

Review

Microplastics in Groundwater: Pathways, Occurrence, and Monitoring Challenges

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Abstract: Microplastics (MPs), defined as plastic particles measuring less than 5 mm, are considered an emerging pollutant. Their presence in the water cycle and their interaction with ecological processes pose a significant environmental threat. As groundwater (GW) represents the primary source of drinking water, monitoring MPs in GW and investigating their potential sources and pathways is of urgent importance. This article offers a comprehensive overview of the primary contamination pathways of MPs from surface water, seawater, and soil into the GW. Moreover, it presents an examination of the occurrence of MPs in GW and identifies the challenges associated with their monitoring in GW. This study also discusses the difficulties associated with comparing research results related to MPs in GW, as well as indicating the need for implementing standardised techniques for their sampling and detection. On the basis of our experience and the literature review, we highlight the importance of understanding the specific hydrogeological and hydrogeographic conditions, collecting representative samples, using sampling devices with comparable specifications and comparable laboratory techniques for MP identification, and preventing contamination at all stages of the monitoring process. This review offers valuable insights and practical guidelines on how to improve the reliability and comparability of results between studies monitoring MPs in GW.

Keywords: microplastics; groundwater; sampling; monitoring; aquifer; borehole



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1. Introduction

In recent decades, the use of plastics has increased to such an extent that they have become indispensable to society [1,2]. In 2022, the global production of plastics reached 400.3 million tonnes, with Europe contributing 14% to this total [3]. While only a small proportion of the plastics produced is recycled or incinerated, the majority is accumulated in natural environments or landfills [4]. MPs have attracted considerable attention as an emerging pollutant and have been recognised as a key contributor to environmental pollution [5–7].

MPs are water-insoluble, solid polymer particles characterised by a size of less than 5 mm. Although the lower limit has not yet been formally defined, particles under 1 µm in size are considered nanoparticles [8]. They differ in terms of their chemical composition, colour, shape, density, size, and other characteristics [9]. The most commonly produced polymer types, according to their chemical composition, are polypropylene (PP; 18.9%), low-density polyethylene (PE-LD; 14.1%), polyvinyl chloride (PVC; 12.7%), high-density polyethylene (PE-HD; 12.2%), polyethylene terephthalate (PET; 6.2%), polyurethane (PUR; 5.3%), and polystyrene (PS; 5.2%) [3]. While there is no standardised method for categorising particles based on their shape [10], some common shapes include fibres, filaments, spheres, fragments, beads, films, and pellets [10,11].

Based on their source, MPs can also be categorised into primary and secondary MPs. Primary MPs are tiny plastic particles released into the environment through the

erosion of products during their use [12,13], e.g., textile fibres and purposely manufactured particles such as microbeads used in cosmetics and medical products, as well as plastic pellets used for the production of plastics [14]. Secondary MPs are MPs resulting from fragmentation due to the weathering of larger plastics when these are released into the environment [13,15].

Although plastic particles smaller than 5 mm had been reported in earlier publications [16,17], the term “microplastics (MPs)” was coined by Thomson et al. [18]. At a workshop organised by NOAA in 2008 [19], the definition of MPs was expanded to include “plastic particles smaller than 5 mm”, without specifying a lower size limit [20].

MPs are present in atmospheric, terrestrial, and aquatic environments [21–28] and thus also in the water cycle [29]. Due to their presence in the environment and the threat they pose to the ecosystem [30], MPs have received considerable attention as newly emerging pollutants [5,6,31,32].

In the environment, primary and secondary MP particles may enter GW via various pathways, e.g., via seawater, rivers, or lakes (GW interaction through the hyporheic zone), or by penetration through soil pores [29,33,34]. To gain a better understanding of these interactions, it is important to compare the presence of MPs in different aquifers under different environmental conditions [35].

GW represents the most important freshwater reservoir on our planet [36,37]. Despite numerous protective measures, the quality of GW sources has been threatened for decades by various contaminants and substandard pumping practices. Rapid population growth and urbanisation of rural areas have intensified MP contamination [38] and pressure on GW systems, leading to impaired water quality [39]. These factors carry far-reaching environmental, economic, and social implications [40].

