

Review

Impact of Microplastics on the Fate and Behaviour of Arsenic in the Environment and Their Significance for Drinking Water Supply

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Abstract: The ubiquitous presence of microplastics (MPs) is a topic of great concern. Not only do MPs themselves represent potential toxicants for human health, they are never found alone in the environment and interact with and adsorb a variety of toxicologically significant pollutants. This review summarises recent work on interactions between MPs and heavy metals in the environment, with a special focus on arsenic, one of the most widespread and problematic water contaminants. Evidence for the adsorption of arsenic onto MP surfaces is given and the recent research into the consequences of this phenomenon for freshwater, marine, and soil environments presented. Finally, the lack of research into the significance of interactions between arsenic and MPs during drinking water treatment is highlighted. The performance of arsenic removal technologies is governed by a multitude of different factors, and with MPs detected in water sources all over the world, data on how these MPs impact the removal of arsenic and, indeed, other major water contaminants are urgently needed.

Keywords: microplastics; nanoplastics; arsenic; heavy metals; drinking water



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1. Introduction

As global awareness of the pervasive presence of microplastics (MPs) and nanoplastics (NPs) in the environment has increased, scientists have begun to investigate not only their direct impact on ecosystems, but also how they effect the fate and behaviour of other pollutants [1,2]. The toxicity of MPs and NPs (referred to collectively in the literature as MNPs) themselves is still the subject of intense research [3], and, as they continue to accumulate in all compartments of the environment [4,5], the uncertainty around the effects of interactions between MNPs and water contaminants is of particular concern in drinking water treatment. Many researchers have reported the presence of MNPs not just in the raw and treated waters at drinking water treatment plants (WTPs) [6], but also in distribution networks [7] and at the tap [8]. WTPs often apply multiple treatment technologies in order to remove a complex variety of contaminants from various water matrices. If MNPs are present at each stage of the treatment process, it would be naive to assume they have no effect on the behaviour of other contaminants. An example of the complexity of the water matrices involved is given by Annex I of the recently updated EU Drinking Water Directive [9], which, in addition to the microbiological quality control criteria, lists more than 100 chemicals whose concentrations must be controlled in drinking water.

However, it is particularly interesting to examine the connection with substances found in drinking water which directly negatively affect human health. One of these substances is arsenic. Thus, this review explores the interactions between MNPs and arsenic, as one of the most widely spread and problematic water contaminants. Arsenic is toxic, carcinogenic, and widely distributed in groundwaters, with the World Health

Organisation (WHO) estimating that the presence of arsenic in drinking water sources continues to negatively impact the health of 140 million people worldwide [10]. Arsenic can be found in groundwaters in several European countries, Bangladesh, India and Pakistan, in the USA and Argentina, and many other countries. Chronic exposure to arsenic can lead to cardiovascular and neurological problems, as well as cancers of the skin, liver, and kidneys [11,12]. In this review, we, therefore, briefly summarise the current thinking on the presence of MNPs and arsenic in the environment, and then focus on the most recent findings of researchers investigating the impact of MNPs on the fate and behaviour of arsenic in the wider environment, in water sources, and during water treatment.

2. Materials and Methods

The literature search for this review was carried out using the following predetermined set of search queries and the search functions of the Google Scholar and ScienceDirect websites:

- NIT: (microplastic OR nanoplastic OR polystyrene OR “polyvinyl chloride” OR polypropylene OR polyethylene OR “polyethylene terephthalate”) AND (arsenic)
- allintitle: (microplastic OR nanoplastic OR polystyrene OR “polyvinyl chloride” OR polypropylene OR polyethylene OR “polyethylene terephthalate”) AND (arsenic OR metals OR contaminants OR pollutants OR carry OR interaction OR adsorption)
- allintitle: (microplastic OR nanoplastic OR polystyrene OR “polyvinyl chloride” OR polypropylene OR polyethylene OR “polyethylene terephthalate”) AND (water OR aqua OR sediment)

The results returned for these search queries were filtered to only display those published in the last 10 years, sorted by relevance according to the search engines, and then assessed manually. At the time of writing, these three search terms return 2040, 914, and 1600 hits in GoogleScholar, although not all the hits are relevant. Of the 62 total citations given in this review, there are 59 scientific papers of which only 24 discuss both MNPs and arsenic in detail. However, the average age of the papers cited in this review is just 3 years, which is a testament to the novelty of this field of research.

