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Review

Trojan horse effects of microplastics: A mini-review about their role as a vector of organic and inorganic compounds in several matrices

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Abstract: The "Trojan horse effect" of microplastics for organic and inorganic contaminants is an interesting topic. So far, the scientific community has focused on microplastics strictly as contaminants, but their role as vectors is still undefined. Adsorption of pollutants follows the Freundlich model by physisorption mechanism. Furthermore, ages and types of microplastics influence the adsorption of pollutants onto microplastics. Moreover, natural particles, like algae particles, present in the environment can interfere in the adsorption mechanisms. Due to their chemical composition of mainly O and N, it has been suggested that natural particles have a stronger adsorption affinity for some pollutants. Furthermore, microplastic's role as vector of pollutants into organisms is controversial. In fact, it has been suggested that the release is species-specific. In *T. japonicus*, accumulation of Hg loaded onto microplastics increased by 2.5 times, whereas a reduction of bioavailability of Hg was observed in *R. lens*.

Keywords: microplastics; vector; pollutants; heavy metals; polycyclic aromatic hydrocarbons; pesticides

1. Introduction

Due to their ubiquity, microplastics have been investigated in various terrestrial [1], marine [2] and atmospheric matrices [3,4]. However, scientific literature suggested the capacity of microplastics

to sorb and concentrate many organic and inorganic contaminants. Therefore, a long-range transport in the environment can be facilitated [5]. However, few studies have investigated their action as vectors [6]. For example, it has been proven that microplastics can adsorb dissolved metals and transfer them into living organisms [7]. Alongside heavy metals, persistent organic pollutants (POPs) are associated with microplastics. The strong hydrophobicity of microplastics enhance the retention of hydrophobic substances such as pesticides like DDT, dioxins, furans, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) [8], liposoluble pharmaceutical compounds like clindamycin and erythromycin [9] and perfluoroalkyl substances (PFASs) [10]. When microplastics act as a vector, they can strongly facilitate the bioaccumulation of microplastics through the food chain [11]. Some areas commonly considered as hotspots for plastic pollution, such as the Mediterranean Sea, can be particularly affected by the action of microplastics as vectors. Due to the limited exchange with other water masses, the widespread accumulation of microplastics can facilitate the accumulation of organic and inorganic compounds as well [12]. Adsorption of pollutants onto microplastics is strongly affected by the physicochemical properties of the microplastic. The chemical and physical characteristics of microplastic particles influence the behavior of contaminants in the environment. Diverse factors, including the properties of the sorbate, such as its partition coefficient, size and functional groups, and environmental conditions, such as pH, temperature, ionic strength and the presence of other compounds, can also impact the nature and behavior of this interaction [9]. The interaction between microplastic particles and adsorbed contaminants could also alter the behavior of microplastics in the environment. This could lead to a modification and, consequently, complication of the risks associated with the microplastic's occurrence in the environmental matrices, as suggested by Tumwesigye et al. [10].

However, the question of whether microplastics can be considered important vectors in the environment has been not clearly assessed. Currently, there are discrepancies among different research groups. For instance, Tumwesigye et al. [10] reported that in water systems, the presence of suspended organic materials is significantly more important compared to the action of microplastics as vectors. On the other hand, experimental evidence seemed to suggest that the action of microplastic particles is crucial due to the increased concentration of pollutants through adsorption on the surface of the microplastics [10]. The adsorbing activity of microplastics and their role as vectors for other pollution has been called the "Trojan horse effect" as they can potentially facilitate the entering of organic and inorganic pollutants into the environment [13].

This mini-literature-review aims to provide an umbrella summarization of knowledge to date, focusing on marine, terrestrial and atmospheric environments and the role of microplastics as vectors for heavy metals (HMs), polycyclic aromatic hydrocarbons (PAHs) and pesticides. This paper critically reviews the literature available to analyze the current status and provide future prospectives.

2. Materials and methods

A search on Scopus database using the keywords "Microplastics" AND "vector" AND "pollutants" AND "marine environment" resulted in 178 papers. Articles were screened by title and abstracts, and 133 papers were excluded. 44.4% of studies included were about heavy metals (HMs), 15.6% focused on polycyclic aromatic hydrocarbons (PAHs) and 4.4% were about pesticides. Papers that focused on other contaminant were not considered in this review. The detailed breakdown of the studies included is shown in Figure 1.