On the environmental level, MPs in GW ecosystems can pose a threat to the stygofauna, which plays a crucial role in removing pathogenic organisms from water [41]. Although there is a lack of research on the effects of MPs on organisms in GW, studies have found that MPs can be harmful to aquatic creatures, as MPs can be ingested or accumulated in the organism’s tissues, affecting their reproductivity, growth, and survival [42]. The impact of MPs varies depending on their characteristics, concentration levels, and duration of exposure [43]. Therefore, monitoring MPs in GW to assess the risk they may pose to the stygofauna is essential.

Due to the presence of MPs in GW, it is crucial to determine the vulnerability of GW to MPs pollution [33]. There is therefore an urgent need to improve our understanding of the mechanisms of MP transport.

This study aims to provide a comprehensive description of the pathway mechanisms for the transport of MPs into GW from rivers, lakes, and seawater, as well as from soil and the unsaturated zone. It presents the findings of previous research on the prevalence and differences of MPs found in GW. The main added value of this literature review is the discussion about the main challenges in monitoring MPs in GW, which is reinforced by our rich experience in this field.

2. Pathways of MPs Transport into the GW

2.1. Transport Mechanisms of MPs to GW from Rivers, Lakes, and Seawater

GW often interacts with surface water and seawater through recharge and discharge. These interactions represent potential pathways for the transport of MPs in GW systems.

MPs can enter rivers and lakes via different sources of pollution, e.g., effluents from wastewater treatment plants (WWTP); sewage sludge; atmospheric deposition; direct public disposal; and runoff from agricultural, recreational, industrial, and urban areas [44,45]. Due to their different origins, these polymers vary in composition, density, shape, and size [46,47]. The physical characteristics of the particles coupled with the hydrodynamic conditions of the open channel flow influence their transport parameters, as they may float or sink depending on these factors [48,49].

Due to their higher surface-to-volume ratio, small MP particles are often subject to an increase in density and size through different processes, such as aggregation with other MP particles, sediments, and organic matter, or the formation of a biofilm on their surface, which in turn affects their transport behaviour [48]. As the density of the particles increases, they tend to settle in the sediments due to the influence of gravity [48–52].

Scherer et al. [26] conducted a study on a river in the German river Elbe and found that the MP content in the sediment was significantly higher than in water. The average concentration of MPs in the sediment was 3,350,000 particles per cubic meter, i.e., 600,000 times higher than the average concentration of 5.57 particles per cubic meter detected in water. This difference is expected to be even greater in lakes due to the lower water flow velocities, which facilitate sedimentation processes [6].

MPs temporarily immobilised in the sediment can be remobilised by high-flow events [53] or by disaggregation of the biofilm formed on their surface. They may be taken up by benthic organisms or transported through the hyporheic zone (HZ) into the GW [54]. This process depends on the relationships between pore diameters and MPs' dimensions [55], particularly in the case of MPs of smaller diameters. Smaller size MPs can move through the pore space from the surface of the streambed into the subsurface layers [48,56]. In a field study conducted by Drummond et al. [48], 23% of MPs were reported to exhibit a hyporheic exchange ratio higher than the sedimentation ratio. This percentage increases to 42% for low-density MPs.

The HZ is an important interface between the stream and the shallow GW system [48]. Its significance lies in the fact that, depending on the situation, water from specific stream sections or the entire river can flow into or out of the local aquifer [57,58]. The transport of MPs through the HZ is conditioned by the properties of the particles, the hydrological and geochemical factors that condition the hyporheic exchange [48,56,57,59,60], including the shape of the streambed, local GW, material heterogeneities in the HZ, and turbulence in the stream [48]. Insight into these factors is crucial for understanding and addressing the problem of MP pollution.

Figure 1 displays the direction of water flow in a channel that either loses or gains water, along with the movement of MPs. When a stream constantly loses water, as shown in Figure 1(1.1,1.2), the water flows through the streambed sediments and reaches the aquifer. As illustrated in Figure 1(1.3), the flow of porewater causes MPs to move into the aquifer and eventually re-enter the water column through hyporheic flow paths [60]. On the other hand, when a stream constantly gains water (Figure 1(1.4)), it flows through the aquifer to the streambed.

Depending on the conditions of the channel, mobile pore-scale MPs in the HZ can be transported by advection from the HZ to the streambed or to the aquifer [56]. Similar mechanisms occur in lakebeds where MPs within sediments can be transported into the GW by continuously moving seeping water [29], which also reflects the bidirectional interaction between the lake and the GW.