3. Microplastics and Arsenic in the Environment

Despite increasing awareness about the need to address environmental issues relating to the presence of plastics in the environment, estimates of annual global plastics production are approaching the order of 1000 megatonnes (Mt), with almost 80% of the plastics produced ending up in landfills or spilled into the environment [5]. Generally, pristine plastics are non-porous and do not carry a surface charge, and are therefore unlikely to adsorb trace metals or metalloids such as arsenic. However, various production processes, and the natural weathering processes which break down plastics into MNPs in the environment, increase the degree of functionalisation on plastic surfaces, creating suitable sites for interactions with metal and metalloid ions [13,14].

Plastic pollution originates from landfills, littering, tyre wear, artificial landscaping, plasticulture, etc. Once plastics enter the environment, they slowly degrade and are subjected to transport via the wind, surface run-off, streams, rivers, etc. [15]. Many MNPs end up in the seas and oceans [16], but they are also found in freshwater bodies, soil, river and lake sediments, and in marine sediments [2]. The co-presence of MNPs and heavy metals and arsenic pollution is therefore only to be expected.

Before discussing interactions between MNPs and arsenic in the various compartments of the environment, it is worth covering some of the more fundamental research work carried out in synthetic matrices in the laboratory. For the Song research group, Dong has recently investigated how MNPs impact the behaviour of arsenic in the environment, with particular emphasis on the uptake of arsenic by crops. They began by investigating the adsorption of arsenic onto two different types of microplastics (Polytetrafluoroethylene—PTFE and Polystyrene—PS) in pure synthetic matrices, before including humic and fulvic acids, common components of the natural organic matter (NOM) usually found in natural waters [17–19] (Table 1). They demonstrated that As(III) is adsorbed onto MNPs from water, and that

the presence of NOM (represented by humic and fulvic acids) dramatically increases that adsorption by about an order of magnitude, depending on the conditions.

Table 1. Adsorption of arsenic and other heavy metals on microplastics.

Type of Microplastics	Particle Size (μm)	BET (m^2/g)	Concentration Range of Heavy Metal (mg/L)	Adsorption Capacity (mg/g)	Matrix	References
Polytetrafluoroethylene (PTFE)	0.01–1	0.95	10–50 (As)	1.05	Synthetic water	[17]
	1–10	0.40		0.94		
	10+	0.32		0.83		
Polystyrene (PS)	0.01–1	0.95	10–50 (As)	1.12	Synthetic water	[18]
	1–10	0.40		1.047		
	10+	0.32		0.92		
	-	-	50 (As)	11.8	Humic and fulvic acid solutions	[19]
Polypropylene (PP)	850	-	50 (Cu)	0.27	Synthetic water	[20]
			50 (Zn)	0.19		

The conclusions of Dong and Song are supported by the results of Fan et al., who investigated the adsorption of Pb, Cu, Cd, and Zn onto polypropylene MPs [20], and demonstrated that PP was able to adsorb significant amounts of these metals from aqueous solutions. Table 1 summarises the finding of these two groups. The particle sizes of the MPs investigated by Dong ranged from 0.1 to 10 μm , whereas the particles investigated by Fan were larger than 850 μm . Arsenic adsorption capacities ranged from around 1 mg/g for PTFE and PS in pure synthetic matrices, up to almost 12 mg/g on PS in the humic acid solutions. Humic and fulvic acids are very commonly present in both surface and groundwaters as part of the NOM, so their impact on the adsorption of arsenic onto PS is of particular significance. However, more research into the effect of other common water constituents would be of great interest in future, especially in real groundwater matrices with different types of NOM.

Note that Dong also investigated the impact of interactions between arsenic and MNPs in freshwater algae [21], in soil bacteria [22] in paddy field soils, in rice seedlings, and in carrot crops [23,24]. These papers are discussed in more detail below in Section 3.4, but, in general, demonstrate that the presence of MNPs can impact how biological systems are able to mitigate the toxic effects of arsenic.

