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Review article

Ecotoxicological impacts associated with the interplay between micro(nano)plastics and pesticides in aquatic and terrestrial environments

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Abstract

Microplastics (size 1 µm–5 mm) and nanoplastics (size 1–1000 nm), commonly referred to as micro(nano)plastics (MNPs), are ubiquitously present in the aquatic and terrestrial environment, where they imminently interact with persistent organic pollutants, such as pesticides, inducing adverse toxicological effects in exposed organisms. MNPs interact with pesticides through adsorption and desorption processes in the environment. Specific interest in the capacity of MNPs' interactions with pesticides requires additional consideration due to the prospective role this nexus plays in changing the environmental transportation, bioavailability, and ecotoxicity of these pollutants. Therefore, this review summarizes studies on the adsorption of pesticides on MNPs and factors affecting that adsorption process, including MNP properties (particle size, surface area, shape, dose), characteristics of pesticides (ionic properties, hydrophobicity), and environmental factors (temperature, pH, ionic strength). Furthermore, the bioaccumulation and associated combined toxicological impacts of pesticides and MNPs in freshwater, marine water, and terrestrial organisms are highlighted. Reviewed studies revealed that MNPs and pesticides undergo bioaccumulation in aquatic and terrestrial organisms and can cause multifaceted impacts, including growth and reproduction impairments, oxidative stress, altered genetic and enzymatic responses, metabolism abnormalities, multigenerational effects, histopathological modifications, neurotoxicity, and hepatotoxicity, among others. Last but not least, research gaps and future perspectives for pesticides and MNP interactions and their interconnected ecological implications are offered.

Keywords: Pesticides; Microplastics; Nanoplastics; Adsorption; Ecotoxicological impacts

1. Introduction

During the past few years, small plastic particles, including microplastics (MPs) and nanoplastics (NPs), commonly termed micro(nano)plastics (MNPs), are topic of major concern in the scientific community and have become an emerging environmental threat globally [1, 2]. MNPs are small fragmented particles with distinctive size (1 nm to <5 mm), color, shape, polymer type, particle density, gravity, and peculiar sources [3, 4]. Depending on their sources, plastic particles may be classified as either primary or secondary MNPs. Primary MNPs are plastic particles manufactured with specific characteristics for use in a variety of applications, such as exfoliating scrubs, cosmetics, and industrial pellets, as well as those used as raw materials in the production of plastic items [5]. However, secondary MNPs are plastic particles released through the degradation of macro- or micro-sized plastic waste in the environment by various processes, including biodegradation, photodegradation, hydrolysis, and mechanical abrasion [6].

Previously, several studies have shown that MNPs can easily be found in water [7], soil [8], air [9], sediment [10] and living organisms including humans [11]. Beaches, urban areas, and landfills are severely contaminated by MNPs, along with agricultural ecosystem also being considerably affected. Due to their continuous accumulation, non-biodegradability and consequent conversion into MNPs via physio-chemical and mechanical degradation, plastics pose remarkable threats to all living beings and the environment [12]. As the whole planet is polluted with MNP pollution, the chances of plastic ingestion by all living beings are quite normal and natural [13]. Food intake is the most common pathway for the MNPs to enter the bodies of organisms, and then accumulated in organs and body tissues [14, 15]. Once absorbed, MNPs can be transported to the lungs, spleen, heart, kidney, brain, liver and reproductive organs as well [16]. Exposure to MNPs causes inflammatory responses, reproduction defects, oxidative stress, suppressed feeding behavior, and successional generation may bring down the evolutionary fitness [17]. Ingestion of MNPs has shown harmful impacts to various species from small invertebrates to large marine animals [17, 18]. Ingestion and transfer of MNPs at different tropic levels via the food chain in aquatic and terrestrial species are extensively reported, representing diverse ecotoxicological impacts of MNPs on higher tropic level consumers including humans [19, 20].

Evaluation of ecotoxicological impacts depends upon how anthropogenic contaminants are dispersed in environment, their probable interaction with MNPs and their mode of action in organisms. This has become very challenging as contamination has resulted from diverse origins and contaminated sites possess many categories of chemical contaminants, ranging from few tens to thousands of contaminants [21]. Moreover, chemicals exhibit an active and unevenly large surface area that permits MNPs to absorb the harmful contaminants including organic compounds [22], pharmaceuticals [23], antibiotics [24] heavy metals [25] and pesticides [26] from the surrounding environment. Therefore, MNPs act as carriers for the transfer and transport of different contaminants through food chain and bring on the risk of toxicity to organisms and humans. MNPs not only transport these contaminants but also increase their environmental prevalence. Adsorption of different contaminants by MNPs is another possibility for amplified contamination of both aquatic and terrestrial environments. The occurrence of MNPs along with different contaminants can induce detrimental impacts to the organisms at all tropic levels [17].

In the company of adsorbed harmful contaminants by the MNPs, pesticides are also primal contaminants of important consideration. Pesticide pollution in soil and water environments has become a leading challenge across the globe [27, 28]. Despite their positive impacts in improving crop productivity and substantially diminishing vector borne diseases, their indiscriminate and unregulated use has triggered drastic concerns about animal and human health in particular [29, 30]. Beside the prohibition and restriction of notable use of currently used pesticides (CUPs) and organochlorine pesticides (OCPs), CUPs and legacy pesticides are still detected ubiquitously in several ecosystems like soil [31], water [32], air [33] and sediments [34]. Pesticides are extensively used for the optimization of agricultural production; however, their movement into water bodies impacts the terrestrial and aquatic environments [35]. Pesticide pollution can unsympathetically impact the biodiversity. Harmful impacts of pesticides on various species include reduction in the survival of three bees (*Apis mellifera, Bombus terrestris, Osmia bicornis*) [36], bioaccumulation and liver damage in small mammals [37], nuclear abnormalities and genotoxic damage in anurans [38], decline in the reproduction behavior of *Daphnia magna* [39], significantly affect the body mass and increases the mortality in tadpole [40], disruption in swimming behavior of goldfish [41]. Excessive use of pesticides can be disastrous for both the soil and aquatic environment, affect the organism’s growth, and bring risks for the downstream organisms and human health via the food chain [42].

MNPs and pesticides are contaminants of worldwide concern coexisted widely in the environment for long period of time. Although plenty of research has been done so far highlighting the individual toxicity of MNPs [43] and pesticides [44], their combined impact on terrestrial and aquatic environments remains poorly understood. The interaction between MNPs and pesticides has not been fully addressed in previous studies. Only a handful of research studies have determined the distinctive properties of MNPs to adsorb pesticides in environment [26, 45-48]. Adsorption of pesticides on

MNPs expand the possibility of pesticide transport and bioaccumulation in aquatic [49, 50] and terrestrial organisms [51]. So far, no comprehensive review is available that specifically highlights the interaction of pesticides and MNPs and associated toxicological impacts in the aquatic and terrestrial environment. Recently, a few review studies summarized the interactions of MPs with pesticides in soils [52] and biotoxicity of MPs and environmental contaminants [53]. Therefore, it is a matter of grave concern to comprehensively evaluate and summarize available studies on the interactions between pesticides and MNPs in both water and terrestrial environments. In this study, the interactions between pesticides and MNPs in terms of co-occurrence, adsorption mechanisms, and factors that affect how pesticides adsorb to MNPs have been pointed out. Also, the combined toxicity of pesticides and MNPs and the mechanisms involved have been studied in freshwater, marine water, and terrestrial environments. Last but not least, research gaps and possible directions for future research are pointed out to help shape future research on how plastic particles and pesticides affect the environment together.

