction of bifenthrin with DOM was probably greater than with MP. Thus, differences between laboratory and realistic environmental conditions may end up in different results. Zocchi and Sommaruga [170] studied two MPs (PE microbeads and PET/PA fibers) and three glyphosate formulations to discover their effects on *D. magna*. The joint addition increased the mortality of each formulation alone, although less with one of them, Roundup Gran formulation. This could be explained by the different adsorption capacities of the formulated herbicide on the MPs. Thus, studies considering various pesticide formulations, which will include different adjuvants, instead of the pure active ingredient, may again bring us closer to more realistic agronomic conditions.

5.2. Terrestrial Ecosystems

MPs are being increasingly considered contaminants of terrestrial ecosystems. However, with respect to soil organisms, only a few studies have been reported, mostly focusing on earthworms as target organisms (Figure 1). As in the aquatic ecosystem, the effects of MPs alone caused generally minimal or negligible effects [171,172]. Thus, when two types of MPs (PS and car tire abrasion) were present in the soil, changes in the activity of multiple biomarkers in *Eisenia fetida* could be detected, but most enzymatic activities recovered after 28 d [173]. However, Tang et al. [174,175] recently informed of the relevant effects of PS (25–30 µm and 90–110 nm) on *E. fetida*, such as damage to digestive and immune systems, reduction in gut microorganisms' diversity and species richness or disturbance of the osmoregulatory metabolism.

Most of the studies reviewed pointed out the capability of some terrestrial organisms to transport and distribute MPs in the soil ecosystem via ingestion. Thus, annelids [42,132–134], soil microarthropods [135,176], molluscs [177], insect larvae [178,179], birds [180] and herbivores [181] are able to ingest MPs. Ingestion mainly depends on the MPs' size and concentration [42,132–134], being smaller particles more easily transported than bigger ones. With the MPs ingestion, adsorbed pesticides could also be introduced into living organisms with subsequent toxic effects. However, the simultaneous presence in the soil of both types of pollutants, MPs and pesticides, and their potential toxicological impact has been less frequently evaluated than in aquatic environments. Nevertheless, various studies that provide some relevant information about possible interactions between these environmental pollutants are available (Table 2).

Mishra et al. [182] addressed the effect on the earthworm *Eudrillus eugeniae* of the MPs PVC and PP together with the organophosphorous pesticide monocrotophos. Both MPs were able to adsorb efficiently the pesticide and, when combined, led to an enhancement of the oxidative stress of *E. eugeniae*, which showed increased lipid peroxidation and enzyme activities, as well as a significant reduction in protein levels. Another earthworm species, *Eisenia fetida*, was investigated in the presence of the soil of MPs and dufulin, a plant antiviral agent [183]. The application of dufulin alone led to the alteration of the relative abundance of 14 metabolites and two metabolic pathways, but the combination of MPs and the antiviral agent resulted in the change in the abundance of 21 metabolites and three metabolic pathways, pointing to a worsening of the metabolic profile. *E. andrei* was also exposed individually or jointly to MPs and the herbicide 2,4-D. The simultaneous exposure resulted in higher toxicity with oxidative alterations, such as increases in glutathione S–transferase and catalase and accumulation of malondialdehydes [184]. The effect of another herbicide, atrazine, on *E. fetida* was evaluated in combination with non-aged and aged low-density PE [185]. In comparison with the herbicide or the MP alone, the combined application increased oxidative stress and led to abnormal expression of genes in *E. fetida*. The alterations induced in *E. fetida* by aged MPs were higher than those by non-aged MPs. For the co-existence of MPs and atrazine, a similar trend for oxidative stress was assessed, while the opposite occurred for the abnormal expression of genes.