3.1. Direct Human Exposure Routes for MPs and Arsenic

The consumption of MNPs in contaminated food and drink is, of course, one of the main routes for human exposure to MNPs. Organisms at lower levels of the human food chain, which can be found in freshwater, marine, and soil environments, are discussed in detail below. However, human food consumption is not limited to these organisms as meat, fish, or crops. Another significant potential source of dietary MNPs is salt. Sathish et al. investigated 14 different sea and bore-well salt brands available commercially in southern India [25]. They estimated that human sea salt consumption led to the ingestion of more than 200 MPs every year. This finding was troubling because As and Ni were both detected on the surfaces of the MPs detected in the sea salts. The possible human health risks of ingestion of MPs contaminated with heavy metals have been investigated by the group of Liu and Wu [26,27]. They have used simulated digestive juices to model the human digestion of MPs, and used the Caco-2 cell line to simulate the cells lining the gastrointestinal tract. In their first paper, they assessed the cytotoxicity and efflux pump inhibition of different particle sizes of polystyrene MPs in the Caco-2 cell line [26]. In their second paper, they demonstrated that the negative impact of MPs on cell integrity was actually reduced by the MP digestion process. They also concluded that intestinal bioavailability of As was in fact reduced when consumed together with polystyrene MPs [27].

Another human exposure pathway for MPs which is gathering interest in the scientific community is inhalation or ingestion of tyre wear particles (TWP) in urban environments. A study by Järnskog et al. carried out in Gothenburg, Sweden endeavoured to quantify and characterise the MPs in TWPs [28]. Cu, Zn, As, Cd, Cr, Ni, and Pb were all detected in these particles, although the concentrations of Cu and Zn were considerably higher than the other metals detected. Their work focused on road dust and stormwater, but the majority of the TWPs detected were found in the smallest particle fraction they investigated (20–100 µm), so transport of these particles through the air is also a real possibility.

3.2. Freshwater Environments

A review by Issac and Kandasubramanian offers a global perspective of how microplastics enter aquatic ecosystems [29]. A more comprehensive investigation into the combined impact of toxic pollutants and microplastics is given by Pandey et al. [1]. The authors' primary concern was focused on how microplastics in the aquatic environment will impact pollutant transport in the North Indian floodplain, but the discussion encompasses all the global issues relating to interactions between MNPs and heavy metals, including arsenic. Selvam et al. researched the role of MPs as vectors for heavy metals not just in surface waters but also in groundwater [30]. As discussed in more detail below, groundwaters are often used as drinking water sources as their separation from the surface affords them better, but not absolute, protection from pollutants. Indeed, MPs were discovered in 9 out of the 24 groundwater samples investigated. Of the MPs detected, polypropylene was found to have the highest capacity for metal adsorption, in the following order: Cd > Mn > As > Pb > Cu > Zn > Cr. Polyethylene MPs were also shown to be significant potential vectors for heavy metals.

He et al. studied the influence of MPs on the sediment transport of nutrients and heavy metals in the Brisbane river, Australia [31]. Principle component analysis showed a clear link between total carbon, total nitrogen, and total phosphorous, and MP abundance in the sediments. The area investigated covers the last 50 km of the Brisbane river before it meets the sea, with the downstream sampling locations being tidal in nature. The authors, therefore, classed the heavy metals investigated by likely origin—marine source, crustal, or anthropogenic. Cu, Cd, Pb, and Zn were classed as anthropogenic and showed high spatial variation in the MPs detected, whereas As was evenly distributed in the MPs at all locations, and was assumed to be of marine origin.

The freshwater algae paper by Dong et al. mentioned above investigates arsenic accumulation in *Chlamydomonas reinhardtii*, focusing on the effect MP particle size has on arsenic uptake rates [21]. These types of algae play an important role in arsenic-contaminated waters, by adsorbing As(III) and metabolising it to less-toxic arsenic species such as As(V), monomethyl As (MMA) and dimethylarsinic acid (DMA). The addition of MPs reduced the *C. reinhardtii* capabilities for both these roles, negatively impacting its ability to reduce the overall toxicity of arsenic-contaminated waters. NPs were found to be more detrimental than MPs in this regard, as they were able to pass fully into the cells.