2. Bibliographic analysis of the available studies

We conducted a comprehensive literature search between November, 2022 and March, 2023 to identify relevant publications on the interactions between micro(nano)plastics and pesticides in the aquatic and terrestrial environments. This search utilized various databases such as Google Scholar, ScienceDirect, and Web of Science, and used several keywords such as "micro(nano)plastics", "pesticides", "microplastics", "nanoplastics", "interaction", "adsorption", "freshwater", "marine water", "terrestrial environment", "toxicity", “impacts", "ecotoxicology", "herbicide", "insecticide", and "organisms", among others. The study included original research papers and review articles (supporting literature) published in English, resulting in the selection of 145 publications, most of which were published in recent years. To analyze the literature in-depth, a bibliometric analysis using VOSviewer Software was conducted. The analysis identified 2233 keywords, out of which 323 met the threshold. The software calculated 194 of the most relevant terms from the title and abstract of the publications, of which 43 irrelevant terms were manually excluded. The Network Visualization map produced by VOSviewer Software comprised of the lines connecting the circles, which indicate the level of confidence in the keywords, the variable font size of the terms indicates their occurrence frequency, and the node curves indicate co-occurrences within the same article. This bibliographic analysis concludes that micro(nano)plastics and pesticides have gained significant attention in recent years.

Fig. 1a represents a Network Overlay visualization map that depicts the literature trends on the interaction of MNPs and pesticides over the last five years. The studies published before year 2020 focused on terms such as sorption kinetic, desorption, freshwater system, PVC, electrostatic interaction, fipronil, sorption process, among others. In contrast, recent years (2020-2023) have seen an increase in toxicological studies on MNPs and pesticides, with a focus on various interactions, toxicity endpoints, species, and related factors. The prominent terms identified include ageing mechanism, hydrophobicity, adsorption, polar microplastics, freshwater, aged microplastic, aquatic organism, difenoconazole, polyamide, sorption capacity, AChE activity, polychlorinated biphenyl, potential risk, organochlorine pesticide, ecological risk, liver, nondegradable microplastics, soil organism, microbe, human health, atrazine, beta cypermethrin, GST, gut microbiota, higher risk, insecticide resistance, invasive pest species, multigenerational effect, mussel, PE microplastic, PS-NPs, terrestrial environment, bioaccumulation, biodegradable microplastics, earthworm, gill, CPF, PS microplastics, zebrafish, human, soil ecosystem, terrestrial organism, herbicide, tissue, glyphosate, malathion, bioaccumulation potential, brain, DOM, ecological risk assessment, neurotoxicity, soil fauna community, among others.

In **Fig. 1b**, a Network Visualization map of data on the impacts of MNPs and pesticide pollutants is presented. The data comprises of 168 items that have been clustered into 11 groups, each represented by a unique color. The links between the clusters have a total strength of 17080, with 3086 links created. Cluster 1 (total link strength of 1120) primarily focuses on the adsorption of chemicals in the environment. The terms in this cluster include " CIP, difenoconazole, freshwater, hydrogen bonding, hydrophobicity, maximum adsorption capacity, polyamide, PVC". Cluster 2 (total link strength of 2269) is dominated by terms such as "atrazine, bioaccumulation potential, biodegradable microplastic, fipronil, Freundlich model, Langmuir model, nondegradable microplastics, PLA, polar microplastics, soil ecosystem, soil fauna community, sorption." Cluster 3 (total link strength of 1585) comprises terms related to the health risks of MNPs and pesticides including "abundance, chemical pollutant, coral reef fish, ecological risk assessment, gill, higher risk, human health, liver, OPP, organochlorine pesticide, polychlorinated biphenyl, and tissue." Cluster 4 (total link strength of 2392) is dominated by terms such as "acetylcholinesterase activity, active ingredient, agrochemical, amphibian, GBH, herbicide, immune parameters, mortality, multigenerational effect, PE microplastics, and PSNPs." Cluster 5 (total link strength of 1868) is characterized by terms such as "beta cypermethrin, DEGs, enzyme, gut microbiota, host, human, insecticide, and insecticide resistance." Cluster 6 (total link strength of 885) comprises terms such as "desorption, ecological risk, electrostatic interaction." Cluster 7 (total link strength of 1925) focuses on the toxicological effects of MNPs and pesticides on aquatic organisms with terms including "aquatic organism, bioaccumulation, brain, malathion, metabolism, neurotoxicity, toxicological effect, and zebrafish." Cluster 8 (total link strength of 679) is characterized by terms such as "PS microplastics, terrestrial environment, transgenerational impact." Cluster 9 (total link strength of 721) comprises terms related to biogenic transport and microplastics, such as "biogenic transport, CPF, LDPE microplastics, and mussel." Cluster 10 (total link strength of 697) is dominated by terms such as "cypermethrin, earthworm, and cyhalothrin." Cluster 11 (total link strength of 611) is comprised of terms such as "degradation, DOM, organic matter, reservoir, sediment, and source."

Fig. 1c-d highlights Sankey diagram for the number of core studies available on the adsorption of pesticides on MNPs (n = 9) and the combined toxicological impacts of pesticides and MNPs (n = 35), implying that 44 studies have been conducted so far on the interaction of pesticides and MNPs and associated toxicological impacts in the environment. Regarding adsorption of MNPs on pesticides **(Fig. 1c)**, five studies have been conducted under aqueous conditions, while four studies have elucidated the adsorption of pesticides on MNPs in a soil environment. As for the ecotoxicological impacts of MNPs and pesticides **(Fig. 1d)**, freshwater, marine water, and terrestrial environments, respectively, comprised 11, 13, and 11 studies. Among MNP characteristics, polystyrene (PS) and polyethylene (PE) were most commonly investigated polymers comprising spherical shapes and MPs were relatively more studied than that of NPs (Table S1-S2). These results indicate that experimental research on the interaction between MNPs and pesticides does not fully account for the peculiarities of environmental conditions. For instance, considering plastic polymers, more than 70 percent of research used PS polymer, which comprises just 5–28% of what is reported in aquatic environments [54]. PS is often employed in laboratory experiments because it is inexpensive, simple to customize for specialized uses, and a widely and readily accessible commodity plastic that has been used for almost a century [55]. Polypropylene (PP) and polyethylene terephthalate (PET) polymers are under-evaluated for their toxicological interactions with pesticides, despite being present in comparable concentrations to PS and PE in the environment.

3. Co-occurrence and adsorption of pesticides on MNPs

MNPs can vigorously act as carriers for persistent organic pollutants [56], including pharmaceuticals [57] and pesticides [58] and sometimes the dose of these pollutants on MNPs exceeded the actual concentration of these pollutants present in the surrounding environment. Therefore, the co-occurrence of chemical pollutants along with MNPs could significantly intensify or alter their overall impact through regulating their mobility and bioavailability in the living system and surrounding environment [2]. MNPs can adsorb different pollutants by being relatively more hydrophobic, having large specific surface area (SSA) and small particle size. Adsorption of pollutants on MNPs depends upon the characteristics of MNPs including degree of crystallinity, point zero charge, polarity, type of polymer, functional groups, and surface topography, as well as properties of matrix such as temperature, pH and salinity [59]. Environmental pollutants with higher hydrophobicity are generally more prone to display high adsorption ability for MNPs [60]. Octanol-water partition coefficient (log K_{ow}) indicates hydrophobicity, therefore environmental pollutants having higher log K_{ow} values tend to adsorb easily on MNPs [61]. Adsorption is the main process linked with the vector/carrier property of MNPs [62].

