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Pollution of agricultural soils by microplastics and their interaction with residual herbicides

Maura Gabriela da Silva Brochado
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MAURA GABRIELA DA SILVA BROCHADO

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Thesis submitted to the Plant Production Graduate Program of the Universidade Federal de Viçosa in partial fulfillment of the requirements for the degree of *Doctor Scientiae*.

Adviser: Kassio Ferreira Mendes

Co-advisers: Gustavo F. de Castro
Lucas de Paula Corredo

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Maura Gabriela da Silva Brochado
Author

Kassio Ferreira Mendes
Adviser

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ABSTRACT

BROCHADO, Maura Gabriela da Silva, D.Sc., Universidade Federal de Viçosa, March, 2025. **Pollution of agricultural soils by microplastics and their interaction with residual herbicides**. Adviser: Kassio Ferreira Mendes. Co-advisers: Gustavo Franco de Castro and Lucas de Paula Corredo.

Agricultural soils contaminated by microplastics (MPs) pose a significant con-cern regarding the efficacy of residual herbicides in controlling weeds. An im-portant part of this study was investigating how MPs interact with three residual herbicides: diuron, hexazinone, and S-metolachlor. The main focus was on identifying the most effective analytical methods for detecting MPs in soil matri-ces and assessing the sorption and desorption behavior of the herbicides. Near-infrared spectroscopy (NIR) and multispectral analysis were used, demonstrating high sensitivity in detecting MPs at various concentrations. High-performance liquid chromatography (HPLC) was used to assess the interaction between MPs and herbicides, enabling the determination of sorption and de-sorption isotherms. MPs were only detected at high concentrations (20%) using X-ray analysis. NIR at 2,300 nm and multispectral analysis at 395 nm showed greater accuracy and sensitivity in distinguishing between all levels of MPs. Scanning Electron Microscopy (SEM) revealed that MPs possess an amor-phous structure, distinct from crystalline soil, which may influence their interactions with other soil constituents. Regarding the interaction of MPs with herbicides, the presence of MPs influenced the sorption of S-metolachlor in the soil, resulting in up to a 10% increase in the amount of the herbicide sorbed, with a sorption coefficient (Kd) of 4.85 L kg^{-1} with the addition of 5% MPs. However, there was no return of S-metolachlor to the soil solution, as demonstrated by a hysteresis (H) of 0.99 for the treatment with 5% MPs, compared to a control treatment with an H of 0.88. Diuron and hexazinone showed little interaction with MPs; the sorbed percentage of diuron was around 40% in all treatments (amended and unamended soils), with a Kd ranging from 1.84 to 2.12 L kg^{-1}. In the case of hexazinone, the behavior was similar, but the sorbed percentage was around 20% for all treatments (amended and unamended soils), with a Kd ranging from 1.63 to 2.03 L kg^{-1}. Only small amounts of both herbicides were taken up by plants. In all treatments (amended and unamended soils), approx-imately 15% of hexazinone and diuron was taken up. These interactions signifi-cantly impact herbicide efficacy in weed control and increase the risk of envi-ronmental contamination. Identifying these polymers and understanding the interaction of residual herbicides with MPs in agricultural soils is crucial for developing

management strategies that consider the presence of MPs, thereby promoting more sustainable agricultural practices.

Keywords: Residues plastic. Contamination. Analytical techniques. Sorption. Desorption

RESUMO

BROCHADO, Maura Gabriela da Silva, D.Sc., Universidade Federal de Viçosa, março de 2025. **Poluição de solos agricultáveis por microplásticos e sua interação com herbicidas residuais**. Orientador: Kassio Ferreira Mendes. Coorientadores: Gustavo Franco de Castro e Lucas de Paula Corredo.

A contaminação de solos agrícolas por microplásticos (MPs) representa uma grande preocupação em relação à eficácia dos herbicidas residuais no controle de plantas daninhas. Este estudo teve como objetivo investigar as interações entre MPs e três herbicidas residuais (diuron, hexazinone e S-metolachlor), com foco na avaliação das técnicas analíticas mais eficazes para detectar MPs em matrizes de solo, além da caracterização dos processos de sorção e des-sorção dos herbicidas no solo. As análises foram realizadas utilizando técnicas como espectroscopia no infravermelho próximo (NIR) e análise multiespectral, que demonstraram alta sensibilidade na identificação de MPs em várias con-centrações. A interação entre MPs e herbicidas foi realizada por meio da cro-matografia líquida de alta eficiência (HPLC), permitindo a determinação das isotermas de sorção e dessorção. A análise por raios X detectou MPs apenas em altas concentrações (20%). O NIR a 2.300 nm e a análise multiespectral a 395 nm demonstraram maior precisão e sensibilidade na distinção entre todos os níveis de MPs. O Microscópio Eletrônico de Varredura (MEV) mostrou que os MPs possuem uma estrutura amorfa, distinta do solo cristalino, o que pode influenciar suas interações com outros constituintes do solo. Em relação a inte-ração dos MPs com os herbicidas, a presença de MPs influenciou a sorção do S-metolachlor no solo, resultando em um aumento de até 10% na quantidade sorvida do herbicida, com um coeficiente de sorção (Kd) de 4,85 L kg^{-1} com a adição de 5% de MPs. Contudo, não houve retorno para a solução do solo do S-metolachlor, como demonstrado pela histerese (H) de 0,99 para o tratamen-to de 5% MPs, comparado a 0.88 H do tratamento controle. O diuron e a he-xazinone apresentaram pouca interação com os MPs, a porcentagem sorvida do diuron foi em torno de 40% em todos os tratamentos (solo tratado e não tratado com MPs), um Kd variando de 1,84 a 2,12 L kg^{-1}. No caso do hexazi-none, o comportamento foi semelhante, mas a porcentagem sorvida foi em torno de 20% para todos os tratamentos (solo tratado e não tratado com MPs), o Kd variou de 1,63 a 2,03 L kg-1. A dessorção de ambos os herbicidas foi baixa, com porcentagens dessorvida em torno de 15% para o hexazinone e diuron em todos os (solo tratado e não tratado com MPs). Essas interações apresentam grandes implicações para a eficácia dos herbicidas no

controle de plantas daninhas, além de aumentar o risco de contaminação ambiental. Identificar es-ses polímeros e compreender a interação dos herbicidas residuais com os MPs em solos agrícolas é crucial para o desenvolvimento de estratégias de manejo que considerem a presença de MPs, promovendo, assim, práticas agrícolas mais sustentáveis.

Palavras-chave: Resíduos plásticos. Contaminação. Técnicas analíticas. Sorção. Dessorção.

SUMMARY

1. GENERAL INTRODUCTION

In modern society, plastics can be considered a universal material and a concern in the Anthropocene (Olivatto et al., 2018). The production of plastics has increased significantly in recent decades due to their application in various products in different sectors. The production of these materials is inexpensive and highly durable. In addition, they are resistant to radiation, chemicals and pressure, among other properties. Due to these characteristics, the demand for these polymers is enormous (Caixeta et al., 2018).

Plastics are considered synthetic polymers composed of macromolecules, high molecular weight chemical structures formed by a large chain of monomers, smaller chemical units linked by covalent bonds and repeated along the chain (Olivatto et al., 2018). The raw material for plastics is mainly derived from petroleum and consists of carbon, hydrogen, silicon, oxygen, chloride and nitrogen. It is produced through a chemical process consisting of the joining of monomers, called polymerization (Derraik, 2002; Andrady and Neal, 2009; Rios, 2010; Oliveira, 2017).

Polymerization occurs through two different processes: addition, in which macromolecules are generated by the insertion of new monomers into an already formed molecular structure and causes the regrouping of chemical bonds, without the suppression of molecules or atoms, and condensation, which consists of the bonding of two monomers, resulting in the release of a smaller molecule, such as water or hydrochloric acid (Kotz et al., 2012; Oliveira, 2017). Among the most common polymers are polypropylene (PP), polyethylene (PE), polyvinyl chloride (PVC), polystyrene (PS) and polyethylene terephthalate (PET), which account for 90% of the world's demand for plastics (Andrady and Neal, 2009; Ma et al., 2018).

In agriculture, these polymers are used to preserve, transport, package and market agricultural products. According to Gamarro and Constanzo (2022) the agricultural sector uses around 12.5 million tons of plastic products each year, with crop and livestock production being the most prominent activities with 10.2 million tons per year collectively, followed by fishing and aquaculture with 2.1 million and forestry with 0.2 million tons. Among the uses of plastics in agricultural production, the most prominent are plastic mulching films, usually made of PE,

with the aim of suppressing weed growth, conserving the soil and reducing the use of pesticides. A study by Sun et al. (2020) showed that the emergence of plastic mulches increased the overall grain harvest and yields of commercial crops by 20%-35% and 20%-60%, respectively.

On the other hand, the growing use of mulching has also led to the pollution of agricultural soils with plastic waste (Zhang and Liu, 2018; Li et al., 2022). According to Choi et al. (2022), agricultural activity is one of the practices that generates the most plastic waste in the soil. Among the various plastic wastes, microplastics (MPs) (Figure 1.1) stand out, defined as particles smaller than 5 mm, mostly resulting from the degradation of plastic waste, which cause various ecological impacts, ranging from the potential threat of accidental ingestion by soil fauna, to the problem of their sorption capacity, concentration and transport of organic pollutants in the soil (Oliveira, 2017; Brochado et al., 2023).

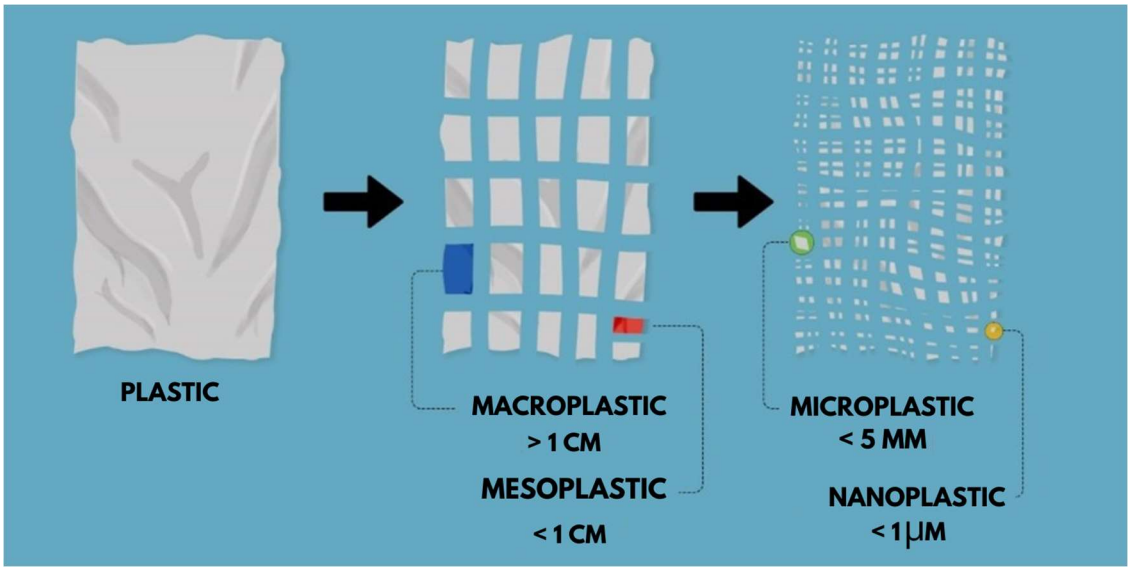

Figura 1.1- Dimensions of plastic waste. Adapted from Aiguobarueghian et al. (2024) and Yang et al. (2024).

The impact of MPs on agricultural crops and their interaction with fertilizers and pesticides is still poorly understood. However, some studies indicate that these polymers can alter the structure of plants in commercial crops (Chen et al., 2019), such as wheat (*Triticum aestivum*) (Qi et al., 2018; Yan et al., 2019; Hale et al., 2020) and tomatoes (*Solanum lycopersicum*). According to Qi et al. (2018), MPs residues affected both the aerial part and the root system of wheat during

its vegetative and reproductive growth. In addition, PM contamination reduced the biomass of spring onions (*Allium fistulosum*), causing changes in root characteristics and soil microbial activities (Machado et al., 2019).

The MPs absorbed by plants not only influence their growth and development, but can also reach the food chain, posing a potential risk to food safety (Zhu et al., 2019; Kumar et al., 2020). In view of this, the characterization of these polymers using efficient and low-cost techniques can contribute to the identification of their composition, allowing for a better understanding of their interactions with organic compounds and their effects on agriculture.

In soils in agricultural environments, for example, MPs have caused drastic changes in soil structure, bulk density and water retention capacity (Machado et al., 2018; Brochado et al., 2023; 2024a; 2024b), as well as influencing nutrient cycling (Zhang et al., 2022) and on some vital activities of the soil biota, such as the enzymatic activities of microorganisms (Zhang et al., 2019b; Xiao et al., 2021; Machado et al., 2019; Rillig and Lehmann, 2020; Rillig et al., 2021; Zhao et al., 2022). In addition, due to their high specific surface area, MPs can also interact with other pollutants such as organochlorine pesticides, polycyclic aromatic hydrocarbons and heavy metals in agricultural soils and, in turn, can affect the environment (Wang et al., 2021; Tian et al., 2022; Brochado et al., 2024a;2024b).

To date, it is known that MPs are strongly present in agricultural environments, due to the numerous routes of entry and distribution of this plastic waste (Yu et al., 2021). These polymers not only cause damage to crops (Kumar et al., 2020), affect the vital activities of the soil (Shafea et al., 2022), but can also influence important processes in agriculture (Zhang, et al., 2022), such as weed control.

In aquatic environments, studies have shown that PMs influence the sorption and desorption processes of herbicides. Wang et al. (2020) evaluated the behavior of simazine, terbuthylazine, atrazine and S-metolachlor in the presence of polyethylene (PE) MPs and observed that this interaction reduced the degradation rate of the herbicides, prolonging their half-life time (DT_{50}). In addition, the MPs affected the sorption of herbicides both on sediment particles and in the water column. The authors suggest that the sorption of herbicides on MPs can reduce their bioavailability, compromising degradation and highlighting the need

to consider these interactions in environmental risk assessments and in the development of mitigation strategies.

Another study, conducted by Ni et al. (2023), analyzed the sorption capacity of the herbicides napropamide and acetochlor in biodegradable and non-biodegradable MPs from agricultural plastic products. The results indicated that biodegradable MPs had a higher sorption capacity compared to non-biodegradable MPs, with this process being influenced by the physicochemical properties of the herbicides, such as water solubility (S_w) and octanol-water partition coefficient (K_{ow}). However, the presence of organic matter in the medium reduced the sorption of the herbicides in the MPs, as well as increasing the desorption rate, an effect that was more pronounced in the biodegradable MPs than in the non-biodegradable ones.

Identifying MPs and determining the level of contamination are essential to understanding their environmental impacts. However, there is still no consensus in the literature on the best technique for identifying and characterizing these materials (Brochado et al., 2024b). Various approaches have been explored for analyzing MPs in agricultural soils and biosolids. Among them, Fourier transform infrared spectroscopy (FTIR) stands out, especially in the attenuated total reflectance mode (ATR-FTIR), which is widely used for PM analysis (Adelugba and Emenike, 2023; Thakur et al., 2023; Circelli et al., 2024). In addition, other techniques such as near-infrared spectroscopy (NIR), X-ray diffraction and scanning electron microscopy (SEM) have been used to characterize these polymers (Circelli et al., 2024; Thakur et al., 2023; Azeem et al., 2023). Density separation using saturated NaCl solution has been shown to be effective in extracting MPs from soil samples (Thakur et al., 2023). The most commonly identified MPs in agricultural environments include polyethylene, polypropylene and polyethylene terephthalate (Thakur et al., 2023; Circelli et al., 2024). Despite advances, there are still no standardized methods for the analysis of MPs in complex matrices such as soil and biosolids, which reinforces the need to combine different analytical techniques to improve the identification and characterization of these contaminants (Adelugba and Emenike, 2023; Azeem et al., 2023).

Once MPs have been identified in the environment, it is essential to understand their interactions with herbicides. The influence of MPs on the behavior of these compounds is directly related to their physicochemical properties, such

as K_{ow}, sorption and desorption coefficients (K_d), S_w, among others (Tang et al., 2021; Brochado et al., 2024a). Peña et al. (2023) point out that the presence of MPs in the soil can modify the distribution and toxicity of pesticides, altering their mobility, bioavailability and, above all, their persistence in the environment. These complex interactions reinforce the importance of studies that assess how MPs can impact the herbicide cycle and, consequently, the environmental risks associated with their use (Tang et al., 2021; Peña et al., 2023).

Thus, the presence of MPs in the soil can significantly alter herbicide behavior, influencing their mobility, bioavailability, and environmental persistence. Moreover, the accumulation of these pollutants in the soil can degrade its quality, affect crop growth, and pose risks to food safety and the environment (Zeng et al., 2013; Li et al., 2022).

Given this, it is essential to conduct studies that not only identify the presence of MPs in agricultural soils but also enhance the understanding of their interactions with organic compounds, such as herbicides. In this context, this study aims to investigate the interactions between MPs and three residual herbicides (diuron, hexazinone, and S-metolachlor), with an emphasis on the sorption and desorption processes of these herbicides in soil. Furthermore, it seeks to evaluate the most effective analytical techniques for detecting MPs in soil matrices, as well as characterizing these polymers.

The scarcity of research in this field underscores the importance of scientific investments to assess the impacts of MP contamination on agricultural activities, considering environmental, economic, and social aspects.

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2. LITERATURE REVIEW[1]

2.1 Sources and distribution of microplastics in agricultural soils

Soils of agricultural land are prone to contamination with microplastics through various agricultural practices (Castan et al., 2021). These polymers can enter these environments through many routes, such as organic fertilizers, irrigation, plastic film cover (mulching), atmospheric deposition, and runoff (Figure 2.1) (Zhu et al., 2019; Li et al., 2022).

Soil fertilization and irrigation are the main agricultural activities that generate plastic waste in agricultural areas (Bläsing and Wulf, 2018). The use of biosolids as fertilizer is a common practice on the continents of North America and Europe. Around 72% of fertilizers used by European countries, such as Ireland and Finland, are derived from these compounds (Bläsing and Wulf, 2018; EPA, 2015; Eurostat, 2016). Every year, up to 700,000 tons of microplastics can enter agricultural fields due to this type of application (Nizzeto et al., 2016b). Recent studies have shown that these biosolids contain at least 300,000 particles of plastic kg^{-1}. In the USA, due to this practice of biosolid application, about 70 kg $year^{-1}$ are introduced into agricultural soils (Koutnik et al., 2021; Castan *et al*., 2021). In addition, irrigation with treated and untreated wastewater (1.000 to 627.000 and 0–125.000 plastic items m^{-3}, respectively) and floods with lake water (0.82 to 4.42 plastic items m^{-3}) or river water (0–13.751 items km^{-2}) are relevant plastic intake routes into the soil (Bläsing and Wulf, 2018).

Another significant way to enter microplastics into agricultural soils is through plastic films. These are usually made of polyethylene and have been used for agricultural production since 1956 (Moine and Ferry, 2019). Its global market has grown steadily, reaching about 2 million tons in 2017 (Moine and Ferry, 2019; Li et al., 2022). Its degradation occurs through sunlight and is later spread in soil tillage operations, mainly in areas with a low recovery rate of dead cover film (Steinmetz et al., 2016; Iqbal et al., 2023).

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[1]BROCHADO, M. G. S.; DE MIRANDA, C.; CARDOSO, J.; MENDES, K. F.; SOUZA, J. J. Microplastics in agricultural soils. In: SOUSA, R. N.; PESSOA, T. N.; MENDES, K. F. (Eds.). **Agricultural soils: impacts on the environment.** Hauppauge, NY, USA: Nova Publisher, 2023. p. 140–180.

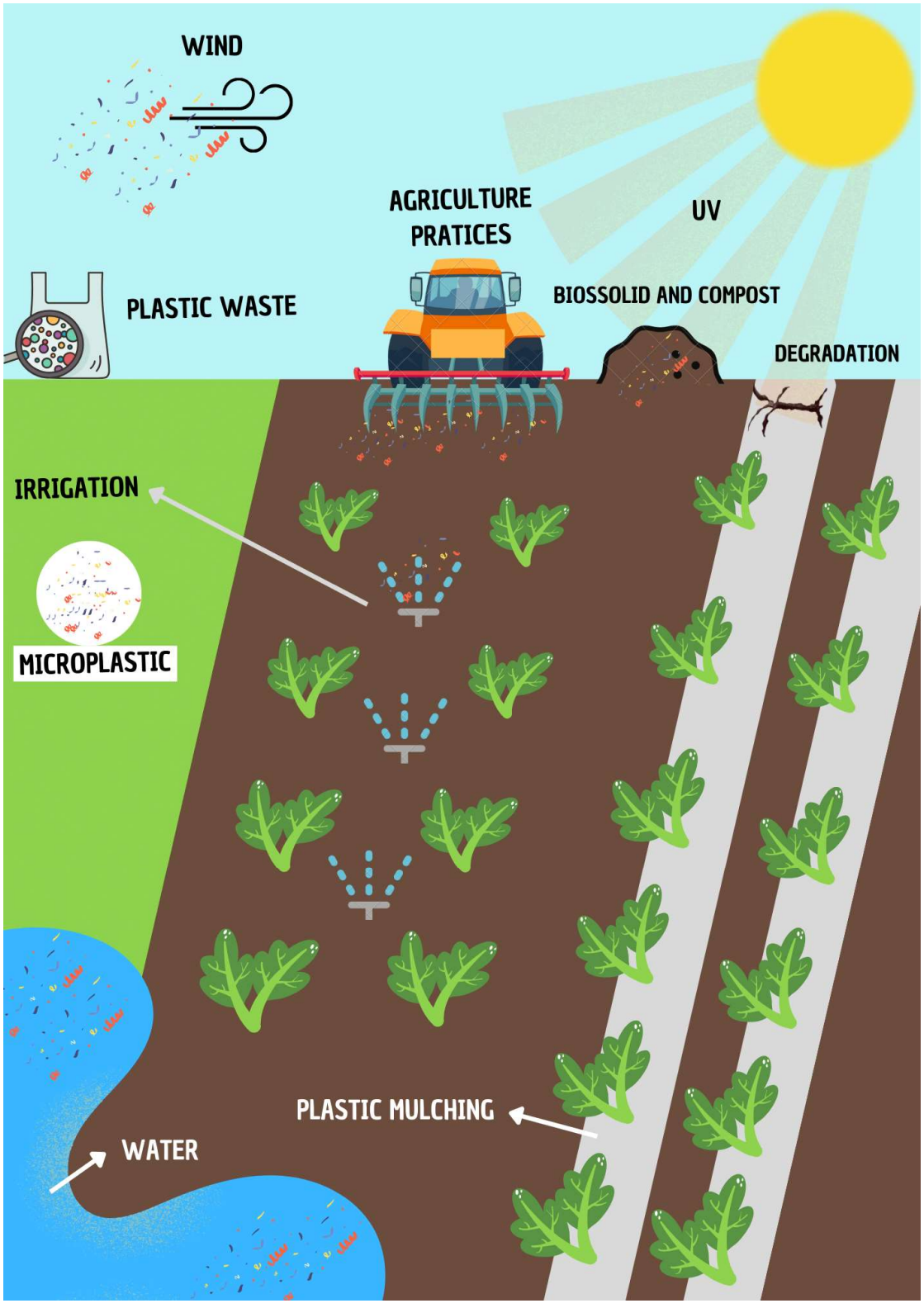

Figure 2.1- Generation and dispersion of microplastics in agricultural soils. Source: Adapted from Pérez-Reverón et al. (2022).

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[1]BROCHADO, M. G. S.; DE MIRANDA, C.; CARDOSO, J.; MENDES, K. F.; SOUZA, J. J. Microplastics in agricultural soils. In: SOUSA, R. N.; PESSOA, T. N.; MENDES, K. F. (Eds.). **Agricultural soils: impacts on the environment.** Hauppauge, NY, USA: Nova Publisher, 2023. p. 140–180.

There are many sources of distribution of microplastics. The existing scientific literature reports that terrestrial environments are the only components of natural systems that can act as a source and route of distribution of microplastics for aquatic environments (Horton et al., 2017; Karbalaei et al., 2018; Kumar et al., 2020; Lechner et al., 2014). In freshwater environments, the main source of microplastics is wastewater, which transports plastics from various sources, such as fragmented plastics and waste from urban runoff tires, polymeric flocculants of wastewater treatments, washed synthetic clothing fibers, and microspheres of cosmetic products and industries (Mengting et al., 2018; Corradine et al., 2019).

Microplastics are composed of various high molecular-weight polymers containing catalysts and additives (Teuten et al., 2009; Zhao et al., 2022). The microplastics transformation in soil is a slow process, which can take decades or even hundreds of years, depending on environmental conditions. (Briassoulis et al., 2015; Zhao et al., 2022). Some studies look for ways to degrade the plastic waste of the environment. Sanluis-Verdes et al. (2022) observed that the saliva of the wax worm larva (*Galleria mellonella*) can oxidize and depolymerize polyethylene, one of the most produced and resistant polyolefins-derived plastics, being the main polymer of mulching.

Further studies should evaluate the effects of microplastic accumulation in agricultural environmentsin tropical condictions. Since research on microplastic scanning methods is in greater concentration in aquatic environments

2.2 Methods for Microplastics Assessments in Soils

The methods usually applied to evaluate microplastics in soils are similar to those developed for sediments, following the principle of isolating plastic particles from the natural matrix for further counting and analysis. However, due to the complexity of the soil matrix, composed of organic and inorganic particles forming peds and heterogeneous properties, there is still a lack of standardized methodologies for microplastics analysis in soils (Junhao et al., 2021; Yang et al., 2021). In this sense, the scientific community has been working on the development of protocols for assessments of microplastics in soils (Grause et al., 2022; Möller et al., 2022; Radford et al., 2021), generally applied successfully through strict contamination and quality control (Corradini et al., 2019a; Yu et al., 2021a).

A brief schematic flow chart is presented, highlighting the steps often used to analyze soil microplastics (Figure 2.2). Here we summarize the main and novel methods for sampling, purification, extraction, and analysis of microplastics in soils, in addition to considerations of measures frequently taken to ensure contamination control and quality assurance of the method to be applied.

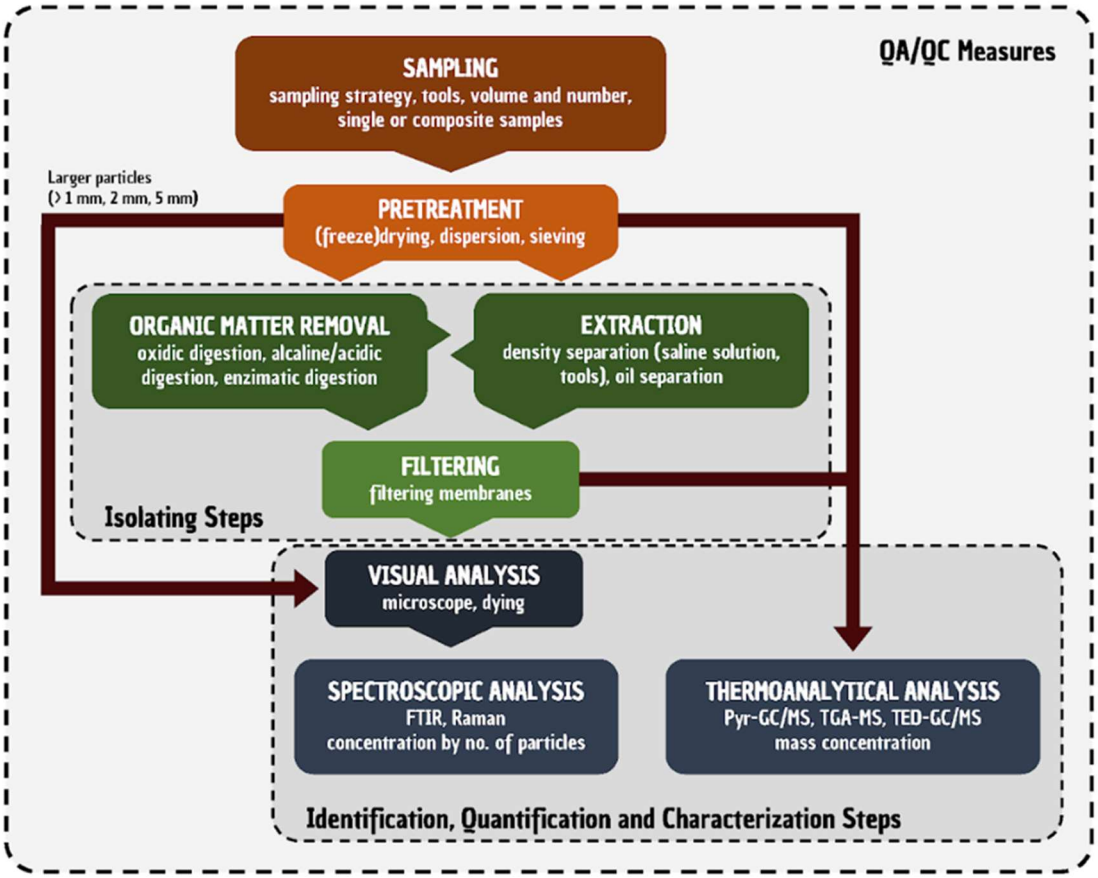

Figure 2.2- Schematic flow chart presenting overall methods often used for microplastics assessments in soils.

