

Review

Does Microplastic Contamination in Agricultural Soils Decrease the Efficiency of Herbicides for Weed Control?

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Abstract: The contamination of agricultural soils by microplastics (MPs) has significant implications for herbicide efficacy and soil health. This study investigates the effects of MPs on critical processes such as the sorption, desorption, and degradation of herbicides, highlighting their influence on these compounds' mobility, persistence, and bioavailability. MPs interact with herbicides through sorption mechanisms, often reducing the availability of these compounds for weed control by retaining them on their surfaces. This sorption not only limits the immediate efficacy of herbicides but also alters their desorption process, resulting in a prolonged release into the soil environment. Additionally, MPs can inhibit microbial activity involved in herbicide degradation, increasing the time degradation of the half-life of these substances and extending their persistence in the environment. These processes collectively enhance the risks of bioaccumulation and environmental contamination. Understanding these interactions is essential for developing strategies to mitigate the impacts of MPs on herbicide performance and promote sustainable agricultural practices.

Keywords: plastic waste; residual herbicides; polymers; pesticides; accumulated in soils



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1. Introduction

Microplastics (MPs) are plastic particles smaller than 5 mm [1]. Researchers estimate that each year, soil and aquatic ecosystems release more than 10 million tons of MPs, and there is growing concern that this volume will continue to increase [1–5]. Currently, the number of MPs in the soil can be up to 23-fold greater than in the ocean, suggesting that the soil may be the main accumulation site for these materials [2,6].

MPs are prevalent in agricultural environments due to the numerous entry and distribution pathways of these plastic residues [7]. These polymers not only cause crop damage [8] and adversely affect vital soil activities [9], but they can also influence important agriculture processes [10].

The production of these small particles can be categorized into primary and secondary sources [11,12]. The primary sources are already manufactured in this size and introduced directly into the agricultural soil [13]. In the agricultural environment, these primary MPs can directly enter the soils by applying biosolids (sewage sludge), organic compounds, and fertilizers that contain these particles previously incorporated [14]. The degradation

of larger plastics in the environment [15], often due to the fragmentation of plastic mulch films used for crop protection or the decomposition of plastic waste used in agriculture [16], initiates the secondary sources of MPs. These plastics are degraded by factors such as sunlight, ultraviolet (UV), mechanical abrasion, and biological activities in the soil [15].

In agricultural soils, MPs can cause drastic changes in soil structure, bulk density, and water retention capacity [17]. Furthermore, they influence nutrient cycling [18] and affect various essential activities of soil biota, such as the enzymatic activities of microorganisms [18–22]. Due to their high specific surface area, MPs can also interact with other pollutants, such as polycyclic aromatic hydrocarbons, heavy metals, and pesticides [23,24], including herbicides, which can influence the effectiveness of weed control [25].

Several studies have highlighted the pervasive presence of MPs in agricultural soils and their interactions with various pollutants, including pesticides and heavy metals [1,7,10,15,19,20]. MPs can alter soil properties, disrupt microbial activity, and impact pollutant dynamics through mechanisms such as sorption [22,23]. Notably, their interaction with herbicides has raised concerns due to their potential to compromise weed control by decreasing herbicide bioavailability and prolonging their environmental persistence [26,27]. Despite these advances, a critical gap remains in understanding how MPs influence herbicides' sorption, desorption, and degradation dynamics in agricultural soils. This review aims to systematically address this gap, providing insights into the implications of MP–herbicide interactions for soil health, environmental sustainability, and agricultural productivity.

Knowledge about the interactions between MPs and herbicides in agricultural soils remains limited, especially considering that some pre-emergence herbicides exhibit residual effects in the soil to ensure effective control of the seed bank [28]. However, if there is an interaction between MPs and herbicides, contamination by these polymers can compromise weed management. The ability of MPs to prolong the persistence of herbicides in the soil, enhance their sorption, and simultaneously decrease their leaching and desorption back into the soil solution is responsible for this (Figure 1).

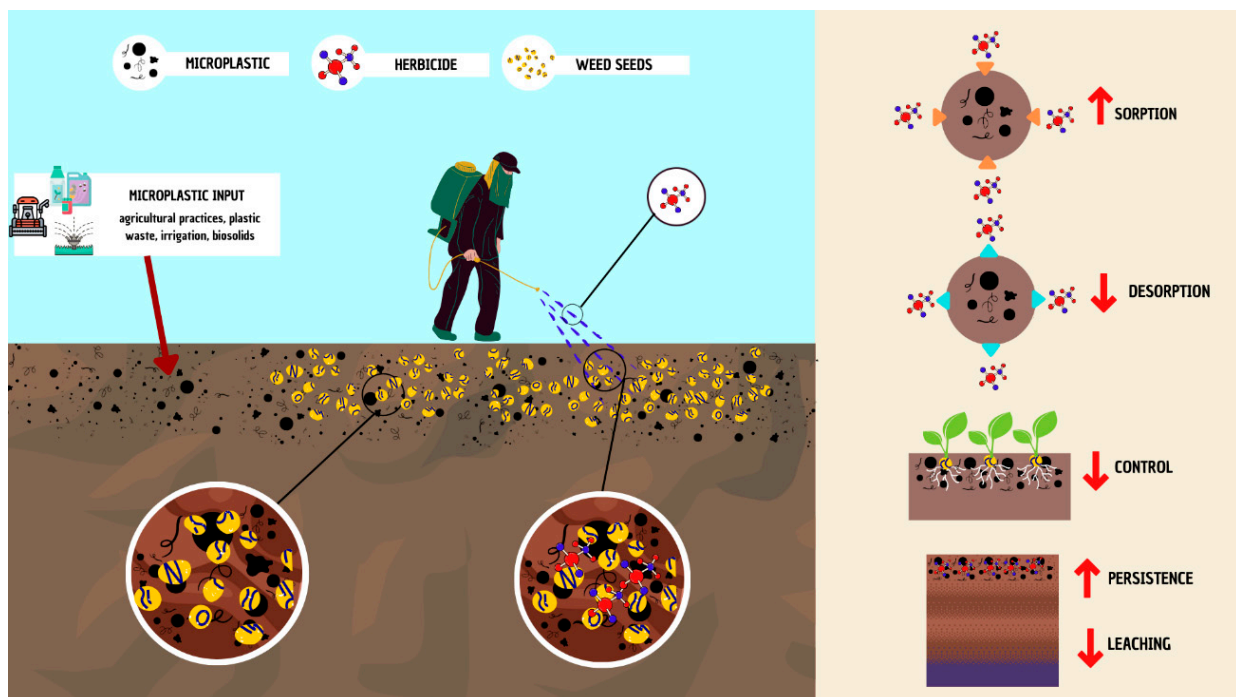


Figure 1. Contamination of arable soils by microplastics (MPs) and their interactions with the behavior and efficacy of herbicides. Source: Adapted from Zhang et al. [29]; Nobre et al. [30]; Wang et al. [31]; and Ni et al. [26].