Huerta-Lwanga et al. [133] and Yang et al. [142] used a soil microcosm to assess the impact of glyphosate and light density PE (<150 µm) on *Lumbricus terrestris*. They found a negative effect of the joint treatment on gallery volume and dry weight, especially at the higher doses (60%). In the burrow's walls the authors found increased concentrations (>65%) of smaller MPs (<50 µm). Since high concentrations of glyphosate and its metabolite were measured inside the burrows, this suggests pesticide transport via earthworms, which would facilitate both MP (smaller particles) and pesticide movement to deeper soil layers.

Table 2. A summary of the effect of microplastics (MPs) and pesticides on terrestrial organisms.

Pesticide	Log K_{ow}	Soil Properties	MPs Employed (Size and Concentration)	Target Organism(s) Experimental Design	Results	Refs
Monocrotophos	−0.22	Soil from an organic field	■ PVC and PP ■ <150 µm ■ 0.25%	■ *Eudrillus eugeniae* ■ Soil microcosm ■ FTIR, SEM ■ Analysis of earthworm tissue	The joint application increased the oxidative stress of *E. eugeniae*, with increased lipid peroxidation level and enzyme activities and a reduction in protein levels	[182]
Dufulin	n.a.	Artificial OECD soil: 70% quartz sand, 20% kaolinite and 10% peat moss	■ Low and high concentrations of MP ■ 10 and 300 mg/kg (bioaccumulation) ■ 300 and 3000 mg/kg (toxicity)	■ *Eisenia fetida* ■ Soil microcosm ■ Bioaccumulation and toxicity tests ■ Biochemical and metabolomics analysis	For both the individual or joint treatments similar accumulation of dufulin in earthworms and in soil, at low MP concentrations. The combination of MPs and dufulin led to a change in the abundance of 21 metabolites and three metabolic pathways, pointing to a worsening of the interference of the pesticide on the metabolic profile of *E. fetida*.	[183]
2,4–D	−0.82	pH 7.45 OM 2.4% Sandy loam	■ Environmental MPs: PE and PET (dominant) + PT, PEVA and PA ■ >3 µm, 3–1.22 µm and 1.22–0.45 µm ■ 100 µg/kg	■ *Eisenia andrei* ■ Soil microcosm (7 and 14 d) ■ Biochemical analyses and gene expression	No differences in the earthworm's weight for mixed or individual treatments. Plastic ingestion occurred, especially for particles >3 µm. Higher ingestion of 2,4–D when mixed with MPs. The mixture MPs + 2,4–D was more toxic, increasing glutathione S–transferase and catalase and accumulating malondialdehydes. Likewise, the DNA integrity in *Eisenia andrei* was significantly affected	[184]
Atrazine	2.7	Agricultural soil	■ Low-density PE ■ 550–1000 µm ■ 0.25%	■ *Eisenia fetida* ■ Soil microcosm (28 d) ■ Aged and non-aged MPs ■ Biomarkers of oxidative stress and gene expression ■ Integrated biological response	The integrated biological response showed that the co-exposure increased oxidative stress but no clear trend for abnormal expression of genes in *E. fetida*. Aged MPs induced higher effects than non-aged MPs.	[185]