2.2.1 Sampling

Representative sampling is a fundamental step to ensure the reliability of data generated after processing environmental samples (Möller et al., 2020; Zhang et al., 2007). Hence, soil sampling for microplastic analysis greatly influences final results and should be carefully planned before field surveys.

The sampling strategy is developed according to hypothesis and objectives, taking into account environmental and pedogenetic factors that may

influence the presence of microplastics in a three-dimensional soil matrix. The soil formation factors (climate, parent material, relief, organisms, and time) determine soil properties such as texture, porosity, conductivity, clay mineralogy, pH, CEC, and others that influence physicochemical interactions between mineral/organic particles and microplastics. Otherwise, land use, potential sources, drainage and wind direction also should be considered in sampling (Möller et al., 2020; Thomas et al., 2020; Weber et al., 2020). Several well-established approaches to soil sampling can be applied to microplastic assessments, as summarized by Möller et al. (2020), such as judgmental (hotspot) sampling [e.g., Yu et al. (2021)], grid or transect sampling [e.g., Piehl et al. (2018)], stratified sampling, and random sampling [e.g., Liu et al. (2018)]. Judgmental sampling is suitable for verifying suspected contamination based on previously known information (e.g., usage history, visual signs of contamination) (Möller et al., 2020). The others are exploratory approaches and suitable for assessing the extent of contamination in homogeneous (random sampling) or previously defined areas (stratified sampling) or identifying area (grid sampling) and linear (transect sampling) contamination gradients (Möller et al., 2020). Additionally, large number of samples increases the representativeness of the sampling, but its application is usually hampered by costly and laborious methods for microplastics analysis (Weber et al., 2020).

Sampling is commonly performed with metal spatulas in quadrants of varying sizes, but using augers is suitable when the objective is to reach lower-depth layers (Weber et al., 2020; Zhou et al., 2020). Larger samples also increase the representativeness of assessments and the chance of finding microplastics (Weber et al., 2020), with sampling reports varying from 50.0 g to 4.0 kg in mass, 320 cm^3 to 5.120 cm^3 in volume, and 0.0625 m^2 to 2500 m^2 in quadrant area (Liu et al., 2018; Huerta Lwanga et al., 2017; Scheurer and Bigalke, 2018; Piehl et al., 2018; Zhou et al., 2018; Zhou et al., 2020). Logically, sampling a very large volume of soil increases logistical and analytical efforts in addition to representing an unsustainable practice depending on the context of the area (Thomas et al., 2020), and therefore it must be carefully evaluated.

The number and volume of samples can be reduced by obtaining composite samples by merging single samples with similar contexts or factors of interest for the research (Möller et al., 2020). Merging the single samples can be done in the field during sampling (Yu et al., 2021b) or in the laboratory (Möller et

al., 2020). However, composite samples are suitable for exploratory studies or for obtaining representative general information (e.g., land use, environmental context, experimental designs), but may be inappropriate for obtaining small-scale variation data (Weber et al., 2020).

Prevention of cross-contamination should already be considered in sampling campaigns. Contact with any plastic material should be avoided when handling samples, but when it is not possible, knowing the materials used can be strategy to trace contamination. Synthetic fibers from clothing are also frequently mentioned sources of contamination (Prata et al., 2019a; Weber et al., 2020), therefore, it is recommended to wear a cotton lab coat while sampling. Contact with the exposed sample should be as little as possible with quick storage (Weber et al., 2020), and Petri dishes can be positioned on site to monitor airborne contamination by opening them to the air during the act of sampling.

Samples are also subject to contamination in storage and transport, so PE plastic bags – widely used for soil sampling – should be avoided and replaced by non-plastic materials. Metal containers (e.g., aluminum, stainless steel) (Weber et al., 2020; Yang et al., 2021) or paper bags can be used as an alternative, but the latter may be unfeasible for soils with very high humidity (bags tend to tear). Exceptionally when it is not possible to eliminate the use of plastic bags, the approach used by Afrin et al. (2021) can be applied to try to quantify the contamination of the transport by shaking samples [microplastic free (MPF) samples] in the same plastic bag used for the transport of environmental samples. Blank samples can be produced by igniting, at 500°C for 3 h (Afrin et al., 2021), a representative sample from the study area. At this temperature all plastic particles should be eliminated, and these samples can also be used as a control for further laboratory procedures.

Whatever the most appropriate soil sampling strategy for the objectives of the microplastic assessment (and related contamination control methods), it should be well described, including a detailed description of the sampling environment and soil characteristics (Weber et al., 2020). This can help reduce historically reported inconsistencies in sampling from microplastics surveys, which consequently resulted in a wide variety of reported units (basis on mass, volume, and area) (Hanvey et al., 2017; Van Cauwenberghe et al., 2015).

2.2.2 Pretreatment

Before proceeding with the challenge of isolating microplastics from the soil matrix for analysis, the samples are subjected to a laboratory pretreatment. As is often practiced for many other analyzes in soil science, the first step usually consists of drying the samples at a maximum temperature of 50-60°C (Junhao et al., 2021; Yang et al., 2021). This temperature range is considered to ensure that minimal or no changes occur in the morphological characteristics of the microplastics potentially present in the samples, since thermal deformation of some polymers can be achieved above 60-70 °C (e.g., PE, PP, PA) (Hurley et al., 2018; Weber et al., 2020; Yang et al., 2021). Drying the samples is important to obtain absolute results (disregarding moisture variations due to weather conditions) (Weber et al., 2020), in addition to facilitating the following steps (Huang et al., 2021).

After drying, the samples must be sieved to isolate particles in an appropriate size range for the research objectives. Samples are usually sieved in 5 mm and 1 mm mesh (respecting the defined size ranges for microplastics) (Wang et al., 2020a) or 2 mm (often used for soil studies) (Corradini et al., 2019b), but some authors use a set of sieves to assess contamination in specific fractions sizes (Michielssen et al., 2016; Zhang et al., 2018a). However, microplastics can be entrapped in agricultural soil aggregates (Zhang et al., 2018a), which can embarrass the further extraction processes (Zhou et al., 2020). Then, large roots and pebbles should be previously removed, and large aggregates should be gently crushed to avoid breaking down microplastics in the sample (Huang et al., 2021). A soil dispersion step is often recommended (Zhou et al., 2020), and can be performed by ultrasonication (Zhang et al., 2018b) since the use of sodium hexametaphosphate – an often-used soil dispersant – has already proved to be an indifferent step (Radford et al., 2021). Alternatively, freeze-drying the samples may be chosen to reduce the stability of the soil aggregates prior to sieving (Möller et al., 2022; Staricka and Benoit, 1995), but it can also contribute to fragmentation of microplastics (Thomas et al., 2020).

2.2.3 Isolating Microplastics from Soil Samples

To analyze microplastics in soil, it is necessary to isolate them from the complex soil matrix, without compromising their morphological characteristics. This is essentially more difficult than removing microplastics from aquatic environments due to the heterogeneity of mineral and organic soil particles (Möller et al., 2020; Weber et al., 2020; Yang et al., 2021). Microplastic could migrate from surface to subsurface horizons through voids and be stored between or into peds. Because of that, it is needed that soil is disaggregated. Soil organic matter influences the formation of aggregates (Zhang and Zhang, 2020), in addition to disrupting the main methods used for the extraction and identification phases due to its density close to that of some polymers (1.0 to 1.4 g cm^{-3}) (Bläsing and Amelung, 2018; Corradini et al., 2019). Therefore, the methods often used for soil samples purification are organic matter removal followed by extraction of microplastics – usually by density separation, although some authors present these processes in reverse order (Möllet et al., 2022; Thomas et al., 2020).

2.2.4 Purification – Removal of Organic Matter

Chemical digestions are the most used techniques to remove organic matter from the soil for further microplastics analysis (Zhou et al., 2020). Among them, the oxidic digestion with hydrogen peroxide (H_2O_2) has been widely and successfully used, without causing significant damage to the microplastic particles (Hurley et al., 2018; Liu et al., 2018; Piehl et al., 2018), but it can take a long time to remove the organic matter (minimum 24 h) (Enders et al., 2020). Several authors also use and point to Fenton's reagent (H_2O_2 in the presence of a Fe^{2+} catalyst) as a more effective and rapid oxidant (Hurley et al., 2018; Yu et al., 2021b), although low efficiencies compared to hydrogen peroxide have already been reported (Radford et al., 2021). However, the suitability of digestion with Fenton's reagent depends on maintaining pH below 3.0 (to avoid precipitation of Fe^{3+} hydroxide) and temperature below 40°C (Zhou et al., 2020).

Alkaline and acidic digestions are also widespread, usually performed with sodium hydroxide (NaOH) or potassium hydroxide (KOH) (Hurley et al., 2018, Enders et al., 2020), and nitric acid (HNO_3) (Scheurer and Bigalke, 2018), respectively. Even though authors have reported better efficiency in the use of HNO_3 against oxidic digestions (Scheurer and Bigalke, 2018), alkaline and acidic

digestions are known to cause more significant damage to polymers [e.g., acrylonitrile butadiene styrene (ABS), PA, PET, polycarbonate (PC)] (Hurley et al., 2018; Zhou et al., 2020) and therefore are rarely recommended. On the other hand, Enders et al. (2020) point out the suitability of digestion with the mixture of KOH with sodium hypochlorite (NaClO) for samples with a high content of biological material.

Enzymatic digestions are considered even more efficient in removing organic matter since using enzymes targets specific soil organic compounds (Möller et al., 2020), they did not cause damage to microplastics (Weber et al., 2020). Enzymatic digestion protocols generally consist of steps with proteases, lipases, pectinases, cellulases, and hemicellulases enzymes, in addition to an oxidative digestion step (H_2O_2 or Fenton) and a previous step with sodium dodecyl sulfate (solubilizer of proteins and lipids of cell walls) (Mbachu et al., 2021; Möller et al., 2022). The results achieved with enzymatic digestion are remarkably improved compared to conventional one-step digestions, but the various steps necessarily followed by filtration can be very labor and time consuming, increasing the risk of cross-contamination (Möller et al., 2022).

2.2.5 Extraction – Removal of Mineral Phase

The extraction step is the one that effectively isolates microplastics for analysis, separating them and removing the mineral phase – the most abundant fraction of the three-phase soil system. Density separation is the most often used technique to separate microplastics from the mineral phase of particle-rich samples, both for soils (Junhao et al., 2021; Yang et al., 2021) and sediments (Van Cauwenberghe et al., 2015). The basic principle considered in density separation exploits the difference in density (ρ) of plastic polymers ($\rho = 0.9 – 1.6$ g cm^{-3}) and particles of the soil mineral phase ($\rho = 2.5 – 2.6$ g cm^{-3}). A saturated saline solution with intermediate density is used to separate the potential microplastics, that will remain floated in the supernatant liquid, while the mineral particles will be deposited on the bottom after stirring and settling times.

Saline solutions of NaCl ($\rho \approx 1.2$ g cm^{-3}), $CaCl_2$ ($\rho \approx 1.4$ g cm^{-3}), $ZnCl_2$ ($\rho \approx 1.5 – 1.8$ g cm^{-3}), NaI ($\rho \approx 1.6 – 1.8$ g cm^{-3}), NaBr ($\rho \approx 1.4 – 1.6$ g cm^{-3}), sodium polytungstate ($3Na_2WO_4 \cdot 9WO_3 \cdot H_2O$; $\rho \approx 1.5 – 1.8$ g cm^{-3}) are commonly used in density separation (Enders et al., 2020; Möller et al., 2020; Thomas et al., 2020;

Zhou et al., 2020). Sodium chloride (NaCl), often used because it is environmentally friendly and low cost, is lighter than many polymers and may underestimate the numbers of commonly used plastics, such as PET (ρ = 1.5 g cm^{-3}) and PVC ($\rho \approx$ 1.58 g cm^{--3}) (Quinn et al., 2017; Zhou et al., 2020). On the other hand, some of the salts that produce higher-density solutions are remarkably expensive and harmful to the environment (e.g., sodium polytungstate, $ZnCl_2$, NaI) (Frias et al., 2018; Möller et al., 2020; Thomas et al., 2020). Solutions of NaBr and $CaCl_2$ have been identified as good alternatives of affordable cost and low toxicity to the environment (Yang et al., 2021). However, the latter is known to cause flocculation of soil organic matter and hinder the identification of microplastics (Scheurer and Bigalke, 2018). Given this variability, the choice of saline solution should also be in line with the research objectives, although denser solutions are better choices for overall assessments (Yang et al., 2021). For statement, Frias et al. (2018) and Thomas et al. (2020) have summarized the main salts used for density separation considering the advantages and disadvantages related to saline solution density, cost, and potential environmental toxicity.

Stirring the samples seeks to promote the contact of all particles with the saline solution, while the decanting time allows obtaining a clear solution to be filtered, which does not interfere with further identification steps. Thus, the reported stirring and settling times vary considerably, ranging from 2 min to 2 h of stirring and from 6 h to 48 h of settling (Afrin et al., 2021; Möller et al., 2022; Weber et al., 2020). The separation containers are also variable, being commonly used glass beakers (Huang et al., 2020), separating funnels (Möller et al., 2021), and centrifuge tubes (Scheurer and Bigalke, 2018). The sample mass and saline solution volume adapt to the separation vessel, ranging from 5 g (Corradini et al., 2019a) to 6 kg (Imhof et al., 2018), with 20 mL to 12 L of saline solution required. Centrifuging samples is useful to reduce the inconvenience of long sample processing time (Weber et al., 2020), although it limits sample mass to 5 – 20 g (Grause et al., 2022), and several replicates are imperative in this case. Some customized separation apparatuses adapted for processing samples for analysis of microplastics promote higher recovery efficiencies (Enders et al., 2019; Imhof et al., 2012; Liu et al., 2019; Möller et al., 2021), but are still difficult to be widely reproduced in the practical reality of other laboratories. Microplastics can remain adhered on the walls of containers used for density separation (Thomas et al.,

2020; Weber et al., 2020), and some authors have used multi-stage procedures to improve the recovery rate efficiency (Quinn et al., 2017; Yang et al., 2021), repeating the separation procedure more than once with the same or different saline solutions (Corradini et al., 2019).

At the end of the density separation step, the supernatant must be collected and vacuum filtered for further analysis of potential microplastics retained in the membrane filter. When the supernatant is collected, the walls of the separation vessel should be rinsed to recover adhered particles, preferably with a plastic-free instrument (e.g., glass syringe), or the collection can be done alternatively by overflow (Horton et al., 2017). Metallic, glass fiber, quartz fiber, cellulosic fiber, PTFE, and PC membranes are used to filter the supernatant solution (Li et al., 2019; Löder et al., 2015; Prata et al., 2019a). The membrane's, mesh is the lower limit of detection of microplastics. Aluminum oxide and PC membranes were reported to be most suitable for analysis in Fourier Transform Infrared Spectroscopy (FTIR) (Löder et al., 2015); fiberglass and PC membranes are suitable for visual analysis assisted by Nile red staining (Prata et al., 2019b); and aluminum coated PC membrane proved to be suitable for analysis by Raman spectroscopy (Oßmann et al., 2017). Therefore, the choice of filtering membrane material can be made considering the subsequent identification steps.

As the density separation procedure can require large volumes of expensive and harmful saline solutions, recycling the solutions is a good strategy to make sample processing more cost-affordable and sustainable (Thomas et al., 2020). This can be done by vacuum filtering the used saline solution and readjusting the solution density by adding salt as necessary (Enders et al., 2019; Rodrigues et al., 2020). However, it is important to consider that recycling the saline solution represents another laboratory step, requiring more labor and time efforts (Thomas et al., 2020).

Oil separation is an alternative to conventional density separation methods, which exploits the lipophilic properties of the polymers to separate microplastics from the soil matrix (Weber et al., 2020; Yang et al., 2021). The procedure is similar to density separation but, in this case, a supernatant layer of oil (containing potential microplastics separated) is collected over a layer of water, while the mineral fraction of the soil remains at the bottom (Crichton et al., 2017). Canola oil (Crichton et al., 2017), castor oil (Mani et al., 2019), and olive oil (Scopetani

et al., 2020) have already been used for this purpose, and the efficiencies achieved are comparable or superior to conventional density separation methods for microplastics > 200 µm (90 – 99% mean recovery rate), but may vary by type of polymer (Scopetani et al., 2020). Another alternative novel method used to isolate microplastics is electrostatic separation (Felsing et al., 2018). Although Felsing et al. (2018) have reported recovery rates around 99% for various size ranges (63 µm - 5 mm), its applicability to cohesive soils with stable aggregates - as most agricultural soils are - is questionable (Möller et al., 2020; Yang et al., 2021).

2.2.6 Identification, Quantification, and Characterization of Microplastics

After being isolated in the filtering membrane, the microplastics must be identified, quantified, and characterized, and the efficiency of these analyses is closely dependent on the quality of pre-processing steps. The sequential methodological procedures presented above are suitable for microplastic analysis by the most often used methods: visual analysis, with the assistance of microscopy, followed by spectroscopic analysis (generally FTIR or Raman). In this way, microplastic-like particles are usually identified in the filtering membrane with the microscope and then confirmed with spectroscopic techniques (Yang et al., 2021). This approach allows for assessing morphological (e.g., color, shape, size) and chemical (type of polymer) characteristics of microplastic particles, and the concentration unit is reported as a number of particles per soil mass, the most used in current research (Weber et al., 2020). Alternatively, thermogravimetric and chromatographic-based techniques are also frequently used and overcome limitations of particle size to be identified/quantified (Junhao et al., 2021).

However, they are destructive methods that prevent the description of morphological characteristics of the particles (Yang et al., 2021), providing results in only mass units (mass of polymer per mass of soil) (Weber et al., 2020). Therefore, it is important to consider that each identification method will be suitable for evaluating specific and perhaps different information about microplastic contamination (Junhao et al., 2021).

2.2.7 Visual Analysis

Visual analysis is the most traditional and almost mandatory identification step since the earlier research on microplastics (Hidalgo-Ruz et al., 2012). Visual analysis makes it possible to determine, in a non-destructive way, the number of particles and their morphological characteristics, mainly color, size, shape, and surface texture (as an estimate of the weathering condition) (Hidalgo-Ruz et al., 2012; Thomas et al., 2020; Yang et al., 2021). This approach is more suitable for large microplastics (> 500 µm), and some authors establish criteria to standardize visual identification, for example: shiny surfaces, intense colors, and sharp geometrical shapes (Corradini et al., 2019a); or no cellular or organic structures are visible, fibers should be equally thick throughout their entire length, particles must present clear and homogeneous colors (Hidalgo-Ruz et al., 2012).

However, this method applied alone is subject to misidentification that leads to an underestimation between 20 – 70% (Möller et al., 2020) of the total microplastic content, or the selection of many false positives – especially for very small particles and in complex environmental matrices such as soil (Thomas et al., 2020; Yang et al., 2021). To help the identification visual inspection can be assisted by staining or heating. The main method of staining microplastics uses Nile Red dye, which fluoresces when exposed to a diverse range of wavelengths (Shruti et al., 2022). Nile Red can also stain on natural organic particles, so co-staining procedures are proposed to differentiate them (e.g., DNA staining with DAPI) (Stanton et al., 2019). On the other hand, heating (3 to 5 seconds at 130 ºC) the filter membranes will cause morphological changes in thermoplastic particles, making it easier to distinguish them (Zhang et al., 2018b). This can also be done by sticking a target particle with a hot needle (“hot needle test”) (Möller et al., 2020). Nevertheless, heating techniques do not reach thermosetting and high-density microplastics, and ignore the presence of natural materials that can be altered by heating (e.g., wax) (Möller et al., 2020).

Even if the visual analysis is assisted, the way to confirm that the composition of a particle is a plastic polymer is through spectroscopic or thermoanalytical chemical identification techniques (Hidalgo-Ruz et al., 2012; Möller et al., 2020; Yang et al., 2021).

2.2.8 Spectroscopic Techniques for Microplastic Analysis

FTIR and Raman spectroscopy are the most often used non-destructive techniques to identify the polymeric composition of microplastic particles (Junhao et al., 2021). Both are vibrational spectroscopy techniques, which detect the spectral fingerprint (in the FTIR or Raman spectral range) corresponding to the vibration of molecules subjected to excitation (Käppler et al., 2016).

FTIR spectroscopy is capable of analyzing particles at a maximum resolution of 10 – 20 µm, and can be used in three modes of operation: transmission, reflection, and attenuated total-reflectance (ATR) (Xu et al., 2019). The transmission mode suffers interference from the filter membrane substrate, and the reflectance mode is influenced by the morphology of the microplastic particle (Xu et al., 2019). The ATR mode requires minimal sample preparation and presents a strong signal-to-noise ratio, but it also requires a proof crystal in contact with the sample, which can cause damage to microplastics (Yang et al., 2021; Xu et al., 2019). Recent optimization technologies enhance the use of FTIR, such as micro-FTIR which allows to detect the microplastics particles visually, and focal-plane-array FTIR (FPA-FTIR) that allows creating a chemical grid map of the sample (Yang et al., 2021), although the latter can be very time consuming (Thomas et al., 2020; Primpke et al., 2017). Other sources of error not linked to the operating modes are in the pre-processing of the samples (e.g., poor identification in visual analysis, inefficient removal of organic matter which causes a high degree of fluorescence), in the analysis of black particles (high absorption of infrared radiation), and the analysis of moist samples (Huang *et al.*, 2021; Junhao et al., 2021; Thomas et al.¸2020).

Raman spectroscopy can theoretically analyze particles below 1 µm, using excitation lasers of 455, 532, 633, and 785 nm (Anger et al., 2018; Xu et al., 2019). Although more commonly used in microplastics research, the 785 nm laser takes longer to deliver the same signal-to-noise ratio than a more suitable 633 nm laser (Anger et al., 2018). Raman also has the advantage of identifying spectra of additives and pigments on the surface of microplastics, although in some cases, they may overlap the spectra of the polymer matrix (Huang *et al.*, 2021; Yang et al., 2021). Raman spectra are less influenced by sample moisture (Xu et al., 2019), but the identification can also be significantly hindered by the high degree of fluorescence promoted by organic compounds (Anger et al., 2018).

FTIR and Raman spectroscopy are suitable for the chemical identification of microplastics (Käppler et al., 2016; Xu et al., 2019), which is done by matching the acquired spectra from the particles with a spectral library database. Besides soil organic matter bounding, pigment coating and weathering of microplastics found in the environment affects the spectra acquired by both techniques, and this issue must be considered when choosing a database (Munno et al., 2020; Yang et al., 2021; Xu et al., 2019). For example, photooxidative degradation promoted by UV radiation can reduce Raman peaks assigned to CH_2 vibrations and CH aromatic rings of the PET structure (Rebollar et al., 2014). In addition to the spectra of weathered polymers, including the spectra of other natural materials potentially present in samples can help to decrease false positive rates (Käppler et al., 2016). Commercial spectral databases are usually used, as summarized by Xu et al. (2019), but the literature has worked to provide free access libraries with information from virgin and degraded polymer spectra for FTIR (De Frond et al., 2021) and Raman (Munno et al., 2020) analysis.

Novel spectroscopic techniques have been evaluated for microplastic analysis, such as visible near-infrared (vis-NIR) (Corradini et al., 2019a; Ng et al., 2020). While combining vis-NIR with machine learning is a fast technique for estimating microplastic abundance that does not require sample pre-processing, it is only suitable for contamination hotspots due to low accuracy (Zhou et al., 2018). Furthermore, the spectra obtained from different soil classes can differ substantially, requiring calibration for each of them, making it difficult to compare results between different soils (Corradini et al., 2019a). vis-NIR also has the drawback of not obtaining morphological data or the polymeric composition of the particles (Zhou et al., 2018).

2.2.9 Thermoanalytical Techniques for Microplastic Analysis

The main thermoanalytical techniques used for the quali-quantitative microplastics analyse are Pyrolysis-gas chromatography-mass spectrometry (Pyr-GC/MS), thermo-gravimetric analysis-mass spectrometry (TGA-MS), and thermal extraction desorption gas chromatography-mass spectrometry (TED-GC/MS) (Thomas et al., 2020; Yang et al., 2021). Thermal analysis explores the thermal decomposition characteristics of polymers, with subsequent analysis of pyrolysates or extracts by mass spectrometry (La Nasa et al., 2020).

Pyr-GC/MS is a powerful and widely used technique for mass quantification of polymers (La Nasa et al., 2020). Pyr-GC/MS explores the controlled thermal degradation of polymer macromolecules which, after being separated by gas chromatography, are identified and quantified in mass spectrometry (La Nasa et al., 2020). However, it is limited to very small amounts of sample (about 5 mg) (Möller et al., 2020). This requires excessive sample purification effort and effective isolation of microplastics, which can be difficult to achieve in complex matrices such as soil, in addition to making the analytical process more prone to contamination (Möller et al., 2020). On the other hand, TED-GC/MS overcomes these drawbacks, combining thermogravimetric analysis to thermally decompose the polymers and analyze the solid phase extract by GC/MS, which requires no pre-processing (except homogenization) of samples up to 100 mg (Dümichen et al., 2017; Huang et al., 2021; Möller et al., 2020). As an alternative to this two-step process, an online TGA-MS simultaneously measures the mass of gases produced by degradation of polymers in the thermal treatment using approximately 50 mg of bulk soil sample, although the results may be affected by high levels of organic matter. (David et al., 2018).

Thermoanalytic techniques are advantageous as they are efficient sensitive methods for the quali-quantitative analysis of microplastics of any size, shape, and composition, with low detection limits and no sample pre-processing required in some cases (Huang et al., 2021; La Nasa et al., 2020; Yang et al., 2021). They are also useful in analyzing organic plastic additives, which are difficult to identify with spectroscopic techniques (La Nasa et al., 2020). However, all thermoanalytical techniques have the same major drawback - they are destructive, so any information about the morphological characteristics of microplastic particles is lost (Möller et al., 2020). This must be carefully considered since morphological characteristics are determinants for the impacts caused by microplastics contamination in agricultural soil ecosystems (Machado et al., 2018).

2.2.10 Quality Assurance and Quality Control Approaches

Microplastics are ubiquitous in the environment and since it is difficult to eliminate the use of any and all plastic materials from the working environment, there is a great risk of contaminating samples during laboratory procedures (Prata et al., 2021). Then, in addition to the care raised in the sampling section, a series

of measures must be taken in the laboratory work to minimize the risk and quantify contamination when it occurs.

Synthetic fibers from clothing are representative sources of contamination (Scopetani et al., 2020), so the laboratory work environment must be clean and restricted, with limited access and airflow (Prata et al., 2021). The sample handler must always wear cotton gowns, and all procedures should ideally take place in laminar flow chambers (not exhausters) (Prata et al., 2021). All solutions and reagents that come into contact with the samples, with the glassware and even those used for cleaning the benches, must be assuredly free of microplastics - which can be achieved by filtering them prior to use (Enders et al., 2019). Obviously, any plastic material should be avoided, and all glassware should be washed vigorously with microplastic-free water before use (Prata et al., 2021). Filter membranes that will be used to filter the microplastics must be heated to at least 450 ºC for 3 hours to avoid previous contamination (Prata et al., 2021).

Procedural blanks should be conducted to assess possible errors due to external contamination (Prata et al., 2021), especially when it is impossible to eliminate all contact with plastic surfaces (Junhao et al., 2021; Yang et al., 2021). A good strategy for doing this is to heat a sample of similar context to the environmental samples at 500°C for 3 h to make them free of microplastics (Afrin et al., 2021), and then conduct all the same laboratory procedures adopted for the environmental samples for further analysis. Atmospheric deposition blanks can also be used by opening Petri dishes to air whenever samples are also opened (Prata et al., 2021).

As there are still no standardized techniques for analyzing microplastics in soils, performing recovery tests has been a frequently adopted and recommended practice to assess the efficiency of the methods used avoiding underestimation (Huang et al., 2021; Way et al., 2022). Recovery tests can be performed by adding microplastics in known concentrations to a clean sample (which may be the same used for process blanks) and conducting these samples through the same laboratory procedures as for environmental samples (Way et al., 2022). Recovery tests are useful not only to estimate the efficiency of the applied method but also to identify possible changes caused in the microplastic particles by the analytical procedures (Huang et al., 2021). For example, Scheurer and Bigalke

(2018) testing their methodology noticed that ABS, PA and PET particles fragment into smaller particles when samples are treated with HNO_3.