Sabilillah et al. very recently published a risk assessment for the consumption of fish from two Indonesian rivers which are contaminated by both plastics and heavy metals [32]. Of the heavy metals, only Cd and Pb were investigated, with the authors reporting that the concentration of these metals was higher in the MPs than in the surrounding waters. The health risk assessment utilised a variety of indices, including the polymer hazard index (PHI), the pollution load index (PLI), estimated daily intakes (EDI), and target cancer risk (TR). The degree of risk was found to depend on the species and size of the fish, as biomagnification can lead to higher levels of heavy metals in fish tissues. Comparison of the human EDI with the acceptable daily intake (ADI) suggested that, although the fish sampled were contaminated with both MPs and heavy metals, they were not at potentially hazardous levels.

Finally, as more knowledge is gained about the impact of MNPs in freshwater systems, there is a need for research which focuses on how to mitigate the risks MNPs present.

Researchers have recently begun to develop improved methodologies for the detection and identification of MNPs in wastewater treatment plants [33]. Investigations have begun into how wastewater treatment plants may be efficiently modified to better remove MNPs from wastewater streams, but the results thus far have proved inconsistent, and the issue of MNPs in the sludge produced by wastewater treatment plants has not been adequately addressed [34]. Given the huge volumes of treatment plant sludge produced globally, more information is required on the behaviour of MNPs in sludge, and how they impact the fate of other sludge contaminants.

3.3. Marine Environments

As rivers approach the sea, the water undergoes very drastic changes in chemical composition. Holmes et al. demonstrated that the increasing salinity and lower pH of estuarine environments reduces the adsorption of Cd, Co, Ni, and Pb onto pre-production plastic pellets, whilst increasing the adsorption of Cr(IV) [14].

Deng et al. investigated the surface sediments of a restored mangrove wetland at the Jinjiang Estuary [35]. They performed a comprehensive analysis of the MPs detected, and compared the abundance of heavy metals in the MPs and in the surrounding sediments. Average accumulated heavy metal contents followed this trend: Zn > Pb > Cu > Cr > Ni > As > Cd > Hg. For all of the metals except Hg, there was no correlation between the sediment and MP concentrations, suggesting that the heavy metals present in the MPs did not necessarily originate from the sediments.

Jeyasanta et al. investigated microplastics in the seas off of Rameswaram Island, India [36]. They found the greatest amounts of MPs in the coral reef and seagrass beds. Polyethylene (PE) was the most common in the water, and Cr, Fe, Hg, and As were all found on the MP surface. Elsewhere, Prunier et al. [16] reported the metal contents of microplastics collected from the North Atlantic subtropical gyre. These MPs were largely PE, and heavy metal and metalloid concentrations ranged from 0.8 µg/g for As to as high as 7000 µg/g for Ti. They also investigated pristine plastic pellets used in plastics production and new packaging materials, where they found significantly lower heavy metal concentrations. They suggested that MPs in the marine environment were therefore adsorbing and thus acting as a sink for heavy metals. This was confirmed by El Hadri et al., who used laser ablation ICP-MS to investigate the surface and subsurface of microplastics from a Guadeloupe beach also subjected to the North Atlantic gyre [37]. The depth profiles of heavy metals in the MPs confirmed the adsorption of heavy metals and they suggested a method to estimate how long MPs were exposed to As concentrations depending upon these depth profiles.

Many other papers demonstrating the adsorption of As onto microplastics found in coastal and marine environments have been published, with Tables 2 and 3 summarising where they have been detected in water and sediments, emphasising the global nature of this issue. In Iran, MNPs were found to be possible vectors of pollution, with positive correlations between MP amounts and concentrations of heavy metals, arsenic, and organic pollutants reported by two different groups [38,39]. In Australia, an ambitious citizen's science project collected and analysed MPs from 37 different locations all over the Australian shore line, and concluded that local land use had a significant impact on the distribution of metals detected on the MPs [40].

The combined impact of MNPs and arsenic on the health of various marine organisms has also been studied. One interesting study on marine microbial communities notes that macro- and microplastics can act as reservoirs for antibiotic (ARGs) and metal resistance genes (MRGs) [41]. Plastics with a wide range of particle sizes were obtained from the North Pacific gyre and the microbial communities on their surfaces were analysed. The MP communities had considerably higher ARG and MRG abundances than the surrounding sea water communities. Arsenic resistance genes were detected in the plastics microbiota, although cobalt, copper, nickel, and multi-metal resistance genes were more common.

Table 2. Studies identifying arsenic adsorption on microplastics present in various waters around the world.