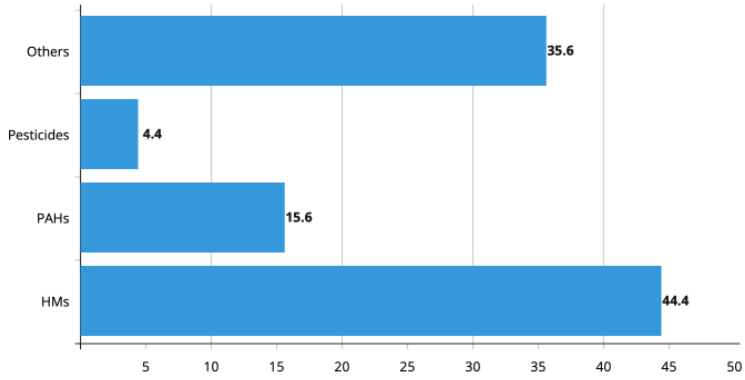

Figure 1. Percentage proportion of papers included by type of pollutants in marine ecosystem.

According to a search conducted on the Scopus database using the keywords "Microplastics", "vector", "pollutants" and "terrestrial environment", a total of 34 papers were found. After screening these papers based on their titles and abstracts, only 2 of them were focused on heavy metals (HMs) and pesticides in the soil, and thus were accepted for this review. The same approach in the research has also been used for the atmospheric environment. "Microplastics", "vector", "pollutants" and "atmospheric environment" have been used as keywords. This research yielded a total of 8 papers, but just one was accepted.

3. Results

3.1. Heavy metals associated with microplastics in marine environment

The high surface-area-to-volume ratio of microplastics serves as carriers of heavy metals and, consequently, increase their accumulation and toxicity in marine copepods [14]. A study by Bai et al. [14] experimentally evaluated the effects of micro-and nano-plastics in increasing the toxicity of mercury (Hg) in marine copepods *T. japonicus*. Briefly, 250 adult specimens of *T. japonicus* were exposed to 1 μg L^{-1} of microplastics and $HgCl_2$ dissolved in seawater prior to short-time exposure for 48 h at 22 °C. First, experimental results showed a gradual adsorption of Hg by polystyrene microplastics (size, 6 μm). Specifically, during the first 36 h, the adsorption rapidly increased and became gradual, reaching the equilibrium after 48 h. Regarding accumulation in *T. japonicus*, experimental evidence showed that the accumulation of Hg was raised by 2.48 times when microplastics were present. Likewise, short-time exposure of Hg and polystyrene microplastics aggravated the toxic effect of Hg, increasing the ROS levels. However, the interaction between Hg and microplastics seem to display species specificity [14]. For example, a work by Pinto et al. [15] reported that microplastics decrease the toxic effects on *Rhodomonas lens*, likely due to the reduction of the bioavailability of heavy metals [15]. Cell viability of *R. lens* was, in fact, seriously affected by exposure to mercury (Hg), where only 8% of cells showed viability compared to the control, i.e., no exposure. When exposed to Hg-loaded to microplastics, cell viability was less reduced, reaching 36% and 45% decreased compared to the control [15]. Likewise, heavy metals have been investigated in microplastics isolated from marine zooplankton from the Mediterranean Sea. Concentrations of heavy metals extracted from marine zooplankton's microplastics ranged from 0.020±0.0003 to

30±2.51 mg kg^{-1}, potentially meaning that heavy metals loaded to microplastics can leach inside the zooplankton body [16]. Furthermore, laboratory experiments seem to suggest that Mn, Zn, As, Cr, Cu, Pb and Ni have a significant release in gastrointestinal solutions, potentially due to the weak bond binding affinity of metal ions to naturally occurring metal-binding proteins in an acidic environment [17]. However, current knowledge is not sufficient to substantiate this hypothesis.

The mechanisms of adsorption of heavy metals onto microplastics has not yet been clearly understood. In a real-life context, environmental conditions strongly influence adsorption dynamics. Moreover, reproducing real-life environmental conditions in a laboratory setting is challenging. However, the adsorption mechanism approximately follows the Freundlich model. The Freundlich model showed that the intensity of the adsorption of Pb and Cu onto microplastics is physisorption. The physioabsorbent process involves a straightforward way of transferring elements. Microplastics will form a thin layer on their surface by weakly bonding with Pb and Cu. Therefore, release into an aquatic environment system can easily occur [18].