2.3 Potential Impacts of Microplastic Contamination on Agricultural Soil Ecosystems

Soil is a life-supporting system that plays a fundamental ecological role in agroecosystems, acting as a substrate for plant growth, which is the main source of food production for society. Agricultural soils are considered a major environmental compartment of microplastic entry and occurrence in continental terrestrial environments (Nizzeto et al., 2016), and this widespread contamination has the potential to interfere with the soil's ability to perform its ecological functions. As microplastics are incorporated into agricultural soil (Rillig et al., 2017), they alter the physical, chemical, and microbial properties of the soil (Zhou *et al.*, 2020), which can affect plant growth performance (Machado *et al.*, 2019) and also impact soil fauna (Huerta Lwanga et al., 2017) (Figure 2.3). Generally, impacts on soil properties are dependent on type (e.g., shape, size, polymer type) and concentration of microplastics (Zhou et al., 2020). Microplastic particles can also release toxic additives (e.g., plasticizers, flame retardants, antioxidants and photostabilizers) or interact with other persistent contaminants (e.g., potentially toxic elements, persistent organic pollutants), posing an additional risk of microplastic contamination to agricultural soils (Figure 2.3) (Zhang et al., 2020a).

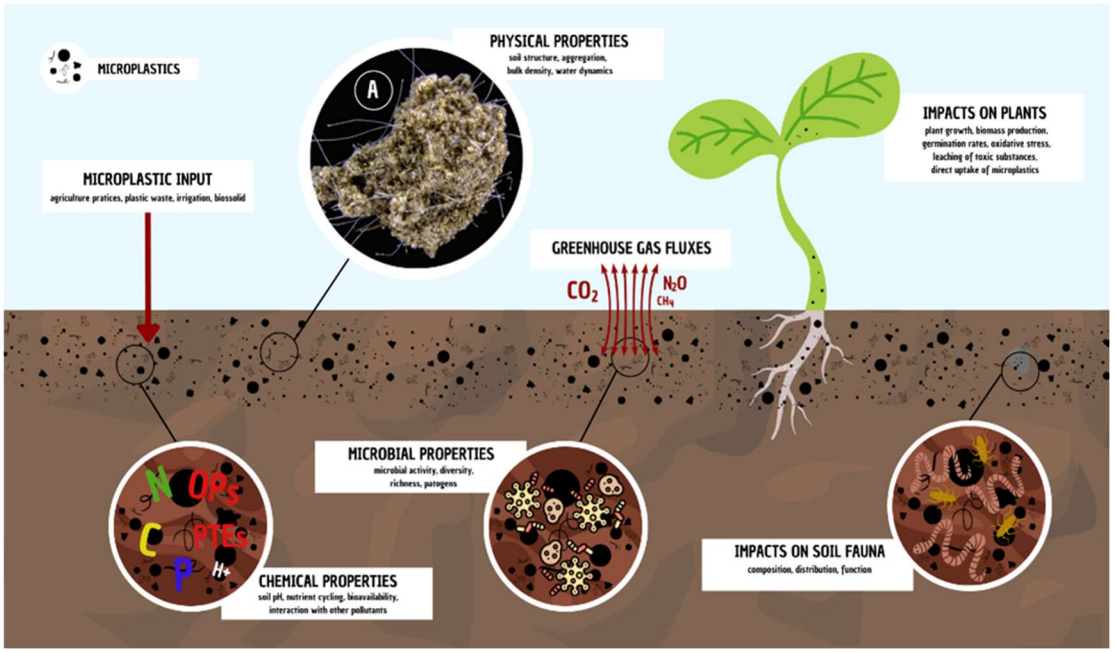

Figure 2.3- Effects of microplastic contamination on soil ecosystems. (A) Interaction between a soil aggregate and microplastic fibers. Source: Adapted from Rillig and Lehamann (2020).

2.3.1 Impacts on physical, chemical, and microbial properties of soils

Microplastic contamination affects soil physical properties such as bulks density, aggregation, water-stable aggregates, and water-holding capacity (Boots et al., 2019; Machado et al., 2018; 2019; Zhang et al., 2018a; Zhang et al., 2019c). Polyester fibers showed concentration-dependent and more representative effects than polyacrylic fibers, polyamide beads, and PET fragments, reducing bulk density and aggregates water-stability, but increasing water holding capacity (Machado et al., 2018), although this increase may be smaller than the increase in evapotranspiration (Machado et al., 2019). Machado et al. (2019) also identified polyester fibers affecting bulk density, soil aggregation, and water dynamics more strongly than five other types of microplastics, which causes greater response drivers in plant traits. Other study, however, did not detect significant changes in the bulk density and hydraulic conductivity (saturated medium) of soils in the presence of microfibers when compared to the control soil, although the volume of pores larger than 30 μm increased at all tested concentrations (Zhang et al., 2019a). A reduction in the mean diameter of water-stable aggregates in three soils containing microplastics compared to a control soil has also already been detected, with HDPE showing more representative effects than synthetic fibers and PLA (polylactic acid, a degradable polymer) (Boots et al., 2019). In this sense, the abundance of microplastic fibers was found to be significantly higher in microaggregates than in macroaggregates from agricultural soil (Zhang et al., 2018b). Meanwhile, even reducing the water-stable aggregates, polyamide, and polyester fibers can increase the formation of macrostructures in the soil (Machado et al., 2018).

Although Lozano et al. (2021) reported a significant decreasing in soil aggregation at all tested concentrations for 12 different types of microplastics, in summary, microplastic fibers (especially polyester) generally cause greater physical changes in the soil environment due to their linear shape – unusual in the soil matrix – and their plasticity, which allow a more efficient interaction between the soil aggregates and microplastic particles (Machado et al., 2018; 2019). Lozano

et al. (2021) also stated that this shape dissimilarity is the key property to determine how significant the impacts of microplastics on the soil are – the greater the difference in microplastic shape compared to the soil matrix particles, the greater the impacts.

As soil physical, chemical, and biological interactions are closely linked, changes in the soil structure and water dynamics affect microbial community responses (Machado et al., 2018; Fei et al., 2020), and there are significant correlations between impacts on soil properties and microbial community composition caused by microplastic contamination (Feng et al., 2022). For example, changes in aggregation dynamics, porosity, and humidity induce the formation of microenvironments that can affect the oxygen pressure and, consequently, the role of aerobic or anaerobic microorganisms (Zhou et al., 2020). Also, the terrestrial plastisphere (microbiome formed on the surface of microplastics) is a suitable ecological niche for several types of microorganisms, including pathogenic fungi (Gkoutselis, et al., 2021). So microplastic contamination also impacts biochemical properties and nutrient cycling in the soil environment.

Several types of microplastics, especially PLA, have already been shown to cause an increase in the activity of urease, phosphatase, and catalase enzymes at high doses (2%), but at low microplastics doses (0.2%) phosphatase activity decreases, just like available levels of P (-11%, PE) and NH_4^+-N (-92%, PLA) (Feng et al., 2022). Machado et al. (2018) highlight that the apparent non-monotonic effects (e.g., more significant impacts with lower doses) enhance the complexity of the microplastic-soil system, considering that interactions of microplastics with the natural matrix of the soil increase at low concentrations. Alternatively, in high doses (7 – 28%) the presence of PP microplastics increased microbial activity and favor the accumulation of dissolved organic C, N and P, increasing the levels of nutrients in the soil (Liu et al., 2017). By improving soil structural properties, polyester fibers increase microbial activity [fluorescein diacetate (FDA) hydrolase] and mycorrhizal hyphae abundance, which can impact the availability of nutrients for plants (Machado et al., 2019). Soils treated with PVC and PE inhibit FDA hydrolase activity but stimulate urease and acid phosphatase activities (Fei et al., 2020). This distinct trend was attributed to changes in diversity and abundance of microbial community, although both declined overall (Fei et al., 2020). Microplastics originating from plastic mulch can act as a special

accumulator of microorganisms, providing an environment for the growth of bacterial communities distinct from the surrounding agricultural soil (Zhang et al., 2019c). Additionally, the diversity of fungal communities is more sensitive to impacts of microplastic contamination than bacterial communities (Fan et al., 2022), and a reduction in the fungi to bacteria ratio was already reported with increasing concentration of low-density polyethylene (LDPE) microplastics (Gao et al., 2021).

Besides microplastics are mainly composed by carbon, they affect the carbon cycle due to these disturbances in soil microbiota and physicochemical properties (Rillig et al., 2021a). For example, microplastic mulching (both LDPE and biodegradable) tend to raise the C:N ratio in the soil (Qi et al., 2020). Consequently, the dynamics of gases emitted from the soil will be affected. Changes in gas fluxes are mainly attributable to effects on soil structure, which govern oxygen supply (Rillig et al., 2021b). Microplastic fibers increase soil aggregation, and consequently increases of soil macroporisity, CO_2 emissions but decrease N_2O emissions. However, the changes in N_2O flux are attributed to anaerobic dynamics in saturated microaggregates (Rillig et al., 2021b). Soils spiked with LDPE microplastics have already shown similar behavior (Gao et al., 2020). On the other hand, by decreasing soil aggregation, PP fragments and LDPE films presented more significant decreases in CO_2 emissions when compared to 10 other types of microplastics, including polyamide fibers, which at high doses inhibit CO_2 emissions, but stimulate them at low doses (Lozano et al., 2021). At the same time, Ren *et al.* (2020) identified that induced changes in N_2O emissions and CH_4 uptake are closely linked to the abundance of specific microbial communities, while CO_2 emissions and dissolved organic carbon did not show significant differences in soils treated with PE microplastic films.

Disagreements in the results between the currently existing studies may reflect differences between the tested doses, types of microplastics, and differences in inherent physicochemical characteristics of the tested soils (Zhou *et al.*, 2020), but plastic additives can also play a role (Lozano et al., 2021). Furthermore, the effects of microplastics contamination in soils may differ, and even be opposite, in the presence or absence of plants (Lozano et al., 2021; Machado et al., 2019). It is also important to note that most experiments historically use virgin microplastics (Horton et al., 2017) and, as weathering significantly alters the

physicochemical properties of microplastics (Liu et al., 2020), the real impacts of microplastics present in the natural soil environment are still gaps to be filled. These observations underscore the need to increase knowledge about the impacts of microplastic contamination on different types of soil that are also subject to varied agricultural uses and practices.

2.3.2 Impacts on Soil Fauna

Soil biota plays essential roles in soil formation, such as litter decomposition, nutrient cycling, and crop growth promotion. Microplastics indirectly impact crops, directly altering soil fauna. Studies show that microplastics especially affect earthworms and nematodes (Ju et al., 2019; Jiang et al., 2020; Kim et al., 2020a; Zhang et al., 2022a; Iqbal et al. 2023). A study conducted by Jiang et al. (2020) observed that the microplastic contamination of soil was able to cause oxidative stress, DNA damage, and alteration in intestinal cells of earthworms. In nematodes, microplastics may be more harmful when kept in soil environments (Kim et al., 2020; Iqbal et al. 2023)

Earthworms play a key role in the degradation of microplastics, as they can ingest microplastic and convert it into smaller particles (Rodriguez-Seijo et al., 2017; Chang et al., 2022). Lwanga et al. (2016) tested the survival and fitness of earthworm (*Lumbricus terrestrial*) at different microplastic concentrations. At the highest concentrations exposed to these polymers in litter, it was possible to observe the mortality of almost 60% of these animals when trying to ingest microplastic.

In addition, other organisms are extremely important in the soil, among them insects. Termites (blattodea:Teermitidea) especially in arid ecosystems that lack earthworms, play an important role in the homogenization of soils, as well as in the selection of mineral particles from the soil for the construction of hills and in the decomposition and distribution of organic matter (De Bruyn and Conacher, 1990). Lenz et al. (2012) showed that these animals can ingest and excrete microplastic particles, but metabolic impacts are still unknown. When walking on the ground, bees (hymenoptera: apidea) can disperse microplastic particles. Solitary bees can even build nests made entirely of plastic fragments (Allasino et al., 2019; Büks et al., 2020). Some ant species (hymenenoptera: Formicidea) are considered an important vector for seed dispersal. Due to the microplastic

particles resembling the size of some species, these animals end up confusing microplastic particles with seeds, performing the dispersion of these polymers (Hughes and Westoby, 1992; Angotti et al., 2018; Büks et al*.,* 2020).

2.3.3 Impacts on Plants

Logically, since microplastics impact soil properties, they can indirectly influence plant growth performance in several ways (Rillig *et al.*, 2019), representing a concern for agroecosystems. Plastic mulching secondary microplastics (both LDPE and biodegradable) on soil decrease wheat (*Triticum aestivum*) biomass production, with effects attributed to impacts on the rhizosphere microbiota, and occur more severe when induced by biodegradable microplastics (Qi *et al.*, 2020). However, the presence of earthworms can alleviate the negative impacts caused by the presence of both types of plastic mulching residues (Qi *et al.*, 2018). Soils contaminated with PLA (another degradable polymer) also cause more severe effects on germination rate and shoot height of *Lolium perenne* than those contaminated with high-density polyethylene (HDPE) (Boots et al., 2019). It is speculated, therefore, that biodegradable microplastics may cause more abrupt and significant effects on the rhizosphere microbiota as they are more easily degraded and may release degradation products with toxic effects (Boots et al., 2019; Qi et al., 2020).

So, it's evident that different types of microplastics also lead to distinct impacts on plant proxies responses. Among seven types of microplastics, soils contaminated by PA beads and polyester fibers had the greatest impact on the growth of spring onions (*Allium fristulosum*), in which the presence of PA microplastics drastically decreases root:leaf ratio and C:N ratio in the leaves and the presence of polyester fibers increased root tissue density and onion bulb biomass (Machado et al., 2019). PA microplastics contain nitrogen in their molecular composition, and perhaps the release of monomers – possibly metabolizable by the soil microbiota – can explain the increase in N levels, while polyester fibers are responsible for causing more significant impacts on soil physical characteristics, which reflects in plant growth (Machado et al., 2018; 2019). Considering biometric parameters (e.g., germination rates, height, biomass, number of leaves) and oxidative stress, PVC microplastics in soil proved to be more toxic to cress (*Lepidium sativum*) than those of PP and PE (Pignatelli *et al.*, 2020). PP microplastics

and, mainly, PVC also induced a more significant decrease in the production of shoot biomass of *Curcubita pepo* than PE and PET, emphasizing the ability of PVC polymer to cause oxidative stress due to favoring the production of H_2O_2 (Colzi et al., 2022). The size of plastic particles also affects indirect impacts on plants. For example, PS microplastics (5 µm) affected more *Vicia faba* biomass production than nanoplastics (100 nm), but nanoplastics caused greater oxidative stress to plants (Jiang *et al.*, 2019).

The indirect toxicity of microplastics to plants is often attributed to the release of toxic substances. For example, the degradation of microplastics – with consequent leaching of toxic compounds – decreased the adverse effects on the germination of *Lepidium sativum* (Pflugmacher et al., 2020). Therefore, the high susceptibility of microplastics interaction with other contaminants worsen the risk to plants (Yang et al., 2021), as they can accumulate pollutants potentially present in agroecosystems environments (e.g., pesticides, potentially toxic elements) (Abbasi et al., 2020; Ramos et al., 2015). PET microplastics can accumulate Cd, Pb, and Zn and act as a vector of these toxic metals to the rhizospheric zone of wheat (Abbasi et al., 2020). The co-contamination of PS and PTFE microplastics with arsenic was able to inhibit the growth of rice seedlings and cause oxidative stress to the plants, although the effects are dependent on the applied concentrations (Dong et al., 2020). Cadmium contents higher than 3 mg kg^{-1} in soils contaminated with HDPE microplastics can enhance bioavailability and promote the accumulation of the metal in strawberry cultivation, reducing the production of biomass and fruits (Pinto-Poblete et al., 2022). However, in another study with Cd-contaminated soil (5 mg kg^{-1}), the presence of PLA and PE microplastics also increase bioavailability but did not cause metal accumulation in maize tissues, although treatments with 10% PLA decreased biomass production and chlorophyll levels in leaves (Wang et al., 2020c). The authors suggest that the attaching of microplastics to the roots and the hydrophobic nature may interfere with the absorption of water and, consequently, of Cd by plants (Wang et al., 2020b). Soil characteristics and experimental setup of each study may also account for such differences. For example, the former uses an andisol mixed with sand (50–50%) at 70% humidity (Pinto-Poblete et al., 2022), which may favor the availability and absorption of water by plants, while the latter uses a farmland soil with moisture maintained at 12–15% (Wang et al., 2020a).

In addition, microplastic particles can directly impact plants, as microplastic can be absorbed and translocated to the aerial parts of apoplastic and symplastic cultures. Subsequently aggregating in the vascular system of the plant (Figure 2.4ac) (Dong et al., 2021a; Iqbal et al. 2023). Microplastics can restrict photosynthesis, affecting chlorophyll production in plant leaves (Figure 2.4A) (Gao et al., 2019; Li et al., 2020a; Iqbal et al. 2023). In the vascular bundles of the stem and the ribs of the leaves, these polymers can suppress the absorption and transport of water and nutrients, which can consequently hinder the growth of the stem and the development of the tissue (Figure 2.4C) (Dong et al., 2020; Chen et al., 2022a; Iqbal et al. 2023).

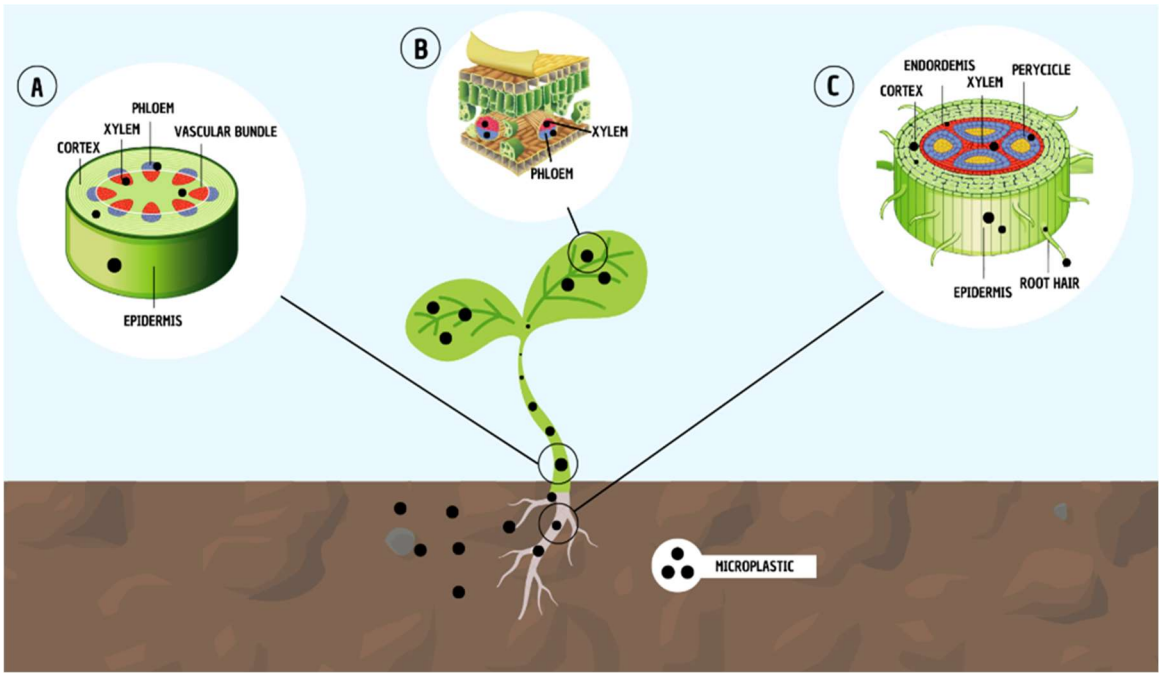

Figure 2.4- An overview of the effects of microplastics on plants. (A) microplastics penetrate the root through the root hair, and (B and C) microplastics are transported to the upper parts of the crop (stem and leaves). Adapted from Iqbal *et al*. (2023).

2.3.4 Interactions of Microplastics with Other Soil Contaminants

Presenting a large specific surface, which is chemically active, microplastics interact with several toxic chemical compounds such as organic pollutants, potentially toxic elements, and antibiotics, and can act as a vector for the transfer of these substances along environmental matrices and the food chain (Cao et al., 2021; Zhang et al., 2020b). Moreover, as microplastics take time to degrade in

the environment, adsorbed toxic compounds or even toxic additives inherent in plastic production can be slowly released to the environment, posing a long-term risk to soil quality (Steinmetz *et al.*, 2016).

2.3.5 Potentially Toxic Elements

Potentially toxic elements are a globally recognized threat to terrestrial and aquatic environments, and the impacts of possible co-contamination with microplastics have attracted the attention of the scientific community (Cao et al., 2021). Microplastics can interact with potentially toxic elements by electrostatic interaction due to the polar surface, by sorption/bioaccumulation by biofilms of the plastisphere or natural soil organic matter, or by interactions involving complexation and co-precipitation of metals (Cao et al., 2021). The point of zero charge (PZC) of microplastics is usually lower than the pH of the environment, so they express a negative charge that can attract cations (Tourinho et al., 2019), including toxic metal cations. The polar nature of microplastic surfaces is due to their physicochemical properties or the presence of chemically active additives, although photo-oxidative degradation can increase their polar character (Cao et al., 2021). Furthermore, soil pH often decreases when contaminated by, for example, polyester fibers, PP and HDPE microplastics (Boots et al., 2019; Cao et al., 2023; Rillig et al., 2021a), which increases the mobility of most toxic elements in soils (Hooda, 2010). Therefore, the presence of microplastics potentially affects the mobility and bioavailability of potentially toxic elements in the soil environment.

Since microplastics have a lower adsorption capacity for metals than pure soil (Feng et al., 2022), their presence generally reduces the adsorption capacity but increases the desorption of metals such as Cd, Pb, and Zn (Li et al., 2021; Zhang et al., 2020a). Thus, PP microplastics can increase Cd bioavailability by decreasing retention by organomineral complexes (Cao et al., 2023). Effects are more pronounced on smaller microplastics due to a higher specific surface area (Zhang et al., 2020a). Results also demonstrate that in soils contaminated by microplastics, the adsorption of, for example, Cd, Cu, and Zn is controlled by intraparticle diffusion (Zhang et al., 2020a; Tang et al., 2021), and the adsorption of Pb is influenced by the concentration of fulvic acids and pH (Tang et al., 2020). However, the transformations caused by microplastics in the chemical speciation

of metals present in soil environment can be more complex. In the Feng et al. (2022) study, for example, extractable Pb concentrations increased at high doses of microplastics, but extractable Zn contents did not change at high doses and even decreased at low doses. Microplastics also lowered the bioavailability of Cu, Cr, and Ni by decreasing their exchangeable fractions (carbonate-bound and Fe/Mn oxide-bound) and increasing organic-bound fractions (Yu et al., 2020). The trend to increase organically bound fractions at the expense of exchangeable fractions has also been observed for Zn, Cu, Cr, Ni, As, Cd, and Pb in soils treated with PE microplastics (Yu et al., 2021a). These changes may occur by adsorption effects or indirect effects caused by the new microenvironments created by the presence of microplastics (so the microplastic type matters), and they occur differently according to the size of the aggregates and time scale (Yu et al., 2020; 2021). Furthermore, microplastics affect the chemical speciation of potentially toxic elements differently, and have a more significant influence on the carbonate-bound fraction of Cu and Zn, Fe/Mn oxide-bound of as, and organic-bound of Cr, Cd, Ni and Pb (Yu et al., 2021a).

2.3.6 Organic Pollutants

Organic pollutants [e.g., antibiotics, pesticides, polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls phthalates (PCBs), polycyclic aromatic hydrocarbons (PAHs)] are also contaminants present in soil, and the potential for their interaction with microplastics is a concern that has been discussed (Chang et al., 2022; Xiang et al., 2022). Among these, PAHs and PCBs are the most often studied (Wang et al., 2020b), and the main mechanisms involved in the sorption of organic pollutants by microplastics are hydrophobic interactions, electrostatic interactions, π-π interactions (esp. between aromatic rings) and hydrogen bonds (esp. between polar molecules) (Chang et al., 2022). As opposed to the interaction with metals, the hydrophobicity of a large specific surface of microplastics favors sorption and accumulation of organic pollutants at higher concentrations than the surrounding environment (Xiang et al., 2022). Therefore, microplastics generally increase the sorption capacity of organic pollutants on soil environments (Chang et al., 2022). There is a clear positive linear trend (R^2 = 0.63) in the relationship between the hydrophobicity of organic pollutants and the sorption coefficient in microplastics, with some exceptions for antibiotics (Chang

et al., 2022; Wang et al., 2020c). The high capacity of microplastics to adsorb PCBs and PAHs, for example, can reduce the bioavailability of these pollutants in the soil environment (Wang et al., 2019). This behavior may be different when other interactions (e.g., van der Waals interactions) play a major role, for example, in a soil contaminated with 10% PE microplastics that have had their ability to sorb pesticides [atrazine and 4-(2,4-dichlorophenoxy) butyric acid] decreased, consequently increasing the bioavailability of these pollutants (Hüffer et al., 2019). Meanwhile, it has already been demonstrated that plastic mulch residues from PE films can accumulate pesticides in amounts much greater than soil particles (584 – 2284 $\mu g_{pesticide}\ g_{plastic}^{-1}$ against 13 – 32 $\mu g_{pesticide}\ g_{soil}^{-1}$) (Ramos et al., 2015).

As already highlighted, weathering changes the physicochemical properties of microplastics, and this will directly affect the dynamics of sorption and interaction with other pollutants. In addition to increasing the specific surface area by physical degradation, (photo)oxidative degradation promotes the formation of oxygen-containing functional groups, which alters the dynamics of surface charges and may increase the ability to adsorb hydrophilic pollutants (Fu et al., 2021). The crystallinity of polymers also greatly influences the sorption behavior of pollutants. More rubbery polymers, such as PE, are more accessible for adsorption of hydrophobic pollutants, but desorption is facilitated, while denser glassy polymers, such as PVC and PS, have lower adsorption capacity but more efficiently trap the sorbed contaminant (Wang et al., 2020c). As a practical example, triclosan is preferentially adsorbed on PE microplastics, but the soil solution promotes desorption from these microplastics more easily than from soil particles or PS microplastics (Chen et al., 2021).

2.3.7 Plastic Additives

In addition to interacting with pollutants in the soil environment, microplastics can release toxic additives such as photostabilizers, fire retardants, plasticizers, and antioxidants (Zhang et al., 2020b). These additives are incorporated into plastic polymers during production to improve the physical characteristics of the materials but pose an additional risk of microplastic contamination on agricultural soils. For example, plastic mulch films contain high levels of phthalate esters (PAEs) – very toxic plasticizing additives (Zhang et al., 2020b), and consequently,

the long-term use of plastic mulch as an agricultural practice raises the levels of these pollutants on soil (Li et al., 2016). It has also been shown that PBDEs – fire retardant additives – can potentially be released from polyurethane microplastics in the application of biosolids (Gaylor et al., 2013). In particular, the leaching of bisphenol A – an additive often used in rigid plastics – from PVC microplastics affected methane production in anaerobic processes (Wei et al., 2019). The weathering of microplastics also plays a role, for example, helping to promote the release of toxic metallic additives from PVC microplastics, thus increasing their bioavailability in the soil environment (Meng et al., 2021).

Based on field studies, Zhang et al. (2021) suggest that the presence of plastic debris contamination has little contribution to the levels of, for example, halogenated fire retardants on soil. However, the release of these toxic additives will impact plant development, microbiota, and soil fauna (Gaylor et al., 2013; Li et al., 2016; Kong et al., 2018), and may be the key explanation for the toxicity of microplastics to organisms (Kim et al., 2020), it is of significant concern for food production and risk to humans.

2.4 Conclusion

Microplastic pollution, extensively investigated in aquatic environments in the last decade, has now attracted attention in soil environments. Through current agricultural practices, agricultural soils receive microplastic inputs from various sources, and impacts of this contamination affect soil properties and crop performance. Microplastics also affect the mobility and bioavailability of other contaminants potentially present in agricultural soils, posing an additional risk for microplastic pollution. Nevertheless, there are still many gaps in the science of microplastics in soil environments, which requires research efforts by the scientific community.

Although several protocols for assessing microplastics in soils have been successfully developed and applied, there are still no standardized methodologies to extract, identify, characterize and quantify microplastics in soil samples, especially for very small microplastics (< 100 µm). This occurs mainly due to the heterogeneity and complexity of the soil matrix. Therefore, there is an urgent need to focus on developing standardized methods to assess microplastics in soils, considering the diverse heterogeneity of soil classes, cropping systems,

and microplastics. The improvement in methods is then substantial to increase understanding of sources, distribution, transport and fate of microplastics in agricultural soil environments.