Sample Type	Type of Microplastic	Particle Size (mm)	Proportion of Total MPs (%)	As conc. in Water ($\mu\text{g/L}$)	Conc. of MPs (Items/L)	As Adsorbed on MPs ($\mu\text{g/g}$)	Location	Ref.
River estuary	PP	0.56–4.5	22	20.56–32.12	7.8 (max 19.9)	0.42–0.96	Punnakayal estuary, India	[30]
	PE		30			0.12		
	Polyamide		38			-		
	PVC		5			-		
Groundwater	Cellulose	0.11–3.6	5	-	4.2 (max 10.1)	-		
	PE		55			-		
	Polyester		10			-		
Coastal water	Polyamide(nylon)	<1	35	0.009–0.32	24 \pm 9–96 \pm 57	3.7–1.24	Rameswaram Island, India	[36]
	PE		26.2–33.4					
	PET		17.1–18.9					
	PA							
North Atlantic	PE	-	-	-	-	0.1–0.8	North Atlantic gyre	[16]
	PE	<1	-	-	-	<10	North Atlantic gyre	[37]
Beach (from sea)	PE	1–5	53	-	-	0.04–1.53	Entire coast of Australia	[40]
	PP		35					
	PS		7					
	PET		2					

Table 3. Studies related to identification and estimation of arsenic adsorbed in microplastics present in sediments.

Sample Type	Microplastic Abundance	Type of Plastic (Percent of Total)	As conc. in Sediments (mg/kg)	As Associated with MPs (mg/kg)	Correlation of As and MPs	Area	Ref.
River sediment	-	PE (70) PA (12) PP (10)	-	-	0.131	Brisbane, Australia	[31]
Coastal sediment	59–217 items/200 g	-	4.56 \pm 2.77	-	$p < 0.01$	Khark Island, Iran	[38]
Coastal sediments	3542–33,561 items/m ²	-	122 220 120	-	-0.733 *	Bandar Abbas, Iran	[39]
Coastal Sediments	-	Cellophane Polyester PP PE	3.01–12.42	0.35–2.89	-0.381 **	China	[42]
Coastal sediment	490–1170 items/500 g	PE PP PET	5.84–8.68	0.64–6.53	$p > 0.05$	Fujian, China	[35]
Coastal sediment	55 \pm 21–259 \pm 88 items/kg	PP PET PA PEST	0.077–0.487	3.7–1.24	$p > 0.05$	Rameswaram Island, India	[36]

* Correlation is significant at the 0.05 level; ** statistically significant at $p < 0.05$.

In a study of sea cucumber farms in the Bohai Sea in China, greater Cd and As concentrations were found in the sea cucumbers than in the marine sediments from the same location [42]. However, in this study, the MPs detected had significantly lower concentrations of these metals than the surrounding sediment. A Korean laboratory studied how combined exposure to NMPs and As effected the health of marine rotifer *Brachionus plicatilis* [43]. They found that for certain in vivo parameters, including reproduction and

swimming behaviour, the presence of NMPs increased As toxicity. Interestingly, they also noted that this effect was strongly dependent on the size of the particles—larger MPs acted as sinks for As, reducing its bioavailability plastic and alleviating toxicity.

The effect of NPs on metals toxicity in fish was investigated by González-Fernández et al., who performed experiments on a fish-brain-derived cell line from seabream with different functionalised NPs: pristine, carboxylic, and amino functionalised [44]. The metals investigated were As and methylmercury (MeHg). As and MeHg were both found to induce oxidative stress in the cell lines, and the functionalised NPs increased the toxicity of both.

Dietary exposure to nanoplastics and arsenic was studied in Canadian (*C. virginica*) and Caribbean (*I. alatus*) oysters by utilising microalgae as an NP vector. Under carefully controlled conditions, bioaccumulation of As was found to be greater in the Canadian oyster species. Toxicity was investigated using a variety of gene expression assays, with greater synergistic effects observed in the Canadian oysters. The combined exposure to NPs and As was considerably more toxic even at low NP concentrations [45]. Another method to assess dietary exposure to MNPs was given by Turner [46], who utilised an avian physiologically based extraction test to simulate seabird exposure to MNPs and a variety of heavy metals, including As. This work studied the kinetics of metals mobilisation during the chemical extraction, which is based on the digestive system of *Fulmarus glacialis*. The MPs were taken from two UK beaches, and extracted heavy metal concentrations ranged from 36.3 µg/g for Cd up to 928 µg/g for Pb (note that the MPs sampled did not contain significant amounts of As). Turner concluded that ingested MPS may represent a significant vector for heavy metal exposure to seabirds.