Given the increasing concern regarding MP contamination in agricultural soils, it is essential to understand how these pollutants interfere with the effectiveness of herbicides, which are crucial for weed management. The interactions between MPs and herbicides can modify the release, mobility, and persistence of these compounds in the soil, directly impacting their efficiency in weed control. Therefore, it is crucial to investigate MPs' impacts on soil properties and the potential environmental risks arising from these interactions. Only with this understanding will it be possible to evaluate the real effects of MPs on the efficiency of herbicides. Furthermore, a comprehensive review of the available evidence on the effects of MPs on herbicide action is essential to guide the adoption of more sustainable agricultural practices and mitigate environmental risks.

2. Material and Methods

The scientific articles were selected using a systematic approach, following the established guidelines for bibliographic reviews. Searches were performed in the Scopus and Web of Science (WoS) databases, both recognized for their comprehensive coverage of scientific literature. The research terms, used between July and September 2024, included combinations such as “*microplastics and herbicides*”, “*microplastics and agricultural soils*”, and “*microplastics and pollutant interactions*”, with results limited to articles published up to 2024.

Inclusion criteria focused on studies that directly addressed interactions between microplastics and herbicides, particularly their effects on soil properties, herbicide persistence, and environmental impacts. Review articles and experimental studies relevant to the topic were prioritized to consolidate research gaps and advancements in the field. Articles lacking experimental data or specific analyses on herbicides and microplastics and those outside the agricultural context were excluded.

The screening process was conducted in two stages: reviewing titles and abstracts to identify potentially relevant articles and thoroughly analyzing the full texts to confirm their relevance. Data were categorized into themes such as soil impacts, herbicide behavior, and environmental interactions, facilitating the synthesis of the available evidence. This systematic approach ensured the inclusion of relevant studies and a comprehensive analysis of the topics investigated.

The figures were created on the basis of the compiled dataset and plotted using the R programming language within the RStudio environment. The most recent version of R (4.3.1) was used to ensure compatibility with advanced libraries and data visualization features. The graphs were generated with the ggplot2 package, which enables the creation of high-quality, customizable visualizations suitable for academic purposes.

3. Results and Discussion

3.1. Studies with Microplastics

The first studies on MPs gained prominence in 2004 when British researcher Richard Thompson coined the term “microplastics”, identifying small plastic fragments in sand and marine sediment samples [32]. Since then, the field of MP research has expanded rapidly, especially after 2010, with growing concerns about the environmental and human health impacts of these materials (Figure 2).

Scopus and Web of Science (WoS) are the main databases for consultation and have indexed 19,830 and 11,494 publications, respectively, as of September 2024. Since 2017, both have recorded more than 200 articles related to MPs per year, and the growth has been exponential. By the end of 2024, both databases expect to surpass the record of 4,729 studies indexed in Scopus and 2,474 in WoS (Figure 2).

The initial research focused mainly on oceans, as it was believed that most MPs accumulated in marine ecosystems [33]. Beyond the marine environment, scientists have begun exploring MPs' effects in terrestrial and freshwater ecosystems. Although these environments are recognized as sources of MP pollution, research is still developing a more complete understanding of the impact in this context [20].

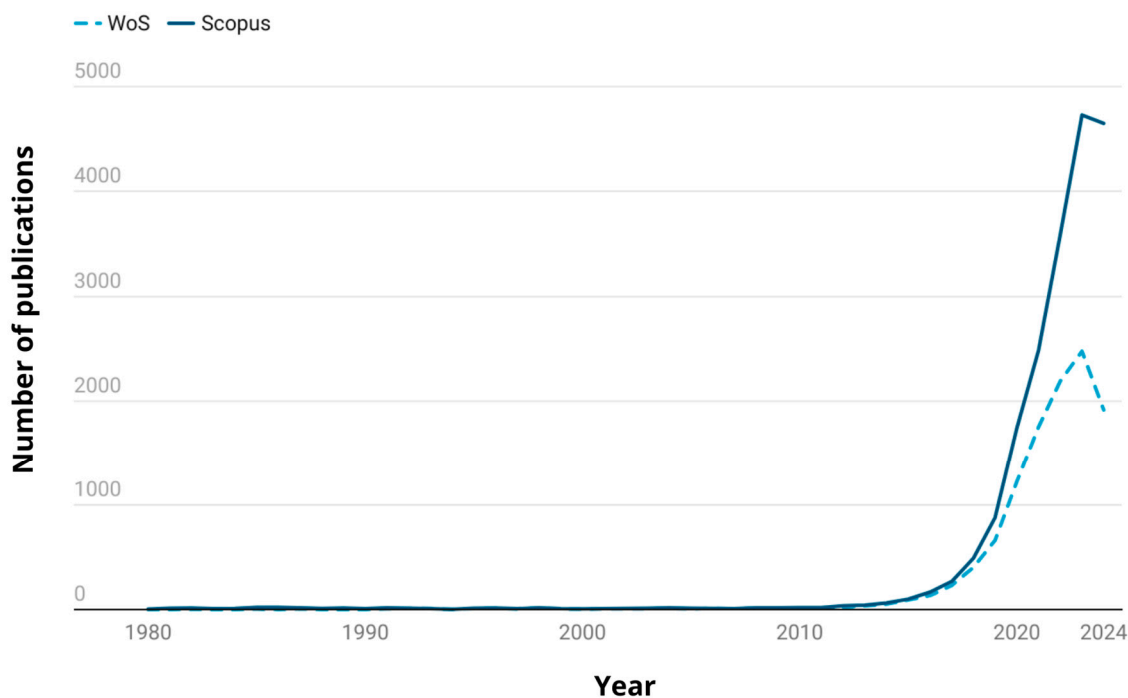


Figure 2. Annual publications on microplastics indexed in Scopus and Web of Science.

These studies revealed that aquatic and terrestrial organisms can ingest MPs, raising concerns about the potential entry of these pollutants into the human food chain. Research has also investigated potential human health risks, such as the neurotoxic and oxidative stress effects caused by MPs in fish [34].

In this context, environmental sciences focusing on water and soil and agriculture, chemistry, medicine, engineering, toxicology, physics, and others account for most publications in Scopus and WoS (Figure 3). As a result, research on MPs continues to evolve, with an emphasis on understanding their long-term ecological and toxicological impacts and the development of standardized methods for sampling and analyzing these pollutants [35].

MP research is a global topic of interest, with more than 150 countries having at least one study indexed in Scopus and WoS. However, some countries are pioneers in MP research, such as mainland China, the USA, Germany, India, and the United Kingdom (Figure 4).

Mainland China has invested significantly in MP research due to its status as the world's largest plastic producer and the growing environmental and political pressure to address pollution caused by these materials. As one of the largest emitters of plastic waste, effectively managing this type of pollution has become essential. Studies have shown that MP pollution affects various ecosystems on China's mainland, including freshwater systems and marine environments such as estuaries and lakes. This research investment aims to better understand the extent of this contamination and its ecological and health impacts and to assist in developing public policies and technological solutions to mitigate the problem [36,37]. Furthermore, mainland China recognizes the need to standardize MP collection and analysis methods to enable more effective comparisons between studies, promoting greater efficiency in environmental management [38].