Recent studies regarding the adsorption of pesticides on MNPs in both the aqueous and soil mediums are summarized in **Table S1**. Among environmental pollutants, pesticides also showed great adsorption efficiency on MNPs when both coexist in aquatic and terrestrial environment [63, 64]. Adsorption of the pesticides on MNPs is a gradual process and both are resistant to degradation, implying that MNPs could enhance the contamination of pesticides in the surrounding environment. For instance, Li et al. (2021) studied the adsorption of three different pesticides including difenoconazole (DFZ), buprofezin (BUP), imidacloprid (IMI) on PE-MPs in aqueous solution with adsorption affinity of the pesticides in the following order DFZ > BUP > IMI, implying that PE-MPs are potential carriers of different pesticides in the aquatic environment. Similarly, the adsorption of flubendiamide (10 mg/L), chlorantraniliprole (5 mg/L) and acetamiprid (1 mg/L) onto PP-MPs (1 mm) and polyester fiber (0.5 mm) were investigated at their 5% and 1% (w/w) contents in soil. All tested concentrations of pesticides with 5% polyester fiber and 5% PP-MPs showed exceptional adsorptions on MPs in soil, proving that MPs in soil matrix also act as carrier for pesticides [65]. The adsorption behavior of four different pesticides including DFZ, carbendazim (CBD), diflubenzuron (DIF), malathion (MAL) on pristine PS-MPs and PE-MPs and aged PE-MPs was investigated in agricultural soil. The adsorption kinetics of the four pesticides indicated that the adsorption ability of aged PE-MPs is much better than that of pristine MPs, which is attributable to the larger surface area of the aged PE-MPs. Aged PE-MP agricultural soil films have more cracks, rough surface and additional oxygen containing functional groups that make the adsorption of pesticides easier [45]. The weathering and aging process of MNPs increases the roughness of the surface area, which further facilitates the adsorption capacity [26]. As described above, MNPs show exceptional adsorption capacity for pesticides. Further discussion on the adsorption of pesticides on MNPs is highlighted in the next section.

4. Factor affecting the adsorption of pesticides onto MNPs

Physicochemical properties of the MNPs (particle size, surface area, shape, dose), characteristics of the organic pollutants (ionic properties, hydrophobicity) and environmental factors (temperature, pH, ionic strength) influence the adsorption of pesticides on MNPs **(Fig. 3)**.

4.1 Plastic particle size, dosage and surface area

MNPs with smaller particle sizes often have a larger SSA, which implies a greater number of adsorption sites on the MNP and thus promotes the adsorption of pollutants. For instance, five pesticides (dipterex-DIP, MAL, DIF, DFZ, and CBD) showed tremendous adsorption on PE-MPs (5 mm) derived from soil plastic film with protrusions and folds, which make it easier to adsorb these pesticides [63]. Similarly, another study also reported that the decrease in the particle size of PS-MPs from 100 μm to 10 μm significantly improved the adsorption of three different pesticides including myclobutanil, hexaconazole, and triadimenol [66]. Similarly, Mo, et al. [67] studied the adsorption of carbofuran (CBF) and CBD on PE-MPs and PP-MPs. The adsorption of CBF was 1.56 mg/g with PE-MPs having a particle size of 830 μm, while its adsorption increased to 2.64 mg/g with 18 μm sized PE-MPs. Similarly, CBF adsorption was 1.39 mg/g with particle size of 830 μm and 2.39 mg/g with 18 μm particle sized PP-MPs. Further, the adsorption of phenanthrene and nitrobenzene on the surface of PS-MPs was also investigated, where the value of log K_{ow} increased with the decrease in the size of PP-MPs [68]. A large SSA of the biodegradable MPs, including PE, PP, and polybutylene adipate-co-terephthalate, favors the adsorption of napropamide/acetochlor herbicide [46]. Smaller-sized PE-MPs (120 μm and 180 μm) showed much better adsorption for OCPs including hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethanes (DDTs) than the large sized particles (2000 μm and 3000 μm). The SSA of PE-MPs was 1.829 m^2/g and 0.644 m^2/g with smaller particle sizes of 120 μm and 180 μm, respectively, while 0.392 m^2/g, and 0.062 m^2/g SSA were recorded with large diameter particles 2000 μm and 3000 μm. Smaller particles increase the contact area and create more sorption sites among MPs and pollutants [48]. Therefore, it is concluded that the particle size affects the pesticides' adsorption capacity, mainly depending on the SSA of plastic particle.

Concentration or dosage of MNPs applied effectively influences the adsorption of organic pollutants including pesticides. Increase in the dosage of MNPs increases the total surface area for the adsorption of organic pollutants, which resulted in generation of more blank sites on the surface of MNPs. Increase in the number of blank sites eventually reduces the unit adsorption of the MNPs [59]. Mo, et al. [67] investigated the impact various MP doses on the adsorption of CBF and CBD on PP-MPs and PE-MPs. As the MP dosage rose from 40 to 200 mg, the adsorption of CBF by PE-MPs reduced from 4.01 to 1.2 mg/g, while the adsorption by PP-MPs fell from 3.98 to 1.03 mg/g **(Fig. 2a)**. Similar trends were seen for the absorption of CBD on PE-MPs and PP-MPs **(Fig. 2b)**. The unit adsorption of MPs decreased as blank adsorption sites increased on the surface of MPs [59]. Similarly, with the increase of MP dosage from 0.5 g/L to 10 g/L, the adsorption of flusilazole (FLU) and epoxiconazole (EPO) gradually increased, while the adsorption capacity of EPO reduced from 0.3089 mg/g to 0.1176 mg/g and 0.3205 mg/g to 0.0865 mg/g from by PE and PS, respectively **(Fig. 2d)**. Besides, the adsorption of FLU by these two MPs also showed the same trend **(Fig. 2c)** [69]. Similarly, the adsorption of five pesticides including CBD, DIF, DIP, DFZ and MAL on PE-MPs significantly reduced as the dosage of MPs increase from 10 to 80 g/L. A 10 g/L dose of MPs was identified as efficient dose of MPs for the adsorption of these five pesticides [68]. A sharp decline in the adsorption of BUP, IMI and DFZ pesticides on PE-MPs was also observed with the increase in the dose of MPs [70].

4.2 Effect of MNP aging

Different changes occur in the structure and functional groups of MNPs under the influence of different environmental factors such as temperature, water and ultraviolet radiations [47, 71]. Plastic debris is susceptible to the ultraviolet radiation, bio-degradation, thermal degradation, oxidation and weathering process that may result in plastic aging [72]. With the increasing aging time, MNPs develop micro-cracks on their surface and become oxidated as well. Aging process affects the mechanisms of adsorption of organic pollutants and adsorption capacities [73]. Aged MNPs have much higher adsorption capability than the virgin MNPs [74]. Aging process of MNPs led towards the oxidation of C-C and C-H bonds, resulting in oxygen containing functional groups, enhancing the hydrophilicity or fortifying the hydrogen bond formation between the organic pollutant and MNPs. Thereby, aging process improves the adsorption affinity for the organic contaminants [75].