3.4. Soils

Although much of the initial concern regarding microplastics in the environment revolved around the oceans, not all MNPs reach the seas. Those which remain in the soil can potentially impact the entire food chain from the ground up. Metals in soils are subject to a wide variety of physical, chemical, and biological processes which govern their fate and bioavailability. Yu et al. performed an in-depth investigation into how the presence of MPs can change those processes for seven heavy metals, including arsenic [47]. They investigated three different soil aggregate size fractions (coarse particulate, micro-aggregate, non-aggregated silt, and clay), and assessed metal speciation in terms of bioavailability. They report that, in general, MPs in the soil reduced metals bioavailability by converting them to more stable organic bound fractions. This decrease in bioavailability was most pronounced in the larger-sized aggregates, and the different metals all behaved slightly differently in each size fraction. It should be noted that their experiments were carried out with significantly higher soil MP concentrations than those usually found in the environment, but still revealed how various soil physiochemical factors can be expected to interact with metals in the presence of MPs.

Large amounts of MPs can of course be detected in certain locations. In a study of 33 soil samples from Guiyu, an area of Guangdong in China which is known for its e-waste dismantling industry, microplastic abundances as high as 34,100 n/kg were reported [48]. The extensive characterisation of MPs in this work included a study of the heavy metals present in the MPs, whereby Pb, Cd, Cr, Ba, Cu, Co, and As were all detected in concentrations ranging from 0.67 µg/g (Cd) to 309 µg/g (Ba, which was also found to be present in commercial pristine PET, although at a lower concentration).

Poor plastic waste management practices are not the only routes for plastics to contaminate soils. Plastic mulch is applied in agriculture to cover certain crops, suppressing weeds and conserving water. These plastic films are subject to weathering processes, creating MNPs. Li et al. studied how a broadly applied fungicide promotes the degradation of plastic mulch and also investigated the leaching of heavy metals from the MNPs during the degradation process [49]. They found that the fungicide prothioconazole promoted MNP degradation, and that biodegradable film MNPs had higher adsorption capacities for heavy metals than regular polyethylene film, due to the greater degree of functionalisation. In

their study, young MNPs were found to act as a sink for soil heavy metals, and they noted that further weathering could result in the re-release of metals back into the environment.

Two groups in China have recently published research on the interactions between MPs and arsenic in soils. Li et al. conducted soil microcosm experiments at three different pH levels and two As concentrations [50]. They then evaluated the effects of these parameters on the bacterial communities in both the soil and MPs. Soil pH was found to have a greater effect on the plastsphere bacterial community than the soil As content, with a greater accumulation of As on the MP itself. One of the most notable findings of this work is that the presence of MPs resulted in greater biotransformation of arsenic, whereby the plastsphere bacterial community was more capable of metabolising As(III) to less toxic forms (As(V) and dimethylarsinous acid (DMA)) than the soil bacterial community alone. Zhu et al. performed a similar study, but investigated fungal and protistan (generally unicellular eukaryotes) communities and performed separately experiments on polyethylene MPs and NPs [51]. The composition of the protist community was more sensitive to the combined threat of As and MNPs than the bacterial and fungal communities. By themselves, As, MPs, and NPs did not negatively impact any of the communities, but the combined exposure of As together with MNPs changed the structure of the protistan community, with a more significant effect observed in the NPs experiment, implying the particle size determines the extent to which MNPs and As combined affect soil ecological function.

The results of a study by Wang et al. on earthworm (*Metaphire californica*) gut bacterial communities [52] present an interesting contrast to these two studies. In this work, earthworms were exposed to As(V), MPs, or As(V) and MPs, and the gut bacteria of the earthworms was investigated. Earthworms exposed to As(V) alone showed significant bioaccumulation of arsenic, and their gut bacteria reduced the As present to the more toxic As(III). Earthworms exposed to both MPs and As(V) demonstrated considerably less bioaccumulation of As, but, more importantly, the MPs significantly inhibited the reduction in As, such that half as much As(III) was present in the earthworm gut [52]. Together with the findings from Li and Zhu [50,51], we can conclude that whether the presence of MNPs increases the ecotoxicity of As in soils depends not just upon the soil type, pH, and particle size of the MPs, but also on the trophic level of the organism.