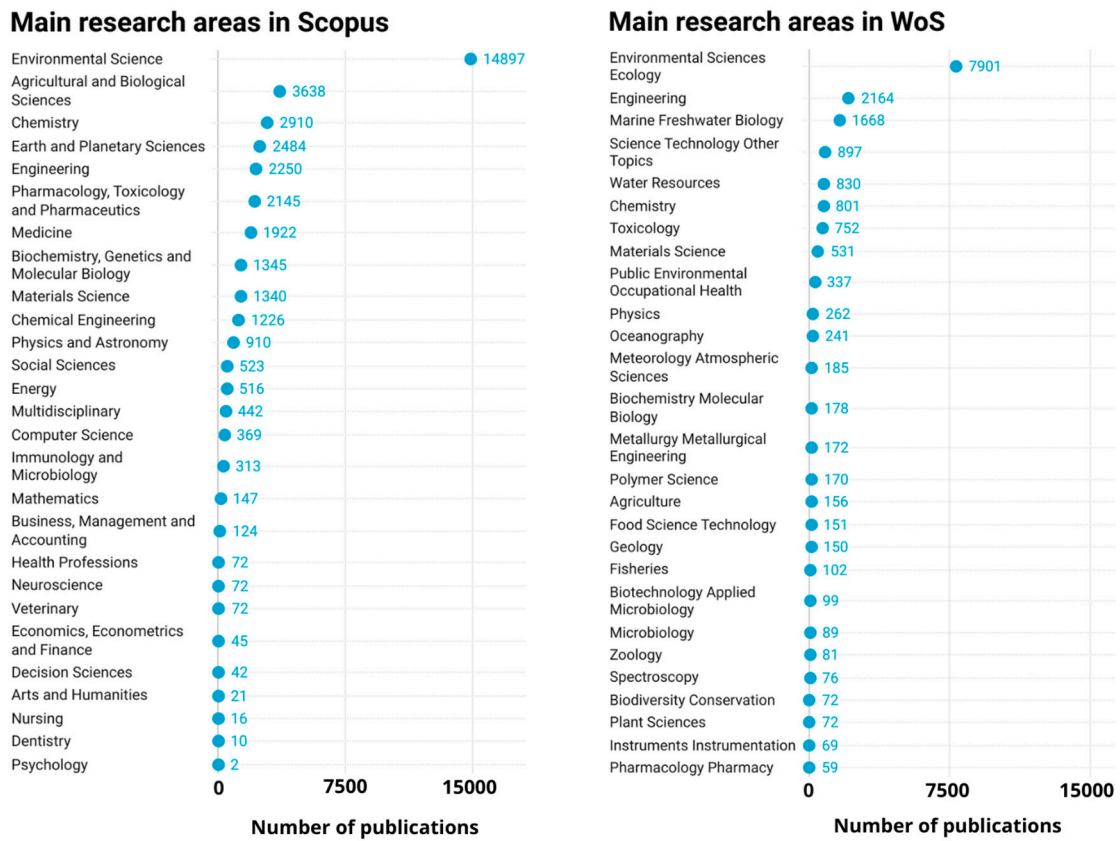


Figure 3. Main research areas by number of publications on microplastics (MPs) indexed in Scopus and Web of Science (WoS).

Publications on Microplastics by Countries/Territories

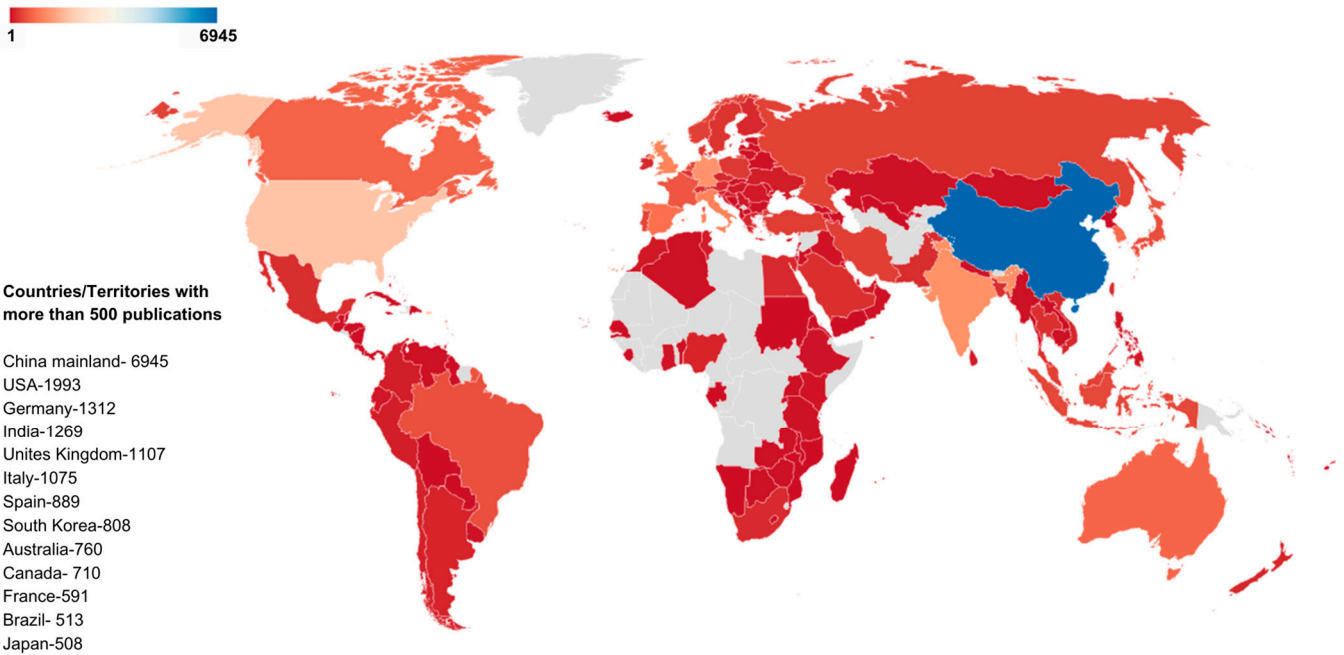


Figure 4. Distribution of publications on microplastics (MPs) worldwide according to the Scopus database.

3.2. Studies with the Interaction of Microplastics and Herbicides

Despite the growing interest in MP research, the interaction with herbicides remains a relatively underexplored topic in the literature. Currently, there are 80 indexed publications in Scopus and 20 in WoS. The first publications appeared in 2013, but the number of studies only increased significantly after 2018 (Figure 5). Although the number of publications is still limited, several research lines are emerging to study the interaction between herbicides and MPs.