The impacts of microplastic contamination on soil ecosystems have been studied, but generally under particular conditions. It is necessary to extend research to holistically explore the effects of microplastics in different environments and soil classes, subject to varied agricultural practices, relating alterations in the soil properties with responses of the microbiota, plants and fauna. Investigations about the interaction and leaching of pollutants by different types of microplastics should also consider this heterogeneity of factors. Biogeochemical context and cycles control the dynamics of contaminants in the environment and should be studied in approaches with microplastics in soils. In addition, field experiments are still scarce, and long-term effects that consider impacts of natural aging processes of microplastics in agricultural soil environments are largely unknown.

Since the mass production of plastics on the planet began in the mid-twentieth century, pollution by microplastics, ubiquitous in various environmental matrices, can be considered an important mark of the Anthropocene. Soil environments are supportive of life and agricultural soils play an important role in the world's food production, but they can act as a reservoir for microplastic pollution. Therefore, it is essential for soil science to understand how this type of pollution occurs, impacts soil ecological functions and, consequently, the organisms that depend on them. Furthermore, evidence of impacts of microplastic pollution on soil environments also reinforces the critical need to seek a sustainable way of dealing with plastic, for example through public awareness, private sustainable initiatives and public policies that regulate production, use and disposal of plastic waste.

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3. DOES MICROPLASTIC CONTAMINATION IN AGRICULTURAL SOILS DECREASE THE EFFICIENCY OF HERBICIDES FOR WEED CONTROL?[2]

Resumo:
A contaminação dos solos agrícolas por microplásticos (MPs) tem implicações significativas para a eficácia dos herbicidas e a saúde do solo. Este estudo investiga os efeitos dos MPs sobre processos críticos, como a sorção, dessorção e degradação de herbicidas, destacando sua influência sobre a mobilidade, persistência e biodisponibilidade desses compostos. Os MPs interagem com os herbicidas por meio de mecanismos de sorção, muitas vezes reduzindo a disponibilidade desses compostos para o controle de plantas daninhas ao retê-los em suas superfícies. Essa sorção não só limita a eficácia imediata dos herbicidas, mas também altera seu processo de dessorção, resultando em uma liberação prolongada no ambiente do solo. Além disso, os MPs podem inibir a atividade microbiana envolvida na degradação de herbicidas, aumentando o tempo de degradação da meia-vida dessas substâncias e estendendo sua persistência no ambiente. Esses processos, coletivamente, aumentam os riscos de bioacumulação e contaminação ambiental. Compreender essas interações é essencial para desenvolver estratégias que mitiguem os impactos dos MPs no desempenho dos herbicidas e promovam práticas agrícolas sustentáveis.

Palavras-chave: resíduos plásticos; herbicidas residuais; polímeros; pesticidas; acumulados em solos.

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

[2]BROCHADO, M. G. d. S.; MAGALHÃES, I. B.; SOARES, J. M.; LIMA, A. d. C.; BORDIGNON, L.; GUEDES, A. G.; CASTILLO, M. R.; MENDES, K. F. Does microplastic contamination in agricultural soils decrease the efficiency of herbicides for weed control? **Microplastics**, v. 3, n. 4, p. 771-788, 2024.

3.1. INTRODUCTION

Microplastics (MPs) are plastic particles smaller than 5 mm (Brochado et al., 2024). 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 (Brochado et al., 2024; Fang et al., 2019; Hu et al., 2021; Law; Thompson, 2014; Sun et al., 2021). 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 (Fang et al., 2019; Guo et al., 2024).

MPs are prevalent in agricultural environments due to the numerous entry and distribution pathways of these plastic residues (Yu et al., 2021). These polymers not only cause crop damage (Kumar et al., 2020) and adversely affect vital soil activities (Shafea et al., 2023), but they can also influence important agriculture processes (Zhang et al., 2022).

The production of these small particles can be categorized into primary and secondary sources (Abbaszadeh et al., 2024; Hanachi et al., 2019).The primary sources are already manufactured in this size and introduced directly into the agricultural soil (Machado et al., 2019). 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 (Zhang et al., 2020a). The degradation of larger plastics in the environment (Rillig, 2012), often due to the fragmentation of plastic mulch films used for crop protection or the decomposition of plastic waste used in agriculture (Waldman and Rillig, 2020), 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 (Rillig, 2012).

In agricultural soils, MPs can cause drastic changes in soil structure, bulk density, and water retention capacity (Machado et al., 2018). Furthermore, they influence nutrient cycling (Zhang et al., 2019) and affect various essential activities of soil biota, such as the enzymatic activities of microorganisms (Rillig and Lehmann, 2020; Rillig et al., 2021; Xiao et al., 2021; Zhang et al., 2019; Zhao et al., 2022). Due to their high specific surface area, MPs can also interact with other pollutants, such as polycyclic aromatic hydrocarbons, heavy metals, and

pesticides (Tian et al., 2022; Wang et al., 2020a), including herbicides, which can influence the effectiveness of weed control (Brochado et al., 2023).

Several studies have highlighted the pervasive presence of MPs in agricultural soils and their interactions with various pollutants, including pesticides and heavy metals (Rillig, 2012; Rillig and Lehmann, 2020; Yu et al., 2021; Xiao., 2021; Zhang et al 2022; Brochado et al., 2023). MPs can alter soil properties, disrupt microbial activity, and impact pollutant dynamics through mechanisms such as sorption retention (Wang et al., 2020a; Zhao et al., 2022). 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 (Ni et al., 2023; Zhou et al., 2022). 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 (Guimarães et al., 2022). 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 3.1).

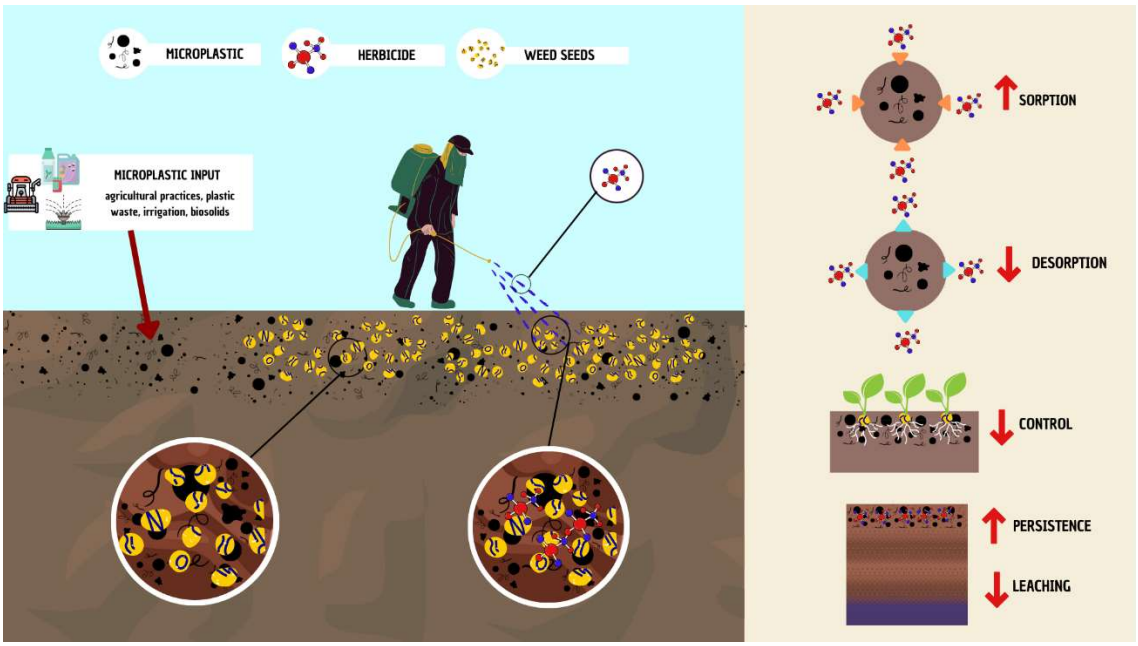

Figure 3.1- Contamination of arable soils by microplastics (MPs) and their interactions with the behavior and efficacy of herbicides. Source: Adapted from Zhang et al. (2020b); Nobre et al. (2022); Wang et al. (2020b); and Ni et al. (2023).

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.

3.2 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.

3.3 RESULTS AND DISCUSSION

3.3.1 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 (Frias and Nash, 2019). 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 3.2).

The initial research focused mainly on oceans, as it was believed that most MPs accumulated in marine ecosystems (Rochman, 2018). 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 (Rillig and Lehmann, 2020).

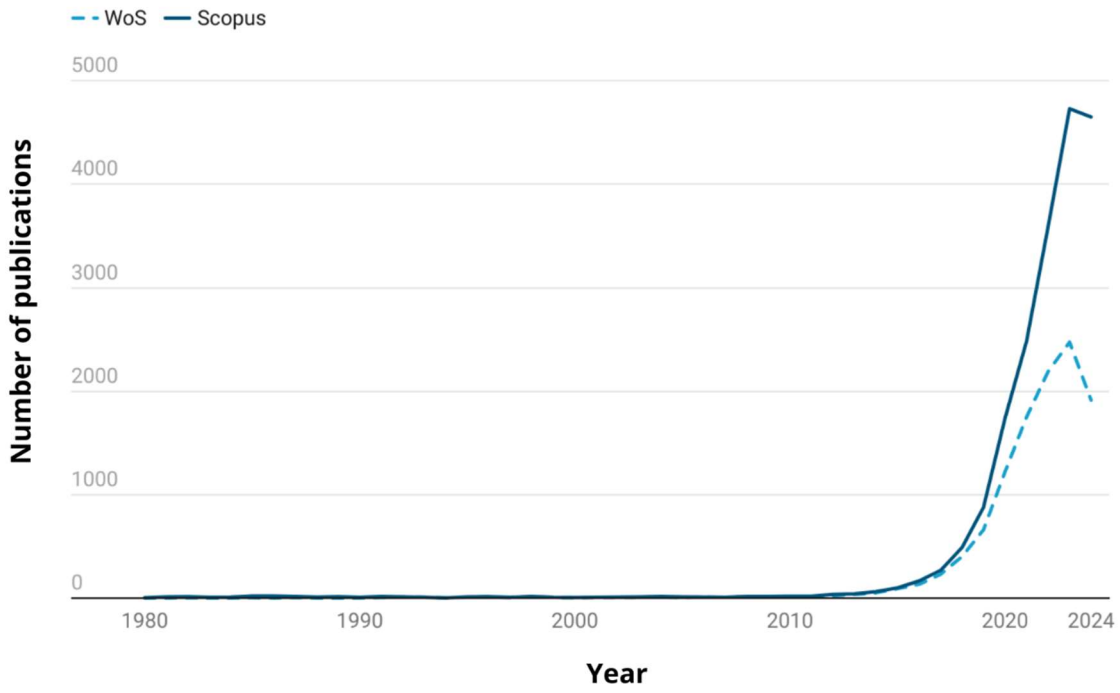

Figure 3.2- Annual publications on microplastics indexed in Scopus and Web of Science.

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 (Barboza et al., 2018).

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 3.3). 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 (Weis, 2019).

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 3.4).

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 (Zhang et al., 2018; Li et al., 2019). 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 (Fok et al., 2020).

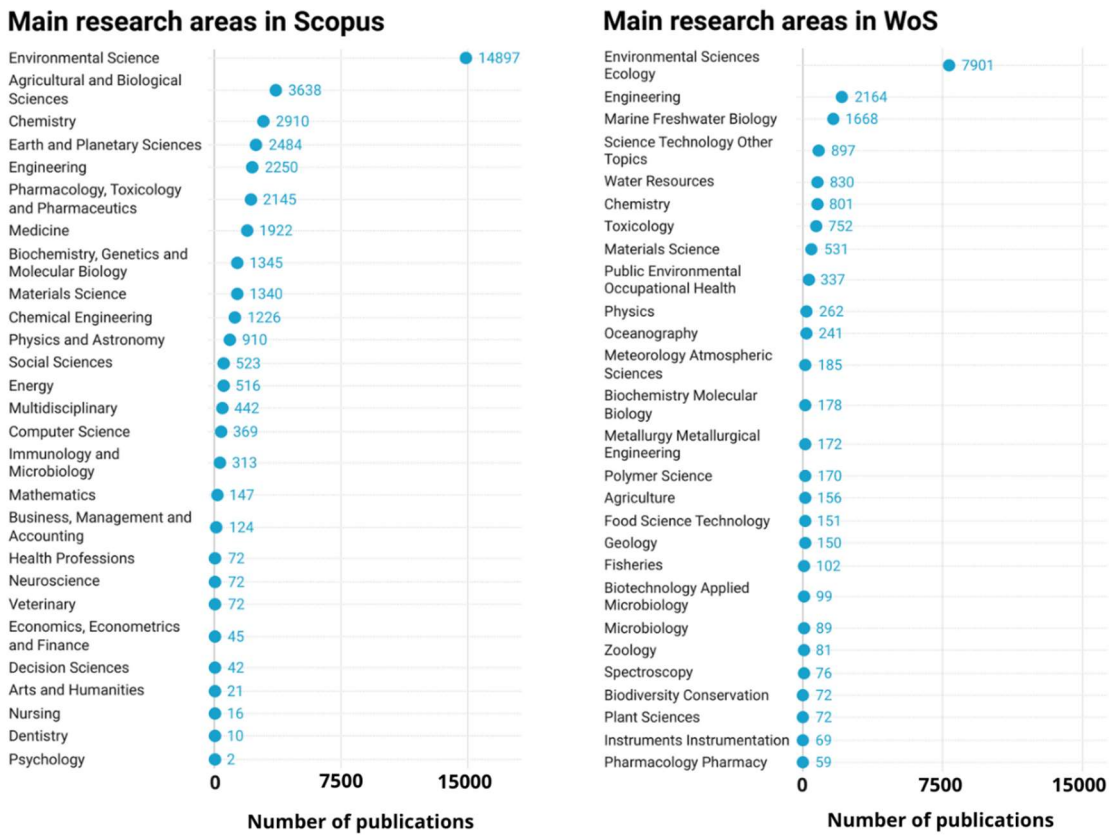

Figure 3.3- Main research areas by number of publications on microplastics (MPs) indexed in Scopus and Web of Science (WoS).

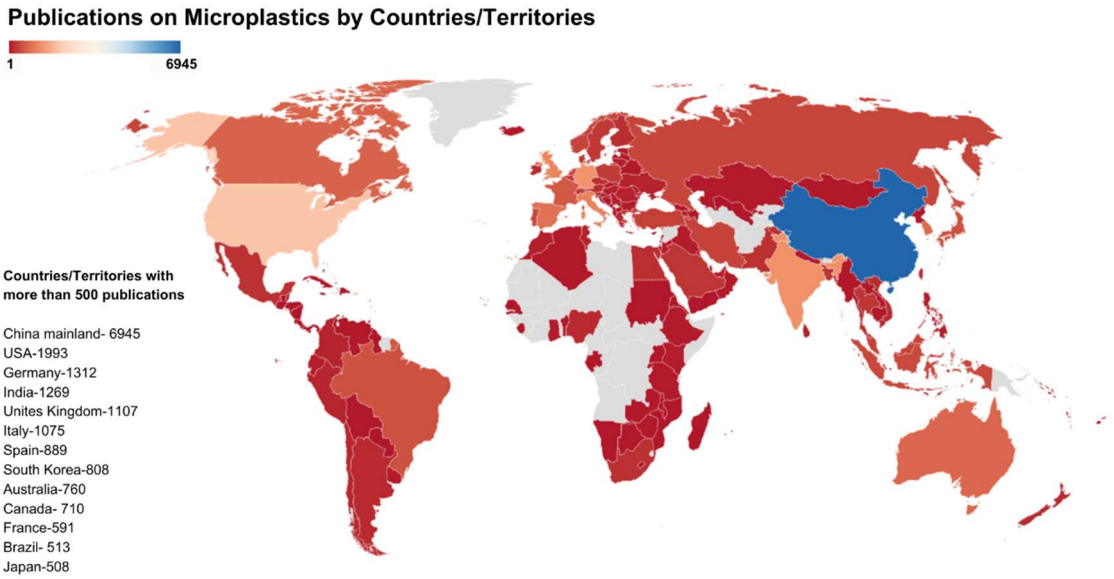

Figure 3.4- Distribution of publications on microplastics (MPs) worldwide according to the Scopus database.

3.3.2 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 3.5). Although the number of publications is still limited, several research lines are emerging to study the interaction between herbicides and MPs.

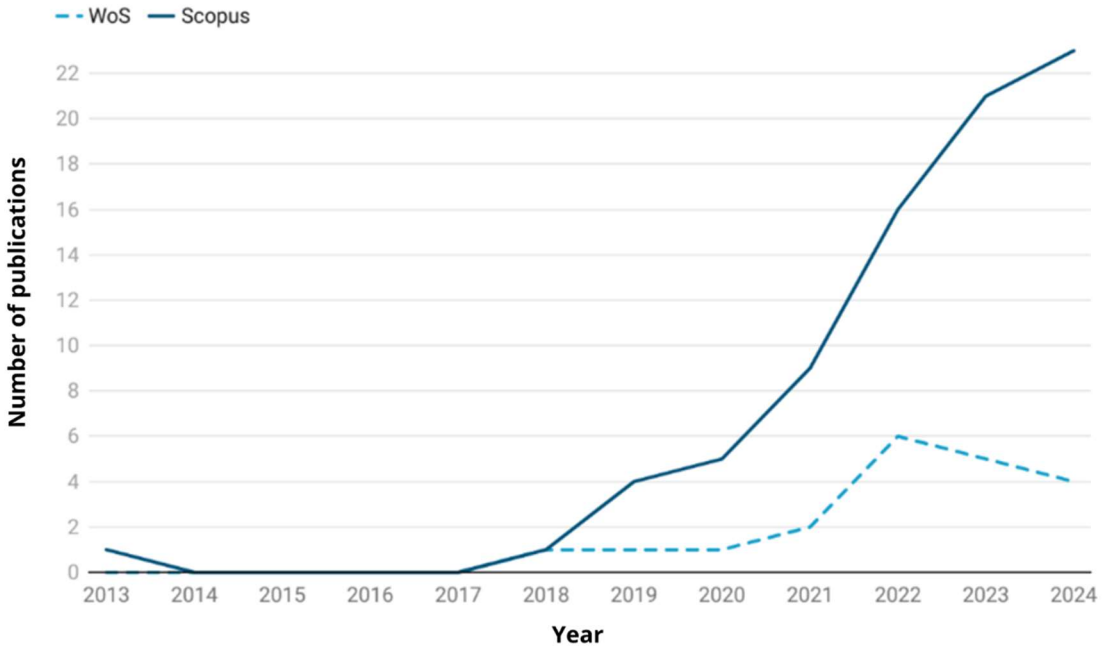

Figure 3.5- Annual publications on microplastics (MPs) and herbicide interaction indexed in Scopus and Web of Science (WoS).

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 (Peña et al., 2023). 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 (Wang et al., 2020b).

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 (Lajmanovich et al., 2021).

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 (Liu et al., 2019).

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.

3.3.3 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 (Machado et al., 2018; Chang et al., 2024; Wang et al., 2022). As summarized in Figure 3.6, 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.

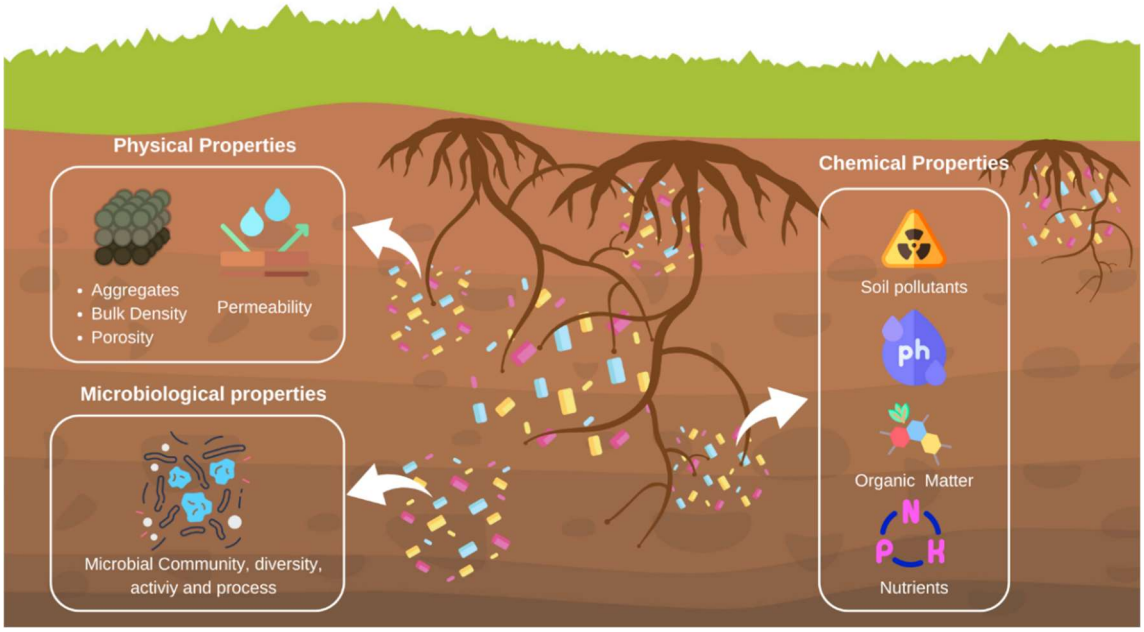

Figure 3.6. Soil properties affected by the presence of microplastics (MPs).

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 (Wang et al., 2022).

MPs can obstruct soil pore spaces and alter water dynamics. For example, Kim et al. (2021) 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 (Wang et al., 2022).

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 (Machado et al., 2018). 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 (Chang et al., 2024). 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 (Gao et al., 2021). 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 (Wang et al., 2022).

MPs in the soil have also been associated with varied effects on organic matter content, directly influencing soil fertility, plant nutrition, and microbial activity (Wang et al., 2022). For instance, Liu et al. (2017) saw that dissolved organic matter broke down less quickly in cultivated loess soils with 28% (w w^{-1}) 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 (Wang et al., 2022). For example, Shi et al. (2022) 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 (Rong et al., 2021). Moreover, amendments with MPs (2000 fragments per kg of soil) significantly increased urease and catalase activities after 15 days (Huang et al., 2019). 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 (Wang et al., 2022).

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. (2021) 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 (Fei et al., 2022). 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 (Ren et al., 2020). Gao et al. (2021) 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. (2021) 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 (Machado et al., 2018). 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.

3.3.4. 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 (Guo et al., 2024). 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 (Lu et al., 2023). In a soilless experiment, Martín et al. (2021) 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 (Sondhia, 2014). 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 (Varah et al., 2019). 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 (Agathokleous et al., 2022). 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 (Agathokleous et al., 2022; Jalal et al., 2021).

Recently, Qiu et al. (2024) 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 (Bao et al., 2024; Guo et al., 2024; Li et al., 2020a; Zhou et al., 2022). 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 (Yang et al., 2018). 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 (Rillig et al., 2017).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 (Huerta et al., 2016).

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 (Nel et al., 2009; Tripathi et al., 2017). In a recent study, Li et al. (2020a) 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 system (Pignatelli et al., 2020; Wu et al., 2020) 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 (Li et al., 2020b).

MPs also act as carriers of chemical contaminants in soil due to their hydrophobic surface and chemical composition, enabling them to adsorb in 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 (Peña et al., 2023). 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 (Fajardo et al., 2022; Roy et al., 2024).

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. (2022) reported concerning levels of particles <10 μm 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.

3.3.5. 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 (Deng et al., 2024). 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 (Büks and Kaupenjohann, 2020).

MPs serve as vectors for organic compounds, altering the sorption and bioavailability of herbicides in the soil (Menéndez-Pedriza and Jaumot, 2020). 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 (Wang et al., 2020a). 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 (Agboola and Benson, 2021). Ions present in the solution compete for sorption sites, reducing the retention of herbicides in the MPs (Agboola and Benson, 2024). 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 3.7), 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 (Kjaer et al., 2011). This high value indicates that it preferentially accumulates in MPs and organic matter, showing low mobility in the soil (Kjaer et al., 2011; Wang et al., 2020a). 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 (Kjaer et al., 2011; Wang et al., 2020a). S_w also influences these interactions. Compounds with low S_w, such as atrazine (S_w = 33 mg/L), are less soluble in water (Souza et al., 2020). 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) (Souza et al., 2020), 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 (Ololade et al., 2015), 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 (Lan et al., 2021) (Figure 3.7).

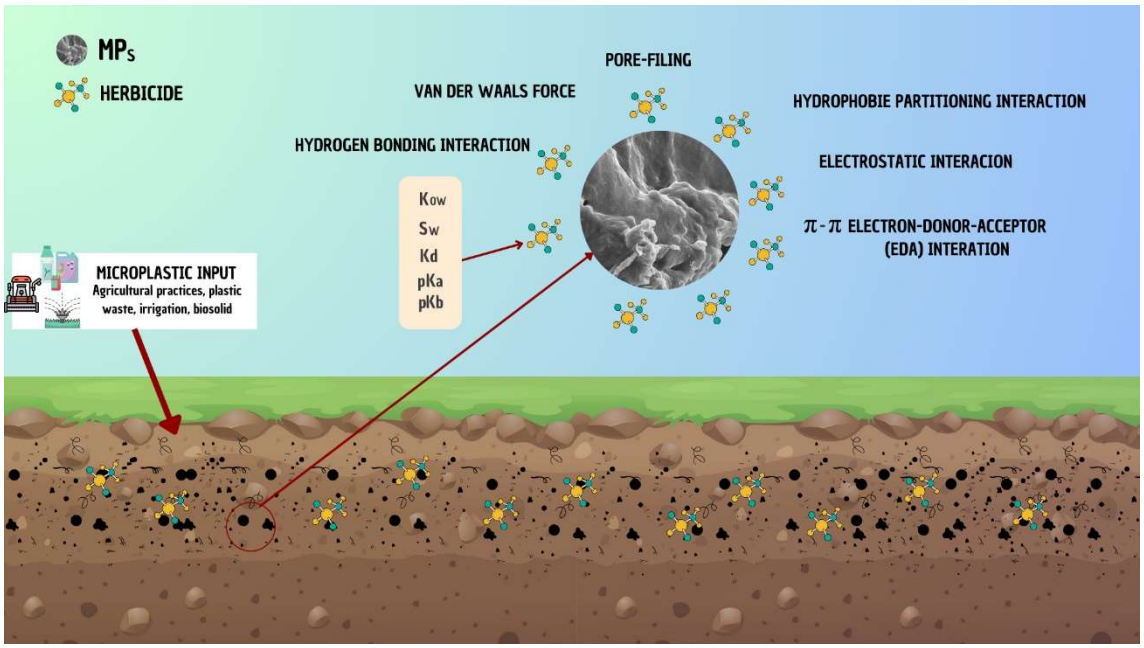

Figure 3.7- Interaction mechanisms between MPs and herbicides in soils. K_{ow}: octanol–water partition coefficient; S_w: water solubility; K_d: distribution coefficient; pK_a: acid dissociation constant; pK_b: base dissociation constant. Source: Adapted from Wang et al. (2020).

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 (Mo et al., 2021; Li et al., 2021; Lv et al.,2023). Pendimethalin, with its high hydrophobicity (K_{ow} = 5.2), exhibits strong sorption to MPs, reducing its bioavailability and potentially compromising its weed control efficacy (Wang et al, 2020). While this reduced bioavailability may mitigate acute toxicity to non-target organisms, it could necessitate higher application rates, further increasing environmental contamination risks (Li et al., 2021). 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 (Mo et al., 2021). Herbicides containing aromatic groups can engage in

π–π interactions with MPs composed of aromatic rings, further enhancing their retention (Wang et al., 2020).

For example, Peña et al. (2023) 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) (Wang et al., 2020). 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 (Li et al., 2021).

A recent study by Lv et al. (2023) 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. (2019) 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. (2021) 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. (2021) 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. (2022) 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 (Yang et al., 2018).

To provide a comprehensive understanding of these interactions, Table 3.1 summarizes key findings regarding herbicide-microplastic interactions. Table 3.1 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

Table 3.1- 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	Lv et al. (2023), Wang et al. (2020)
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. (2011), Wang et al. (2020)
Simazine	Polystyrene	Reduction in degradation and alteration in microbial community	Reduction in microbial degradation rate	Alterations due to high sorption capacity	Zhou et al. (2022), Liu et al. (2019)
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. (2018), Souza et al. (2020)
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. (2021), Lan et al. (2021)

K_{ow}: Octanol–water partition coefficient.

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.