The aging process also affects the adsorption behavior of pesticides on the MNPs. For instance, the adsorption of four different pesticides, including MAL, CBD, DFZ, and DIF, was investigated on pristine and aged PE-MPs. Aged PE-MPs showed much better adsorption of these pesticides as compared to the pristine PE-MPs due to an increase in the number of adsorption sites, and cracks appeared on the surface of the aged PE-MPs [45]. Photoaging of MNPs also plays a crucial role in the adsorption of pesticides. In the photo-aging process, sunlight irradiation changes the structure of the polymer and significantly alters the physio-chemical properties of the MNPs. The aging process considerably alters the intrinsic charge on the surface of MNPs and affects their adsorption capacities. The aging process increases the SSA of MNPs, improves crystallinity, and boosts negative surface charge on aged MNPs [76]. Liu, et al. [26] investigated the adsorption mechanism of IMI pesticide on biodegradable polylactic acid (PLA) MPs exposed to ultraviolet irradiation. During photo-aging process, oxygen containing functional groups present on the surface of aged biodegradable PLA-MPs were broken down into smaller fragments and adsorption of IMI pesticide onto PLA-MPs enhanced after effective photo-aging. Similarly, Wang, et al. [77] studied the adsorption behavior of aged and pristine MPs. Target MPs such as PP, PE and PS along with their corresponding aged MPs were tested for the adsorption of atrazine (ATZ). Aged MPs showed much better adsorption for ATZ (aged PE 0.940 mg/g, aged PP 0.677 mg/g, and aged PS 0.663 mg/g) than the pristine (PS 0.565 mg/g, PE 0.535 mg/g and PP 0.410 mg/g) **(Fig. 2e)**. **Figure 2f** depicts the pertinent outcomes of the intraparticle diffusion model of various phases of ATZ adsorption on MPs. In addition to surface interactions, intraparticle diffusion seems to have contributed to the rate-controlling mechanism for the adsorption of ATZ on MPs [77, 78]. Similarly, in another study, Langmuir and Freundlich isotherms confirmed that the aged pellets of different MPs such as low-density polyethylene (LDPE), polyvinyl chloride (PVC), PP, polyamide (PA, N6), PS and polyethylene terephthalate (PET) showed tremendous potential for the adsorption of endrin and endosulfan (α + β) insecticides [79]. Microbial-mediated aged MPs also showed tremendous potential in adsorption of pesticides. Microbial aging process fabricated new pores/cracks and cavities on the surface of PLA-MPs, which lead to the improved adsorption of the ATZ, microbial aging process forms microbial film that resulted in the agglomeration of PLA-MPs particles further facilitating the adsorption of ATZ [47]. Hence, it is concluded from the above-mentioned studies that aging of MNPs improves their adsorption affinity towards pesticides.

4.3 Polymer crystallinity

On the basis of crystallinity, plastic polymers are classified into three categories, including crystalline, semi-crystalline, and amorphous forms [61]. A crystalline form of MPs has ordered structure where polymeric molecules are organized in regular pattern [80]. Crystalline polymer regions are commonly expressed as volume and mass fractions [81, 82]. A symmetrical, fixed, and ordered carbon chain defines a higher degree of crystallinity, which restricts the movement of organic compounds as it requires high energy for movement, thus resulting in decreased adsorption of organic compounds. Whereas in the amorphous region of MPs, a more disordered carbon chain is observed, this disorderliness in an important carbon chain allows the free movement of organic compounds, creating more free volume for adsorption [83]. The adsorption of polychlorinated biphenyls (PCBs), and OCPs (BHC alpha isomer, endosulfan, lindane, DDD, methoxychlor, chlorpyrifos (CPF), hexachlorobenzene, mirex, heptachlor, heptachlor epoxide, endrin, cis-nonachlor, cis-chlordane, trans-chlordane, trans-nonachlor, DDT, dichlorodiphenyldichloroethylene (DDE), Dieldrin, Aldrin) onto six MPs including PET, high density polyethylene (HDPE), PVC, LDPE, PP, and PS was investigated. Highest adsorption of these OCPs and PCBs was observed in PVC as it presented higher surface area and lower level of crystallinity in its polymer due to lack of weathering [84].

Chain configuration, glass transition temperature (Tg), and complexity of the polymer alter the crystallinity of MPs. Plastic polymers having a Tg value below the ambient temperature are referred to as rubbery polymers, while polymers having a Tg value higher than the ambient temperature are referred to as glassy polymers. Molecular linkage between the glass polymer is usually dense, which obstructs the movement of organic compounds, whereas movement of organic compounds is relatively easy in rubbery polymers as they have free volume due to inner cavities, which upgrade the adsorption. Adsorption of ATZ along with other four organic compounds was investigated on three polar MPs such as polyurethane (PU), polycaprolactone (PCL), polybutylene succinate (PBS), and nonpolar PS-MPs. Results indicated that the adsorption of all five organic compounds, including ATZ, by polar MPs was two times higher than that of nonpolar PS-MPs. Higher adsorption by the polar MPs, including PU, PBS, and PCL, was dominated due to the rubbery domain of the polar MPs [61]. Similarly, biodegradable MPs, including PBS and PLA, showed tremendous potential for the adsorption of fipronil pesticide, compared to the adsorption on non-biodegradable MPs such as PS, PE, PP, and PVC. Surface functional groups and the spatial organization of the rubbery domain in biodegradable MPs played a vital role in the adsorption of fipronil [85]. PE, being a rubbery plastic polymer with a low level of crystallinity, showed extensive adsorption potential for two OCPs such as DDT and HCH. Internally, PE-MPs possess a huge area of amorphous zone that supplies more SSA for the adsorption of DDTs and HCHs [48].

4.4 Effect of temperature

Temperature significantly alters the interaction between organic compounds and MNPs. A change in temperature affects the solubility of organic compounds and the surface tension of the medium [86]. Organic compounds adsorb easily on MNPs under certain low temperatures due to an increase in surface tension and a decline in the solubility of organic compounds. Adsorption rate of organic pollutants decreases with increase in temperature [87]. A decrease in temperature from 20°C to 4°C favors the adsorption of CPF pesticides on PAN6 (a petroleum-based polymer) and polyhydroxybutyrate (PHB) (biopolymer). This result is attributed to the decrease in temperature, which further decreases the solubility of CPF in water. On average, 90% adsorption of α-endosulfan pesticide on PAN6 was observed at 4°C, while it reduced to only 50% at 20°C [88]. On the contrary, some thermodynamic studies suggest that higher temperatures are conducive to the adsorption of pesticides. Li, et al. [70] reported that increasing temperature (278 K, 288 K, 298 K) favor the adsorption of IMI, BUP and DFZ on PE-MNPs. It indicates that the adsorption was spontaneous and endothermic. Similarly, the adsorption of four pesticides (CBD, DIP, DIF, MAL, and DFZ) on PE-MPs also increases with the increase in temperature from 298K to 318K [63]. The adsorption behavior of another four pesticides, including CBD, DIF, MAL, and DFZ, on pristine and aged PE-MPs was investigated. Both pristine PE-MPs and aged PE-MPs spontaneously adsorbed these pesticides. This study also concluded that the adsorption was an endothermic process and that increases in temperatures (298K, 308K, and 318K) improved pesticides' adsorption [45].