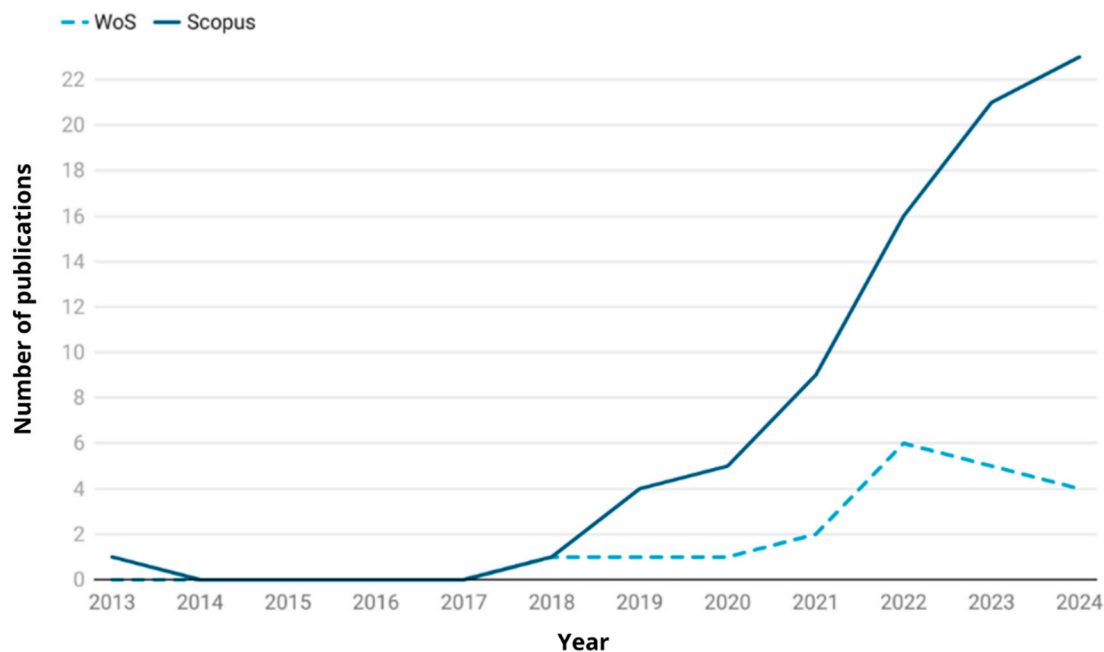


Figure 5. Annual publications on microplastics (MPs) and herbicide interaction indexed in Scopus and Web of Science (WoS).

Research on the interaction of MPs and herbicides spans several specific areas, addressing different impacts and mechanisms in terrestrial and aquatic ecosystems. One of the main research lines focuses on soil interactions and changes in soil properties. Many studies have investigated how MPs in the soil affect herbicide adsorption, mobility, and degradation. MPs can increase herbicide persistence in the soil by acting as carriers for pollutants. They can also alter the physical and chemical structure of the soil, impacting herbicide retention capacity and their mobility through the soil profile [39]. Another research focus is the interaction with plants and its effects on plant performance. Studies have shown that the presence of MPs can influence plant growth and health, interfering with nutrient absorption and root development. Additionally, the presence of MPs and herbicides can exacerbate plant stress, negatively affecting biomass and photosynthesis [40].

Research on aquatic environments investigates how MPs and herbicides interact in water systems, altering herbicide toxicity and behavior. Studies on aquatic organisms have shown that MPs increase the toxicity of herbicides like glyphosate, exacerbating harm to ecosystems and aquatic biodiversity [41].

The effects on soil microbiota represent an emerging area of research focusing on the impacts of the combined presence of MPs and herbicides on soil microbial communities. These studies investigate how the presence of both MPs and herbicides affects soil health, including microbial activity and organic matter decomposition, potentially disrupting essential biogeochemical cycles [42].

Concerns about the ecological impacts of these combined pollutants on terrestrial and aquatic ecosystems are driving the steady growth of research on the interaction between MPs and herbicides. The primary areas of investigation include soil interactions, plant health, aquatic toxicity, and effects on microbial communities. While it is already

known that MPs can increase the persistence and toxicity of herbicides in the environment, studies continue to explore the long-term implications for biodiversity and ecosystem health. This field of research is crucial for guiding future mitigation strategies and environmental regulations.

3.3. Impact of Microplastics on Soil Properties

MPs originate from various sources and have accumulated in soils, presenting in various shapes, sizes, and polymeric compositions. This heterogeneity leads to a range of impacts on soil properties, which can be positive, negative, or negligible. Unlike soil particles, MPs exhibit significant variations in shape, weight, and surface charge, potentially altering the entire spectrum of soil properties. The impacts of the presence and accumulation of MPs on soil properties can be classified into chemical, physical, and biological effects.

The literature reports a wide range of results, with different effects observed depending on the combinations of MP types and soil characteristics [17,43,44]. As summarized in Figure 6, the physical properties affected by MPs include soil structure, aggregation, porosity, bulk density, and water retention. MPs also influence chemical properties like pH, organic matter content, nutrient availability, and pollutant dynamics. Moreover, MPs can alter the microbiological community, affecting organisms' diversity, activities, and related processes and altering greenhouse gas emissions.

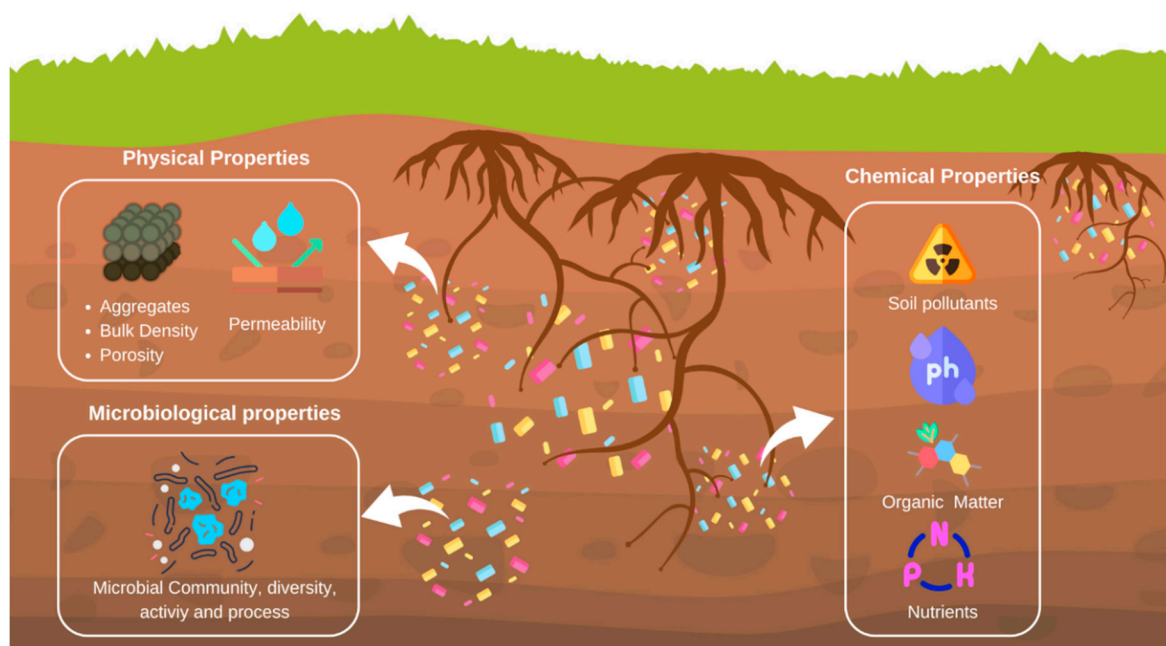


Figure 6. Soil properties affected by the presence of microplastics (MPs).