Table 2. *Cont.*

Pesticide	Log K_{ow}	Soil Properties	MPs Employed (Size and Concentration)	Target Organism(s) Experimental Design	Results	Refs
Glyphosate	−6.28	OM 0.2% Sandy soil	■ PE (light density) ■ <150 µm ■ 0–60%	■ *Lumbricus terrestris* ■ Soil microcosm ■ Earthworm burrow, gallery volume and weight	The mixed treatment, at higher doses, had a negative effect on gallery volume and dry weight, and diminished earthworm activity. Increased concentrations (>65%) of smaller MPs (<50 µm) were found in the burrow's walls. High concentration of glyphosate and its metabolite inside the burrows suggests pesticide and MP transport via earthworms, even to deeper soil layers.	[133,142]
Chlorpyrifos	4.7	OECD artificial soil: Kaolin clay 20%, quartz sand 70%, peat 10% (pH 6.5)	■ PE (low density) ■ 5 mm, and 250 µm–1 mm	■ *Eisenia fetida* ■ Soil microcosm ■ Biomarkers: AChe and lipid peroxidation ■ MPs sprayed with the pesticide	Earthworms escaped from the soil layer treated with the insecticide and MPs, by moving to the bottom of the microcosm. Though earthworms can ingest small-sized MPs, in which the concentration of the insecticide increased, no effect on AcChe was observed, then avoidance by moving away from the pollutant was the mechanism proposed.	[136]
Chlorpyrifos	4.7	Artificial sandy soil: 50% sand, 50% loamy silt OM 0.2% pH 6.4	■ Low-density PE and bio-MP (85% PBAT) ■ 50–150 µm ■ 0, 7 and 28% in feeding litter	■ *Lumbricus terrestris* ■ Mesocosm with the insecticide at three different concentrations	The growth and survival of the earthworms remained unchanged with PE alone, while the bio-MP reduced both endpoints. In combination with the insecticide, PE was more toxic than bio-MP, possibly due to the different adsorption capacities of the MPs	[143]

Table 2. *Cont.*

Pesticide	Log K_{ow}	Soil Properties	MPs Employed (Size and Concentration)	Target Organism(s) Experimental Design	Results	Refs
Simazine and three pharmaceuticals	2.3	pH 5.5 Total OC 1.77%	■ PE (blue, fluorescent blue and white microbeads) ■ 212–300 µm	■ *Vibrio fischeri*, toxicity of soil leachates ■ *Caenorhabditis elegans* and *Zea mays*, toxicity ■ DNA, total bacteria, diversity indices, metanogenic functional content	Adsorption depended on the pollutant and type of MP. The combined addition (MPs + pollutants) decreased the toxicity to *V. fischeri* in comparison with single additions. No effect on *C. elegans* (likely due to the big plastic size). A negative effect on the root development of *Z. mays* was assessed, possibly due to physical blockage of the roots by MPs. Disturbance of soil microbiome by the simultaneous presence of MPs and the pollutants, but not different from MPs alone. MP or mixed treatment enriched Proteobacteria (in particular, Alphaproteobacteria) and both had a potential impact on the C and N cycling in the soil	[126]
Glyphosate	−6.28	Agricultural soil	■ Low density PE	■ Collection of invertebrates ■ Field experiment ■ Three managements: Control, herbicide and herbicide with MP ■ Herbicide and metabolite analysis	Residues of glyphosate were detected in the invertebrate's tissue. No significant differences in invertebrate diversity between the joint treatment or the one with glyphosate, but both were lower than the control. No relationship between MP amount and glyphosate concentration in soil, nor with the concentration of glyphosate in the tissue of invertebrates.	[186]
Chlorpyrifos	4.7	Standard agricultural soil	■ PE fibers (220 µm) and crumb rubber (<180 µm) ■ 0.05, 0.5 and 1.5%	■ *Porcellio scaber* ■ Microcosm (3 wk) ■ Analysis of immune biomarkers and AChe	Total haemocyte count increased for the co-exposure, more with fibers than with crumb rubber. Plastics reduced the bioavailability of chlorpyrifos. However, no consistent results were found for the immune processes.	[154]
Chlorpyrifos	4.7	Lufa 2.2, agricultural soil Loamy sand pH 5.5 OC 1.72%	■ PE fibers (220 µm) and tire particles (<180 µm) ■ Low (0.05%) and high (0.5%)	■ *Porcellio scaber* and *Folsomia candida* ■ Microcosm (3–4 wk) ■ AChe and electron transfer system (ETS)	Joint addition decreased AChe and induced a change in ETS, in comparison with the insecticide alone, but depended on the MP type and concentration. Higher effects of tire particles than PE, especially for *P. scaber*, more sensitive.	[187]
Glyphosate	−6.28	Model minerals: Calcite and iron hydroxides	■ PS with different functional groups ■ PS, PS–COOH, PS–HCO3, PS–NH2	■ *Oryza sativa* cells ■ Rice cells culture and cell viability assays	Glyphosate, adsorbed by the functionalized PSs, reduces the potential toxicity to *O. sativa* cells	[112]