3.4 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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4. WHAT IS THE MOST EFFECTIVE ANALYTICAL METHOD FOR QUANTIFICATION AND IDENTIFICATION OF MICROPLASTICS IN CONTAMINATED SOILS?[3]

Resumo

A crescente preocupação com a contaminação por microplásticos (MPs) em solos agrícolas devido ao uso excessivo de plástico é uma questão global. O objetivo deste estudo foi determinar qual técnica analítica é mais eficaz para a análise de MPs em solos agrícolas. Foram utilizadas espectroscopia no infravermelho próximo (NIR), microscopia eletrônica de varredura (MEV), análise multiespectral e difração de raios X para analisar seções de solo argiloso contendo diferentes porcentagens de MPs brancos virgens, variando de 0 a 100%. A análise por raios X detectou MPs apenas em altas concentrações (20%). No entanto, a NIR a 2.300 nm e a análise multiespectral a 395 nm demonstraram maior precisão e sensibilidade na distinção entre todos os níveis de MPs. O MEV mostrou que os MPs possuem uma estrutura amorfa, distinta do solo cristalino, o que pode influenciar suas interações com outros constituintes do solo. Esses achados destacam o valor da NIR e da análise multiespectral na identificação e quantificação precisa dos MPs no solo. Planos de manejo eficientes dependem de uma maior conscientização sobre o impacto ambiental dos MPs.

Palavras-chave: caracterização de polímeros; poluição por plásticos; técnicas de detecção; contaminantes no solo; agricultura sustentável

Abstract

The increasing concern over microplastics (MPs) contamination in agricultural soils due to excessive plastic use is a worldwide concern. The objective of this study was to determine which analytical technique is most effective for the analysis of MPs in agricultural soils. Near-infrared spectroscopy (NIR), scanning electron microscopy (SEM), multispectral analysis, and X-ray diffraction were used to analyze sections of clay soil containing varying percentages of virgin white MPs from 0 to 100%. X-ray analysis only detected MPs at high concentrations (20%). However, NIR at 2.300 nm and multispectral analysis at 395 nm demonstrated greater accuracy and sensitivity in distinguishing between all MPs levels. SEM revealed that MPs have an amorphous structure that is distinct from crystalline soil, potentially influencing their interactions with other soil constituents. These findings highlight the value of NIR and multispectral analysis in accurately identifying and measuring MPs in soil. Efficient management plans rely on increased awareness of MPs' environmental impact.

Keywords: polymer characterization; plastic pollution; detection techniques; contaminants in soils; sustainable agriculture

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[3]BROCHADO, M. G. S.; NORONHA, B. G.; LIMA, A. C.; GUEDES, A. G.; SILVA, R. C.; DIAS, D. C. F. S.; MENDES, K. F. What is the most effective analytical method for quantification and identification of microplastics in contaminated soils? **Environmental Geochemistry and Health**, v. 46, n. 7, p.1-18, 2024.

4.1 INTRODUCTION

Since its invention in the early twentieth century, global plastic production has shown steady annual growth, reaching a milestone of 359 million tons in 2018 (Caixeta et al., 2018; Kurniawan et al., 2021). Projections suggest that this trend will continue, with an expected increase of approximately four times the current rate by the year 2050 (Kurniawan et al., 2021). The increased use of plastics has led to a signifcant generation of waste, raising signifcant concerns in environmental and socio-economic contexts. In this context, it is especially critical to highlight the pollution that micro and millimeter-sized plastics cause (Montagner et al., 2021).

Among the various plastic waste types, microplastics (MPs) are emerging as a signifcant concern due to the impacts they are causing on soil health and quality (He et al., 2018). Thompson et al. (2004) created the term "MPs" to refer to small plastic fragments measuring less than 5 mm.

MPs are present in water (Pivokonsky et al., 2018), air (Dris et al., 2017; Rezaei et al., 2019), and soil (Brochado et al., 2023; Kim et al., 2021). Because of their ubiquitous presence in the environment, they pose various risks to ecosystems and human health. According to Senathirajah et al. (2021), our average weekly consumption of MPs is approximately 5 g per person. This quantity is roughly equivalent to the weight of a credit card. Research has shown that using MPs without meaning can harm important parts of the human body. Researchers have discovered these MPs in various parts of the human body, including the heart (Persiani et al., 2023), lungs (Amato-Lourenço et al., 2022), placenta (Braun et al., 2021), digestive tract (Fournier et al., 2023), blood (Çobanoğlu et al., 2021), and urine (Hefernan et al., 2020).

Analysis of MPs in environments provides crucial information about pollution levels and potential organism exposure to residues. In agricultural environments, these MPs can impact the development of crops such as wheat (Triticum aestivum) (Qi et al., 2018), green onions (Allium fstulosum) (Machado et al., 2019), and tomatoes (Solanum lycopersicum) (Bosker et al., 2019). Machado et al. (2018) say that MPs can have a big efect on microorganisms' structure, bulk density, ability to hold water, nutrient cycling, and enzyme activities. All

these things are important for soil life (Zhang et al., 2019; Xiao et al., 2021; de Souza Machado et al., 2019; Rillig & Lehmann, 2020; Rillig et al., 2021; Zhao et al., 2022).

Several methods are currently used to verify MPs contamination in the soil. These include controlled chemistry, enzymatic digestion, near-infrared spectroscopy (NIR), fuorescence spectroscopy, scanning electron microscopy (SEM), and three-dimensional X-ray analysis (Li et al., 2020). Vignesh et al. (2024) have carried out a study of MPs in water and sediment pollution. Using NIR in the spectral range of 500–4.000 cm^{-1} in the middle infrared region, these authors identifed the presence of polymers. In organic fertilizers and water, the identifcation was carried out by means of Raman spectroscopy (Jacob et al., 2024; Xu et al., 2024). Other techniques, such as electrostatic separation and scanning diferential calorimetry, have also been shown to be efcient for this purpose (Kurzweg et al., 2024). Researchers use these methods to characterize, detect, and measure the presence of MPs in the soil, thereby improving our understanding of the environmental impact that this type of pollution causes (Brochado et al., 2023).

Scientifc research widely recognizes the impact of MPs on the environment and human health as an emerging and highly relevant feld. The characterization and quantifcation of these residues are essential to support informed decision-making. Advancing the development of efcient and cost-efective analytical methods is crucial for improving analyses and understanding the currently available options. However, it is important to highlight that the number of studies addressing this topic is still limited. Most studies focus on only one of the techniques discussed in this study, whereas it explores multiple key techniques for identifying MPs in agricultural soil. This underscores the urgent need for further research to provide a solid knowledge foundation for scientists, producers, and academics involved in this area of study. The objective of this study was to determine which analytical technique is most effective for the analysis of MPs in agricultural soils, thereby contributing to the advancement of research in this field.

4.2 MATERIAL AND METHODS

4.2.1 Microplastics

The polyethylene microspheres were obtained as a "virgin" material with the following characteristics: particle size of 600 µm, natural color, melting point between 100–115 °C, bulk density between 350 and 370 g/cm^3, and a melt flow index of up to 30 g/10 min. The material was acquired from Bianquimica (Diadema, São Paulo, Brazil).

4.2.2 Soil

The soil samples were collected from the topsoil layer (0–20 cm) of areas that had not been treated with herbicides in the past three years at the *Unidade de Ensino, Pesquisa de Extensão em Produção de Grandes Culturas e Bioenergia* (UEPE/GCBE) *da Universidade Federal de Viçosa*. The samples were classified as *Latossolo Vermelho* (Oxisol in the USDA Soil Taxonomy) according to the Brazilian Soil Classification System (EMBRAPA, 2018; IUSS, 2022). They were air-dried for 10 days and subsequently sieved through a 2 mm mesh, then stored at room temperature. This soil was classified as clayey, with a 53% clay content, 1.98% organic matter (OM), pH 4.88, and an effective cation exchange capacity (CEC) of 3.99 $cmol_c\ dm^{-3}$. The soil's physical and chemical properties include 0 mg dm^{-3} P, 18 mg dm^{-3} K, 0.36 $cmol_c\ dm^{-3}$ Ca, 0.8 $cmol_c\ dm^{-3}$ Mg, 3.5 $cmol_c\ dm^{-3}$ H + Al, and 12% Base Saturation.

4.2.3 Sample preparation

The samples were composed of 6 g of material, with increasing proportions of MPs relative to the initial mass of pure soil, as follows: 0, 0.1, 0.5, 1.0, 5.0, 10.0, 20.0, 30.0, 50.0, 70.0, and 100% w w^{-1}., with four replicates at each level.

4.2.4 Physicochemical analysis of microplastics

The determination of the amount of carbon (C), oxygen (O), hydrogen (H), and nitrogen (N) in the MPs was performed using an elemental analyzer. 100 mg of the MPs sample was weighed into a tin capsule. The capsule was then sealed and placed in the apparatus, which operates by subjecting the samples to combustion in an atmosphere of pure oxygen (99.99%). A thermal conductivity

detector (TCD) quantifies the gases formed by this combustion. Equation 1 presented the mass balance equation, which we used to estimate the oxygen content.

$$O = 100 - (C + H + N + Mineral) \quad (1)$$

The content of inorganic minerals was determined through energy dispersive X-ray fluorescence spectrometry (XRF/EDX) using the D8 Discover model by Agilent Technologies in Santa Clara, CA, USA.

To do this, 1 g of the MPs was weighed, and then it was placed in a polyethylene cup with an internal diameter of 20 mm and covered with a 6 µm thick polypropylene film. The sample was irradiated in triplicate for 300 s under vacuum conditions using an energy-dispersive X-ray fluorescence spectrometer. An X-ray tube operated at 15 kV (from Na to Sc) and 50 kV (from Ti to U) to irradiate the samples. The current was automatically adjusted (up to a maximum of 1 A). A 10 mm collimator was used, and detection was performed with a Si (Li) detector cooled with liquid nitrogen.

4.2.5 Acquisition of X-ray images

For X-ray analysis, Faxitron MX-20 equipment (Faxitron X-ray Corp., Wheeling, IL, USA) was used, configured with an exposure time of 19 s and a 30 kV setting. The samples were individually positioned inside the equipment, 20 cm from the X-ray source. The acquired images were saved in Tiff format and analyzed using the ImageJ software (ImageJ2 Version, Bethesda, Maryland, USA).

4.2.6 Multispectral analysis

For multispectral analysis, the Croma Seed prototype (Viçosa, Minas Gerais, Brazil) was used, providing UV–VIS-NIR images in the spectra from 395 to 940 nm with a total of 8 spectral bands (Figure 4.1a). The soil samples previously described were placed inside the equipment, and subsequently, images were captured and saved in Tiff format (Figure 4.1b).

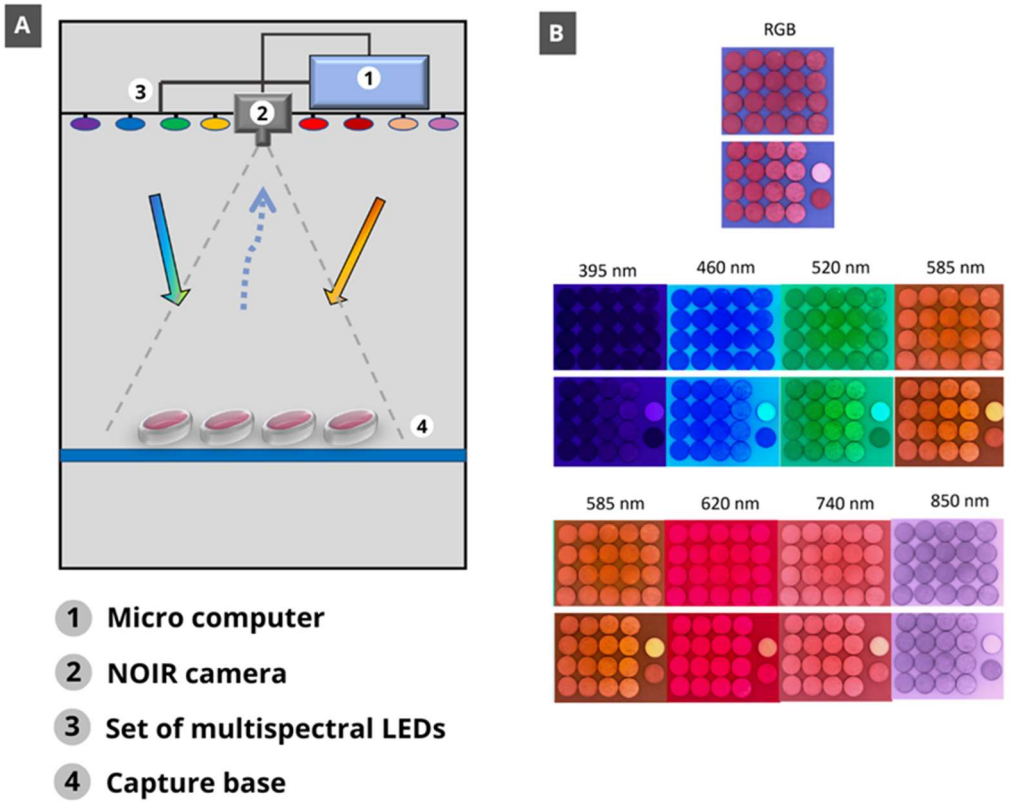

Figure 4.1- Prototype Model of Croma Seed (a), Croma Seed Equipment (b), and Image of the Spectral Bands of the MPs samples (with smaller proportions of MPs in the top row and larger proportions in the bottom row)

For the analysis of the images and the extraction of reflectance values, the ImageJ software (ImageJ2 Version, Bethesda, Maryland, USA) was employed. The process involved opening the image, selecting the region of interest using the threshold method with the Otsu segmentation technique (Otsu, 1979), and obtaining the average grayscale values of pixels for each spectral band. Equation (2) then converted these values into reflectance:

$$R(\%) = (((PVi * 100)/Bi) - P)/((Bi - P)) * 100 \quad (2)$$

Where:

R (%) is the estimated reflectance in percentage;

PV is the mean pixel value for each spectral band;

Bi is the reference white value (in this case, barium sulfate with an estimated reflectance of 98% was used);

P is the reference black value (in this case, activated carbon nanoparticles with an estimated reflectance of 0.05% were used).

After collecting the spectral curves from the samples, they were individually plotted to check for quality and the presence of noise using the Nira package for R-Project (Medeiros et al., 2020).

4.2.7 Near-infrared analysis (FT-NIR)

For the determination of the near-infrared spectrum, the FT-NIR equipment (Antaris II model, Waltham, Massachusetts, USA) was used. The contaminated soil samples were placed in a quartz glass reducing ring and positioned at the equipment's aperture for reading. To prevent external interference, the reducing ring with the sample was covered with a metal cylinder. Following this procedure, readings were taken in the spectral range of 1000 to 2500 nm, totaling 1122 spectral bands collected for each sample. The results were expressed in reflectance (log 1/R).

After collecting the spectral curves from the samples, they were individually plotted to check for quality and the presence of noise using the Nira package for R-Project (Medeiros et al., 2020).

4.2.8 Spectral data analysis

Both multispectral and FT-NIR spectral data underwent several pre-processing steps. These included autoscaling (AU), multiplicative scatter correction (MSC), standard normal variate (SNV) normalization, and the application of Savitzky-Golay first- and second-order derivatives (Savitzky and Golay, 1964) with a variable window. For classification model development, 70% of the data was allocated for training, while the remaining 30% was reserved for testing. Additionally, a tenfold cross-validation was performed on the training data to ensure model robustness. Each preprocessed dataset was subjected to partial least squares (PLS) analysis, a statistical technique well-suited for predictive modeling, particularly when dealing with datasets containing many correlated independent variables (Barker and Rayens, 2003). The PLS analysis was implemented using the Caret package (Kuhn, 2008) within the R software environment (R Core Team, version R.2.2). The model's performance was measured by a number of factors, including the root mean square error of calibration (RMSEC), the calibration coefficient of determination (R^2c), the root mean square error of cross-validation (RMSECV), the cross-validation coefficient of determination (R^2cv), the

root mean square error of prediction (RMSEP), and the number of latent variables (LVs) used in both the training and test datasets. Furthermore, during model construction, the most significant wavelength ranges were identified, providing insights into the factors influencing prediction model accuracy.

4.2.9 Scanning electron microscopy (SEM) analysis

SEM (JEOL model JSM-6010LA, Akishima, Japan) was used to evaluate the physical surface morphology changes of the MPs. The MPs particles were mounted on a metal sample holder using carbon-conductive tape and sputtered with a 9 nm thick gold layer in a metal coater. This procedure is employed to enhance the material's conductivity, resulting in higher-quality images. Image capture was carried out with secondary electron (SE) detection in the SEM, operating with a 20 kV electron beam

4.3 RESULTS

4.3.1 X-ray analysis

In the radiographic analyses, it was not possible to accurately measure the amounts of MPs ranging from 0.1 to 10% contamination since these particles are not visible in this setting, making it hard to get clear detections (Figure 4.2). Concerning the different concentrations of MPs incorporated into the soil, the detection capability only became discernible from the 15% proportion onward, extending up to the concentration of 100%. The radiographic approach showed its limitations by not being suitable for quantities below 15%, as these proportions hindered the effective identification of densities.

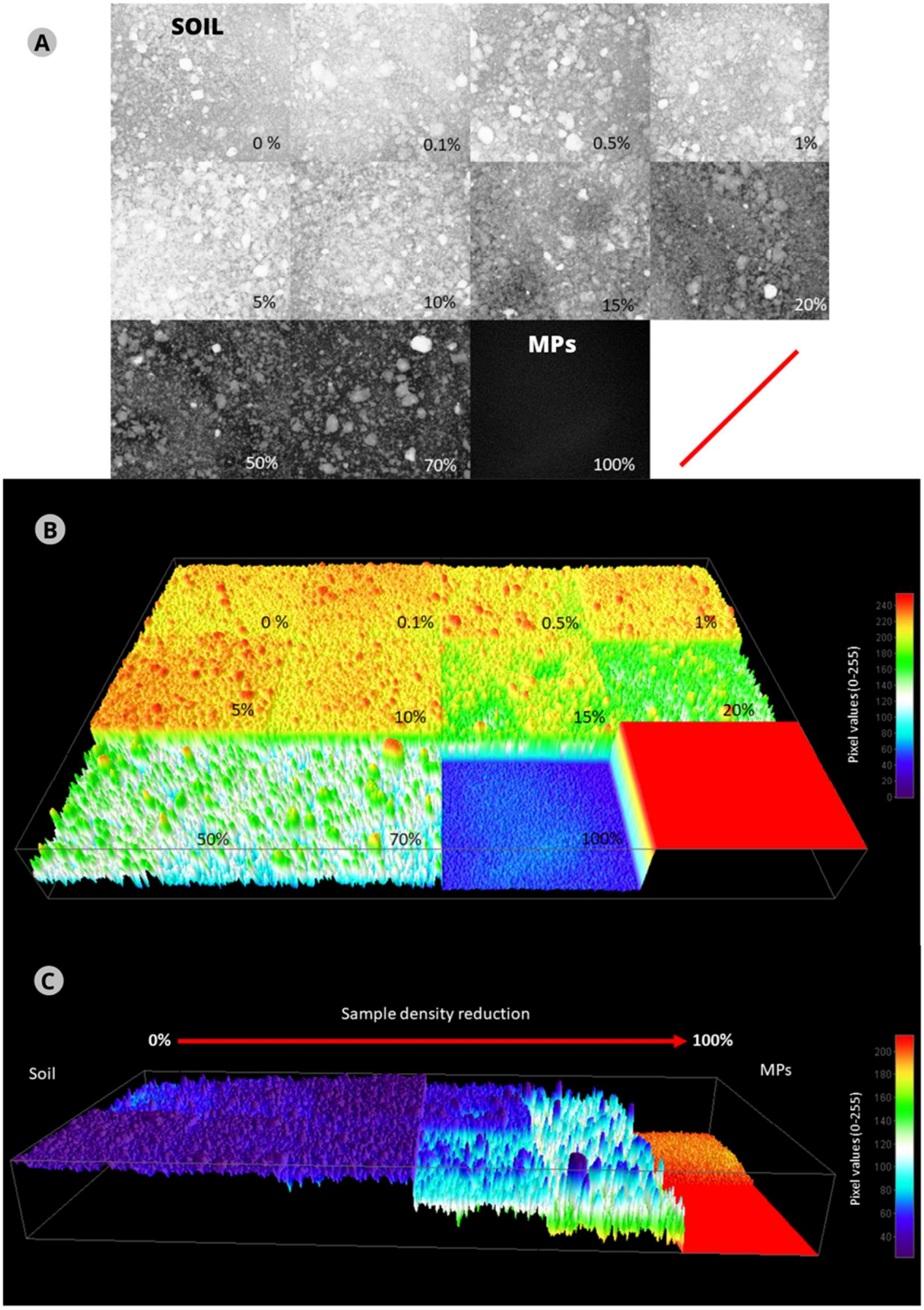

Figure 4.2- Quantification and identification of MPs in soil contaminated with the proportions of MPs 0, 0.1, 0.5, 1.0, 5.0, 10.0, 20.0, 30.0, 50.0, 70.0, and 100% (w w^{-1}) based on **a** X-ray images and **b** and **c** 3D projections

This limitation stems from the fact that MPs have a lower density compared to the soil. As a result, during the radiography technique application, X-rays passed directly through the MPs, creating gaps between these particles and the soil components. This occurrence was particularly pronounced in the presence of larger amounts of soil, which is why the images appear darker at higher proportions of MPs (Figure 4.2a). The soil absorbs X-rays more due to its density, leading to the creation of radiopaque soil images. This becomes clear when comparing it to the treatment with MPs, which are penetrated by X-rays due to their lower density.

Figure 4.2b and c illustrate this behavior. In the 3D representations, at a contamination level of 15%, the images display a higher quantity of empty spaces. This behavior reflects the density difference between the particles, which allows X-rays to pass through the MPs due to their differing densities compared to soil. The whiter and bluer the areas, the stronger the indication of these empty spaces, emphasizing the relationship between density, X-ray penetration, and space formation in the matrix.

4.3.2 Multispectral analysis

In the multispectral analysis, Figure 4.3 displays the graphs of the spectral signatures of the samples. The MPs' spectral signatures differ significantly from other signatures that include soil mixtures. Additionally, it is noteworthy that the MPs exhibit considerably high reflectance, playing a crucial role in quantification. A pronounced disparity in the proportions is observed, indicating that the higher the concentration of MPs, the higher the reflectance of the signature.

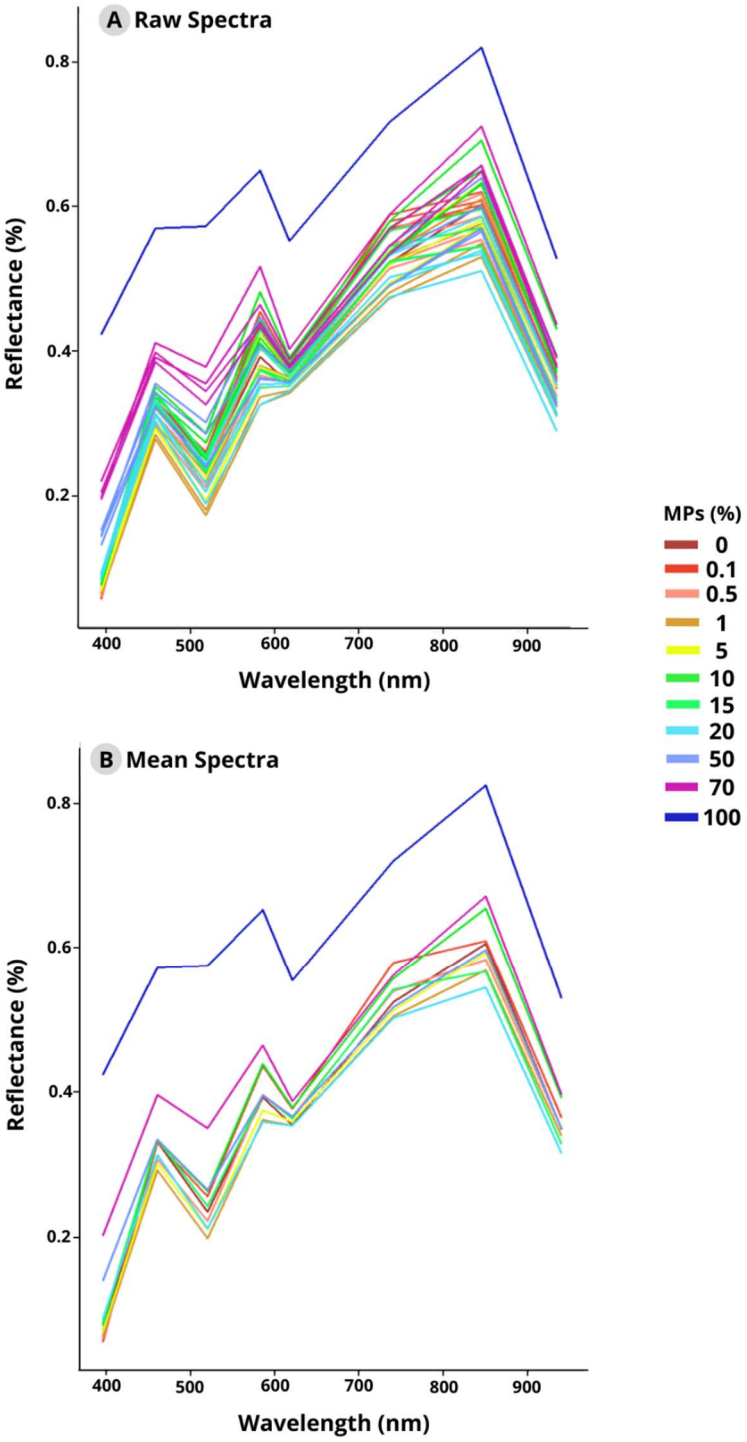

Figure 4.3- Reflectance spectra of soil samples contaminated with the proportions of MPs 0, 0.1, 0.5, 1.0, 5.0, 10.0, 20.0, 30.0, 50.0, 70.0, and 100% (w w^{-1}), highlighting the spectral signature. (A) Raw multispectral spectra (B) Average spectra.

In the ultraviolet range, it is possible to identify an increase in reflectivity that decreases as the proportion of MPs is reduced. The trend persists until the red region, where the proportions are at their lowest. Regions near the red spectrum, specifically between 600 and 700 nm, exhibit greater absorption (Figure 4.4). It is important to note that this spectral pattern remains consistent across all samples, emphasizing inherent cohesion.

Figure 4.4 shows that Principal Component Analysis (PCA) makes it easy to tell the difference between groups. Figure 4.4 spectrum demonstrates a strong correlation between the presence of MPs and spectral bands. It is noteworthy that there is a direct correlation between the levels of reflection and the number of MPs present. As the concentration of MPs in the soil increases, there is a corresponding increase in reflection, as vividly demonstrated in the PCA analysis. In this context, the representative vectors of the spectral bands prominently point towards the MPs group, identified as the cluster on the right, displaying proportions of 70% and 100% (Figure 4.4).

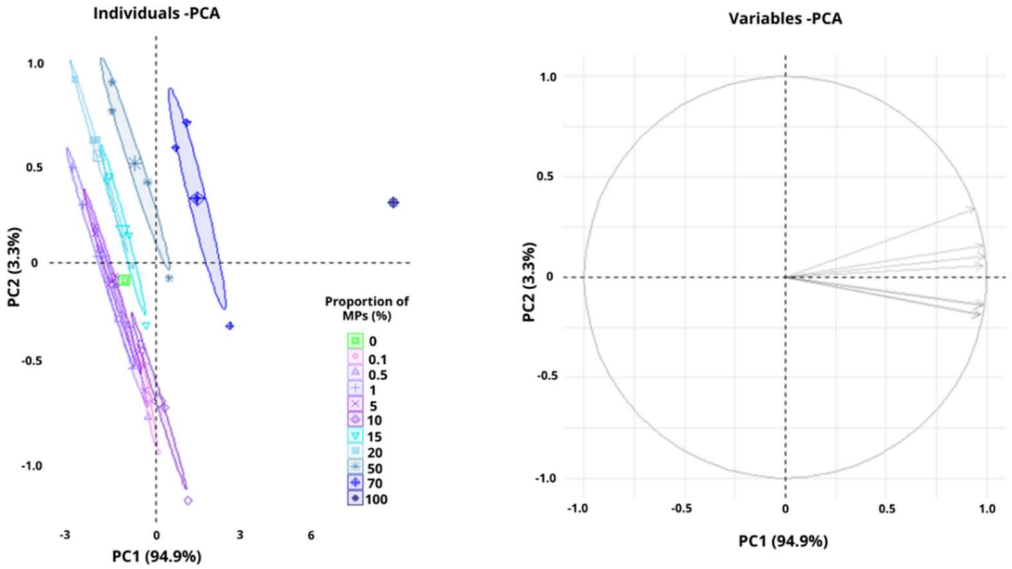

Figure 4.4- Principal Component Analysis (PCA) scores and weights of PC1 × PC2 in soil contaminated with the proportions of MPs 0, 0.1, 0.5, 1.0, 5.0, 10.0, 20.0, 30.0, 50.0, 70.0, and 100% (w w^{-1}).