Regarding physical properties, the presence of MPs in various forms—spheres, fragments, fibers, foams, films, and pellets—can harm soil structure. The differences in shape, weight, and charge between MPs and soil particles can hinder soil aggregation, which is crucial for maintaining porosity. This, in turn, influences water transport, aeration, soil stability, and microbial activity [44].

MPs can obstruct soil pore spaces and alter water dynamics. For example, Kim et al. [45] demonstrated that MP contamination in the soil disrupts vertical water flow and modifies the physical structure, impacting both the contaminated and adjacent layers. The physical impacts of MPs, including reductions in soil bulk density, porosity, and permeability, arise due to the differences in shape, weight, and charge compared with soil particles. MPs hinder soil aggregation by interfering with the binding forces among soil

particles, reducing pore space connectivity. This impacts water transport, aeration, and soil stability, affecting microbial activity and plant root penetration [44].

Polyacrylic fibers, polyamide spheres, polyester fibers, and polyethylene fragments were evaluated in sandy clay soil. It was observed that soils contaminated with MPs generally exhibit a reduction in bulk density [17]. The findings revealed that spherical MPs, due to their size similarity with soil particles, have a less significant impact on soil properties than fibers and fragments, highlighting the potential limitations of visual identification methods. Additionally, the concentration of MPs plays a critical role, with lower concentrations sometimes exerting more significant effects than higher concentrations, reflecting non-monotonic responses.

Regarding chemical properties, soil pH is a crucial indicator of the physicochemical properties [43]. Studies have reported a decrease in soil pH following MP contamination. This decrease is attributed to the release of lactic acid from the mineralization of aliphatic polyesters, such as polylactic acid, which form cracks on the polymer surface. The increase in soil organic matter, which negatively correlates with soil pH, may also correlate with this pH reduction [46]. However, non-biodegradable MPs, such as polyethylene (PE) and polypropylene (PP), may influence pH differently. These MPs can leach additives and other chemicals that alter ionic concentrations, potentially buffering or changing the pH over time [44].

MPs in the soil have also been associated with varied effects on organic matter content, directly influencing soil fertility, plant nutrition, and microbial activity [44]. For instance, Liu et al. [47] saw that dissolved organic matter broke down less quickly in cultivated loess soils with 28% (w/w) polypropylene particles. This meant that more nutrients, especially nitrogen and phosphorus, were released and accumulated in the soil solutions. Conversely, MPs can contribute to organic carbon levels and facilitate the release of dissolved organic carbon (DOC). Soil bacteria can degrade MPs, particularly bioplastics, into soluble carbon, resulting in higher concentrations of DOC in soils with elevated MP levels [44]. For example, Shi et al. [48] reported a significant increase in soil DOC after adding 1% MP to various soils. At 25 °C, soil containing 1% polylactic acid exhibited the highest DOC content, with increases of 16% and 24% in black soil and loess soil, respectively, compared with the control treatments. Given these contradictory results, further research is needed to elucidate the impacts of MPs on soil organic matter and related processes.

MPs in the soil can also significantly influence nutrient dynamics, particularly concerning soil organic matter and microbial activity. Studies have shown that low-density polyethylene (LDPE) MPs at concentrations of 2% and 7% disrupt soil bacterial networks and alter functional groups involved in the nitrogen cycle [49]. Moreover, amendments with MPs (2000 fragments per kg of soil) significantly increased urease and catalase activities after 15 days [50]. Specifically, adding MPs notably stimulated catalase activity, likely due to the increased soil porosity caused by polyethylene fragments. The increase in urease activity, crucial for the nitrogen cycle, promoting the hydrolysis of nitrogen-containing organic matter, was also observed. However, research on the effects of MPs on soil micronutrients, such as Fe, Mn, Zn, and Cu, still needs to be deeply explored, indicating the need for more studies to explore the impacts of various MPs on soil health and plant growth [44].

Furthermore, MPs influence soil nutrient availability through various mechanisms, with effects depending on their type, shape, concentration, and size. Studies have reported mixed impacts: MPs such as polyvinyl chloride (PVC) and PE can reduce nitrogen and phosphorus availability, while others show minimal or even positive effects like reduced nitrate leaching due to improved soil aggregation. Key mechanisms include the release of nutrient-like elements (e.g., phosphorus and nitrogen) from MPs during degradation and their ability to adsorb nutrients, especially when aged or weathered. MPs also alter microbial communities, enzyme activities, and symbiotic relationships, such as those with arbuscular mycorrhizal fungi, which play a crucial role in nutrient cycling. Additionally, MPs can modify soil structure, improving aggregation and porosity and enhancing nutrient retention or oxygen diffusion for microbial processes. Despite these findings, the variability

in outcomes underscores the need for further research, particularly on micronutrients and long-term effects.

Biologically, MPs significantly impact microbial community composition, diversity, and activity in the soil. Ng et al. [51] observed a divergence in bacterial communities in soils treated with polyethylene terephthalate (PET) and LDPE, with a reduction of 0.4% in PET and 3% in LDPE. Adding 1% and 5% PE and PVC MPs to agricultural soils with low pH and high nitrogen levels decreased the number and types of bacteria, with PE having a larger effect than PVC [52]. MPs can induce the formation of specialized microbial networks adapted to the metabolism of these materials, threatening microbial ecology and biogeochemical cycles with potential ecological-scale consequences [53]. Gao et al. [46] reported that adding MPs increased total phospholipid fatty acids (PLFA) but decreased nutrient use efficiency, microbial diversity, and functional genes. This addition favored the growth of tolerant microorganisms, inhibiting the more sensitive ones, leading to the formation of specialized microbial communities and disrupting global carbon and nitrogen cycles. Furthermore, Rong et al. [49] discovered that LDPE MPs affected the competition for niches and nutrients, with microbial community responses influenced by resistance to disturbance and resilience, which affect recovery rates following disturbances.

Studies indicate that the diversity of MPs—encompassing variations in polymer type, particle structure, surface oxidation state, and size—should be considered when assessing their effects on soils. Considering the different types of MPs as a homogeneous stressor can compromise the accuracy of environmental risk assessments [17]. Moreover, the synergy between MPs and other contaminants, such as herbicides, deserves special attention. Therefore, additional research is needed to elucidate the interactions and mechanisms between MPs and different soil properties and types. Understanding MPs' potential risks and environmental impacts is crucial for improving risk assessments and developing more effective mitigation strategies.