Pollutant properties from PPDB (https://sitem.herts.ac.uk/aeru/ppdb/en/atoz.htm (accessed on 24 February 2023)). Log K_{ow}, octanol/water partition coefficient. OC/OM, content in organic carbon/matter. SEM, Scanning electron microscopy. FTIR, Fourier transform infrared spectroscopy. AChe, acetyl cholinesterase. PP, polypropylene. PE, polyethylene. PS, polystyrene. PVC, polyvinylchloride. PA, polyamide/nylon. PET, polyethylene terephthalate. PEVA, Polyethylene vinyl acetate; PBAT, polybutylene adipate terephthalate. n.a., not available.

The size of the MPs is an important feature to be taken into account when dealing with living organisms. However, most of these studies were conducted without soil. So, *Caenorhabtidis elegans* and *Vibrio fischeri* were used as targets by Martín et al. [125] to evaluate, without soil, the effects of simazine and the pharmaceutical ibuprofen together with white and fluorescent blue PE microbeads (250–300 μm). Due to the large MP size, nematodes could not ingest them and negligible effects were assessed on both *C. elegans* and *V. fischeri* endpoints, unless the concentration of simazine increased to 15 μM. Kiyama et al. [188] also suggested that *C. elegans* could discriminate plastics based on size. A different approach established that MPs could reduce the negative impacts on the nematode *C. elegans* of toxic compounds present in plant litter because MPs could effectively retain the toxic phenolic compounds [189]. Furthermore, Lei et al. [190] showed that the effect of MPs on *C. elegans* was size-dependent, by comparing PS at 100–500 nm and 1–5 μm. They found that the 1 μm group induced the lowest survival rate, the largest decrease in body length and the shortest average lifespan, possibly because this size was appropriate for ingestion. All MPs and NPs led to similar behavioral toxicity and enhancement of oxidative damage.

Rodríguez-Seijo et al. [136] also evaluated the behavior and enzyme activity of *E. fetida* when exposed in the soil to a mixture of two sizes of MPs and chlorpyrifos. The authors confirmed the inhibition of acetylcholinesterase activity, as well as the release of the insecticide from the MPs. However, the chlorpyrifos level in the earthworm did not change because *E. fetida* individuals avoided the contact with the polluted plastic, moving away from it. *E. fetida* could have used taste and olfaction cues to discriminate plastics, as proposed for the nematode *C. elegans* [188] or the insect herbivore *Bradisia difformis* [191]. The impacts of the same insecticide, chlorpyrifos, combined with PE and a bio-MP were recently assessed in *L. terrestris* [143]. The bio-MP reduced significantly the earthworms' growth and survival, while PE showed no significant effect. On the contrary, the combined treatment PE + insecticide was more ecotoxic than bio-MP + insecticide. Thus, the insecticide would have been adsorbed on the MPs, making it more or less accessible to the earthworms, depending on the MP composition. Fajardo et al. [126] studied how the co-presence of four organic pollutants (the herbicide simazine and three pharmaceutical products) and three different PE formulations affected various soil organisms, including *C. elegans*. After incubation in soil for 30 d the authors found no effects on *C. elegans* endpoints (growth, reproduction or survival). Another study considered three soil managements (unmanaged and adding glyphosate with/without MPs) and evaluated the impacts on different invertebrates [186]. The authors found no significant differences in invertebrate diversity between the combined treatment and that with glyphosate alone, but both were lower than the control. The concentration of MPs in soil was not related to the concentration of glyphosate neither in the soil, nor in the tissue of invertebrates.