Hydraulic gradients along the streambed and lakebed are the key drivers of hyporheic exchange [61,62]. Hydraulic conductivity, in turn, controls the flow rates of hyporheic exchange. If the material below and adjacent to the river channel is saturated (Figure 1(1.1)), the flow rates are controlled by saturated hydraulic conductivity. If the channel is perched above the underlying water table (Figure 1(1.2)), leakage is controlled by unsaturated hydraulic conductivity, which is much lower in value. Therefore, the transport of MPs under these conditions will be slower [57]. Hydraulic conductivity depends on various factors, including the materials present in the sediment [63]. For example, lakebeds retain sediments from the runoff, streamflow, and shoreline erosion. These sediments usually consist of organic matter, have a finer texture, and are less permeable; thus, they limit the rates and locations of the exchange [64]. Nevertheless, numerous studies have shown that there is still considerable interconnectivity between the two systems, even when sediments have low hydraulic conductivity [65–67].

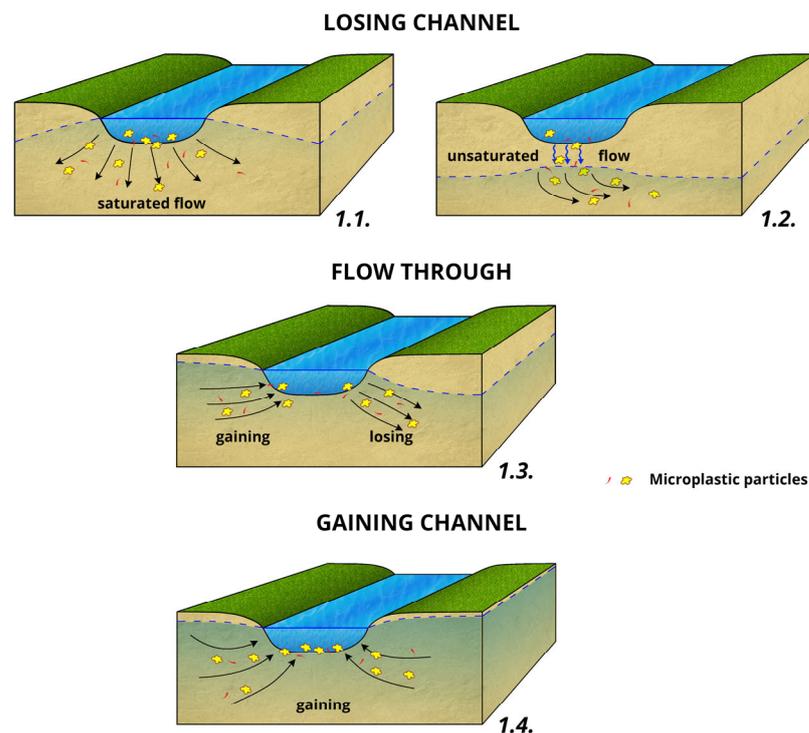


Figure 1. Pathways of MPs from the river channels: From the channel to the aquifer if (1.1) the material below and along the riverbed is saturated, or (1.2) the channel is above the lower GW level. (1.3) In and out of the channel to the aquifer. (1.4) From the aquifer to the channel. Adapted from Hoehn [57] and Singh and Bhagwat [29].

The spatial and temporal changes in water flow lead to corresponding changes in hydraulic gradients and hydraulic conductivity. This flow variability plays a crucial role in shaping fluvial hydrosystems by causing fluctuations in the water depth of the river channel laterally and along the longitudinal profile, thus creating or enhancing hydraulic gradients along the watercourse. This phenomenon is particularly pronounced in rivers with smaller drainage basins [61].

In general, the hydraulic conductivity in a river corridor decreases from the headwaters towards the lowlands. As a result, the exchange between surface and hyporheic waters is more pronounced in the headwaters of the river than in the lowlands. This trend can also be observed on a smaller scale, where the heads of the riffles act as infiltration zones while the tails of the riffles serve as discharge zones [26,56,61].

Fluctuations in seasonal flows have a considerable effect on hyporheic exchanges. In humid climates, the GW feeds the river during dry periods, while wet periods cause changes in flows from the surface to the hyporheic and floodplain water and vice versa due to river-level alterations. In arid climates, the vertical hydraulic gradient strengthens during the dry season, resulting in a shift from discharge to recharge in the direction of surface GW exchange [61].

In karstic limestone areas, fractures or conduits in the limestone regulate the main flow pathways through secondary porosity-dominated rocks, thereby intensifying interactions between the surface and the ground. During intense or prolonged rainfall, the recharge cannot drain fast enough, and the GW can rise above the ground level [68,69]. These dynamics can accelerate the migration of MPs from the surface into the GW [70].