These changes in soil properties affect the overall dynamics of the ecosystem and play a critical role in the interaction between MPs and herbicides. For instance, alterations in soil structure and water retention capacity can influence the transport and bioavailability of herbicides, while reduced microbial activity may slow the degradation of these compounds. Thus, MPs' modification of the soil's physical, chemical, and biological properties determines their interactions with herbicides, directly affecting their efficacy and environmental persistence.

3.4. Potential Risks and Environmental Impacts of MPs

The presence of MPs in the terrestrial environment results in direct negative impacts. However, their interaction with herbicides amplifies ecological risks for non-target plants and soil organisms. Due to their large specific surface area and hydrophobicity, MPs function as sorbents for herbicides and other pesticides, with the potential to alter their bioavailability and persistence in the soil. MPs' sorption capacity can slow down herbicide degradation, increase toxicity to non-target plants, and impact the ecosystem of other terrestrial organisms.

In a maize cultivation study, the coexistence of MPs significantly reduced the bioconcentration of atrazine [6]. Similarly, rice research indicated that the interaction between MPs and the herbicide quinclorac reduced the crop's injury damage by activating the plant's antioxidant system [54]. In a soilless experiment, Martin et al. [55] observed that the detrimental effects on lettuce (*Lactuca sativa*) were more severe when contaminated with either MPs or other contaminants rather than by a mixed solution of both. This suggests that MPs may sorb contaminants, thus decreasing their availability and associated toxicity.

Studies on the potential impact of the interaction between MPs and herbicides acting in the soil on non-target plants are still incipient. Despite this, the examples demonstrate that, although MPs can reduce the phytotoxic impact of herbicides on agricultural crops, the same can occur with weeds, suggesting a potential increase in herbicide resistance. Furthermore, MPs can retain herbicides in the soil, reducing their leaching and immediate

bioavailability for plant absorption or consumption by other organisms and soil microorganisms. This reduced efficacy of herbicides on target plants at the recommended doses poses a risk of intensified use of the products and a consequent increase in soil and ecosystem contamination [56]. Therefore, it is important to include the study of MP contamination in agricultural soils in agricultural planning to mitigate environmental damage.

The intensive use of herbicides for weed management in agricultural systems presents significant challenges. Weed resistance to herbicides diminishes control effectiveness and increases production costs [57]. The high sorption capacity of the MPs can cause some of the herbicide molecules to become unavailable to the target plants, reducing the control's efficacy.

The interaction between MPs and herbicides can prolong the degradation of these chemicals, resulting in their extended presence in the environment. Chronic exposure to sublethal concentrations allows weed adaptation. As the availability of herbicides decreases, the selection pressure for resistant weed species may increase over time. This occurs because plants that survive sublethal herbicide doses are more prone to developing resistance, exacerbating transgenerational negative effects [58]. Supported by evolutionary theory, the hormesis phenomenon justifies that low pesticide concentrations can lead to increased growth and biomass production as an adaptive response to more severe stresses, increasing survival chances [58,59].

Recently, Qiu et al. [60] gathered research on plants' genetic expression responses to stress induced by MPs, revealing that MPs, as a stress factor, affect genetic expression and regulatory networks in plants. More research is still needed to identify genes linked to microplastics, underscoring the pressing need for studies to comprehend the molecular toxicity of MPs and the specific mechanisms involved.

Several studies have examined the coexistence of MPs and herbicides, addressing dissipation and adsorption in the soil, degradation, transport, and bioaccumulation [6,27,61,62]. Overall, the accumulation of MPs in the soil appears to decrease herbicide degradation and increase the half-life of the herbicide. Despite this, there are gaps in the research regarding the potential risk of enhanced herbicide resistance in weeds due to the reduced efficacy of herbicides. Consequently, further investigation into the interactions between MPs and herbicides is still necessary concerning the response of weed plants to the adsorption and desorption behavior of herbicides in biodegradable and non-biodegradable MPs over time.

In addition to the risks associated with the behavior and survival of weeds, the impact of MPs on soil organisms also requires attention. A study investigating glyphosate revealed that while MPs did not affect the degradation of the herbicide, microbial respiration in soil was altered in treatments with higher concentrations of MPs [63]. Moreover, MP residues can be ingested by earthworms and other soil organisms, which play a significant role in the redistribution of MPs to deeper layers through excrement, burrows, and even by adhering to the exterior of their bodies [64]. This transport of MPs increases the exposure of other soil organisms, prolongs the residence time of herbicides, and favors the possible arrival of MPs to groundwater, carrying herbicides and other adsorbed contaminants with them.

The consequences of the interaction between MPs and herbicides go beyond immediate toxicity. MPs can directly and indirectly affect ecological processes at the level of organic matter decomposition, nutrient cycling, and productivity. When incorporated into feces and soil particles, MPs and herbicides can be ingested and transferred to other organisms [65].

The soil supports the development of plants and, by acting as a reservoir for MPs, creates conditions for these particles to be absorbed by the roots and their subsequent transportation to other plant tissues. The hydrophobic nature of MPs, as well as the cellulose cell walls of plants, favors the sorption of nanometric plastic particles onto the root surface, leading to the accumulation and blockage of pores and root channels and thereby impeding water absorption [66,67]. In a recent study, Li et al. [62] demonstrated that MPs can penetrate the stele of lettuce and wheat plants through fissures in the emergence areas of secondary roots and observed signs of MPs located in the vascular system, epidermis, xylem vessels, and cortical tissue of wheat. Higher transpiration rates increased the absorption of

MPs, suggesting that the water movement through transpiration acts as the main driving force for the transport of plastics within plants.

Studies have shown that the presence of MPs affects plant development, potentially influencing plant metabolism and productivity by inhibiting seed germination, reducing plant height, producing biomass, interfering with photosynthetic pigments, and interfering with the antioxidant defense system [68,69]. On the other hand, research indicated that certain types of MPs had no significant effect on root and leaf activity or significantly increased the length, volume, and diameter of the roots, depending on the particle size [70].

MPs also act as carriers of chemical contaminants in soil due to their hydrophobic surface and chemical composition, enabling them to adsorb herbicides and other pesticides and heavy metals, prolonging their persistence and mobility in soil. Pesticides quickly adhere to the surfaces of MPs, with the diffusion rates influenced by the characteristics of both the pesticides and the MPs [39]. The dynamics of contaminants with MPs make them more susceptible to bioaccumulation in soil organisms due to the delayed degradation of herbicides and other associated chemicals, especially in plants with shallow roots and bacterial communities [71,72].