4.5 Effect of pH

In adsorption studies, pH plays a very crucial role as it alters various chemical and biological reactions. Changing pH affects the adsorption of organic pollutants on MNPs. Increasing pH causes the dissociation of dissociable organic contaminants, resulting in the subsequent generation of hydrophilic substances, which stimulate the electrostatic repulsion between the organic contaminants and MNPs as a result of the decline in the hydrophobic effect. Wang, et al. [68] reported that the adsorption of CBD and DIP on PE-MPs decreases as a result of subsequent rise in range of pH from 3 to 6. Maximum adsorption of MAL was also observed at pH 4. Whereas, the adsorption of DIF and DFZ initially increases with the increase in pH, albeit it keeps stable with a continued increase in pH. Most pesticides are ionic in nature, and the ionization constants (pKa) of these pesticides usually differ from each other due to their important functional groups. That is why pesticides' behavior in an environment is strongly influenced by the changing pH [89]. Lan, et al. [45] reported that the adsorption of DFZ on positively charged PE-MPs increased due to the electrostatic attraction between MPs and pesticide as pKa value of DFZ was 2.94. Whereas maximum adsorption of DIF, CBD, and MAL were not observed at 6 pH, the values of pKa were 8.6, 6.8, and 4.2 for DIF, MAL, and CBD, respectively. It indicates that the change in pH is determined by the change in the properties of pesticides instead of the surface properties of MNPs. A lower level of pH (5.95) favored the maximum adsorption of α-endosulfan pesticide on 6 different MPs, including polyethylene-co-vinyl acetate (PEVA), LDPE, PEVA6, unplasticized PVC, PP, and PS-MPs granules [90]. The adsorption capacity of pesticides is affected by electrostatic interactions under acidic conditions (i.e., low pH), while in alkaline conditions, adsorption is primarily simulated by the hydrophobic interactions. Jiang, et al. [91] stated that the rise in pH from 7 to upward reduces the electrostatic interaction and boost up the hydrophobic interaction between the butachlor (BUT) pesticide and three different MPs including PP, PVC and PE.

4.6 Effect of dissolved organic matter

Dissolved organic matter (DOM) widely participates in all important biogeochemical cycles of the terrestrial and aquatic environment as it has a variety of functional groups on its surface [92]. They show powerful interactions with MNPs to change their mobility and characteristics. DOM interacts with MNPs through hydrophobic interaction and complexation, thereby affecting the adsorption ability of MNPs. They also compete with organic pollutants for sorption site [93, 94]. They also influence the migration of pesticides in the natural environment [3] and inhibit the adsorption of pesticides by MNPs. For instance, the presence of DOM in the form of humic acid (HA) and oxalic acid declined the adsorption of FLU pesticides from 35.02–48.67% on PS-MPs and from 15.99–32.00% on PE-MPs. Whereas, the adsorption capacity of PS and PE for binary pesticides system (FLU + EPO) decreased by 44.36–51.35% and 36.13–37.93%, respectively [69]. Similarly, the presence of glycine and oxalic acid decreases the adsorption of two pesticides, CBD and CBF on PP and PE by 7.25%–24.29% and 19.27–48.02%, respectively. The effect of DOM on CBD was slightly lower than that on CBF, as CBD shows much stronger bonding with these MPs. Fast rate of CBD adsorption indicated powerful interaction while much higher adsorption capability meant ample binding sites [67]. The adsorption capacity of ATZ on PP-MPs was reduced from 0.41 mg/g to 0.23 mg/g with the addition of HA (10 mg/L). This decline in the adsorption of ATZ was attributed to the competitive behavior of both HA and ATZ for binding sites [77]. HA sometime acts as a bridge for the vital interaction between the MPs and the organic pollutants. After adsorbing on the surface of MPs, HA forms complexes with these organic pollutants [95]. Increasing the concentration of HA from 0-10 mg/L decreases the adsorption of thiacloprid (THIA) pesticides on microfibers and pristine MPs. While increasing the concentration of HA from 25-50 mg/L increases the adsorption of THIA. A significant decrease in the adsorption of THIA was observed due to the competitive behavior between HA and THIA for the adsorption sites. Whereas, a higher adsorption of THIA was observed at a higher level of HA (50 mg/L). The higher adsorption of THIA was mainly attributed to the bridging effect of HA between the THIA and MPs [96].

4.7 Effect of salinity and ionic strength

Salt ions and different organic pollutants also compete with each other for adsorption sites, thereby decreasing the adsorption of organic pollutants on MNPs. The addition of NaCl (0–100 mg/L) significantly reduces the adsorption of S-metolachlor (S-MET) by three different MPs, including PP, PVC, and PE. PVC showed the highest adsorption capacity for S-MET under the interference of exogenously applied sodium chloride (NaCl). While the adsorption capacity of PE and PP considerably decreases with the increasing concentration of salt ions and displays clues of recovery in later stages, it declines again when the salt concentration reaches its maximum level [97]. The addition of NaCl (0.5%) significantly improved the adsorption of EPO and FLU on PE and PS-MPs, whereas, 2% and 3.5% of NaCl significantly ($p < 0.05$) reduced the adsorption of both pesticides on MPs [69]. The main phenomenon behind the improved adsorption is the "salting out" effect, which means that the existence of salt ions improves the hydrophobic adsorption of organic pollutants on MNPs as the solubility of organic compounds decreases in water medium. Whereas, when ionic strength reaches a certain level, it may accelerate the decomposition of organic compounds, eventually leading to a decline in the overall concentration of organic compounds and, hence, a decrease in their adsorption onto MNPs. An increase in salinity (NaCl) from 0.01-0.4M decreases the adsorption of tebuconazole (TEB) by 26% and 44% onto PP-MPs and PS-MPs, respectively. In contrast to this, the adsorption of TEB on PA-MPs slightly improves (10%) with the increase in salinity. An increase in salinity reduces the electrostatic repulsion among MPs and TEB, which could be a possible reason to improve the adsorption on MPs [98].

5. Eco-toxicological implications of MNPs and pesticides

MNPs and pesticides undergo bioaccumulation in aquatic and terrestrial organisms and can cause multifaceted impacts, including growth and reproduction impairments, oxidative stress, altered genetic and enzymatic responses, metabolism abnormalities, multigenerational effects, histopathological modifications, and neurotoxicity, hepatotoxicity, among others **(Fig. 4)**. A summary of recent studies highlighting the combined toxicological impacts of pesticides and MNPs in freshwater, marine water, and terrestrial organisms is given in **Table S2**.

5.1 Freshwater organisms

Freshwater ecosystems are perceived as non-negligible source of plastic pollution [11]. There are rising concerns regarding the toxic impacts of co-exposure to MNPs and pesticides on different freshwater organisms. Previously, several freshwater organisms like zebrafish, common carp, crustaceans, tadpoles, and diatoms have been studied for the potential toxic impacts of MNPs and pesticides (Table S2). Although relevant studies on freshwater organisms are scarce, relatively more studies have been conducted using zebrafish. For instance, Varshney, et al. [99] reported the elevated bioaccumulation of PS-NPs in terms of their fluorescence in the ocular, pericardium, gastrointestinal, and cranial regions of zebrafish exposed to PS-NPs and DDE mixtures, compared to control and individual NPs and DDE exposure groups **(Fig. 5a)**. This study further found 1915 significant differentially expressed genes (DEGs) (downregulated: 1263; upregulated: 652) in zebrafish after exposure to NPs + DDE through RNA sequencing analyses. Moreover, a significant reduction in velocity, distance traveled and movement of larvae was observed as result of DDE+PS-NPs and DDE exposures. Chen, et al. [100] also found that MPs can produce behavioral abnormalities in zebrafish such as hyperactive swimming at the concentration that other toxicological end points may not produce. However, MNPs have the ability to reduce the bioaccumulation of various organic pollutants and demonstrate the suppressing effect. For instance, PS-MPs declined the bioaccumulation of DFZ inside zebrafish, decreased the oxidative stress and specific changes occurs in the gene expression owing to the exposure of DFZ (Li et al. 2022a). These studies exhibited that the interaction between the MNPs and other pollutants makes it very precarious to understand their joint toxicity to aquatic organisms.