It has been reported that natural particles in the marine ecosystems play a more important role as vectors compared to microplastics, both pristine and aged [10]. The knowledge about this mechanism is quite controversial. For instance, it has been experimentally proven that natural particles, like algae particles, show a stronger adsorption affinity for some heavy metals such as copper (Cu) than polystyrene and polyethylene microplastics (size, 15–30 μm) [19]. The contrasting adsorption capacity of natural and microplastic particles seem to be due to chemical functional groups and, thus, electrostatic forces and covalent bonding. The complex composition of algae particles, like proteins, silica, hydroxyls, high oxygen- and nitrogen-containing, provide O and N ligands for complexing Cu ions. On the other hand, microplastics are characterised by functional aromatic groups (C-H, C=O, C-O-C). Therefore, the absence of oxygen group determines low absorption capacity of metals [19]. On the contrary, some experiments showed that virgin microplastic polyethylene has preferential adsorption for cadmium (Cd), cesium (Cs) and zinc (Zn) over sediment particles. This means that the polyethylene microplastics (i.e., 32–38 μm, 38–45 μm, 45–53 μm, 53–63 μm and 63–75 μm) are able to retain these heavy metals more effectively than the sedimentary particles present in the marine environment [20]. Likewise, an experimental exposure of mussels to microplastics loaded to natural and microplastic particles proved that mussels exposed to the natural route showed lower levels of mercury than those exposed to microplastics [21].

Furthermore, adsorption of heavy metals onto microplastics might be related to the age of microplastics. Aged microplastics showed a stronger adsorption affinity for heavy metals than virgin ones. Particularly, aged polyvinylchloride fragments (1.6 x 0.8 mm in size) accumulated Cu and Zn in a larger measure than virgin polystyrene microbeads (0.7–0.9 mm) [19,22–24]. A simulated aging of microplastics, i.e., polystyrene (PS) and polyethylene terephthalate (PET), in the laboratory through exposure to high temperatures for 168 h has shown an increase in Cu adsorption capacity [24].

The type of polymer seems to affect the transport of heavy metals as well [25,26]. For instance, polyamide microplastics showed the highest adsorption ability for Cr (VI) because of hydrophilic amide groups, compared to polyethylene and polypropylene microplastics [25]. Hydrophilic amide groups are strongly basic and can form stable complexes with metal cations. Furthermore, heavy metal adsorption is influenced by pH. Specifically, experimental evidence showed that the adsorption capacity of microplastics for Cu (II) was the best at pH 7. In addition, coexistence of several heavy metals determined the adsorption competition effect between them [24]. However, it is worth considering that metals are usually assembled into plastic polymers mainly as fillers (i.e., calcium

carbonate, magnesium hydroxide), stabilizers (i.e., calcium-zinc, barium-zinc, cadmium, lead) and pigments (i.e., cadmium, lead, zinc, chrome) to give color to plastics. Therefore, it could be difficult to discern between metals accumulated from the environment and metals intentionally load to microplastics [22].

3.2. PAHs associated with microplastics in marine environment

Microplastics have been reported to adsorb persistent organic pollutants (POPs), with particular regards to polycyclic aromatic hydrocarbons (PAHs). Particularly, virgin and aged polyethylene microplastics have shown the ability to adsorb fluoranthene and phenanthrene. However, aged microplastics adsorb the tested PAHs more, as for heavy metals. Furthermore, it emerged that substances present in the water systems could interfere in the adsorption process. For instance, fulvic acid reduced fluoranthene adsorption on microplastics but increased phenanthrene adsorption on both types of microplastics [27]. Experimental evidence suggests that the type of polymer can affect the ability of adsorption. Phenanthrene shows a stronger affinity for polyethylene compared to nylon. The maximum quantities of phenanthrene adsorbed by polyethylene and nylon fibers were 146.4 μg g^{-1} and 131.8 μg g^{-1}, respectively. Additionally, screening polyethylene fibers is faster than screening nylon fibers within the first two hours, with sortation quantities of 88.7 % and 77.8 %, respectively. However, the data collected so far is not sufficient to fully understand the kinetics of the adsorption/desorption process. The pseudo-first order model for phenanthrene sorption shows a poor linear relationship, indicating that it is not suitable for representing the kinetics. In contrast, a good adherence to the pseudo-second order equation has been observed when plotting data in the t/qt graph [28].