The result of the bioaccumulation of MPs and associated chemical substances implies potential contamination in plants, soil organisms, and water reservoirs, but they can also be transferred to animals and humans. The contamination of MPs in the ecosystem threatens the food chain through herbivorous animals, everyday salads, and drinking water, exacerbating public health risks. A review by Campanale et al. [73] reported concerning levels of particles $<10\ \mu\text{m}$ in fruits and vegetables, as well as variations in the nutritional values of some edible vegetables due to MPs interactions. Besides the direct effects of contamination by MPs, they can serve as a pathway for contamination by agricultural pesticides and heavy metals in plants and animals, whose toxic effects will depend on the ability of the substances and particles to interact with the organism.

Given these findings, it is imperative to conduct more research on the bioaccumulation of MPs and their associated contaminants, investigate the possible interactions between these polymers and organic contaminants present in the soil, such as herbicides, and assess the implications of these interactions for environmental and food security.

3.5. Interaction of Microplastics and Herbicides in Soil

With the increasing accumulation of MPs in the environment and the associated risks, it is essential to understand how these polymers interact with other contaminants, such as the herbicides widely used in agricultural practices [74]. In the soil, these interactions can influence herbicides' mobility and persistence, affecting their effectiveness in weed control and increasing the risks of long-term environmental contamination [75].

MPs serve as vectors for organic compounds, altering the sorption and bioavailability of herbicides in the soil [76]. These interactions involve hydrophobic partitioning processes, where nonpolar herbicides migrate to the plastic phase of MPs, and surface sorption mechanisms that involve hydrogen bonds, π - π interactions, electrostatic interactions, and Van der Waals forces [23]. Moreover, herbicides can accumulate in the micropores of MPs, increasing their retention and persistence in the environment (Figure 7).

Environmental factors, such as pH, ionic strength, and dissolved organic matter, also critically influence these interactions. For example, pH variations can alter the compounds' charges, modulating the electrostatic interactions [77]. Ions present in the solution compete for sorption sites, reducing the retention of herbicides in the MPs [78]. As a result, these interactions can decrease the effectiveness of herbicides by reducing their availability for weed control while increasing their persistence, intensifying the risks of environmental contamination.

The physicochemical characteristics of herbicides, such as acid/base dissociation constants (pK_a and pK_b), K_{ow} , and S_w (Figure 3), directly influence these interactions, as they determine the behavior of these compounds in the soil and their affinity for MPs. Herbicides with high K_{ow} values are more hydrophobic and tend to accumulate in MPs

through hydrophobic partitioning, reducing their availability in the soil. An example is the herbicide pendimethalin, which has a K_{ow} of 5.2 [79]. This high value indicates that it preferentially accumulates in MPs and organic matter, showing low mobility in the soil [23,79]. Conversely, herbicides with low K_{ow} values, such as glyphosate ($K_{ow} = 3.2$), exhibit a greater affinity for the aqueous phase and a lower tendency to accumulate in MPs, making them more mobile and bioavailable in the soil [23,79]. S_w also influences these interactions. Compounds with low S_w , such as atrazine ($S_w = 33$ mg/L), are less soluble in water [80], which enhances their adsorption on the surfaces of MPs, especially in dry soils, increasing the retention of the herbicide and reducing its leaching. By contrast, herbicides with high S_w , such as glyphosate ($S_w = 12,000$ mg/L) [80], exhibit lower adsorption in MPs and greater mobility in the soil, which can lead to loss through leaching. Additionally, the pK_a and pK_b values influence the ionic state of these compounds. Herbicides with low pK_a values, such as 2,4-D ($pK_a = 2.8$), are more likely to be neutral in acidic soils [81], facilitating their interaction with MPs. By contrast, more soluble and predominantly ionic compounds at neutral or alkaline pH have a reduced propensity for hydrophobic partitioning, although they may interact with MPs through electrostatic adsorption [82] (Figure 7).

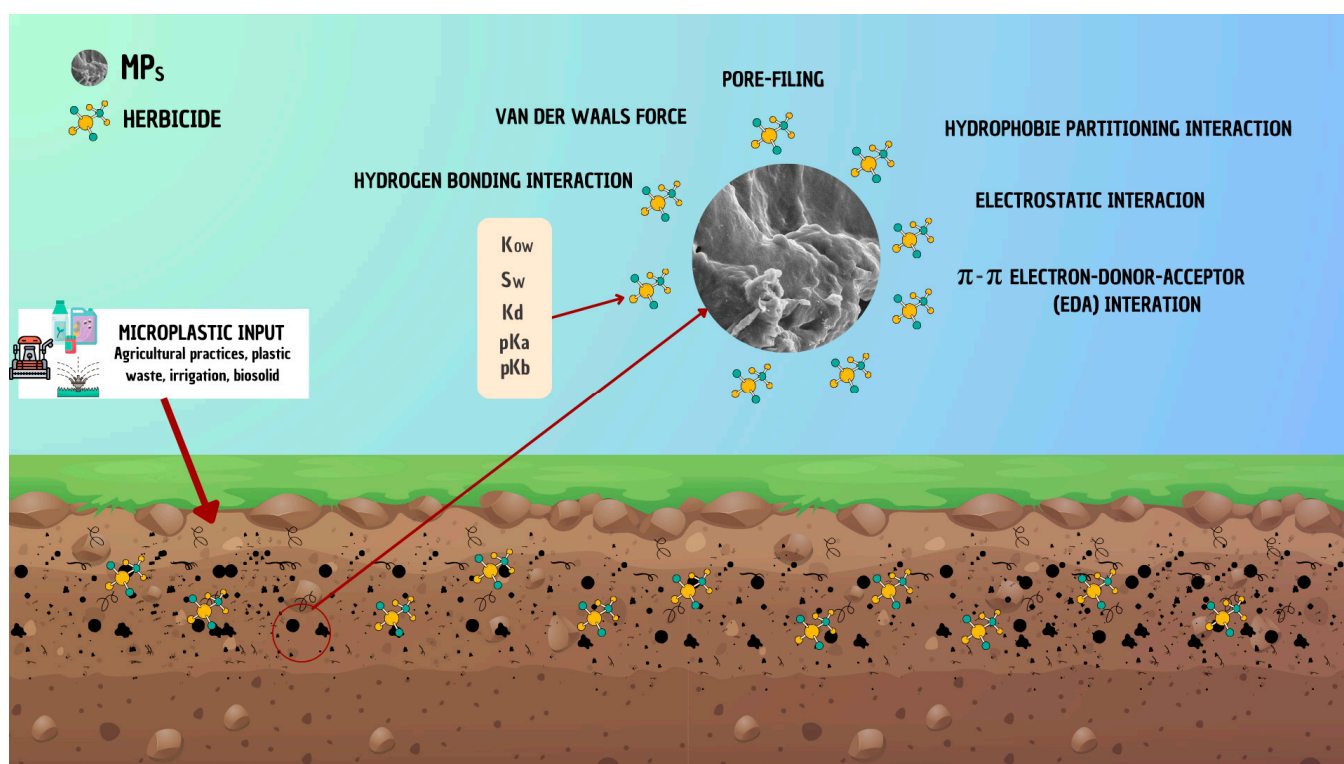


Figure 7. Interaction mechanisms between MPs and herbicides in soils. K_{ow} : octanol–water partition coefficient; S_w : water solubility; K_d : distribution coefficient; pK_a : acid dissociation constant; pK_b : base dissociation constant. Source: Adapted from Wang et al. [23].