Induction of oxidative stress is one of the basic mechanisms responsible for the elevated toxicity mediated by MNP and pesticide exposure. Luo, et al. [101] revealed that the combined exposure to IMD (100 μg/L) and PS-MPs (20 μg/L) for 2-days significantly suppressed the growth of zebrafish by altering the biochemical parameters related to oxidative stress and the level of glycolipid metabolism. Even at these low levels, both IMD and PS-MPs induced considerable hepatotoxicity in zebrafish particularly in terms of gene transcription. Similarly, Nogueira, et al. [102] reported a higher level of fluorescence associated with the elevated ROS levels in terms of toxic units in *D. magna*, exposed to glyphosate (Gly) and PS-NP individually and in mixture, compared to the control group **(Fig. 5b)**. The multigenerational studies showed that the presence of MNPs and organic pollutants including pesticides can cause significant decline in the survival rate, hinder maternal health, reduce nutritional status, cause abnormal ovarian development and lower the reproduction in aquatic organisms [2]. For instance, the parental exposure (F0) to PS-NPs and Gly mixture generates defects in the reproduction parameters in F1 and F2 generation in *D. magna*, compared to individual exposure [102]. Similarly, Zocchi and Sommaruga [103] observed a significant increase in the mortality of *D. magna* after combined exposure to Gly and PE-MPs or PA-MPs. Similarly, life history traits including mortality, number of neonates, number of broods and longevity in *D. magna* were considerably altered after combined exposure to MPs and insecticide deltamethrin (DM), compared to their respective single exposures [104]. These detrimental impacts significantly weakened the defense mechanisms in daphnid colonies, which are at the base of the aquatic food chain. On the other hand, Duong [105] found that the acute exposure to methoxychlor increased mortality and induced significant changes in the locomotive ability of *D. magna*, whereas the binary mixture of methoxychlor and MPs displayed a distinctive response, where impacts on mobility and mortality were deferred. The perceived effect proposes that MPs act as defense vectors for pesticides, reducing the influence vulnerable species may experience as a result of subsequent exposure.

Exposure to both MNPs and pesticides can directly affect reproduction and offspring growth. For example, Nugnes, et al. [106] reported that the seven days exposure to PS-MPs and insecticide IMD mixture causes a significant inhibition in the reproduction, as well as DNA damage induction in *Ceriodaphnia dubia*. Chen, et al. [107] studied the impact of long-term exposure (60 days) to PE-MPs with Gly pesticide on common crap (*Cyprinus carpio L.*) and found massive decline in mRNA expression of tight junction genes (*ZO-1*, *claudin-2* and *occludin*) in brain. This binary mixture provoked the micro-biome modification in gut of the freshwater common carp. Lajmanovich, et al. [108] conducted a study to examine the toxicity of PE-MPs along with two different herbicides like Gly based herbicides (GBH) and glufosinate ammonium based herbicide (GABH) to determine the realist contamination of these xenobiotic on freshwater anuran tadpole at 48 hours experimental assay, and reported that, at the exposed tadpoles exhibited significant alteration in the enzyme biomarker, reducing the activities of important enzymes including carboxylesterase (CbE) and acetylcholinesterase (AChE). In contrast, coexistence of MNPs with organic pollutants like pesticides can reduce their toxicity as well. For example, Hao, et al. [109] found that the adsorption behavior of PS-MPs to diuron pesticide alleviated the intracellular damage induce by the diuron to the freshwater diatom *Cyclotella meneghiniana*, whereas, diuron eased the physical damaged induced by the PS-MPs to the *Cyclotella sp*. Likewise, studies on histopathological modifications, bioaccumulation of organic pollutants and neurotoxicity to MNPs and pesticides exposure in freshwater organisms are comparatively scarce and need further experimentation.

5.2 Marine organisms

Recently, different studies have shown MNPs pollution is extensively widespread in marine environment [7, 110]. They are considered emerging threats to marine organisms because they can be ingested and accumulated by marine organisms through different trophic levels [111]. MNPs and pesticides are commonly found in marine environments globally. Combining exposure to MNPs and pesticides induces eco-toxicological effects on the physiology and behavior of marine organisms. Bringer, et al. [112] assessed the effects of sub-chronic exposure to chlortoluron alone or in combination with HDPE- MPs on the growth and valve activities in the Pacific oyster *Crassostrea gigas* in a 24-day experiment. HDPE-MPs alone or in combination with chlortoluron considerably affected the shell growth and valve activities in tested bivalve. Similarly. Bellas and Gil Luna [113] also observed a sharp decline in the growth of marine copepod *Acartia tonsa* under combined exposure to PE-MPs and CPF. A rapid decline of 60% was detected in survival rate after 24 hours of exposure at lethal concentration of (LC50) 0.1 µg/L, whereas zero survival was observed after 48 hours of exposure at similar concentration.

The harmful toxicological impacts of MNPs and other organic pollutants start with the ingestion of MNPs by marine organisms. Dietary exposure to MNPs along with other contaminants negatively affects the growth and development of marine organisms. Rios-Fuster, et al. [114] reported that the co-exposure to LDPE-MPs enriched diet for fish with OCPs and PCBs significantly enhanced the toxicity in juvenile gilthead seabream *Sparus aurata* and the toxic effects of these pollutants were more pronounced in liver than in the muscle of *S. aurata*. Similarly, juvenile sea bass *Dicentrarchus labrax* were fed with feeds having PP-MPs either virgin or polluted with other contaminants such as CPF, DDE and benzophenone-3 (BP-3) for 60 days. A synergistic action of chemical pollutants and PP-MPs generated an inflammatory like effect in the distal intestine via up-regulation of *tnf-α* and cytokine *il-6* expressions. This raises concern regarding the function of MPs in the bio-magnification and bioaccumulation of these contaminants, which could in turn induce negative impact on intestinal microbiota in fish (Montero, et al. [115]. Ingestion of MNPs can either directly cause lethal effects or mortality or sub lethal effects through inducing injuries or variations in the composition and diversity of intestinal microbiota [116].

MNPs and OCPs are greater inhibitors of enzymatic activities in marine organisms. Inhibition of cholinesterase (ChE) enzymatic activity is widely recognized as a toxicity biomarker for MNPs and pesticides. For instance, Albendín, et al. [117] observed that ChE activity was significantly declined in invertebrate *Artemia salina* by the co-exposure of PVC-MPs and CPF pesticides. Inhibition of ChE causes obstruction of neuronal function and AChE dissolves into acetic acid and choline, which are vital for the proper functioning of the nervous system. Another study by Albendín, et al. [118] reported that the exposure to MPs and CPF pesticides significantly inhibited ChE activity in mussels and head tissues of *Solea senegalensis*. Results revealed that inhibition of ChE activity led to the obstruction of neurotransmitters, ultimately affecting nerve function. The combined exposure to pesticides and MPs disturbs the activities of antioxidant enzymes as biomarkers of external stress. For instance, Hanachi, et al. [119] also found a substantial reduction in catalase (CAT) and glutathione peroxidase (GPx) activities in rainbow trout *Oncorhynchus mykiss*, under combined exposure to MPs and CPF for 96 hours. In another study, Hanachi, et al. [120] studied that the combined exposure to PE-MPs and CPF significantly decreases the nutritional parameters (protein content, composition of fatty acids and amino acids) in rainbow trout. The combined application of PE-MPs and CPF causes physical micro injuries on the gut wall and leads to disturbances in amino acid and fatty acids synthesis.