While extensive research has been devoted to the transport of MPs through rivers and lakes, comparatively little attention has been paid to their transport through interactions between seawater and GW. However, the mechanisms involved in seawater–GW interactions are similar to those observed in river or lake–GW interactions.

The mixing of seawater with GW resources is a natural process known as seawater intrusion [29]. This phenomenon is primarily caused by prolonged changes in coastal GW levels, which can be triggered by many factors, including pumping, land use change, climate change, or sea level fluctuations [71]. Research has shown that seawater contaminants can enter GW through seawater intrusion [72,73]. The presence of MPs in seawater raises concern about the potential infiltration of MPs into GW through the mechanisms of seawater intrusion [29]. The high demand for fresh water in coastal areas has led to intensive GW extraction, resulting in elevated hydraulic gradients that drive seawater towards the inland area [29] and may increase the infiltration of MPs in GW.

Li et al. [74] investigated the impact of GW–seawater displacement on the transport behaviours of marine plastic particles through experiments on flow chamber systems and packed column systems. Their results confirm that plastic particles can enter the aquifer via seawater intrusion. Particles that attach to porous media during this process are more easily moved by GW–seawater displacement, especially when there is low ionic strength as the colloids attached to porous media tend to detach [75]. As a result, these particles can return into the seawater.

2.2. Transport of MPs through the Soil and the Unsaturated Zone to GW

MPs can enter the soil through poorly managed landfills, agricultural activities, the use of untreated wastewater for irrigation, flooding, bioturbation, atmospheric deposition, and illegal dumping of waste [76–78]. Agricultural activities can have a significant impact on the presence of MPs in the environment. For example, once in the soil, plastic mulches used in modern agricultural systems can be degraded to MPs and transported into the GW [54,77,79].

Larger plastic particles in soils can undergo degradation due to UV radiation, physical abrasion, and biological processes, thus transforming into MPs [80,81]. The generated MPs and MPs of primary origin can undergo fragmentation and phototransformation due to UV radiation and physical forces. In combination with aging, these processes can lead to the production of smaller MPs [82–84] with rougher surfaces, oxygen-containing functional groups, and more specific surface areas. These properties improve their capacity to adsorb pollutants from the environment, e.g., heavy metals and pesticides [85–88].

Due to their small size and large surface area, soil organisms such as earthworms, collembolans, and mites can transport MPs from the soil surface into deeper layers by various mechanisms such as pushing, ingestion, egestion, and adhesion to their exterior [89–91]. Invertebrates can also indirectly influence the transport of MPs by creating macropores in the soil, which serve as conduits for the transport of MPs through the process of leaching [89]. In addition to their direct or indirect transport by soil organisms, MPs can also reach deeper soil layers via percolating water [92]. Conversely, the presence of plant roots in the soil tends to retain or lift MPs along the soil profile [93].

The unsaturated zone provides an important link between the land surface and the GW [93]. MPs that permeate the soil can cross the unsaturated zone and reach the GW [88]. The processes of transport and binding of MPs to the substrate depend on particle properties, soil properties, and environmental factors [39,87,92]. Recent column experiments (Table 1) have investigated the impact of different environmental factors or particle properties on the transport or retention behaviour of MPs [87,94–100].

Particle properties such as surface hydrophobicity, density (which depends on the chemical composition or plastic material), shape, and size can influence the transport of MPs through porous media [98]. Smaller and regular shapes have better mobility than larger and irregular particles. While particle size and shape are the main determinants of MP transport, particles with higher hydrophobicity and density exhibit greater migration [98,100,101].

Table 1. Column experiments under unsaturated conditions investigating MP transport influenced by different experimental factors and MP properties.