It is for this reason that the next papers presented herein concern organisms further up the food chain, investigating the impacts of As and MNPs on factors which effect crop production. Two papers by Dong et al., mentioned above, were carried out in paddy fields soils. The first one investigated how polystyrene (PS) MPs affected arsenic volatilisation from arsenic-contaminated paddy soils [53]. The MPs reduced the water-soluble As and increased As volatilisation, suggesting that, overall, the presence of PS MPs reduced the amount of As which was available for uptake by rice. In their next work, they also studied nutrients in rice rhizosphere soil [22]. Polystyrene (PS) and polytetrafluorethylene (PTFE) MPs in two different MP sizes were investigated (0.1–1 μm and 10–100 μm) and were added to topsoil samples with two different levels of arsenic contamination (high and low). Soil nutrients (organic matter content, available nitrogen, and available phosphorous), soil enzyme activities, and soil microbes were all investigated. The authors noted that paddy fields usually flooded, creating anoxic conditions where soil microbes can reduce As(V) to As(III). Without arsenic contamination, MPs reduced the availability of all the nutrients mentioned. In the presence of both MPs and arsenic, soil organic matter availability was increased, but phosphorous and nitrogen availability was reduced. The soil enzymes investigated are mainly due to microbial activity, and enzyme activity was reduced with increasing As concentrations. This effect was mitigated somewhat by the addition of MPs, which again acted as sinks for As, reducing its bioavailability.

Two more papers from the same group investigating carrots and rice seedlings were actually carried out in hydroponic facilities. This allowed the combined uptake and toxicity of As and MPs to be investigated without the confounding effects of all the complicated physical, chemical, and biological processes which occur in soils. In the rice seedlings paper, both PS and PTFE MNPs affected transpiration and stomata in rice seedlings by inhibiting

the rice seedlings' root vigour. This made the rice seedlings more vulnerable to inhibition of the RuBisCO enzyme by As(III), reducing their capacity for photosynthesis [23]. This effect was mitigated somewhat by the MPs inhibiting root activity, restricting the ability of the rice seedlings to uptake As(III), although this would also impair nutrient uptake. As(III) was shown to be less toxic to rice seedlings in the presence of PS than PTEE. In the carrot paper, biomass, soluble proteins, soluble sugar, and carotene were analysed [24]. The presence of As was observed to actually increase the uptake of PS MPs by the carrot roots. The presence of higher concentrations of As also distorted the cell walls sufficiently to allow PS MPs to enter the cells, increasing the overall amount of MPs which were able to enter the carrot.

4. Interactions between Microplastics and Arsenic during Water Treatment

In lower- and middle-income countries, which often do not have the financial and human resources to implement solutions, the presence of arsenic in drinking water represents a serious hurdle to achieving UN sustainability goals SDG3, SDG6, and SDG9, relating to good health and wellbeing, clean water and sanitation, and reduced illness from hazardous chemicals [54]. For this reason, thousands of research papers are published every year looking for more economically and environmentally sustainable arsenic removal technologies. However, considering the body of evidence presented above which relates to how the fate of arsenic and heavy metals in nature can be greatly influenced by the presence of MNPs, papers discussing the interactions between MNPs and As (or heavy metals) during water treatment are rare.

To illustrate this, three separate review papers were published in 2019 alone relating to MPs in drinking water. Koelmans et al. discussed the work carried out thus far to identify and quantify MPs in freshwater and drinking water [55], with a particular focus on analysing the sampling, analytical, and quality control methodologies applied by researchers aiming to detect MPs. Novotna et al. also presented work detailing where MPs have been discovered in drinking WTP [56]. Finally, Eerkes-Medrano et al. presented recent findings on the human health implications of MPs in drinking water. None of these excellent review papers covered how MPs might impact the removal of other water contaminants during drinking or wastewater treatment.

This gap in understanding is of particular concern when we consider the dominant role plastics play in drinking water supply infrastructure—plastics are commonly used in the construction of the adsorption column, tanks, and reservoirs, and a significant proportion of the pipe networks. The WTPs and supply networks themselves are thus a potential source of MNPs in drinking water [7,8], suggesting that the presence of MNPs during water treatment is fundamentally unavoidable.