This agreement in vector orientation and MP clustering suggests a significant positive correlation. The clear separation between clusters, which correlates with the quantity of MPs present in the soil, confirms this relationship. Therefore, it is plausible to infer that these results denote a strong association, allowing for the segmentation of these distinct groups, which exhibit noticeable variations.

The PCA explains a significant percentage of 98.2% of the total variation. The first component along the X-axis encompasses a substantial explanation of 94.9% of the variation, while the results along the Y-axis represent 3.3% of the explained variation. These values indicate that the groups differ noticeably due to their distinct characteristics, making it possible to discriminate between them through multispectral analysis.

A predictive analysis was devised utilizing partial least squares (PLS) to assess the capability of the apparatus to classify MPs in soil. We assessed different preprocessing techniques (Table 4.1). The original data and the data after autoscaling (AU) preprocessing produced comparable results. This suggests that preprocessing did not significantly impact the model's quality. The model displayed minimal prediction errors (RMSEC and RMSEP) and good correlation (Rc and Rp near 1). The SNV method (with type = max) did not work at the original and AU data. Larger errors in calibration and prediction (RMSEC and RMSEP) and a slight decrease in correlation coefficients (Rc and Rp) demonstrated this. The MSC preprocessing performed noticeably worse than the other approaches, as evidenced by the biggest prediction errors (RMSEP) and lowest prediction correlation coefficients (Rp). While it still had a relatively good correlation coefficient, the first-order derivative with a window length of 5 (SG deriv = 1) produced greater calibration and prediction errors than the original data. As a result, we used the original data to develop the prediction model, which produced the best results in terms of high correlation and low prediction error (Figure 4.5).

Table 4.1- PLS model parameters based on different types of preprocessing: multispectral analysis.

Pre-Processing	RMSEC	Rc	RMSECV	Rcv	RMSEP	Rp	LV	Decision
Original data	2.657504	0.996494	3,879514	0.992541	3.910407	0.992445	8	0.992048
AU	2.657504	0.996494	3.879514	0.992541	3.910407	0.992445	8	0.992048
SNV (type=max)	3.49666	0.993922	5.040263	0.987386	7.983935	0.975231	6	0.978659
MSC	3.926181	0.992331	5.694228	0.983852	10.51607	0.950699	6	0.959009
SG (deriv=0, poly-order=2, win-dow_length=3)	2.657504	0.996494	3.879514	0.992541	3.910407	0.992445	8	0.992048
SG (deriv=0, poly-order=2, win-dow_length=5)	2.657504	0.996494	3.879514	0.992541	3.910407	0.992445	8	0.992048
SG (deriv=1, poly-order=2, win-dow_length=5)	4.729979	0.98885	5.961941	0.98224	6.876717	0.983032	5	0.981946

AU = Autoscaling; SNV = Standard Normal Variate; MSC = Multiplicative Scatter Correction; SG = Savitzky=Golay derivative; RMSEC (Root Mean Square Error of Calibration), RC (R Squared of Calibration), RMSECV (Root Mean Square Error of Cross Validation), RCV (R Squared of Cross Validation), RMSEP (Root Mean Square Error of Prediction), VL (Latent Variable).

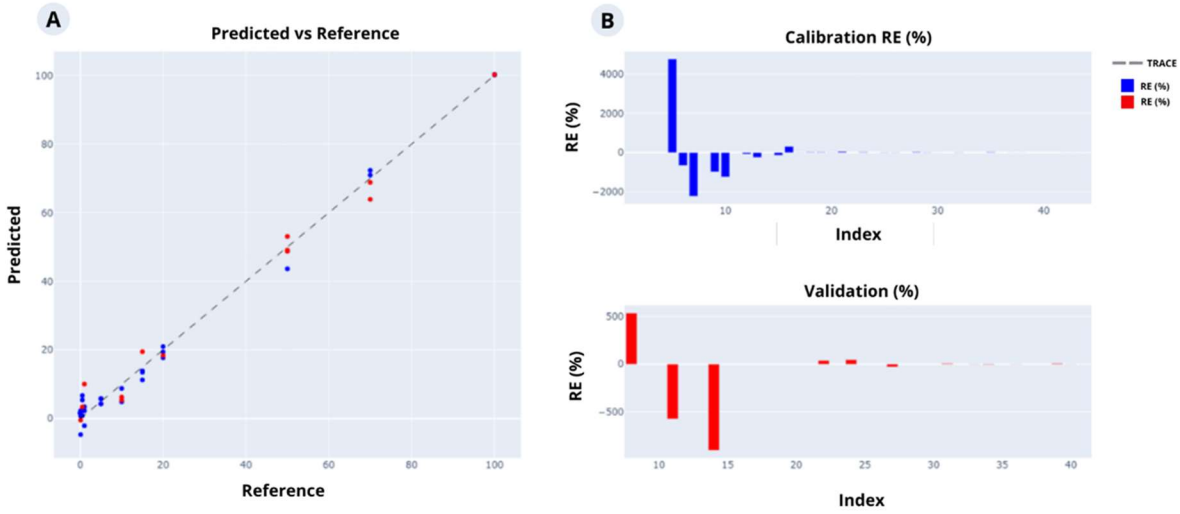

Figure 4.5- Cross-validation of the PLS model using spectral variables between 395 - 940 nm. A) Displays a regression plot comparing the predicted and actual MPs values. The black line represents the reference line; the closer the predicted MPs scores are to this line, the better the quality of the fit. B) The PLS model presents a Relative Error (RE%) plot for calibration and validation.

4.3.3 Near-infrared analysis (FT-NIR)

The analysis of NIR (Figure 4.6) allows us to explore spectral characteristics in greater depth. This enriched analysis provides us with a greater number of spectral bands, expanding the possibilities for investigation. Both generalized

multivariate models and quantification can employ these data, expanding the scope of potential applications.

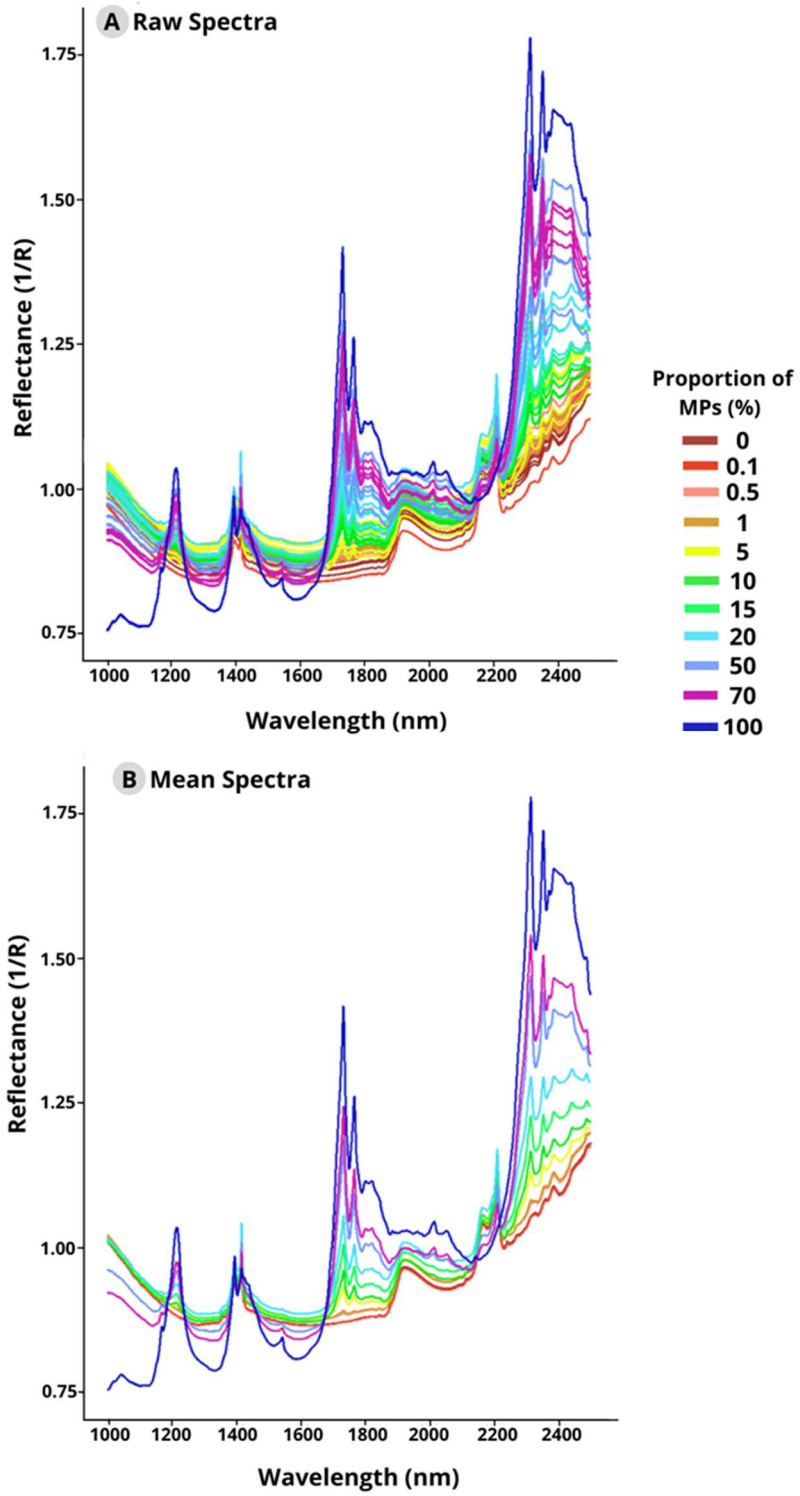

Figure 4.6- Reflectance spectra of soil samples contaminated with the proportions of MPs 0, 0.1, 0.5, 1.0, 5.0, 10.0, 20.0, 30.0, 50.0, 70.0, and 100% (w w^{-1}), highlighting the spectral signature. (A) Raw NIR spectra (B) Average spectra.

The regions in the wavelength ranges between 1.660–1.860 nm, 1.950–2.100 nm, and 2.300–2.500 nm (Figure 4.6) showed absorption peaks that allowed us to visualize the separation of the classes and proportions of MPs in terms of reflectance. In this case, the clear difference shows that there is a straight line between the MPs' reflectance and their spectral properties. This means that the NIR method could be used to identify and classify soil samples that contain MPs (Figure 4.7).

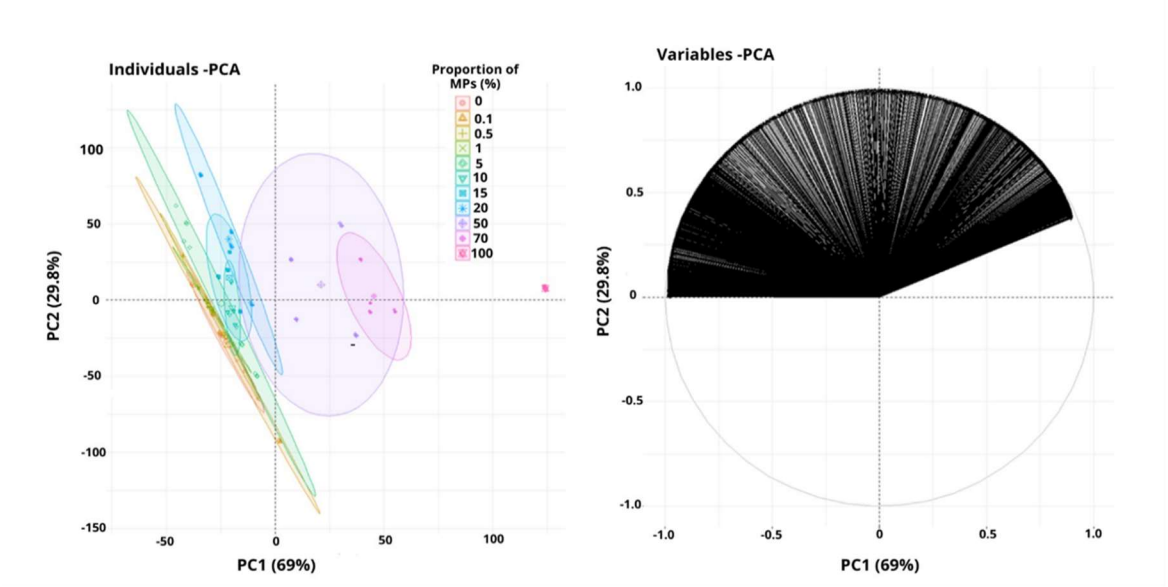

Figure 4.7- Principal Component Analysis (PCA) scores and weights of PC1×PC2 in soil contaminated with proportions of MPs 0, 0.1, 0.5, 1.0, 5.0, 10.0, 20.0, 30.0, 50.0, 70.0, and 100% (w w^{-1}).

The PCA analysis of the NIR spectrum revealed more comprehensive information, although it may be subject to some complexity due to the large number of spectral bands. Prediction models may need to filter noise and information to identify the optimal bands for MPs identification and quantification. Nevertheless, considering all spectral bands, the reliability reached 98.8%.

The groups without MPs are primarily located in quadrants 1, 2, and 3, whereas samples with MPs typically fall into quadrants 3 and 4. This trend suggests a clear correlation between the quantity of MPs and reflectance in the near-infrared region. Cluster analyses provide an insightful view of the intrinsic relationships between MPs' presence and their spectral characteristics.

Regarding the predictive analysis using PLS, various preprocessing methods were evaluated (Table 4.2). The original data demonstrated moderate correlation and relatively high prediction errors, suggesting that preprocessing could enhance the model. The MSC method proved to be the best individual pre-processing method, presenting the lowest calibration and prediction errors and the highest correlation coefficients. The combinations of methods showed the best overall results, with the lowest calibration and prediction errors and the highest correlation coefficients. Specifically, combining SG (deriv = 1, polyorder = 2, window_length = 11) and SNV yielded the best overall results. This is why it was chosen to be the basis for the prediction model (Figure 4.8).

Table 4.2- PLS model parameters based on different types of preprocessing: Near-Infrared Analysis (FT-NIR).

Pre-Processing	RMSEC	Rc	RMSECV	Rcv	RMSEP	Rp	LV	Decision
Original data	15.78463	0.888555	16.32929	0.880233	14.4399	0.868006	1	0.868595
SG (deriv=0, polyorder=2, window_length=15)	3.060827	0.996035	3.74797	0.99405	3.482409	0.990987	6	0.991148
AU	3.032296	0.996109	3.742824	0.994067	3.46978	0.991052	6	0.991199
SNV (type=max)	3.398402	0.99511	3.631714	0.994414	3.797736	0.989299	6	0.989768
MSC	2.528597	0.997296	3.107246	0.995915	2.885667	0.993833	6	0.993938
Combinations								
SG (deriv=1, polyorder=2, window_length=11)) + SNV	1.456084	0.999104	2.808564	0.996667	2.386061	0.995797	6	0.995475
SG (deriv=1, polyorder=2, window_length=17)) + SNV	1.815127	0.998607	2.7451	0.996817	2.491019	0.995407	6	0.99534
SG (deriv=1, polyorder=2, window_length=11)) + MSC	1.440816	0.999123	2.672142	0.996982	2.517731	0.995311	6	0.995228
SG (deriv=2, polyorder=2, window_length=23)) + SNV	1.368031	0.999209	2.752998	0.996799	2.512314	0.995411	6	0.995218

AU = Autoscaling; SNV = Standard Normal Variate; MSC = Multiplicative Scatter Correction; SG = Savitzky=Golay derivative; RMSEC (Root Mean Square Error of Calibration), RC (R Squared of Calibration), RMSECV (Root Mean Square Error of Cross Validation), RCV (R Squared of Cross Validation), RMSEP (Root Mean Square Error of Prediction), VL (Latent Variable).

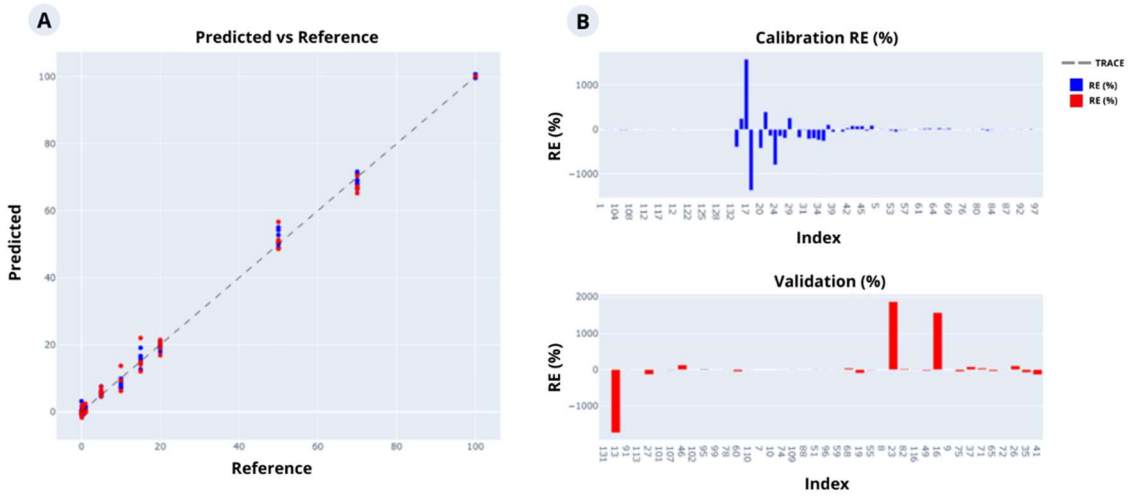

Figure 4.8- Cross-validation of the PLS model using spectral variables between 1.000 – 2.500 nm. A) Displays a regression plot comparing the predicted and actual MPs values. The black line represents the reference line; the closer the predicted MPs scores are to this line, the better the quality of the fit. B) The PLS model presents a Relative Error (RE%) plot for calibration and validation.

4.3.4. Scanning electron microscopy (SEM) analysis

Scanning Electron Microscopy (SEM) analysis at different contamination levels in Figure 4.9 allows for the identification of material morphology, but it does not allow for direct quantification of MPs. As observed in figure 4.7, as the contamination by MPs increases, there is a corresponding increase in the dimensions of the materials analyzed.

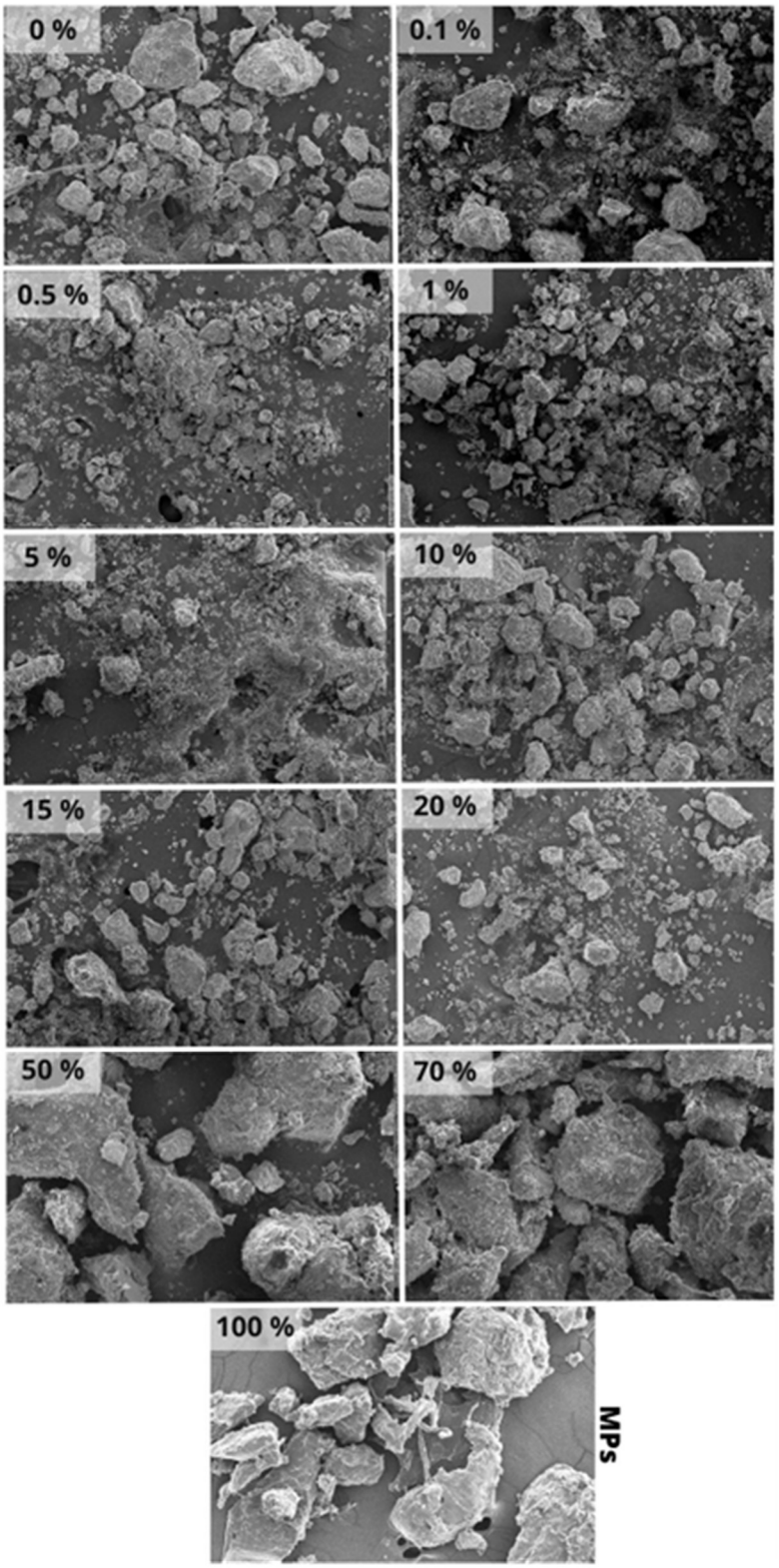

Figure 4.9- Scanning Electron Microscopy (SEM) of soil contaminated with the proportions of MPs 0, 0.1, 0.5, 1.0, 5.0, 10.0, 20.0, 30.0, 50.0, 70.0, and 100% (w w^{-1}). Scale of 10 µm and 100x zoom.

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Furthermore, figure 4.10 provides relevant insights into the morphology of the particles in question. It became evident that the morphology of MPs is amorphous, meaning it is characterized by the absence of a regular and repetitive molecular organization. This also translates into distinctive physical and optical properties. In contrast to the soil, which displays characteristic crystalline diffraction patterns, the structure of MPs does not exhibit these distinct patterns. Moreover, MPs tend to exhibit isotropic behavior, indicating that their properties do not vary significantly with different orientations, compared to the soil's structure that is crystalline.

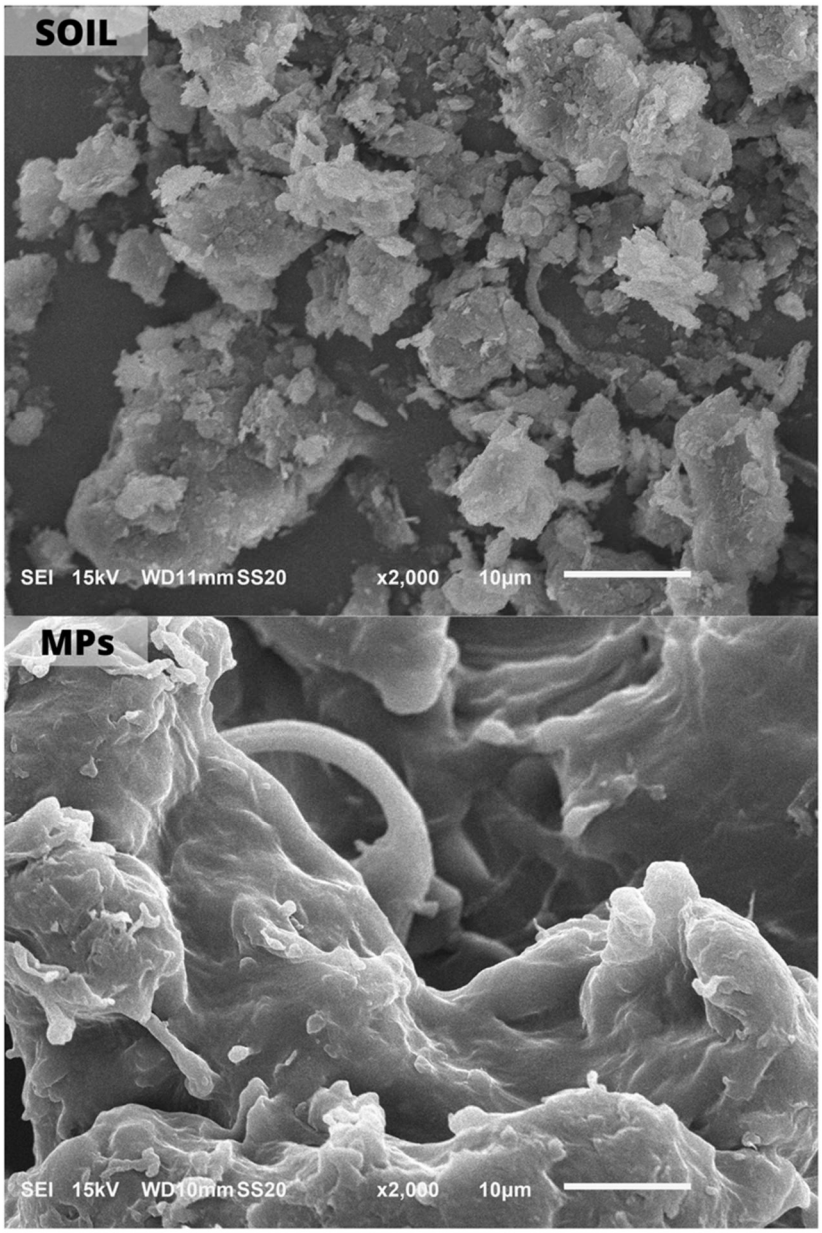

Figure 4.10- Scanning Electron Microscopy (SEM) of 100 % isolated microplastics (MPs) and 100 soil particles. Zoom x2000 and 10 µm

4.4 DISCUSSION

Quantifying MPs in soils presents challenges due to the lack of standardized and labor-intensive methods (Corradini et al., 2019). However, increasing awareness of the effects and risks associated with MPs has spurred research efforts to find alternative approaches for their identification and quantification. Models developed using X-ray data have proven inadequate for quantifying MPs in soils. According to Bonse (2008), X-ray technology is an imaging technique that utilizes X-rays to produce images of objects opaque to visible light. X-

rays, being a form of electromagnetic radiation, can penetrate dense objects such as soil (Demattê et al., 2010). However, MPs have low density, rendering this technique inefficient for their analysis (Li et al., 2018).

Multispectral analysis, on the other hand, has proven to be highly effective at quantifying MPs in soil. This technique, by segmenting the spectrum into multiple bands, enables the identification of MPs based on the characteristics of their absorption or reflection spectra (Park and Crozier, 2013). Notably, using a low-cost prototype for this analysis increases its efficiency. Multispectral imaging strikes a balance between data quality and acquisition speed, thereby facilitating strategies for MP classification and identification (Choi et al., 2024; Tatem et al., 2008). Although previous studies have showcased the capability of hyperspectral techniques in rapidly identifying MPs in soil, multispectral analysis emerges as an equally promising alternative (Shan et al., 2018). Furthermore, the application of support vector machines has also demonstrated significant potential for monitoring polyethylene MPs in soil.

NIR is one of the most powerful and widely available techniques for the reliable detection and identification of MPs in soils (Paul et al., 2018). This instrument measures the amount of light reflected from a surface in the wavelength range of 350 to 2500 nm, providing a percentage of reflectance for each wavelength. Peaks observed during spectral reading are generally associated with energy absorption by molecular vibrations of chemical bonds, such as OH, CH, CO, and NH bonds. Furthermore, functional groups that also absorb energy at specific wavelengths, such as CH_3, C = O, and NO_2, can have peaks at different wavelengths (Stuart, 2004). In this study, we observe discrepancies in absorption in the wavelength ranges highlighted in the average of the NIR spectrum (1.660–1.860 nm, 1.950–2.100 nm, and 2.300–2.500 nm). This method relies on the molecular vibrations of the functional groups in MPs. This is possible because these polymers have unique patterns of absorption and reflection in the NIR spectrum, which lets us figure out what kind of polymer it is (Silva et al., 2020). Correlating these data with the chemical composition of the sample enables the prediction of the composition of new sample sets. Researchers have well-documented the utility of vis–NIR techniques in directly analyzing the elemental composition of soil samples (Viscarra Rossel et al., 2016; Gandariasbeitia et al., 2017; Conforti et al., 2017; Corradini et al., 2019).