Regarding the effects, it emerged that combined exposure to benzo[a]pyrene-loaded microplastics enhanced toxic effects compared to single exposure, i.e., only benzo[a]pyrene, in the seaworm *Hediste diversicolor* [29]. Likewise, a combined exposure of fluoranthene and microplastics of polyethylene or polyhydroxy butyrate (10–90 μm) increased levels of reactive oxygen species (ROS) in the muscle tissue of *Mytilus edulis* mussels, as well as a relevant decrease in the activity of the enzyme catalase (CAT) [30]. On the contrary, experimental evidence suggested that combined exposure to microplastics and pyrene did not lead to a magnification of the acute effects on *Lates calcarifer.*

Morphological characteristics of the digestive tract of living organisms can affect the ability to desorb/adsorb PAH from microplastics, as for heavy metals. For example, a work by Ito et al. [31] proved that polyethylene microplastics (250–300 μm) have been able to desorb PAHs differently, according to the type of organs. To be precise, the amount of desorbited PAH was significantly higher in the red seabream than in the mummichog. PAH desorption showed significant variations depending on the part of the intestine considered. In the red seabream, the highest concentration of desorbed PAH was recorded in the mesentery (cecum pyloric and stomach), followed by the posterior intestine and finally by the stomach itself. In mummichog, maximum desorption also occurred in the anterior intestine followed by the middle and posterior intestines. Thus, the red capon mesentery and the anterior intestine of mummichog showed increased desorption capacity of the PAHs. This suggests that the morphological characteristics of the digestive tract on the one hand and the breakdown constant of the PAHs on the other can influence the ability to desorb PAH from PE microplastics [31].

3.3. Pesticide associated with microplastics in aquatic environment

Pesticides can be absorbed onto microplastics in the aquatic environment through hydrophobic and electrostatic interactions [32].

Elseblani et al. [11] have extracted metal and organic contaminants, including some pesticides, from microplastics. A combination of methanol and acetonitrile (1:1) was added for the extraction from microplastics sample. The mixture was subjected to ultrasound bath at 50 °C for 30 min and then mechanically shaken for 24 h. The extracts were concentrated by rotary evaporation and injected in the LC-MS/MS. The analysis led to the identification of 19 compounds, where 9 corresponded to pharmaceuticals and pesticides. Naphthalene acetamide, pyroquilon, diazinon, chlorpyrifos and pyrimethanil were detected. In over half the samples, more than 60% of the total concentration of pesticides is made up of chlorpyrifos and permethrin [11]. Chlorpyrifos, a former insecticide, has the potential to remain in MPs derived from PE agricultural greenhouse and mulch film, as well as PP plant protection tubes [33,34].

Until now, only limited research has addressed the eco-genotoxic impacts on organisms in freshwater ecosystems resulting from the combined exposure of microplastics and other pollutants such as pesticides. Nugnes et al. [13] evaluated chronic and sub-chronic effects of PS individual and in combination (binary/ternary mixtures) with a drug (Acyclovir (AC)) and a pesticide (imidacloprid (IMD)) in *Ceriodaphnia dubia* crustacean. Several toxicity and genotoxicity indicators, such as survival, growth, genetic markers and key enzymes involved in metabolism, were measured. The results demonstrated that exposure to polystyrene microplastics, in combination with pesticides and antiviral drugs, increased toxicity in the tested organism. Reductions in organism survival and growth were observed, as well as an increase in DNA damage and genotoxicity markers. These findings indicate that the interaction between polystyrene microplastics and pesticides/antiviral drugs can lead to increased toxic and genotoxic effects on aquatic organisms. Therefore, microplastic pollution and exposure to contaminated chemicals may pose a significant threat to the aquatic ecosystem [13].

3.4. Heavy metals associated with microplastics in terrestrial environment

A work by Zhou et al. [35] extracted microplastic particles from 24 sampling sites in the suburb of Wuhan City, China. The results showed that the concentration of microplastics ranged from $2.2x10^4$ to $6.9x10^5$ particles kg^{-1} of soil. From each sampling site, 400 plastic particles with a size range of 200–5000 μm were randomly selected for the extraction of heavy metals. To remove any adhered material, plastic particles were placed in an ultrasonic bath. Afterward, the samples were digested with aqua regia (a mixture of HCl: HNO_3 in a ratio of 3:1). The concentration of heavy metals, including cadmium (Cd), chromium (Cr), lead (Pb), silver (Ag), copper (Cu), antimony (Sb), mercury (Hg) and manganese (Mn), was analysed using inductively coupled plasma-mass spectrometry (ICP-MS). The identification of iron (Fe) was conducted using inductively coupled plasma-optical emission spectrometry (ICP-OES). The results revealed that the microplastic particles in the soil contained varying levels of heavy metals. The heavy metal content in the microplastic particles correlated positively with the metal content in the soil, indicating that the levels of metals in the soil strongly influence the heavy metal content in the microplastic particles. Notably, the average Cd content in the microplastic particles was higher than in the soil at 17 out of the 24 sites [35]. The metals present in MPs can be either adsorbed onto the surface of the particles or inherently present within the

composition of the MP particles, as far as metals are added into the synthetic polymer as stabilizers, pigment or catalyst [36].