Reference	Factor	Column Characteristics (cm)	Polymer	Shape	Media Material	Max Infiltration Depth (cm)	dMPs/dMedia	Rainfall Intensity
Waldschläger and Schüttrumpf. [96]	/	19.40 × 30.00	CoPA; PA; PE; PET; PP; PS; PVC; SBR	Fibre; fragment; pellet; pellet cubic; sphere	Glass sphere	0.00–30.00	0.05–3.33	4600 mL/min
Ranjan et al. [97]	Wet-dry cycles	9.00 × 33.00	PE; PET; PP	Fragment	Sand	6.00–>30.00	<0.02–1.40	2.5–7–7.5 mm/h
Gao et al. [98]	Wet-dry cycles and presence of DOM	4.00 × 25.00	PA; PE; PET; PP	Pellet	Sand	0.00–13.50	0.017–2.14	/
Zhang et al. [99]	Artificial rainfall	39.00 × 9.00 × 29.00	PET; PE	Particle; fibre: film	0.03% MO; 0.77% clay; 17.27% silt; 81.73% sand	7.00	/	15.00 mm/day
		39.00 × 9.00 × 29.00	PET; PE	Particle; fibre: film	0.03% MO; 0.77% clay; 17.27% silt; 81.73% sand	6.00	/	25.00 mm/day
	Natural rainfall	39.00 × 9.00 × 29.00	PET; PE	Particle; fibre: film	0.03% MO; 0.77% clay; 17.27% silt; 81.73% sand	5.00	/	3.10 mm/day
O'Connor et al. [100]	/	25.00 × 4.00	PE	Spheres	Sand	7.500	0.05	83 mm/day
	/	25.00 × 4.00	PE; PP	Spheres	Sand	3.500	0.07–1.39	83 mm/day

Various media factors such as pH, humic acids, organic matter content, and electrolytes can lead to fluctuations in MP transport. However, as indicated by recent studies [102,103], these factors do not have a significant impact. Dong et al. [103] conducted a column experiment to investigate the effects of electrolyte concentration, pH, and humic acid on the transport of MPs. The study found that the mobility of PET MPs increased with decreasing electrolyte concentration, rising pH, and increasing humic acid concentration. The study also proved that the density and shape properties of PET MPs have a greater impact on their transport behaviour in porous media than the experimental chemical conditions.

Soil texture and MP size are both important factors that influence the movement of MPs through the soil. As MPs move through the soil, they travel through the spaces between the soil particles. If these spaces are smaller than the MPs, they can become trapped in the soil. The ratio between the size of the MP (dMP) and the size of the soil particles (dMedia) is a major factor influencing this process. Studies by Gao et al. [98], Ranjan et al. [97], and Waldschläger et al. [96] have shown that MPs tend to migrate deeper into the soil when the ratio of dMP/dMedia is less than 0.11. This ratio has been identified as the most important factor influencing the migration of MPs [98].

Soil layering may inhibit movement by enhancing MP deposition in the upper soil horizons, making MP transport in multilayer aquifers more complex [39]. Macropores, on the other hand, can promote preferential flow, increasing the likelihood of MPs reaching the GW [39,92,104]. To determine the size of MPs that can be transported through sediments, it is necessary to analyse the lithology and identify the pores and fissures in the soil [39].

In experiments with dry–wet cycles in a sandy soil column, O'Connor et al. [100], Ranjan et al. [97], and Gao et al. [98] found that weather patterns involving rainfall events followed by dry periods determined the depth of MP transport more than the volume of water flowing through the column.

Zhang et al. [99] conducted a leaching experiment to investigate the vertical migration of MPs under simulated and natural rainfall. Their experiment also showed that natural rainfall resulted in higher vertical migration compared to simulated rainfall. This emphasises the importance of conducting experiments under realistic environmental conditions to more accurately predict the distribution and fate of MPs in the natural environment.

3. Occurrence of MPs in GW

Early research on MPs focussed primarily on marine environments, with an emphasis on analytical approaches and reporting of data from monitoring campaigns [105]. The scope of studies focusing on freshwater environments remains limited. According to a recent review, 87% of the database of studies on MPs is associated with oceans, while only 13% refers to fresh water [106]. Few studies have been conducted on the detection of MPs in GW [2,25,33,59,107,108]. Table 2 summarises the results of the field studies selected for this review.

Currently, there is no standard procedure for the sampling and analysis of MPs in GW, and recent studies agree that there is an urgent need to standardise the sampling and analysis protocols [15,35,39,59]. Consequently, studies assessing the occurrence of MPs in GW are difficult to compare as they use different sampling and analytical approaches [15]. In addition, a multitude of factors can contribute to the variations in the number of MPs detected in GW across different studies, e.g., population density [109], climatology, hydrology, geology, land use of the study area [110], the presence of a particular source of contamination [111], and the distance between the surface and the aquifer [112].