Corradini et al. (2019) used vis–NIR techniques to identify and quantify LDPE, PET, and PVC MPs in soil samples. For this purpose, the researchers used a spectroradiometer with a working range of 350 to 2500 nm, predicting MP concentrations with an accuracy of 10 g kg^{-1} and a detection limit of approximately 15 g kg^{-1}. Another study by Paul et al. (2019) successfully identified soil contaminated with MPs at levels above 0.5 to 1.0% w w^{-1}.

Soil properties investigated by NIR spectroscopy are mostly associated with the estimation of organic carbon, as well as physical, chemical, and hydrological properties, and there is little research on soil contamination (Piccini et al., 2024). This study's developed classification model suggests potential methods for verifying the presence of MPs in the analyzed soil. Despite this, the soil composition in an agricultural area remains unrestricted, making NIR characterization more challenging (Bellon-Maurel et al., 2010), as factors such as chemical composition, size, and texture can interfere with spectral reading. Furthermore, the degradation of MPs in the environment also affects their composition.

Identifying MPs is critical but understanding their characteristics can help us understand how these polymers interact with organic pollutants. Bhat (2024) did a study using scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM–EDS). The study identified 25 distinct types of MPs, including Nylon 66, Polytetrafluoroethylene, Polypropylene, High-Density Polyethylene, and Polyethylene. Soil organic matter, inherently amorphous (Zhao et al., 2023), bears resemblances to MPs, complicating the identification process. However, the SEM method emerges as an excellent option for discerning MPs particles due to the significance of their shape and size in interactions with pollutants and impacts on soil properties, microbial activities, and plant growth (He et al., 2022).

4.5 CONCLUSION

Overall, the results of this study highlight the urgent need to use highly sensitive techniques, such as multispectral analysis and NIR in the range of 395 to 2.300 nm, to accurately identify and quantify the levels of MPs in the soil. This study serves as a preliminary step, showing the potential utility of these tools and recommending the conduct of future studies on different soil types to understand their composition, origin, structure, and application. Furthermore, it is crucial to consider that the majority of MPs present in the environment are of secondary

origin and have different shapes and colors, highlighting the need for more research in this area.

Additionally, the effective characterization of MPs' structures through SEM, in contrast with soil, highlights the importance of advanced analytical approaches. The many effects that MPs have on the environment are very complicated. For example, they can change the porosity and aggregation of soil, hurt the diversity of microbes, and make it easier for contaminants to move around. As a result, a thorough understanding of these polymers is critical for a comprehensive assessment of their environmental impact, as well as the development of effective management and mitigation strategies.

These methodological advancements not only contribute to environmental preservation but also promote sustainable practices in terrestrial ecosystems. Furthermore, these methodological advancements lay a solid foundation for future research that aims to expand our understanding of MPs' effects on soil and natural systems, thereby enabling more efficient management of the challenges these pollutants pose in our environment.

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5. HOW DOES SOIL CONTAMINATION BY MICROPLASTICS INTERFERES THE SORPTION AND DESORPTION PROCESSES OF THREE HERBICIDES?

Resumo:

O aumento do uso de plásticos na agricultura resultou na acumulação de microplásticos (MPs), que podem interagir com herbicidas e alterar seu comportamento ambiental. Este estudo teve como objetivo avaliar a influência de diferentes proporções de MPs na sorção e dessorção de três herbicidas em solo. Hexazinona, diuron e S-metolachlor foram introduzidos no solo em concentrações de 0% (controle – solo não modificado), 1, 5, 10, 15, 20 e 100% (m m^{-1}) de MPs, com a adição de 2 g de material (solo ou MPs). As isotermas de sorção e dessorção foram determinadas utilizando o método de equilíbrio em batelada, seguidas da análise dos herbicidas por cromatografia líquida de alta eficiência. Os resultados indicaram que a presença de MPs alterou a sorção de S-metolachlor em aproximadamente 10% no solo enriquecido com 5% de MPs, com valores de K_d variando de 3,20 a 4,85 L kg^{-1} no solo não modificado, sugerindo um aumento na retenção do herbicida na presença de MPs. Para hexazinone e diuron, a sorção nos tratamentos com MPs foi comparável ao controle, com comportamento semelhante observado na dessorção. Esses achados sugerem que a presença de MPs no solo pode modificar o destino ambiental dos herbicidas, potencialmente afetando sua eficácia no controle de plantas daninhas e aumentando o risco de contaminação ambiental, particularmente em solos agrícolas poluídos por esses polímeros.

Palavras-chaves: hexazinone; diuron; S-metolachlor; polímeros; resíduos plásticos

Abstract:

The increasing use of plastics in agriculture has resulted in the accumulation of microplastics (MPs), which can interact with herbicides and alter their environmental behavior. This study aimed to evaluate the influence of different MP proportions on the sorption and desorption of three herbicides in soil. Hexazinone, diuron, and S-metolachlor were introduced into soil at concentrations of 0% (control – unamended soil), 1, 5, 10, 15, 20, and 100% (w w^{-1}) MPs, with the addition of 2 g of material (soil or MPs). Sorption and desorption isotherms were determined using the batch equilibrium method, followed by herbicide analysis via high-performance liquid chromatography. The results indicated that the presence of MPs altered S-metolachlor sorption by approximately 10% in soil amended with 5% MPs, with K_d values ranging from 3.20 to 4.85 L kg^{-1} in unamended soil, suggesting increased herbicide retention in the presence of MPs. For hexazinone and diuron, sorption in the MP treatments was comparable to the control, with similar behavior observed in desorption. These findings suggest that the presence of MPs in soil can modify the environmental fate of herbicides, potentially affecting their efficacy in weed control and increasing the risk of environmental contamination, particularly in agricultural soils polluted with these polymers.

Keywords: hexazinone; diuron; S-metolachlor; polymers; plastic residues.

5.1 INTRODUCTION

Large volumes of plastic products are widely used in agriculture. Mulching films, irrigation pipes, and packaging are examples of materials that, due to continuous wear and tear associated with limited recovery, remain in agricultural fields for long periods (Brochado et al., 2023; 2024). Thus, microplastics (MPs) are created by soil breaking down and ageing, among other changes (Thompson et al., 2004; Ni et al., 2023).

When considering the presence of MPs in agricultural soils, it is important to highlight that their interaction with organic pollutants, such as herbicides, can have negative impacts. Studies have shown that MPs can adsorb pesticides, and this adsorption depends on the hydrophobicity of the pesticide and the type of MPs involved (Šunta et al., 2020). Furthermore, this interaction can reduce the soil's capacity to retain pesticides, potentially increasing their mobility through soil systems, which affects the behavior of these compounds in the environment (Šunta et al., 2020).

Factors such as the type of MPs, their composition, particle size, and surface structure influence the interaction between herbicides and MPs (Nern et al., 1996; Wang et al., 2020). Furthermore, MPs in soil have the potential to negatively impact soil biota and plant growth (Kumar et al., 2020). Biosolids, wastewater irrigation, and polymer-based agrochemicals are some of the things that put MPs into agricultural soils (Kumar et al., 2020).

MPs have a large contact surface and hydrophobicity, characteristics that make them excellent sorbents of organic pollutants (Yilimulati et al., 2021; Koyuncuoğlu et al., 2021; Dissanayake et al., 2022; Peña et al., 2023), and decisively influence sorption and desorption processes, for example. Water-soluble herbicides can adhere to the surface of MPs in aquatic environments, while lipophilic herbicides can be absorbed by MPs with similar characteristics (Peña et al., 2023). The presence of MPs in soil increased atrazine sorption capacity (Guo et al., 2024). Juck et al. (2024) compared aged and non-aged MPs, observing that aging increases the polarity and decreases the hydrophobicity of MPs, resulting in lower sorption of terbuthylazine on aged MPs compared to non-aged MPs.

These aspects are fundamental to understanding the environmental impacts of these compounds and MPs on ecosystems. Ni et al. (2023) analyzed the sorption capacities of two herbicides, napropamide and acetochlor, on both biodegradable and non-biodegradable MPs derived from agricultural plastic products. The authors found that the physicochemical properties of the herbicides affected why biodegradable MPs were better at absorbing them than non-biodegradable ones.

Several factors influence the interactions between herbicides and MPs. Water solubility (S_w), lipophilicity-octanol-water coefficient (K_{ow}), particle size, electrical charge, chemical reactivity, chemical stability, and polarity play significant roles in these interactions (Jiang and Li, 2020). Pre-emergent herbicides have a residual effect on the soil, effectively controlling the soil seed bank (Guimarães et al., 2022). Agriculture widely uses herbicides like hexazinone, diuron, and S-metolachlor, but our understanding of their interactions with these polymers remains limited.

Knowing the physicochemical characteristics of herbicides is essential to understanding the possible interactions they may have with these MPs, as these characteristics can influence their environmental behavior (Junaid et al., 2023). Hexazinone, whose chemical name is 3-cyclohexyl-6-(diethylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione, is a systemic herbicide that is highly soluble in water (33 g/L at 25°C) (PPDB, 2024; PUBCHEM, 2024a), a characteristic that facilitates its absorption by plant roots. This herbicide's K_{ow} is 1.17 (PPDB, 2024; PUBCHEM, 2024a), which indicates low lipophilicity. This herbicide is relatively persistent in the soil, with a degradation half-life (DT_{50}) ranging from 30 to 180 days (Bouchard et al., 1985). Its high S_w suggests a potential for leaching, which can lead to contamination of groundwater and surface water (Silva, 2022; Porto et al., 2024).

Diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea] is a systemic herbicide with low S_w (42 mg/L at 25°C). When it comes to soil, diuron has a DT_{50} that can range from 30 to 365 days and a K_{ow} of 2.85, which means it is moderately lipophilic (Rocha et al., 2013; Guzella et al., 2020). Surface runoff and erosion can transport diuron to water bodies due to its low S_w and strong sorption to soil organic matter (Martins et al., 2019; Almeida et al., 2020). S-metolachlor [(S)-2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxyethyl)acetamide] has a high S_w

(1.050 mg/L at 25°C) (PPDB, 2024; PUBCHEM, 2024c). This herbicide's K_{ow} is 2.90, indicating moderate lipophilicity, and its DT50 in soil ranges from 15 to 70 days, indicating moderate persistence (Bedmar et al., 2017). Due to its high S_w, S-metolachlor presents a risk of leaching into groundwater in sandy or slightly clayey soils, especially under high precipitation conditions (Marín-Benito et al., 2021).

This study investigated the sorption and desorption processes of the herbicides hexazinone, diuron, and S-metolachlor in soil contaminated with six different proportions of MPs. Understanding the complex interactions between MPs and herbicides can aid in developing more effective strategies to preserve soil health, water quality, and biodiversity, thereby promoting the sustainability of agricultural systems, and ensuring long-term food security.

5.2 MATERIAL AND METHODS

5.2.1 Microplastic (MPs)

Polyethylene microspheres were purchased as a primary material with the following characteristics: granulometry of 600 µm, natural color, melting point between 100-115°C, apparent density between 350-370 g/cm³, and a fluidity index of up to 30 g/10 min. The material was purchased from Bianquimica (Diadema, São Paulo, Brazil).

5.2.2 Soil

Soil samples were collected from the surface layer (0-20 cm) of areas not treated with herbicides in the last three years of the Experimental Research Unit (20°46'02.0"S, 42°52'14.0"W, 700 m altitude). The samples were classified as *Latossolo Vermelho* (Oxisol in the USDA Soil Taxonomy) according to the Brazilian Soil Classification System (EMBRAPA, 2018; IUSS, 2022). They were air-dried for 10 days, then sieved through a 2.0 mm mesh and stored at room temperature. As described in Table 5.1, this soil was classified as clayey in texture.

Table 5.1- Physicochemical attributes of the soil

Sand	Silt	Clay	Soil texture
---------- Kg Kg^{-1}----------			
0,331	0,135	0,534	Clay

OC	pH	P	K	Ca^{+2}	Mg^{+2}	H+Al	CEC	BS
%	H_2O	----- mg dm^{-3}-----		---------- $cmol_c dm^{-3}$----------				%
1,15	4,88	0,0	18	0,36	0,08	3,5	3,99	12,3

Source: Laboratory of Soil Analysis Viçosa LTDA, Viçosa, MG, Brazil. Potential of hydrogen (pH), Organic carbon (OC), Phosphorus (P), Potassium (K), Calcium (Ca), Magnesium (Mg), Potential acidity (H + Al), Cation Exchange Capacity (effective) (CEC), Base Saturation (BS).

5.2.3 Scanning Electron Microscopy (SEM) Analysis

The SEM (model JSM-6010LA, JEOL, Akishima, Japan) was used to evaluate the changes in the physical morphology of the MPs surface. The MPs particles were mounted on a metal sample holder using conductive carbon tape and sputtered on the metallizer with a 9 nm gold layer. The secondary electron (SE) detector in the SEM, operating with an electron beam of 20 kV, captured the images. The images were colored using MountainsLab® software (Norcross, Georgia, USA).

5.2.4 Sorption and desorption studies

The herbicides were added to the soil at concentrations of 0% (control, unmodified), 1, 5, 10, 15, 20, and 100% (w w^{-1}) of MPs, corresponding to 0.0, 0.1, 0.2, 0.3, 0.4, and 2.0 g in a total of 2 g of material (soil or MPs). In field terms, these proportions are equivalent to 5, 50, 100, 150, 200, and 1000 t ha^{-1}, respectively. The analytical standards of the herbicides hexazinone, diuron, and S-metolachlor were purchased from Sigma-Aldrich Company (Missouri, USA) with chemical purity > 98%. The stock solutions of the herbicides were prepared from the standard at a concentration of 500 mg L^{-1} in acetonitrile, and the working solutions were prepared from this. The guidelines "106, Adsorption-Desorption Using a Batch Equilibrium Method" (OECD, 2000) guided the establishment of the methodology for the sorption and desorption study. In the sorption study, from

the stock solution of hexazinone, diuron, and S-metolachlor (500 mg L^{-1}), working solutions were prepared in 0.01 mol L^{-1} $CaCl_2$ solution with five concentrations of hexazinone, diuron, and S-metolachlor (mL g^{-1}): 1xD, 2xD, 3xD, 4xD, and 5xD, where D corresponds to the highest recommended dose of the herbicide in the field, being 500 g a.i. ha^{-1} for hexazinone, 320 g a.i. ha^{-1} diuron, and 1200 g a.i. ha^{-1} for S-metolachlor, assuming a soil density of 1200 kg m^{-3} and incorporation depth of 0.10 m.

For each substrate, we added 2g of soil and 10 mL of a 0.01 mol L^{-1} $CaCl_2$ solution in triplicate to falcon-type tubes. The tubes were then placed on a horizontal shaking table in a semi-dark room with a controlled temperature of 20±2°C and remained under agitation for 24 h until they reached equilibrium concentrations for all herbicides (Ma et al*.,* 2006). Subsequently, they were centrifuged at 3500 rpm for 7 min in a refrigerated centrifuge (~4°C) (model K14-4000, KASVI, São José dos Pinhais, Paraná, Brazil), and finally two aliquots of 1 mL each were extracted from the supernatant for quantification by High-Performance Liquid Chromatography, HPLC, Shimadzu LC 20AT (Kyoto, Japan), photodiode array detector (Shimadzu SPD-M20A) and stainless steel C18 column (Shimadzu VP-ODS Shim-pack 250×4.6 mm diameter).

5.2.5 Chromatographic conditions

Queiroz et al. (2006) adjusted the chromatographic conditions for the analysis of hexazinone, following the adaptations proposed by Sousa *et al.* (2018). The analysis proceeded using a mobile phase composed of water and acetonitrile in a ratio of 50:50 (v/v), with a flow rate of 1.12 mL min^{-1}, an injection volume of 20 µL, a detection wavelength of 254 nm, and a column temperature maintained at 30°C. For S-metolachlor, the chromatographic conditions were based on the study by Long et al. (2014), with specific adjustments. A mixture of acetonitrile and water that had 0.01% phosphoric acid added to it was used as the mobile phase. The injection volume was 10 µL, the flow rate was 1 mL min^{-1}, the detection wavelength was 190 nm, and the temperature of the column oven was kept at 30°C. For the diuron analysis, the chromatographic conditions were adapted from the study by Pontes Jr. et al. (2024), using a mobile phase composed of water and acetonitrile in a ratio of 50:50 (v/v), with a flow rate of 1.12 mL min^{-1},

an injection volume of 20 µL, a detection wavelength of 254 nm, and a column temperature maintained at 30°C.

The desorption study was performed under the same conditions as the sorption. To the falcon tubes containing soil and with hexazinone, S-metolachlor, or diuron sorbed, 10 mL of the $CaCl_2$ 0.01 mol L^{-1} solution (without herbicide) was added again. All tubes were shaken on a horizontal shaking table for 24 h at 200 rpm to reach the re-equilibrium time (Ma et al., 2006). After the shaking period, the vials were centrifuged, and 1 mL of the supernatant was pipetted in duplicate for HPLC quantification. The amount desorbed was calculated by the difference between the herbicides sorbed in the soil and the amount remaining in the supernatant.

The equilibrium (Ce) and sorbed (Cs) concentrations of the treatments were quantified for statistical analysis of the data obtained.

5.2.6 Statistical analysis

The equilibrium concentration and sorbed concentration data were analyzed using Linear and Freundlich regression models.

The sorption coefficient (K_d, L kg^{-1}) was also calculated at C_e = 2.0 mg L^{-1} (an intermediate value of the equilibrium concentrations studied in the sorption), using the following Equation (1):

$$K_d = C_s/C_e \quad (1)$$

where C_s is the amount of herbicide sorbed in the unamended soil and pure MPs (mg kg^{-1}) (2):

$$C_s = (C_i - C_e) \times V/M \quad (2)$$

where C_i is the pesticide initial liquid concentration (mg L^{-1}), C_e is the equilibrium liquid concentration (mg L^{-1}), V is the volume of herbicide solution added (mL) and M is the mass of soil (g).

The sorption coefficient (K_d, L kg^{-1}) normalized to the OC content of the pure MPs and unamended soils (K_{oc}, L kg^{-1}) was calculated as follows (3):

$$K_{oc} = (K_d/\%OC) \times 100 \quad (3)$$

The desorption K_d value for desorption was also calculated for comparison to the sorption K_{dp}.

The Freundlich model and its distribution coefficient were derived from Equation (4):

$$K_f = C_s/C_e^{1/n} \quad (4)$$

where n (dimensionless value) can range from 0 to 1, depending on the heterogeneity in the sorption sites.

The same sorption coefficient was also standardized, considering the soil OC content (K_{foc}) (5):

$$K_{foc} = (K_d/\%OC) \times 100 \quad (5)$$

The hysteresis index (H) was calculated by Equation (6):

$$H = 1/n_{desorption}/1/n_{sorption} \quad (6)$$

Figures for the variables K_d, K_f, K_{oc}, and K_{foc} were created using SigmaPlot® software (version 13.0, Systat Software Inc., Point Richmond, CA, USA). Sorption and desorption percentages were represented using Sankey diagrams, generated with SankeyMATIC software (version 1.7.0, Germany).

To assess the significance of the correlation coefficients, a Student's t-test was performed with a significance level of $p<0.05$.

5.3 Results and discussion

5.3.1 Scanning Electron Microscopy (SEM)

Figure 1 presents the SEM analysis of the materials used in the study. The image shows that pure MPs have an amorphous structure (Figure 5.1 A), characterized by a wide and irregular contact surface. In contrast, soil exhibits a well-defined crystalline structure (Figure 5.1B).

Figure 5.1- Scanning Electron Microscopy (SEM) of 100% pure microplastics (MPs) (A) and 100% (B) soil particles. Zoom × 100 and 100 µm

The amorphous structure of MPs, being looser and more flexible, offers a larger and more heterogeneous surface area, which increases their sorption capacity for chemical compounds, such as herbicides (Wang and Wang, 2018; Mo et al., 2021; Prajapati et al., 2022). The crystalline structure of soil, with its regular and well-defined surfaces, limits this interaction since more ordered regions tend to have lower sorption capacity (Borggaard et al., 1990). Because of this, the more crystallized something is, like soil, the less organic compounds it can soak up (Wang and Wang, 2018; Torres et al., 2020; Mo et al., 2021).

Knowing the morphological characteristics of MPs and soil is essential to understanding, in more depth, the potential interactions between these materials and herbicides (Brochado et al., 2024). Furthermore, these morphologies can be decisive in herbicide sorption and desorption processes.

5.3.2 Sorption and desorption

5.3.2.1 Sorption-Desorption Isotherms of Herbicides

The sorption and desorption isotherms of hexazinone, diuron, and S-metolachlor in soil with different proportions of MPs were adjusted using the Freundlich and Linear models. The strong and good models used are shown by the high coefficients of determination (R^2) in Tables 5.2, 5.3, 5.4, 5.5, 5.6, and 5.7.

Additionally, the values of 1/n in Tables 5.2, 5.3, 5.4, 5.5, 5.6, and 5.7 described the unique behavior of each herbicide. Hexazinone and diuron presented Type C sorption isotherms (constant partition) (Limousin et al., 2007), indicating a linear relationship between the herbicide and the soil with no preference for specific sorption sites. In other words, the increasing concentration of the herbicide did not influence the sorption (Figures 5.2 and 5.3).

In contrast, S-metolachlor presented a Type L (Langmuir) isotherm (Limousin et al., 2007), characterized by a strong interaction between the soil (sorbent) and the herbicide (sorbate) (Figure 5.4). As the concentration of herbicide in the soil increases, sorption decreases in this isotherm. This occurs due to competition for limited sorption sites, which become saturated as the solution's solute concentration increases.

Table 5.2- Freundlich and linear models sorption isotherms parameters for hexazinone applied to soil amended with proportions at 0 (unamended soil), 1, 5, 10, 15, 20, and 100% (pure) (w w^{-1}) microplastics (MPs).

MPs% (w w^{-1}) +soil	Freundlich					Linear			
	K_f	K_{foc}	1/n	*p*-value	R^2	K_d	K_{oc}	*p*-value	R^2
	($mg^{(1-1/n)}$ $L^{1/n}$ kg^{-1})					(L kg^{-1})			
0 (unamended soil)	1.17 (0.86-1.48) [a]	101.98 (101.67-102.29) [a]	1.23±0.30[b]	0.0038	0.95	1.63 (1.35-1.91) [a]	142.20 (141.92-142.48) [a]	0.0037	0.91
1	0.78 (0.67-0.89)	68.10 (67.99-68.21)	1.81±0.16	0.0002	0.99	2.02 (1.75-1.29)	175.64 (175.37-175.91)	0.0026	0.94
5	1.00 (0.59-1.41)	87.56 (87.15-87.97)	1.58±0.45	0.0069	0.95	2.03 (1.58-2.48)	176.69 (176.24-177.14)	0.0099	0.86
10	0.99 (0.65-1.32)	86.26 (85.92-86.60)	1.41±0.38	0.0056	0.95	1.69 (1.36-2.02)	147.15 (146.82-147.48)	0.0062	0.89
15	1.18 (0.75-1.32)	103.28 (102.85-103.71)	1.33±0.42	0.0084	0.93	1.86 (1.45-2.27)	162.27 (161.86-162.68)	0.0084	0.87
20	0.97 (0.64-1.30)	84.34 (84.01-84.67)	1.41±0.39	0.0056	0.95	1.66 (1.34-1.98)	144.72 (144.40-145.04)	0.0061	0.89
100 (pure)	1.61 (1.21-2.01)	140.29 (139.89-140.69)	1.61±0.29	0.0060	0.93	1.67 (1.30-2.04)	145.24 (144.87-145.61)	0.0059	0.86

[a]Number in parentheses are confidence intervals of the mean (*n* = 3). [b]Mean value ± standard deviation of the mean.

Table 5.3- Freundlich and linear models desorption isotherms parameters and hysteresis coefficient (H) for hexazinone applied to soil amended with proportions at 0 (unamended soil), 1, 5, 10, 15, 20, and 100% (pure) (w w^{-1}) microplastics (MPs).

MPs% (w w^{-1}) +soil	Freundlich						Linear			
	K_f	K_{foc}	1/n	H	*p*-value	R^2	K_d	K_{oc}	*p*-value	R^2
	($mg^{(1-1/n)}$ $L^{1/n}$ kg^{-1})						(L kg^{-1})			
0 (unamended soil)	12.67 (4.40-20.94) [a]	1100.62 (1092.35-1108.89) [a]	1.91±0.62[b]	0.64	0.0142	0.89	5.93 (4.46-7.40) [a]	515.13 (513.66-516.60) [a]	0.0154	0.84
1	4.11 (2.45-5.77)	357.20 (355.54-358.86)	0.91±0.38	1.98	0.0247	0.78	4.34 (3.03-5.65)	377.01 (375.70-378.32)	0.0252	0.78
5	6.70 (4.88-8.52)	582.28 (580.46-584.10)	1.36±0.30	1.16	0.0032	0.94	5.83 (5.06-6.60)	506.44 (505.67-507.21)	0.0030	0.95
10	10.72 (4.79-16.65)	931.23 (925.30-937,16)	1.62±0.50	0.87	0.0089	0.90	6.36 (4.91-7.81)	552.48 (551.03-553.93)	0.0141	0.86
15	17.70 (12.24-23.16)	1537.57 (1532.11-1543.03)	2.03±0.30	0.65	0.0007	0.98	7.34 (5.94-8.74)	637.61 (636.21-639.01)	0.0086	0.90
20	16.01 (9.38-22.64)	1391.37 (1384.74-1398.00)	1.94±0.36	0.73	0.0019	0.96	6.78 (5.46-8.10)	588.96 (587.64-590.28)	0.0095	0.89
100 (pure)	4.06 (2.33-5.79)	353.03 (1038.34-1744.40)	1.09±0.44	1.48	0.0160	0.75	3.57 (2.39-4.75)	310.12 (308.94-311.30)	0.0162	0.75

[a]Number in parentheses are confidence intervals of the mean (*n* = 3). [b]Mean value ± standard deviation of the mean.

Table 5.4- Freundlich and linear models sorption isotherms parameters for diuron applied to soil amended with proportions at 0 (unamended soil), 1, 5, 10, 15, 20, and 100% (pure) (w w^{-1}) microplastics (MPs).

MPs% (w w^{-1}) +soil	Freundlich					Linear			
	K_f	K_{foc}	1/n	*p*-value	R^2	K_d	K_{oc}	*p*-value	R^2
	($mg^{(1-1/n)} L^{1/n} kg^{-1}$)					(L kg^{-1})			
0 (unamended soil)	2.89 (2.84-2.94) [a]	251.48 (251.44-251.52)	0.68±0.03[b]	0.0001	0.99	1.99 (1.89-2.09) [a]	173.21 (173.11-173.31) [a]	0.0003	0.99
1	2.81 (2.77-2.84)	244.34 (244.30-244.38)	0.70±0.3	0.0001	0.99	1.88 (1.89-2.09)	164.09 (163.99-164.19)	0.0003	0.99
5	2.72 (2.69-2.75)	237.02 (236.99-237.05)	0.69±0.02	0.0001	0.99	1.99 (1.86-2.12)	173.21 (173.08-173.34)	0.0006	0.98
10	2.88 (2.81-2.95)	250.62 (250.55-250.69)	0.72±0.04	0.0001	0.99	2.12 (1.42-2.81)	184.16 (183.46-184.86)	0.0009	0.98
15	2.74 (2.72-2.77)	238.85 (238.83-238.87)	0.67±0.01	0.0001	0.99	1.87 (1.17-2.57)	162.96 (162.26-163.66)	0.0001	0.99
20	2.63 (2.61-2.66)	229.28 (229.26-229.30)	0.70±0.01	0.0001	0.99	1.84 (0.97-2.70)	159.92 (159.06-160.78)	0.0002	0.99
100 (pure)	2.40 (2.15-2.65)	208.702 (229.03-29.53)	0.70±0.19	0.0024	0.93	1.67 (1.31-2.03)	145.76 (145.40-146.12)	0.0187	0.87

[a]Number in parentheses are confidence intervals of the mean (*n* = 3). [b]Mean value ± standard deviation of the mean.

Table 5.5- Freundlich and linear models desorption isotherms parameters and hysteresis coefficient (H) for diuron applied to soil amended with proportions at 0 (unamended soil), 1, 5, 10, 15, 20, and 100% (pure) (w w^{-1}) microplastics (MPs).