Finally, a terrestrial arthropod, the isopod *Porcellio scaber*, presented also increases in haemocyte count when MPs and the organophosphorus insecticide chlorpyrifos were simultaneously present [154]. The same authors [187] evaluated again the effect of chlorpyrifos together with PE fibers and tire particles, not only on *P. scaber*, but also on the springtail *Folsomia candida*. The effects on both arthropods depended on MP type, diminishing both MPs the bioavailability of the insecticide. In addition, tire particles, especially at high concentrations, were able to reduce the mortality of *P. scaber* induced by chlorpyrifos, but not PE fibers. Differences in the arthropods' responses could be attributed to the soil niches inhabited by each organism, being the more sensitive *P. scaber* mainly exposed to soil contaminants while springtails, less affected, were rather exposed to soil pore water.

In summary, it has been established that potential adverse effects on living organisms may occur by the co-presence in the soil of different MPs and pesticides. Concerning plants, scarce research studies can be found in the literature that couple with the joint effect of MPs and pesticides. Recent studies have highlighted the effective uptake and translocation of MPs by plants by using innovative techniques, such as fluorescently labeled PS microbeads detected by SEM and CLSM [192], Pd-doped nanoplastics by μ-XRF [193] or pyrolysis GC-MS [194], among others.

If only MPs are considered, inconsistent results were observed in relation to their effect on plants [195]. Zang et al. [18] reported an enhancement of the plant biomass of wheat (*Triticum aestivum*) due to the presence of MPs in soil (PVC and PE), probably because MPs diminish soil density and alter the water-holding capacity and water-stable aggregates, thus reducing penetration resistance for plant roots, and enhancing soil aeration, with a positive effect on root growth. Lian et al. [196] found increased seedling root elongation by 89–123% with the presence of PS NPs. On the contrary, negative effects on above-ground and below-ground wheat parts by low-density PE and biodegradable starch-based MP have been also reported, with higher negative effects by biodegradable MP [197,198]. In rice, which is a plant species more sensitive to MPs than wheat or lettuce [84], negative effects of different types of MPs have been reported: reduction in height and dry weight, decrease in primary root length and nutrient uptake or increased oxidative stress [199–201]. In cherry radish, PVC significantly induced more phytotoxicity than PP or PA, reducing plant growth [202]. A similar finding was priorly reported by Pignatelli et al. [203], who observed that long-term exposure to PVC caused more oxidative stress in *Lepidium sativum* than PP or PE. Some other studies showed low or negligible effects by various MPs in seed germination, seedling growth or biomass production in wheat [196,204], in the growth and yield of wheat plants even at extremely high plastic doses [95], or in seed germination or plant growth of *Sorghum saccharatum* and *L. sativum* [205]. Contradictorily, different sizes of green fluorescent microspheres or PET MPs have been reported to delay seed germination and affect the growth and physiological responses of *L. sativum* [79,203].

Similarly to MPs alone, the interaction with pesticides caused different effects on plant growth and development. Thus, Fajardo et al. [126] showed that leaf growth of maize (*Zea mays*) was initially inhibited, but this effect declined over time; whereas, a 47% reduction in root growth was measured with the simultaneous addition of pollutants and MPs. The mixed treatment led to an enrichment of the bacterial community (especially Proteobacteria) and predicted a potential impact on the C and N cycle in the soil environment. Likewise, another experiment, which was run in solution, showed that PE in combination with ten organic pollutants including three pesticides (alachlor, diuron and pentachlorophenol) caused no effect (*L. sativum*) or a low decrease (*Sinapsis alba*) of the early growth of both plant species [116]. On the contrary, Martín et al. [125], who also ran the experiment without soil, found higher negative effects for *Lactuca sativa* by the individual (white/blue PE or pollutants alone) than by the mixed treatments, possibly because pollutants adsorbed onto the MPs. Similarly with lettuce and in solution, the same conclusions were drawn by Yan et al. [206], who studied the effects of PS and a copper-based pesticide ($Cu(OH)_2$ nanowires). In the co-exposure, PS partially suppressed the hazardous effects on lettuce growth induced by the pesticide, diminishing plant stress. A very recent study [207] evaluated, in solution, the effect of PS and the herbicide quinclorac on *Oryza sativa*. It was shown that the combination of PS and the herbicide reduced the damage to rice by affecting the metabolism of a variety of amino acids and sugars and by activating the rice antioxidant enzyme system. Finally, the viability of *O. sativa* cells using glyphosate and PS or functionalized PS was established by Chi et al. [112]. The mixed treatment exhibited combined toxicity, altering metabolic activity and inflicting physical damage. However, in the presence of minerals, increased adsorption (Table 1) would immobilize them and reduce their uptake by plant root cells, alleviating the negative effects.