Recent studies have identified various MP contamination sources in GW, including septic tanks, landfills, sewage treatment plants, and agricultural areas [109,113–115]. A significant correlation has been found between MP abundance in GW and the total concentration of antibiotics, proving that sewage treatment plants are a source of contamination [109]. Several studies have attempted to determine the impact of landfills on the occurrence of MPs in GW. They show that municipal and informal landfills, including abandoned municipal landfills, are sources of MPs that can contaminate GW. Informal landfills, which are built without proper construction and operated with a lack of environmental protection measures, are a cause for concern due to their insufficient protection and poor management [115]. Wan et al. [115] found a concentration of 11 to 17 MP/L of MPs in GW around an informal landfill, while Leideu et al. [113] investigated the presence of MPs in GW around a former municipal landfill located in an alluvial aquifer and found even wider concentration range of 0.71 to 106 MP/L. In addition, a study from Chennai, South India, reported higher levels of MPs in GW samples in the vicinity of municipal solid waste landfills, ranging from 2 to 80 MP/L [114]. MPs originating from industrial wastewater can also be an important vector for the transfer of heavy metals [2].

The capacity of karst systems to transport MPs into GW has been demonstrated in three studies from different parts of the world. The highest concentrations were reported from Italian cave water, where 12 to 54 MPs/L was measured, with no difference between tourist and non-tourist areas [116]. In a ground-breaking study from the USA, Panno et al. [25] discovered the presence of MPs in karst aquifers with an average of 7 ± 4.3 MP fibres per litre. Private septic tanks appear to be the source of MPs that can enter GW through sinkholes in the investigated area. In a remote area of China without a specific source of pollution, a low MP concentration was reported (ranging between 0 and 4 MP particles/L) [117].

Even fewer studies have been conducted on the occurrence of MPs in alluvial aquifers, namely, only two. However, recent studies by Esfandiari et al. [110] and Samandra et al. [108] have shed some light on this topic. In Iran, they found MPs in the range of 0.1 to 1.3 MP/L [110]. In contrast, much higher concentrations were detected in Australia, averaging 38 ± 8 MP/L in an unconfined alluvial aquifer [108].

Sample volume in the studies included in this review [2,25,108–110,113–115] ranged from one to twenty litres. When measuring MPs, a small sample volume can lead to an overestimation [118]. A minimum sample size of five hundred litres is necessary to ensure reliable results [15,119,120]. However, only two studies, both from Korea, sampled this many litres or more directly from GW [112,121]. These studies were conducted in a fractured rock aquifer and showed differences in the number of MPs detected. The first study reported MP concentrations between 0.02 and 3.48 MP/L. Their chemical composition was similar to the results of previous studies conducted on soils from the same area,

suggesting that the MPs present in the soils are leaching into the GW [121]. The second study detected fewer MP particles, with results ranging from 0.006 to 0.193 MP/L [112]. The highest MP concentrations were detected at the lowest altitude points, suggesting that the distance between the surface and the aquifer may be a factor in the entry of MPs into the GW [112].

The most frequently reported types of MPs in GW were PP and PE, which are also the most extensively manufactured types of plastics on the global scale [3] and the most highly prevalent types in marine environments [122], rivers [123], lakes [124], freshwater sediments [125], and soils [126,127]. The large amount of PP and PE particles in these environments poses a significant risk to the environment partly due to their potential to adsorb metals even at low concentrations [2]. To mitigate their negative impact, it is therefore crucial to understand the transport parameters of these particles.

The correct classification of MP particles in GW is important as the MP shapes detected can provide information about their source [128]. For example, MP fibres originate from the degradation of synthetic textiles and represent the predominant shape of MPs in wastewater treatment plant (WWTP) effluents [129]. Their presence may therefore indicate contamination from a WWTP effluent. On the other hand, fragment shapes are typical for weathering degradation of MPs, and their presence in GW may indicate contamination from a soil source [121]. Understanding the transport parameters of MP fibres and fragments is crucial for predicting GW contamination by MPs, as these are their most prevalent forms in GW [130].

It is crucial to ensure reliable and comparable results across different types of aquifers. Therefore, analysing the presence of MPs in different types of aquifers must be conducted using the same methodology for their sampling, quantification, and identification.

Table 2. Summary of the results of the analysed field studies investigating the presence of MPs in GW.