In the 4 years since these reviews were published, more research has been carried out into the role of MPs as adsorbents of heavy metals, although those investigating the deliberate utilisation of MPs during water treatment tend to focus on specifically designed resins, as discussed in a review by Zhao et al. [57]. However, it is one thing to selectively apply a well-characterised known resin in the laboratory to adsorb heavy metals or other contaminants under static hydraulic conditions, but quite another to predict what effect the ever-increasing concentrations of the complex mixtures of MPs already present in water sources might have on existing water treatment technologies operating in carefully optimised continuous flow conditions. Drinking water treatment plants for the removal of arsenic often employ complex treatment lines [58] so research is required to establish whether the proven presence of MNPs in drinking water sources helps or hinders the removal of specific pollutants such as As. The following technologies are currently widely applied for the removal of As from drinking water: aeration/preoxidation, coagulation/flocculation followed by sedimentation/sand filtration, adsorption on a wide variety of adsorbents, ion exchange, and membrane processes. Sarkar et al. investigated the removal of MPs at a WTP by a pulse clarifier, and correlated MP abundance with turbidity, phosphates, and nitrates [59]. In future, there is an urgent need for similar investigations,

whereby, in addition to the removal of MNPs using these various processes, attention must also be paid to how MNPs affect As removals.

Finally, if the role MNPs play as vectors for metals is a cause for concern, then it makes sense to investigate technologies which can mitigate this concern. In a paper by Ye et al., a method to remove heavy metals from the surface of MPs is proposed [60]. They investigated a catalytic removal and separation method which applied a magnetic biochar for the activation of the oxidation process. As usual, in heavy metal removal treatments, the goal can be to not destroy the metal elements, but merely to partition them into a more stable solid material which can be more safely disposed of. The catalytic process proposed by Ye et al. oxidises the surface of the MPs, breaking down the MPs and freeing the Pb investigated into solution. This then allowed it to be reabsorbed on the magnetic biochar. As a result, the bioavailability of the Pb is significantly reduced.

5. Current and Future Perspectives

Global plastics production is approaching 400 million metric tonnes annually, whilst global plastics recycling levels are only around 10%. The large-scale degradation of plastics into micro- and nanoplastics in the environment is therefore unfortunately set to continue. The toxicity of MNPs themselves is still the subject of intense research, but it seems clear from the research summarised above that MNPs have a significant influence on the behaviour of arsenic in the environment. The affect MNPs can have on living organisms, by increasing arsenic adsorption and/or reducing the efficiency of their metabolic conversion of toxic As(III) into less toxic forms, is of particular note. By hindering the metabolic mechanisms responsible for arsenic detoxification, the presence of MNPs is reducing the tolerance of those organisms to arsenic-rich environments.

It is also necessary to emphasise the necessity for further investigations in regions with elevated concentrations of arsenic in the soil and groundwater, especially in rural areas with poor plastic waste management. This will allow for improved human health exposure estimates and more effective risk assessment into the impact of plastics on agriculture in areas with arsenic-containing soils.

Meanwhile, work on improving arsenic removal technologies has been the subject of intense research ever since the early 1990s, when large quantities of arsenic were discovered in the tube wells of Bangladesh [61], and when the WHO lowered their recommended maximum concentration of arsenic in drinking water from 50 to 10 µg/L [62]. This work continues, but more attention must be paid to take into account possible interactions of arsenic and MNPs during treatment, especially when equipment made of plastic materials is used extensively in water treatment plants and in distribution systems. The works presented in this review demonstrate the growing interest in MNPs as a significant variable in the fate and behaviour of arsenic, but specific information on how MNPs impact the performance of common arsenic removal technologies such as coagulation and flocculation, adsorption, and membrane processes is also urgently required.

To conclude, this review focussed on scientific efforts to resolve the connection between two major global pollutants, MNPs and arsenic. However, there are still many other pollutants whose co-existence with MNPs remains under investigation in all compartments of the environment. How do MNPs impact the fate and transport of those other pollutants, and the toxicological effects the pollutants express in organisms at all trophic levels? Finally, as in all areas of MNP research, it is still necessary to work on the development of standard methods for sampling and analysis, which would enable a better comparison of the obtained results and a more efficient assessment of the impacts of MNP on the behaviour of those other pollutants.

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