6. Conclusions

Due to the worsening of plastic pollution worldwide, specifically in the soil ecosystem, this review has focused on the interactions of two soil pollutants that deserve special attention, MPs and pesticides. Pesticides comprise a series of chemical compounds whose purpose is the control of pests and diseases but whose chemical composition and properties vary considerably. Likewise, MPs consist of a wide array of different polymer types with different sizes, shapes, and additives, which makes it difficult to draw general conclusions. MPs by themselves are considered emerging pollutants in terrestrial ecosystems since they

have the capacity of modifying soil properties (including structure, bulk density, porosity, chemical composition, pH or EC) and exerting harmful effects on the structure, enzymatic activity, population and diversity of soil biota, as well as on other living organisms, such as invertebrates or plants. Despite the many variables that must be taken into consideration regarding both MPs and pesticides, it is possible to outline some concrete ideas.

As it has been shown, plastics have the ability to retain pesticides, especially the more hydrophobic ones, thus reducing their instant availability for leaching, degradation, uptake by plants or ingestion by other organisms present in soils. Therefore, pesticides will not be able to attain the target pests at the recommended doses, plastics carrying pollutants may be ingested or uptaken by non-target organisms, or polluted plastics may be desorbing the pesticides over time, constituting a time-dependent releaser of pesticides in the ecosystem. Therefore, the co-presence of MPs and pesticides in soils may cause disturbances in medium- and long-term periods with adverse effects on soil-living organisms that will be dependent on the particular MP/pesticide system. In general, aged MPs produce higher effects than pristine MPs on environmental pesticide fate and on pesticide toxicity to living organisms, because aging gives rise to the appearance in plastics of new functional groups or microcracks that favor pesticide retention. Environmental soil factors, such as pH, DOM, salinity, etc., seem to play minor or changing roles in the interactions between MPs and pesticides, mainly depending on the properties of both pesticides and MPs. MPs may serve as an entryway for pesticides into terrestrial animals and the occurrence of toxic effects will depend on the ability of the pesticide to interact with the biosystem of the organism. Due to a lack of specific information, further research is strongly recommended to fully understand the mechanisms that participate in pesticide uptake and translocation by crops cultivated in soils contaminated with MPs. In any case, the ability of MPs to retain pesticides appears to be crucial since it controls the bioavailability of the contaminants to either animals or plants.

In light of the foregoing, environmental legislation should provide clear guidelines and include precautionary measures concerning the inputs in soil of plastics, not only because they may be potentially harmful on their own, but also due to the interactions with pesticides and other organic pollutants reaching the soil.

Author Contributions: All authors have equally contributed to the design of the work, search for literature, original draft preparation, writing, review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

DOC	dissolved organic carbon
DOM	dissolved organic matter
MP	microplastic
NP	nanoplastic
OC	organic carbon
PA	polyamide
PBAT	polybutylene adipate terephthalate
PBS	polybutylene succinate
PE	polyethylene
PET	polyethylene terephthalate
PLA	polylactic acid
PP	polypropylene

PS	polystyrene
PVC	polyvinyl chloride
Tg	glass transition temperature
WWTP	wastewater treatment plant

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