Reference	Country	Landfill/Aquifer Type	Sampling Procedure				Analytical Method				Results		
			Well Cleaning before Sampling *	Pump	Filter	Sampled Volume (L)	Sample Treatment	MPs Detection and Quantification	Quality Control	MP Concentration (MP/L)	Main MP Type	Main, MP Shape	Size of Detected MPs (μm)
Kim et al. [112]	Korea	Fractured rock mass and basal aquifer	5 min	Peristaltic pumps	Stainless steel—20 μm	500	50 mL of 30% H_2O_2 24 h—20 μm steel mesh filter—density separation 40 mL solution $\text{Li}_2\text{O}_{13}\text{W}_4^{-24}$ and ultra-pure water—metal filter	μ -FT-IR	Field blanks	0.006–0.192	PP, PE, PET	Fragments and fibres	20–50
Cha et al. [121]	Korea	Weathered and/or fractured rock aquifers	Yes	Peristaltic pump	Stainless steel—100 and 20 μm	300–500	30% H_2O_2 solution for 24 h—20 μm stainless-steel filter—40 mL solution of a Li_2WO_4 —20 μm stainless-steel filter—dried at room temp	μ -FT-IR—Imaging microscope	Lab blanks/field blanks	0.02–3.48	PP, PE	Fragments	50–100
Panno et al. [25]	USA	Cracked and open karst aquifer	/	/	0.45 μm	2	Dried at 75 $^\circ\text{C}$ for 24 h	Dissecting microscope—py-GCMS	Lab blanks	Average 7.00 St. dev. 4.30	PE	Fibres	<1500
Shu et al. [117]	Southwest China	Karts aquifer	Yes	Extruded outlet device	0.45 μm	1	30% H_2O_2 at 65 $^\circ\text{C}$ and 100 rpm for 12 h—250 mL saturated NaCl 2 min—dried at 50 $^\circ\text{C}$ for 24 h	Stereoscopic microscope—RAMAN—FT-IR	Lab blanks	0.00–4.00	PS, PP, PET	Fibres	3–20
Balestra et al. [116]	Italy	Cave waters	/	/	Silver—0.8 μm	1	Dried for 2 h at 40 $^\circ\text{C}$ —2 mL of 15% H_2O_2 30 min—dried for 2 h at 50 $^\circ\text{C}$	UV flashlight under a microscope—Infrared (IR) spectroscopy	/	12.00–54.00	PE, PVA	Fibres	100–990
Selvam et al. [2]	South India	Costal aquifer	/	12 V Teflon pump	Stainless steel—50 μm	20	30% H_2O_2 and Fe (II) solution—micro-line filter paper—diluted with deionised water	Stereoscopic microscope— μ -FT-IR—Atomic Force Microscopy	Field blanks	0.00–4.30	PA, PE	Fibres	120–2500
Shi et al. [109]	North China	Drinking water source	Yes	/	Polycarbonate—5 μm	1	30 mL of 30% H_2O_2 24 h at 40 $^\circ\text{C}$	Optical microscope— μ -FT-IR	Lab blanks	4.00–72.00	PA, PE, PP, PVC, PS	Fragments	<50

Table 2. Cont.

Reference	Country	Landfill/Aquifer Type	Sampling Procedure				Analytical Method				Results		
			Well Cleaning before Sampling *	Pump	Filter	Sampled Volume (L)	Sample Treatment	MPs Detection and Quantification	Quality Control	MP Concentration (MP/L)	Main MP Type	Main, MP Shape	Size of Detected MPs (μm)
Samandra et al. [108]	Australia	Alluvial unconfined aquifer	Yes	Bailer	Polycarbonate— $15\ \mu\text{m}$	1	40 mL of 30% H_2O_2 for 12–24 h at $60\ ^\circ\text{C}$ —density separation with 35 mL of a saturated CaCl_2 solution	LDIR	Field blanks, method blanks. Positive control: Lab control	Average 38.00 ± 8.00	PE, PP, PS, PVC	Fragments	18–491
Esfandiari et al. [110]	Southwest Iran	Alluvial aquifer	30 min	/	Paper— $2\ \mu\text{m}$	20	250 mL of 30% H_2O_2 1 day—filter paper $2\ \mu\text{m}$ —dried at room temp	Binocular microscope—RAMAN—SEM	Lab blanks, Positive control: Lab control	0.10–1.30	PS, PE, PET	Fibres	< 500
Ledieu et al. [113]	France	Landfill—alluvial groundwater	Yes	Supernova 21 pump	Metal— $10\ \mu\text{m}$	8.8–10.2	Alumina filter $0.1\ \mu\text{m}$ —100 mL of 30 wt% H_2O_2 48 to 72 h—ultrasonic bath—densimetric separation with NaI solution—JAMSS unit 24 h	μFTIR	Lab blanks, field blanks	0.71–106.70	PE, PP	/	32–2758
Manikanda et al. [114]	South India	Landfill	/	/	/	1	/	Dissecting microscope—SEM—ATR—FTIR	/	2.00–80.00	Nylon, PP, PS	Pellets, foam, fragments, fibres	/
Wan et al. [115]	South China	Landfill	/	/	Stainless steel $150, 75, 45$ and $25\ \mu\text{m}$	4	40 ml 0.05 M Fe (II) solution and 40 ml 30% H_2O_2 — $0.45\ \text{mm}$ filter membrane—density separation	LDIR Chemical Imaging System	Blanks in the entire procedure	11.00–17.00	PE, PP, PET	Fibres	20–150