Toxicological interactions between MNPs and pesticides suggest that MNPs can easily alter the bioavailability of pesticides. Similarly, CPF showed toxicological impacts on *A. tonsa* [113] and *O. mykiss* [120], which were considerably enhanced in the presence of MPs, and demonstrated that the bioavailability of CPF increased in the existence of MPs. Likewise, much higher bioaccumulation of MPs along with MAL in tissues of fiddler crab *Minuca ecuadoriensis* resulted in a significant high mortality (80%) through synergistic effects [121]. Similarly, Villegas, et al. [122] also reported a higher bioaccumulation of MPs in combination with MAL and ethyl-parathion pesticides in two different species of fiddler crabs including *Leptuca festae* and *Minuca ecuadoriensis*. The highest bioaccumulation was observed in gill tissues, followed by the digestive tract and the hepatopancreas.

Histopathological alteration has also been reported by different studies during the past few years in fish tissues as a biomarker to measure the consequences of MNPs and chemical exposures. For instance, the application of CPF alone or in combination with PS-MPs showed enormous histopathological alterations such as necrosis and infiltration of inflammatory cells in rainbow trout [123]. It is a widely accepted phenomenon that the combined exposure to MNPs and organic pollutants triggers greater biological and physiological alteration than that induced by the stressor alone. Fernández, et al. [124] found that the combined exposure of HDPE-MPs and CPF causes an extreme reduction of physiological parameters like absorption rate (AR), respiration rate (RR), clearance rate (CR), scope for growth (SFG), commencement of bacterial activities and reduction of peroxidase activity in marine mussels *Mytilus galloprovincialis*. Conversely, Hao, et al. [109] observed an antagonistic phenomenon during the combined exposure of PS-MPs and diuron pesticide on marine diatom *Skeletonema costatum*. Individual exposure of both these stressors causes significant inhibition in the growth *Skeletonema sp*, while their combined exposures affect their respective toxicities, as MNPs reduced the intracellular damage induce by the diuron and diuron alleviated the physical damage produced by the PS-MPs to *Skeletonema sp*. Burić, et al. [125] addressed the effect of two MPs including PS-MPs and polymethylmethacrylate (PMMA) MPs along with cypermethrin insecticide on sea urchin *Arbacia lixula*. Combined exposure led to developmental abnormalities, damage to the zygote, skeletal abnormalities, and the deaths of a significant number of larvae. Consequently, it must be stated that the consequences of combined exposure to MNPs and pesticides on marine creatures of varying tropic levels are still in their infancy, are mostly unknown, and that further research is needed. Similarly, the inner mechanisms of action and adverse outcome pathways of these xenobiotics on marine megafauna (dolphins, whales, sharks, rays, and seals) are largely unclear, and further research is needed.

5.3 Effect on terrestrial organisms

A number of recent studies have shown the potential impacts of MPs [126, 127] and pesticides [128] pollution on terrestrial ecosystem. MNPs and pesticides interact with terrestrial organisms such as fungi, terrestrial invertebrates, pollinators, and animals to regulate crucial ecosystem functions and services. MNPs in soil interact with different pesticides that are used to protect plants and improve yield. Most of the studies carried out with the combined exposure of pesticides and MNPs are on aquatic ecosystems; only a few studies address their combined effects on terrestrial organisms. Earthworms are among the most commonly used model organisms in studies on the terrestrial environment, and the effects of MNPs and pesticides on earthworms are relatively better studied. Recently, Ju, et al. [129] stated that combined exposure to CPF and LDPE-MPs exhibited much stronger impacts on the growth and survival of common earthworms *Lumbricus terrestris*. More recently, Fu, et al. [130] reported that combined exposure to PE-MPs and IMI displayed significant inhibition in the growth and subsequent weight loss of earthworms, compared to that of PE-MPs and IMI single exposures. These results might be attributed to the inhibitory effect of IMI on the growth and feeding behavior of earthworms, and to the ingestion of MPs by earthworms in a concentration that may restrict the intake of food and ultimately inhibit the growth of the earthworm [131].

Similarly, Eisenia fetida earthworms tend to ingest higher concentrations of PE-MPs and tris (2-chloroethyl) phosphate (TCEP), resulting in stunted growth and high weight loss [132]. When *E. fetida* was exposed for 14 days to soil containing LDPE-MPs and CPF contaminants, a significant decline in the activity of AChE enzymes was observed. This study further suggests that the concentration of LDPE-MPs (5 mm) and CPF (9 mg/kg) released into the soil was sufficient to induce a neurological disturbance in *E. fetida* [133]. Cheng, et al. [134] discovered that the combined exposure to LDPE-MPs and ATZ for 28 days induces DNA impairments in *E. fetida*. The co-exposure further caused oxidative stress in terms of excessive generation of reactive oxygen species (ROS), a substantially decrease in the activities of important antioxidant enzymes including superoxide dismutase (SOD), glutathione S-transferase (GST) and catalase (CAT) and a considerably increase the level of 8-hydroxydeoxyguanosine (8-OHdG). Baihetiyaer, et al. [135] also found a considerable increase in the oxidative stress and alteration of the genetic expression of *annexin* (ANN) and *HSP70* genes in *E. fetida* under combined exposure to PLA-MPs and IMI. Similarly, combined exposure of environmental MPs and 2,4 dichloro-phenoxy-acetic acid (2-4-D) herbicide induce oxidative stress in earthworm (*Eisenia andre*i). MPs boost up the bioaccumulation of 2-4-D herbicide in earthworm, which disturbs the lysosomal membrane stability (LMS) and induces severe oxidative stress. In addition, after 14 days of exposure, MPs were detected in the tissues of worms treated with single MPs and MPs and 2,4-D mixture, but not in those exposed to individual 2,4-D or the control group [136] **(Fig. 5c)**.

The size and concentration of MNPs and pesticides are very important features when dealing with the toxicological implications of both MNPs and pesticides on terrestrial animals. For instance, *Caenorhabtidis elegans* were used as a target organism by Martín, et al. [137] to assess the impacts of simazine (herbicide) together with PE microbeads (250–300 μm). *C. elegans* could not ingest MPs due to their large size and insignificant effects were observed on *C. elegans* toxicological endpoints until the concentration of simazine was enhanced up to 15 μM. Li, et al. [138] exposed *C. elegans* PS-NPs and two OCPs (chlordane and HCH) and found that the single exposure to PS-NPs at 1.0 mg/L did not show any influence on rate of survival, while joint exposure with chlordane and HCH showed tremendous reduction in survival, body length and life span of *C elegans*. These results indicate the inhibitory effects of PS-NPs and OCPs on the growth and development of nematodes. On the other hand, Fajardo, et al. [139] studied the impact of co-presence of three different formulation of PE-MPs and simazine (herbicides) on *C. elegans* and after successful incubation of 30 days, authors did not observe any impact on toxicological endpoints including growth, survival and reproduction.

Terrestrial arthropods *Porcellio scaber* showed tremendous disturbance in haemocyte count as a result of a significant decline in the activity of AChE, when MPs (polyester and crumb rubber) and CPF were concurrently present. A significant reduction in the total haemocyte count was discovered with the exposure of the maximum concentration (2.0 mg/kg) of CPF [140]. On the other hand, Selonen, et al. [141] evaluated the impact of CPF along with tire particles and polyester fibers, not only on *P. scaber* but also on springtail *Folsomia candida*. No or zero effects on survival were detected with polyester fibers, however the tire particles treatment greatly altered the toxicity of CPF and led to the subsequent reduced in mortality of F. candida and *P. scaber*. MPs impacted the CPF induced suppression of AChE activity. CPF is the largest inhibitor of AChE activity. The decline in its inhibition suggests a lower existing concentration of inhibitor. The capability of MNPs to store the pesticides appears to be highly significant since it governs the bioavailability of pollutants for organisms at various tropic levels.