These interactions influence herbicide behavior in soils, as demonstrated by specific examples. For instance, MPs derived from polyethylene have been shown to enhance the sorption of atrazine, reducing its leaching and increasing its persistence in soil, which may heighten long-term contamination risks [83–85]. Pendimethalin, with its high hydrophobicity ($K_{ow} = 5.2$), exhibits strong sorption to MPs, reducing its bioavailability and potentially compromising its weed control efficacy [23]. While this reduced bioavailability may mitigate acute toxicity to non-target organisms, it could necessitate higher application rates, further increasing environmental contamination risks [84]. These examples highlight the dual role of MPs in modifying herbicide dynamics, simultaneously mitigating and exacerbating associated risks.

Molecular size also affects the mobility of herbicides, with larger compounds showing a greater tendency to accumulate in the micropores of MPs, hindering their availability and transport in the soil. Moreover, polar functional groups, such as hydroxyls and carboxyls, facilitate the formation of hydrogen bonds and electrostatic interactions, particularly with MPs that possess oxidized surfaces [83]. Herbicides containing aromatic groups can engage in π - π interactions with MPs composed of aromatic rings, further enhancing their retention [23].

For example, Peña et al. [39] reviewed the interaction between microplastics and pesticides in soils, demonstrating that microplastics can increase pesticide retention through sorption mechanisms. This process reduces the bioavailability of pesticides and prolongs their environmental persistence, emphasizing the role of microplastics in altering pesticide behavior in agricultural soils. Similarly, studies have shown that the herbicide pendimethalin exhibits strong sorption to MPs due to its high hydrophobicity ($K_{ow} = 5.2$) [23]. This behavior reduces its mobility and bioavailability in the soil, potentially impacting its efficacy in weed control. Sorption occurs both through Van der Waals forces and the filling of micropores, with the surface area of the MPs being a determining factor in the retention of contaminants [84].

A recent study by Lv et al. [85] revealed that MPs derived from polyethylene significantly enhance the sorption of atrazine, reducing its leaching potential and increasing its persistence in the soil environment. This interaction underscores the importance of considering polymer type when evaluating herbicide dynamics. Furthermore, Liu et al. [86] reported that polystyrene MPs delayed the degradation of 2,4-D, extending its environmental half-life. This delay, attributed to reduced microbial activity in the presence of MPs, illustrates the complex interplay between MPs, soil microbiota, and herbicide degradation pathways. These findings highlight how MPs modify the fate of herbicides in soils, raising concerns about long-term ecological risks.

Furthermore, Torres et al. [87] investigated the affinity of biodegradable MPs for hydrophobic compounds, identifying that electrostatic forces, Van der Waals interactions, hydrogen bonds, and π - π interactions play essential roles in sorption. In another study, Zhang et al. [88] investigated the interaction between polyethylene microplastics and organochlorine pesticides in soil. The study demonstrated that microplastics increased pesticide sorption, reducing their bioavailability in soil suspensions, highlighting the role of microplastics in modifying contaminant dynamics in terrestrial environments. This behavior was attributed to hydrophobic interactions and the chemical affinity between MPs and metolachlor, which could decrease the herbicide's effectiveness in weed control while prolonging its environmental persistence.

Consequently, Zhou et al. [27] showed that the presence of MPs in the soil reduced the degradation of the herbicide simazine, prolonging its half-life and altering the microbial community. All tested concentrations observed this effect, indicating greater herbicide persistence and environmental risks. Although MPs did not affect the degradation of glyphosate in Chinese soils, their presence altered microbial activity, demonstrating that microbes can indirectly influence soil ecology and modify the persistence of contaminants [63].

To provide a comprehensive understanding of these interactions, Table 1 summarizes key findings regarding herbicide-microplastic interactions. Table 1 outlines the physicochemical properties of herbicides, the mechanisms of sorption, kinetic behavior, and isotherms, offering insights into how these processes influence herbicide persistence and environmental impact.

These studies collectively highlight that the presence of MPs in the soil can compromise the efficiency of herbicides, altering their behavior, increasing their persistence, and directly impacting weed control. However, a significant gap remains in research regarding the interaction between MPs and herbicides, emphasizing the necessity for further investigation to elucidate these dynamics.

Table 1. Herbicide–microplastic Interactions: physicochemical properties, mechanisms, kinetics, and isotherms.

Herbicide	Microplastic	Interaction Mechanism	Kinetics	Isotherms	References
Atrazine	Polyethylene	Sorption via Van der Waals forces and micropore filling	Rapid sorption, depending on herbicide and MPs characteristics	Linear and Freundlich, depending on conditions	Ly et al. [85], Wang et al. [23]
Pendimethalin	Polyethylene	High sorption due to high hydrophobicity ($K_{ow} = 5.2$)	Slow due to accumulation on MPs	Freundlich due to high affinity for MPs	Kjaer et al. [79], Wang et al. [23]
Simazine	Polystyrene	Reduction in degradation and alteration in microbial community	Reduction in microbial degradation rate	Alterations due to high sorption capacity	Zhou et al. [27], Liu et al. [86]
Glyphosate	Various types	Higher soil mobility due to low sorption on MPs	Kinetics influenced by pH and ionic charge	Variable isotherms with greater mobility	Yang et al. [63], Souza et al. [80]
2,4-D	Polystyrene	Sorption facilitated by polar functional groups and π – π interactions	Sorption affected by polar groups and molecular size	Freundlich behavior in organic matter-rich environments	Mo et al. [83], Lan et al. [82]

K_{ow} : Octanol–water partition coefficient.

4. Concluding Remarks

MPs in agricultural soils pose significant challenges to herbicide efficacy and the sustainability of agricultural practices. The sorption of herbicides onto MPs reduces their bioavailability to target plants, impairing weed control and potentially contributing to weed resistance to herbicides. Additionally, MPs adversely impact soil health by destabilizing microbial communities and disrupting essential nutrient cycles, further compounding the ecological risks associated with their presence.

The interactions between MPs and herbicides present a complex balance of risks and mitigations. While MPs can prolong the persistence of herbicides in the environment, amplifying ecological risks, they may also reduce immediate bioaccumulation and toxicity by sequestering herbicides. This dual role highlights the need to clarify the conditions under which MPs amplify or mitigate the environmental impacts of herbicides.

This review comprehensively explored these interactions, emphasizing the importance of advancing our understanding of these processes to enable more accurate risk assessments. Addressing these impacts requires a deeper understanding of MP and herbicide dynamics, the development of sustainable agricultural practices, and effective public policies to mitigate plastic contamination in agricultural systems.

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