MPs% (w w^{-1}) +soil	Freundlich						Linear			
	K_f	K_{foc}	1/n	H	*p*-value	R^2	K_d	K_{oc}	*p*-value	R^2
	($mg^{(1-1/n)}$ $L^{1/n}$ kg^{-1})						(L kg^{-1})			
0 (unamended soil)	4.21 (3.81-4.61) [a]	365.71 (365.31-366.11) [a]	0.52±0.06[b]	1.32	0.0002	0.96	4.85 (4.46-5.24) [a]	421.31 (420.92-421.70) [a]	0.0001	0.98
1	3.85 (3.74-3.96)	334.44 (365.60-365.82)	0.50±0.02	1.42	0.0001	0.99	4.30 (3.87-4.72)	373.53 (373.10-373.95)	0.0001	0.97
5	3.57 (3.51-3.62)	310.12 (310.06-310.18)	0.47±0.01	1.47	0.0001	0.99	3.98 (3.62-4.33)	345.73 (345.37-346.08)	0.0001	0.97
10	4.49 (4.00-4.98)	390.04 (389.55-390.53)	0.53±0.07	1.38	0.0003	0.95	5.14 (4.22-6.05)	446.50 (445.58-447.41)	0.0008	0.91
15	4.42 (3.80-5.03)	383.95 (383.33-384.57)	0.51±0.09	1.33	0.0006	0.93	5.06 (3.00-6.11)	439.55 (438.49-440.60)	0.0012	0.88
20	3.10 (2.64-3.56)	269.29 (268.83-269.75)	0.32±0.08	1.19	0.0011	0.84	3.01 (1.98-4.04)	261.47 (260.44-262.50)	0.0023	0.74
100 (pure)	3.86 (3.54-4.17)	335.31 (335.09-335.63)	0.48±0.05	1.47	0.0001	0.97	4.41 (3.66-5.16)	383.09 (382.34-383.84)	0.0007	0.91

[a]Number in parentheses are confidence intervals of the mean (*n* = 3). [b]Mean value ± standard deviation of the mean.

Table 5.6- Freundlich and linear models sorption isotherms parameters for S-metolachlor applied to soil amended with proportions at 0 (unamended soil), 1, 5, 10, 15, 20, and 100% (pure) (w w^{-1}) microplastics (MPs).

MPs% (w w^{-1}) +soil	Freundlich					Linear			
	K_f	K_{foc}	1/n	*p*-value	R^2	K_d	K_{oc}	*p*-value	R^2
	($mg^{(1-1/n)}$ $L^{1/n}$ kg^{-1})					(L kg^{-1})			
0 (unamended soil)	3.05 (1.94-4.16) [a]	265.38 (264.27-266.49) [a]	0.78 ± 0.30 [b]	0.0081	0.90	3.20 (2.32-4.07) [a]	278.15 (277.28-279.02) [a]	0.0355	0.81
1	2.59 (2.09-3.09)	225.51 (225.01-226,01)	0.59±0.14	0.0014	0.95	3.00 (2.75-3.65)	260.77 (260.32-261.22)	0.0069	0.93
5	4.77 (3.25-6.29)	415.05 (413.53-416.57)	0.89±0.23	0.0029	0.95	4.85 (3.96-5.73)	421.57 (420.69-422.45)	0.0119	0.90
10	3.46 (2.86-4.06)	300.82 (300.22-301.42)	0.58±0.10	0.0008	0.97	4.52 (3.98-5.06)	392.99 (392.46-422.45)	0.0035	0.95
15	4.96 (3.75-6.17)	430.95 (429.74-432.16)	0.68±0.14	0.0012	0.96	6.42 (5.51-7.33)	558.21 (557.31-559.11)	0.0058	0.94
20	5.17 (4.58-5.76)	449.19 (448.60-449.78)	0.63±0.06	0.0001	0.99	7.32 (7.22-7.43)	636.66 (636.56-636.76)	0.0001	0.99
100 (pure)	12.09 (4.45-19.73)	1050.50 (1042.86-1058.14)	0.56±0.20	0.0043	0.94	33.20 (29.85-36.56)	2884.64 (2881.34-2887.64)	0.0022	0.97

[a]Number in parentheses are confidence intervals of the mean (*n* = 3). [b]Mean value ± standard deviation of the mean.

Table 7. Freundlich and linear models desorption isotherms parameters and hysteresis coefficient (H) for S-metolachlor applied to soil amended with proportions at 0 (unamended soil), 1, 5, 10, 15, 20, and 100% (pure) (w w^{-1}) microplastics (MPs).

MPs% (w w^{-1}) +soil	Freundlich						Linear			
	K_f	K_{foc}	1/n	H	*p*-value	R^2	K_d	K_{oc}	*p*-value	R^2
	($mg^{(1-1/n)}$ $L^{1/n}$ kg^{-1})						(L kg^{-1})			
0 (unamended soil)	5.43 (3.09-7.76) [a]	471.69 (469.35-474.03) [a]	0.55±0.141[b]	1.43	0.0026	0.88	13.33 (11.91-14.75) [a]	1157.96 (1156.54-1159.38)[a]	0.0004	0.96
1	67.94 (49.35-86.52)	5901.85 (5883.26-5920.44)	1.30±0.08	0.46	0.0001	0.99	31.69 (29.44-33.94)	2752.86 (2750.61-2755.11)	0.0001	0.98
5	21.27 (17.64-24.90)	1847.69 (1844.06-1851,32)	0.93±0.05	0.96	0.0001	0.99	25.09 (23.71-26.47)	2179.53 (2178.15-2180.91)	0.0001	0.99
10	13.48 (3.37-23.59)	1171.16 (1161.05-1181.27)	0.75±0.23	0.77	0.0026	0.86	22.42 (18.96-25.88)	1947.59 (1944.13-1951.05)	0.0009	0.93
15	16.96 (7.96-25.96)	1474.07 (1465.07-1483.07)	0.80±0.170	0.85	0.0011	0.93	26.11 (23.24-28.98)	2268.14 (2265.27-2271.01)	0.0004	0.96
20	12.69 (8.04-17.34)	1103.14 (1098.49-1107.79)	0.71±0.119	0.89	0.0006	0.95	23.69 (20.92-26.46)	2057.91 (2055.14-2060.68)	0.0004	0.96
100 (pure)	11.31 (2.41-20.21)	983.00 (974.10-991.90)	0.52±0.234	1.08	0.0050	0.79	34.43 (32.24-36.62)	2990.88 (2988.69-2993.07)	0.0001	0.98

[a]Number in parentheses are confidence intervals of the mean (*n* = 3). [b]Mean value ± standard deviation of the mean.

5.3.2.2 Hexazinone

The results indicate that hexazinone sorption in soil with different proportions of MPs was similar in both treatments without MPs and those amended with MPs (Table 5.2). In the soil without MPs, the K_f value varied from 1.17 to 1.61 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1} in the treatment with 100% MPs. In the linear model, the K_d value showed an even smaller variation, going from 1.63 L kg^{-1} in the soil without MPs to 1.67 L kg^{-1} in the soil with 100% MPs, indicating a small change. In contrast, K_{oc} increased from 142.20 L kg^{-1} in the soil without MPs to 145.24 L kg^{-1} in the treatment with 100% MPs. The parameter 1/n, which reflects the linearity of sorption, increased from 1.23 to 1.61 in the soil with 100% MPs, suggesting that sorption becomes more linear with increasing MPs content.

On the other hand, desorption showed different sorption dynamics, particularly at lower MPs content (Table 5.3). In the treatment with 1% MPs, K_f was 4.11 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1}, while in the unamended soil, the value was 12.67 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1}. In the linear model, the same pattern was seen. The control treatment had a Koc of 515.13 L kg^{-3}, while the soil that had 1% MPs added had a Koc of 377.01 L kg^{+3}. Despite this initial discrepancy, as the amount of MPs in the soil increases, the values of K_f (4.06 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1}) in the treatment with 100% MPs become very close to those of the soil amended with 1% MPs, which can be explained by the saturation of the sorption sites or by the stabilization of the interactions between MPs, soil, and herbicide. Zhang et al. (2021) observed a similar behavior: as the diameter of MPs increases, the sorption capacity of hexazinone decreases, indicating the saturation of the sorption sites, which may influence the sorption and desorption behavior of the herbicide.

This is because hysteresis values (H) show the difference between how herbicides are absorbed and released from the soil (Table 5.3). For example, in the treatment with 1% MPs, the H value was 0.91, indicating lower retention and greater ease of desorption of hexazinone, compared to the unmodified soil, where H was 1.91, indicating greater retention. Small amounts of MP appear to reduce the soil's sorption capacity. As the proportion of MPs increases, H values also increase, as in the treatment with 5% MPs (H 1.36), reflecting greater retention of the herbicide.

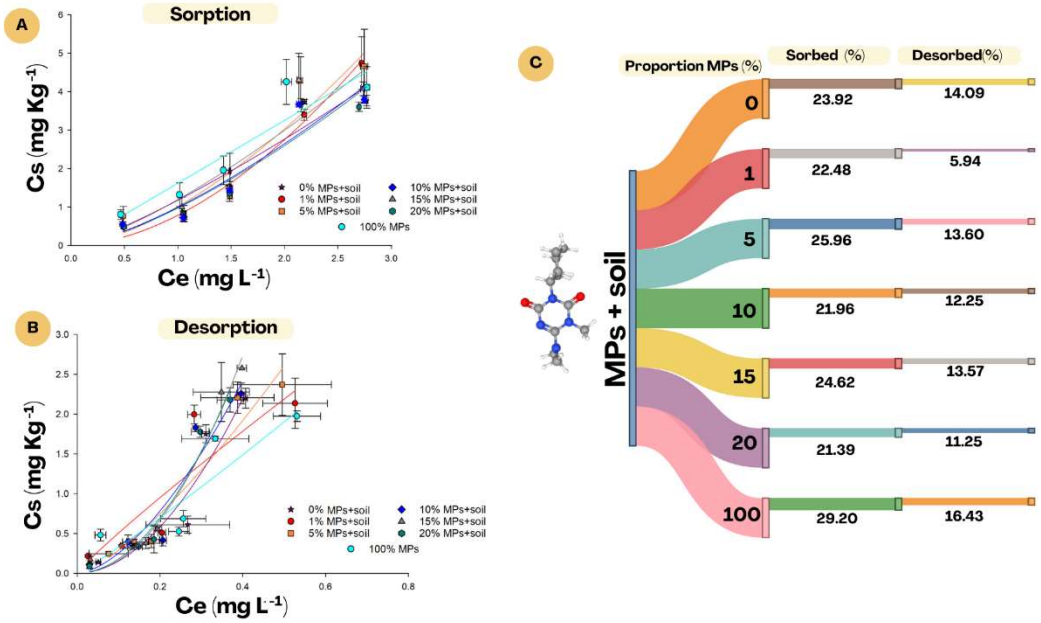

Figure 5.2- (A) Freundlich model sorption and (B) desorption isotherms for hexazinone applied to soil amended with proportions at 0 (unamended soil), 1, 5, 10, 15, 20, and 100% (pure) (w w^{-1}) microplastics (MPs). Vertical and horizontal bars represent the standard error of mean (*n* = 3) of equilibrium concentrations (Ce) and soil concentration (Cs), respectively. Symbols may obscure the error bars. (C) Sankey diagram illustrating the percentages of hexazinone sorbed and desorbed relative in the unamended and MPs-amended soil.

The Cs of hexazinone sorption in the soil increased as the Ce of hexazinone in the soil solution increased (Figure 5.2A). This behavior suggests that herbicide sorption by the soil is a concentration-friendly process. When adding MPs to the soil, a behavior similar to that of the treatment without MPs was observed (Figure 5.2A). For instance, the 1% MPs proportion showed a sorbed percentage of 22.48%, while the treatment without MPs showed a sorbed percentage of 23.92% (Figure 5.2C). All proportions showed desorption around 12%, except for the treatment with 1% MPs, which reached 5.94%. The physicochemical properties of the pesticides can explain this behavior. Wang et al. (2020b) studied pesticides such as carbendazim, difenoconazole, malathion, dipterex (trichlorfon), and diflubenzuron, whose log K_{ow} was critical in the extension of their sorption in MPs. These pesticides, due to their specific characteristics, presented differentiated interactions with MPs, mainly influenced by the Log K_{ow} and S_w values. Hexazinone is an herbicide that has a low Log Kow (0.67) and a high S_w of

33,000 mg/L at 25°C (PPDB, 2024). This indicates a reduced interaction with MPs, leading to less absorption. Huffeer and Hofmann (2016) have demonstrated that compounds with lower Log K_{ow}, such as nitrobenzene, high S_w, and low K_d, exhibit less interaction with MPs.

This moderate sorption and higher desorption ratio can be explained by analyzing the 1/n parameters in the Freundlich sorption models (Table 5.2). As the proportion of MPs increases, the 1/n value decreases, indicating a more limited sorption of hexazinone in soils with MPs. Furthermore, in the Sankey diagram (Figure 5.2C), the sorption percentages are very similar to those observed in the unamended soil, as is the case for desorption. This suggests that the herbicide's physicochemical properties reduced its interaction with MPs. Initially, herbicides can be adsorbed on the outer surface of MPs through Van der Waals forces, which are weak interactions between molecules (Zhang et al., 2021). However, because these forces are relatively weak, herbicides on the surface can be desorbed comparatively easily, especially when the internal pores of MPs provide more space or more favorable energy for the compound to move (Hu et al., 2021). This results in faster desorption than sorption because the movement of herbicides to the internal pores reduces the amount of herbicide present on the external surface, facilitating their release into the soil solution (Wang et al., 2020a). In other words, the forces holding hexazinone on the surface of MPs are not strong enough to prevent them from being released when the internal pores are available for diffusion (Li et al., 2020). Therefore, the desorption rate may be higher than the sorption rate in this context. Furthermore, due to its high S_w and low K_{ow}, hexazinone has a higher propensity to leach into the soil profile. This effect is amplified by its low sorption to the soil, especially in environments contaminated with MPs (Yang et al., 2018), which further facilitates its mobility and potential for contamination of deeper layers.

5.2.2.3 Diuron

The interaction between the herbicide diuron and the soil, both in the presence and absence of MPs, is shown in Figure 5.2. The results indicate that (Cs) increased as the (Ce) of diuron in the solution (Ce) increased (Figure 5.3A). This behavior indicates that the sorption of the herbicide by the soil tends to be more efficient as the concentration increases. However, the addition of MPs to

the soil affected the sorption of the herbicide, with a tendency to reduce sorption at all Ce concentrations (Figure 5.3A). The presence of 10% MPs reduced the sorption of the herbicide by approximately 10% compared to the soil treatment without MPs. This occurs because diuron is a polar herbicide, containing functional groups such as urea and phenyl, which influence its interactions with the soil (Araújo, 2012) and with MPs (Wang et al., 2020a). On the other hand, primary polyethylene (PE) MPs exhibit nonpolar characteristics, resulting in low affinity for polar solvents, such as diuron (Kumar et al., 2020). Because diuron and MPs are not electrically charged the same, as the amount of MPs in the soil rises, sorption decreases (Bhagat et al., 2022).

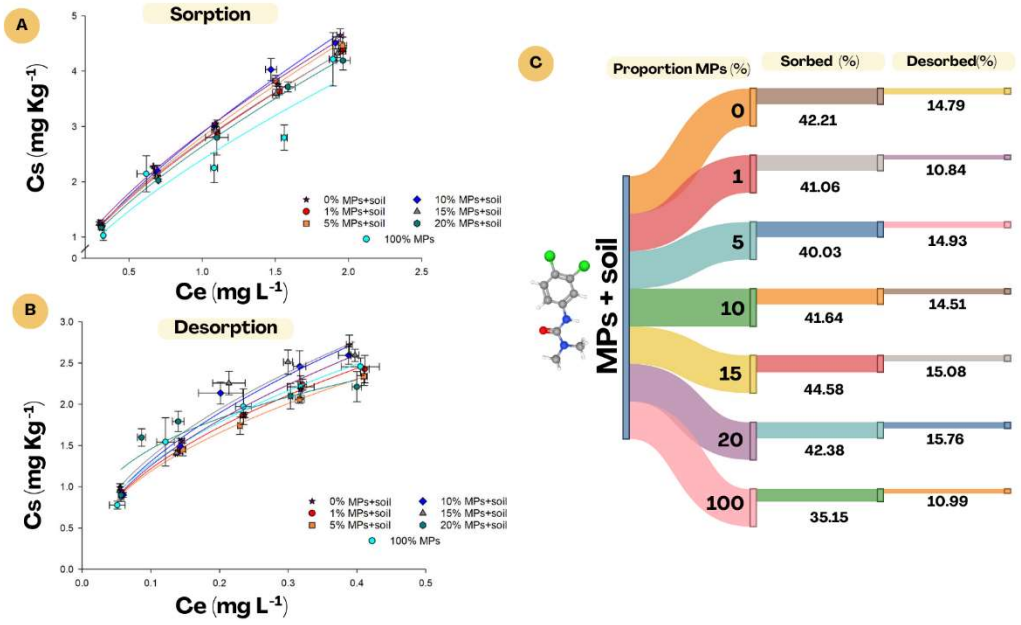

Figure 5.3- (A) Freundlich model sorption and (B) desorption isotherms for diuron applied to soil amended with proportions at 0 (unamended soil), 1, 5, 10, 15, 20, and 100% (pure) (w w^{-1}) microplastics (MPs). Vertical and horizontal bars represent the standard error of mean (*n* = 3) of equilibrium concentrations (Ce) and soil concentration (Cs), respectively. Symbols may obscure the error bars. (C) Sankey diagram illustrating the percentages of diuron sorbed and desorbed relative in the unamended and MPs-amended soil.

In the study by Xu et al. (2020), two contaminants with distinct polarities were used: diazepam (a polar compound) and phenanthrene (a nonpolar compound). Due to the low affinity between nonpolar MPs, such as PE, and polar compounds, such as diazepam, the sorption of these compounds to the soil was

reduced. This effect may increase the mobility of polar contaminants, while the sorption of nonpolar compounds, such as phenanthrene, was favored by PE MPs (Xu et al., 2020).

Diuron desorption in soil follows a behavior similar to that of sorption, with an increase in the concentration of desorbed diuron (Cs) due to the equilibrium concentration in the solution (Ce). The presence of MPs in the soil influenced desorption, with a slight reduction in the amount desorbed in soils with a higher proportion of MPs (Figure 3B). In soils with 15% MPs, diuron desorption was approximately 12% lower compared to the treatment not modified with MPs, which was 14.79%. In the Sankey diagram, it is possible to observe more clearly that as the MPs increased, the percentage sorbed and the percentage desorbed were lower, such as the 100% MPs treatment, which was approximately 1/3 lower than the treatment without MPs.

MPs compete with soil particles for diuron sorption. The surface of MPs can sorb part of the diuron, resulting in a smaller amount of diuron available for desorption from soil particles (Costigan et al., 2022). This competition was more pronounced in soils with a higher proportion of MPs, which explains the reduction in desorption observed. As a result, this competition can make diuron more mobile, which raises the chance that it will leach into deeper soil layers and maybe even reach groundwater (Xu et al., 2020).

K_f showed a reduction from 2.89 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1} in soil without MPs to 2.40 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1} in 100% MPs, suggesting that MPs compete with soil particles for diuron sorption, reducing the herbicide retention capacity (Table 5.4). Similarly, the reduction in Kd from 1.99 L Kg^{-1} in soil without MPs to 1.67 L Kg^{-1} in 100% MPs confirmed the trend of reduced sorption. Furthermore, K_{oc} decreased from 173.21 L Kg^{-1} in soil without MPs to 145.76 L Kg^{-1} in the treatment with 100% MPs. In desorption, K_f values ranged from 4.21 mg$^{(1-1/n)}$ $L^{1/n}$ kg^{-1} in soil without MPs to 3.86 mg$^{(1-1/n)}$ $L^{1/n}$ kg^{-1} in soil with 100% MPs, while K_d values decreased from 4.85 to 3.01 L kg^{-1} in the same interval (Table 5.5). This behavior suggests that the presence of MPs increases the herbicide's mobility in the soil. The constancy of 1/n values close to 0.5 indicates a slight nonlinearity in the desorption process, except for the soil with 20% MPs, where a greater linearity was observed (1/n = 0.32). With the addition of MPs, H showed an increasing trend, ranging from 1.32 to 1.47, which suggests a more difficult desorption in soils with

MPs. These findings indicate that the presence of MPs in the soil alters diuron's retention and desorption dynamics, potentially affecting its efficacy and weed control.

The reduction in K_f observed with increasing MPs concentration in the soil can be explained by the reduction in the sorption capacity of soil particles due to competition with MPs (Chen et al., 2022). Studies show that the presence of MPs in agricultural soils can increase the mobility of contaminants such as heavy metals and pesticides, reducing their sorption and increasing desorption. This occurs because MPs act as vectors that compete for interactions with contaminants, which was observed, for example, in soils contaminated with cadmium and MPs, in which there was a decrease in sorption and an increase in metal desorption (Zhang et al., 2019). This behavior was also confirmed in pesticide studies, in which the presence of MPs altered the sorption and desorption dynamics, reducing the retention of compounds such as atrazine (Lv et al., 2023).

5.2.2.4 S-metolachlor

As the proportion of MPs in the soil increases from 0% to 100%, the sorption Cs value also increases for a given Ce (Figure 5.4). This indicates that S-metolachlor has a higher affinity for MPs than for soil, resulting in greater sorption of the herbicide in the presence of MPs. This trend is more pronounced at high proportions of MPs (100%), suggesting that MPs have a superior capacity to sorb the herbicide compared to pure, unamended soil. Desorption analysis (Figure 5.4B) shows that the amount of herbicide released into the solution decreases as the proportion of MPs in the soil increases, indicating that S-metolachlor, once sorbed by MPs, does not return to the solution, evidencing more effective retention by MPs. Samples with high amounts of MPs (20% and 100%) have the lowest desorption. Soils without MPs (0%), on the other hand, have higher desorption, which means the herbicide can be released more easily from the pure soil.

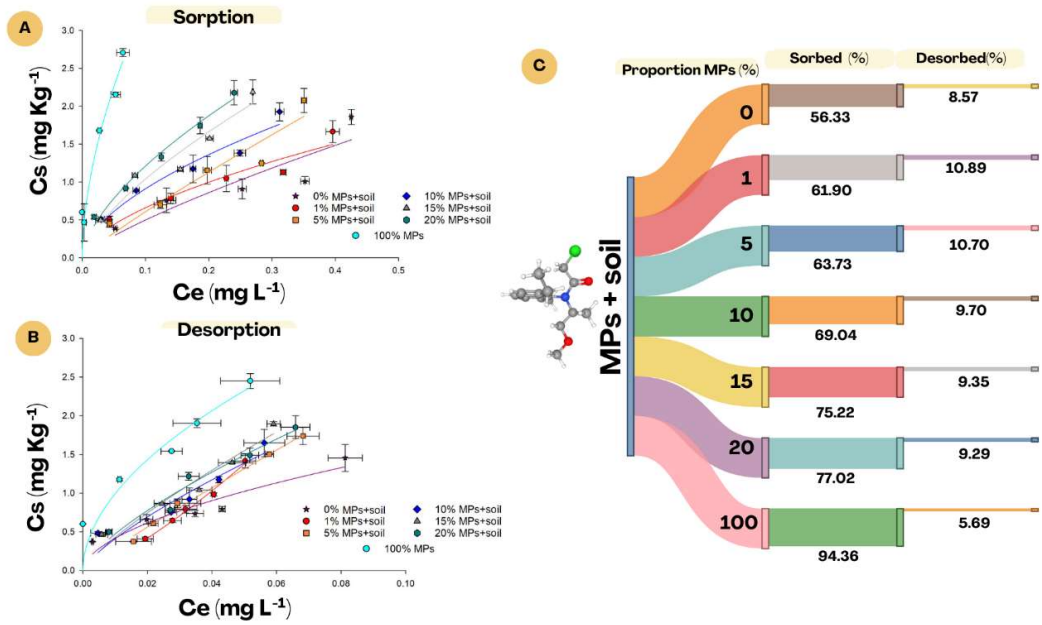

Figure 5.4- (A) Freundlich model sorption and (B) desorption isotherms for S-metolachlor applied to soil amended with proportions at 0 (unamended soil), 1, 5, 10, 15, 20, and 100% (pure) (w w^{-1}) microplastics (MPs). Vertical and horizontal bars represent the standard error of mean (*n* = 3) of equilibrium concentrations (Ce) and soil concentration (Cs), respectively. Symbols may obscure the error bars. (C) Sankey diagram illustrating the percentages of S-metolachlor sorbed and desorbed relative in the unamended and MPs-amended soil.

In the Sankey diagram, it is observed that the sorption of the herbicide is 56.33% without MPs (0%) and increases to 94.36% with pure MPs. Simultaneously, as the proportion of MPs increases, the desorption decreases from 8.57% to 5.69% with the increase in the proportion of MPs. These results show that MPs have a greater capacity to sorb S-metolachlor and a lower tendency to release it, demonstrating a strong interaction between the herbicide and the polymer.

The parameters of the Freundlich and linear sorption isotherms for S-metolachlor in soils with different proportions of MPs (0% to 100%) are presented in Table 6. The parameters K_f and K_d, which reflect the sorption capacity of the herbicide, increase with the proportion of MPs, going from 3.05 $mg^{(1-1/n)}\ L^{1/n}\ kg^{-1}$ in soil without MPs to 12.09 $mg^{(1-1/n)}\ L^{1/n}\ kg^{-1}$ in soil with 100% MPs. This pattern suggests that S-metolachlor has a greater affinity for MPs than for unamended soil. The values of K_{foc} and K_{oc}, which normalize the sorption coefficients by soil OC, also increase with the concentration of MPs, confirming the greater sorption capacity of MPs. The K_{foc} varied from 265.38 L kg^{-1} in the unmodified soil to 1050.50 L kg^{-1} in the treatment with 100% MPs. The K_{oc} followed the same behavior,

increasing from 278.15 L Kg^{-1} in the unmodified soil to 2884.64 L Kg^{-1} in the soil with 100% MPs. The Freundlich parameter 1/n, which indicates the sorption intensity, decreases with the proportion of MPs, suggesting a more favorable sorption and less dependence on the herbicide concentration in the presence of MPs.

The parameters of the Freundlich and linear desorption isotherms, as well as H, which quantifies the irreversibility of sorption, are presented in Table 7. The K_f values ranged from 3.05 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1} in the unamended soil to 12.09 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1} in the 100% MPs treatment. The K_d ranged from 3.20 to 33.20 L Kg^{-1}, indicating that desorption increases with the MPs proportion, suggesting that S-metolachlor is more firmly retained in the MPs than in the soil. The H, which ranges from 1.08 to 0.46 with different MP proportions, suggests that the presence of MPs makes the sorption process less reversible, with greater hysteresis in soils with low MP levels (1%). This reflects greater herbicide retention and lower desorption. As the proportion of MPs increases, H decreases, possibly due to the saturation of sorption sites or the formation of weaker interactions at high MP levels.

Several complementary factors explain the strong interaction between S-metolachlor and MPs in soil. First, MPs, being predominantly nonpolar, provide a compatible surface for the sorption of lipophilic compounds, as is the case with S-metolachlor (Wang et al., 2020). Despite being moderately polar (Zemolin et al., 2014), S-metolachlor has a K_{ow} of approximately 2.64 (PPDB, 2024), which indicates its affinity for organic phases. This makes it easier for it to interact with MPs, which are nonpolar compounds (Torres et al., 2021). This leads to strong sorption. Furthermore, in soil, hydrophobic interactions between S-metolachlor and MPs play a determining role. The presence of MPs, which are hydrophobic, favors the binding of S-metolachlor to their surfaces to the detriment of polar soil particles. The herbicide's mobility in the soil decreases due to these hydrophobic interactions, as the MPs retain it, reducing its desorption and increasing its sorption (Qu et al., 2021). This behavior is corroborated by studies that show high retention of S-metolachlor in soils with MPs, evidencing the low desorption of the herbicide in the presence of these particles (Ćwieląg-Piasecka, 2023).

The herbicide's retention in the MPs reduces its availability for weed control, compromising its effectiveness in the field. Furthermore, this retention increases the risk of environmental contamination, as the herbicide can remain in

the soil for longer, potentially accumulating and migrating to other areas, which increases the chances of contamination of groundwater and adjacent ecosystems.

5.3 CONCLUSION

The presence of MPs in agricultural soil influences the sorption and desorption processes of the three herbicides studied. For S-metolachlor, MPs increased their sorption, reducing their mobility in the soil, which may compromise their effectiveness in weed control and increase the risk of environmental accumulation. In contrast, the herbicides hexazinone and diuron showed less interaction with MPs, resulting in greater mobility and potential for contamination of groundwater and surface water. These results suggest that soil contamination by MPs can alter the environmental behavior of herbicides, varying according to their physicochemical properties. As a result, it is critical to consider MPs in agricultural management, as their presence may compromise the sustainability and safety of agricultural ecosystems. To ensure herbicide efficiency and environmental protection, strategies for mitigating the impact of MPs should be explored.

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