This finding is consistent with previous studies by Holmes et al. [37], which demonstrated that the adsorption capacity of metals by plastics is influenced by environmental conditions. For example, lead adsorption became relatively constant when the pH was above 6, while cadmium adsorption increased with increasing pH [37]. However, Brennecke et al. [23] found that the adsorption capacity of metals depends also on the type of polymer, with PVC particles relevantly accumulating higher levels of copper (Cu) compared to polystyrene (PS) particles [23].

3.5. Pesticides associated with microplastics in terrestrial environment

Regarding pesticides, a study conducted by Sunta et al. [32] investigated the interaction between two type of MPs and a combination of pesticides with alluvial soil. The study focused on examining the adsorption of three pesticides, acetamiprid (ACE), chlorantraniliprole (CAP) and flubendiamide (FLU), at concentration of 1, 5 and 10 mg L^{-1} onto 5% of polyester (PES) fibers and polypropylene (PP) particles (with a size range of 50–1000 μm) in the soil.

The adsorption of each pesticide onto PES and PP was tasted in soil samples containing the microplastics and the pesticide. The mixtures were continually stirred for 1 h and then filtered through stainless steel sieves (1.0 mm for the mixture with PES and 0.5 mm for the mixture with PP). The pesticides were extracted from microplastics through sonication with 1 mL of acetonitrile (ACN), purified using filtration through a CA filter and analysed using HPLC-DAD.

Results showed that out of all tested pesticides, FLU (from 1154 to 3815 ng g^{-1}) was the most adsorbed onto microplastics surface, followed by CAP (from 964 to 3737 ng g^{-1}) and ACE (from 277 to 690 ng g^{-1}). This indicate that more hydrophobic is the substance, the higher is the significant adsorption on MPs, regardless of the type and morphology.

Therefore, MPs decrease the retention capacity of pesticides in the soil and allow for their distribution in the environment [32].

3.6. Microplastics as a vector in the atmosphere environment

A work by Ortega et al. [38] discusses the role of atmospheric microplastics and nanoplastics as primary carriers of air pollutants. Specifically, the study focuses on the case of polyethylene terephthalate (PET). The authors investigated the connection between the chemical properties of PET and its ability to adsorb and transport air pollutants, such as CO, CO_2, NO, N_2O, NO_2, NH_3 and SO_2. The results indicate that the adsorption of air pollutants onto PET-aMPs occurs through two mechanisms: inner surface adsorption and outer surface adsorption, influenced by the molecular polarity (dipole moment) and atomic constitution (effect of electronegativity). Air pollutants such as NO, NO_2, CO, NH_3 and SO_2 prefer outer surface adsorption, while N_2O and CO_2 favour inner adsorption [38]. The mechanistic information provided in this article will contribute to a better understanding of hazards and risks associated with atmospheric and airborne plastic debris, as well as their impact, cotransportability and interaction with the environment. However, further research is a needed to fully comprehend the impact of atmospheric microplastics on air quality.

4. Conclusions

The role of microplastics as vectors of organic and inorganic contaminants is still an underexplored topic. Reproducing real environmental conditions in the laboratory is still a challenge. The discrepancies found in different studies may be attributed to this. The mechanisms of adsorption/desorption of contaminants from microplastics are influenced by various factors, including the porosity of the plastic material, the age of the microplastics and the type of polymer. Similarly, environmental conditions such as pH seem to influence the adsorption/desorption behavior.

Scientific evidence is necessary to assess the actual impact of microplastics as vectors compared to natural particles. In this regard, the scientific knowledge available so far is still contradictory. Therefore, further studies are necessary to assess the role of microplastics as vectors and understand if this could pose further dangers to organisms and the environment as a means of contaminant concentration.

Use of AI tools declaration

The authors declare they have not used Artificial Intelligence (AI) tools in the creation of this article.

Conflict of interest

Cristina Di Fiore and Pasquale Avino are Guest Editors for AIMS Environmental Science and was not involved in the editorial review or the decision to publish this article. All authors declare that there are no competing interests.

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