Gut microbiota is the key target of MNPs and pesticides as reported in different studies [142, 143]. Sun, et al. [144] investigated that the mice exposed to EPO experienced massive impairment in the intestinal barrier as EPO significantly affected the gut microbiota and paved the way for the enormous invasion of PS-MPs, which in turn PS-MPs altered the ability of the liver to metabolize EPO. Thus, this increased accumulation leads to oxidative stress, tissue damage and different metabolic disorders in the kidney and liver. Similarly, Meng, et al. [145] also reported a massive dysbiosis of gut microbiota in mice upon exposure to azoxystrobin (AZO). Further investigations on different organisms in the terrestrial ecosystem are required to explore the metabolic disorders that occurred as a result of disturbances in the gut microbiota. Finally, urgent research is needed to investigate the distribution of MNPs and pesticides in the terrestrial environment. It is also crucial to examine how combined exposure to MNPs and pesticides interrupts physiologically essential functions. Further investigation should include different communities from terrestrial ecosystems, like ecotoxicological models like plants, birds, rodents, microbial assemblages, and other organisms of a higher tropic level in the food chain.

6. Research gaps and future perspectives

The co-occurrence, fate, and toxicological impacts of pesticides and MNPs in aquatic and terrestrial organisms have been highlighted in a limited number of studies so far. More precise and wide-ranging research work focusing on these features can deliver better insight into the ongoing scenario regarding the bioaccumulation, biomagnification, and transport of both pesticides and MNPs in living organisms. Since the available studies are limited to a very few types of the most commonly used pesticides and MNPs, more studies are needed to investigate the combined eco-toxicological impacts of pesticides and MNPs associated with diverse MNP characteristics (particle size, surface area, shape, dose), pesticide properties (ionic properties, hydrophobicity), and some other environmental factors (temperature, pH, ionic strength). So, to have a brief understanding of the eco-toxicological implications of pesticides and MNPs in the environment, the following research gaps should be carefully considered, and some extra efforts are required.

1) Adsorption of pesticides onto MNPs required a complete and comprehensive investigation as their imperative interactions are strongly influenced by environmental factors. MNP characteristics (such as polymers: PS, PP, PE, and PVC; shapers: fiber, sphere, and pellet; types: primary vs. secondary MPs, among others) chemical properties of pesticides, contact time, and environmental conditions all significantly modify the availability and transport of pesticides and MNPs and the effectiveness of their interactions. A lot of adsorption experiments have already been performed under controlled laboratory conditions, while adsorption of pesticides by MNPs under natural conditions is complex and needs comprehensive examination. Potential impacts of MNPs and pesticides on aquatic and terrestrial organisms at environmentally realistic concentrations of MNPs along with pesticides and other contaminants are desired to draw a firm conclusion.
2) This review revealed that a very limited amount of data is available regarding the co-occurrence of MNPs and pesticides in the environment, so a significant research gap is still available for the estimation of the co-occurrence of MNPs and pesticides in different geographical areas and several environmental components, including air, water, and terrestrial ecosystems. Concentration and abundance of MNPs and pesticides in lakes, rivers, estuaries, wetlands, etc. are dynamic and depend upon the prevailing meteorological, hydrological, and topographical properties. Thus, long-term monitoring is desired for beneficial modeling of MNPs and other contaminants.
3) A very limited amount of data is available regarding the formation of MNP-associated biofilms and their potential impact during the interaction of

pesticides with MNPs. Plastic biofilms may not only intensify the uptake of pesticides and other pollutants but also boost or decrease their combined toxicity. The formation of biofilms and their characteristics could be an attention-grabbing research subject that requires more investigation in this field.

4) MNP and pesticide contamination is a common issue when it comes to beverages, food items, and fodder crops (exposed to pesticides); therefore, more evident and profound insight research is needed to be performed to list out the food items under threat of chemical contamination. It is equally important to figure out the concerns associated with the biomagnification and bioaccumulation of pesticides and MNPs via the food chain.
5) Biodegradable and aged MPs have displayed much better vector characteristics than the non-biodegradable ones. New research is required to address the adsorption behavior of pesticides on biodegradable MNPs and their associated toxicity.
6) Smaller plastics lead to bigger problems. Various chemical and physical characteristics of a diverse range of plastic pollution, like macroplastics, MPs, and NPs, will eventually result in deviating hazards and fates in the environment. Quantifiable data are quite inadequate owing to the analytical complications involved in identifying NPs in multifaceted matrices. Therefore, systematic studies to apprehend the transport, fate, and biological interactions of NPs with pesticides and other pollutants are limited. Additional exploration with this topic may display how nano-scale interactions vary from micro-scale interactions and change toxicity.
7) Although different studies have been performed, there is deficient evidence

available concerning the combined toxicological implications of MNPs and pesticides on higher-trophic level organisms such as fish, reptiles, birds, mammals, and amphibians inhabiting aquatic and terrestrial environments. Multigenerational and multidimensional research studies are required to study the impacts of these contaminants on organisms of different trophic levels.

8) In typical environmental conditions, MNPs of different sizes and shapes can be found in the water column, where they can absorb different types of pollutants before organisms feed on them. Consequently, additional studies are desired to evaluate the dose-dependent biological impacts of MNPs alone and when combined with other pollutants, such as pesticides, as MNPs act as a vector that could improve the effect of other pollutants.

7. Conclusion

Contamination of both aquatic and terrestrial environments with MNPs is likely to persist owing to the continual growth of plastic production and consumption. MNPs have obtained mounting research consideration during the past few years. Research has added a significant understanding of the transformation, transport, fate, and environmental impact of MNPs. MNPs have the ability to accumulate a diverse range of hazardous pollutants, including antibiotics, pharmaceuticals, pesticides, and other organic contaminants. This review has focused on field investigations and experimental research on the occurrence, adsorption, and combined toxicity of pesticides with MNPs. The presence of pesticides alongside MNPs is a concern of great public interest owing to their drastic risks to the environment and health of all living systems. Interaction between pesticides and MNPs is dominated by the adsorption mechanisms that transform their combined toxicity, change their environmental behavior, and induce subsequent ecological risk. Furthermore, the adsorption of pesticides onto MNPs favors the concentration of plastic additives and associated chemicals, and this phenomenon further increases the environmental risk of MNP contamination. Co-contamination of pesticides with MNPs induces hazardous impacts to both aquatic and terrestrial organisms and even threatens human health via the food chain. Persistent, precarious estimation and knowledge propagation linked with the risk of pesticide and MNP contamination are indispensable, specifically since the problem is mounting and will continue for a long period of time.

CRediT authorship contribution statement

Muhammad Junaid: Conceptualization, methodology, data mining, analysis, and writing original draft. **Zohaib Abbas:** Conceptualization, methodology, data mining, analysis, and writing original draft. **Junaid Ali Siddiqui:** Data mining, analysis, writing and review. **Shulin Liu:** Data mining, analysis, writing and review. **Shamas Tabraiz:** writing and review. **Qiang Yue:** Data mining, analysis, writing and review. **Jun Wang:** Supervision, conceptualization, funding, writing, review, and revise.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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