Notes: * When yes, it was mentioned that the water discharged before sampling was at least three times the volume of water in the borehole or/and the physico-chemical water parameters were stable.

4. Challenges in GW MP Research

On the basis of our experience and analysis of the research articles listed in Table 2, we identified several challenges associated with the monitoring of MPs in GW. The main challenge is that there is currently no internationally agreed upon sampling method and MP detection procedure [131]. The challenges associated with sampling methods and sample analysis associated with quality assurance are described below.

4.1. Challenges Associated with Sampling Methods

Researchers conducting research on MPs in GW face several challenges in the field of GW sampling. Firstly, they need to select a suitable sampling site and then the correct sampling technique to ensure high-quality samples and comparable results. The important aspects of both are described below.

a. Sampling point selection

Improper selection of the sampling point is a major concern, as it can lead to incorrect or questionable results. The sampling point must be defined on the horizontal and vertical scale (depth). To determine the optimal sampling location, we need to know the precise hydrogeographic conditions of the sampling site and the positions of the available boreholes or pumping stations.

In this context, Viaroli et al. [39] note the lack of information on the hydrogeographic properties of sampling points in many studies on MPs in GW. In order to conduct reliable research, sampling from a borehole requires consideration and inclusion of the following hydrogeographic features of the sampling sites: (a) data on the lithological profile of the sampling site, (b) data on the protection and maintenance of the sampling site, (c) data on the quality status of the sampling site, and (d) data on the borehole design (drilling method, borehole material, borehole depth and height, quantitative borehole capacity). For a correct interpretation of the pathways and origins of the detected MPs, it is also important to understand which GW (aquifer) enters the borehole [119].

There appears to be a lack of specific guidelines in the literature for determining the optimal depth for sampling in a well or below the GW table. In some articles, the depth at which sampling was performed is not mentioned [109,110,113]. Selvam et al. [2] state that sampling was carried out at a depth of 2–5 m. Samandra et al. [108] report that sampling was performed at the mid-point of the screened interval of the boreholes. Although further studies are required on the appropriateness of the sampling depth, it is expected that sampling should be carried out at the level of the screened section of the borehole. Sampling a few metres below the water table may result in sampling stagnant water from the well rather than from the aquifer itself, depending on the hydrogeological conditions of the aquifer and the pumping force.

When selecting the sampling points, the maintenance of the sampling boreholes must also be taken into account. Inadequate maintenance of the sampling points can lead to the presence of plastics and consequently MPs at the sampling points, which should be avoided. Boreholes that are open to the atmosphere and constructed with plastic materials should be avoided as they can be a source of contamination. However, some of the articles analysed report sampling in open or plastic-lined boreholes [108,110].

When sampling from a spring, it is possible to take samples either directly from the spring or from a pumping system. Sampling from a spring can lead to problems with air pollution, so it is important to sample as close to the spring as possible. If this is not possible, the distance at which sampling was performed should be indicated. On the other hand, sampling from a pumping system can lead to MP contamination due to the potential use of plastics in the construction of the facilities. Nevertheless, it is beneficial to compare the data from both sampling points in order to validate the reliability of the results.

b. Sampling procedure

Sampling with the pumping system

When sampling from a well, obtaining the necessary amount of sample water requires the use of pumping systems consisting of the pump and the filtration system which allow for the filtration of large amounts of water at the sampling point. Typically, the pumping systems also contain plastic parts that can potentially contaminate the sample. Of the articles analysed, only one indicates the use of Teflon-made pumps [2], while some [112,113,121] mention the type of pump used without specifying its material composition. All components of the pumping system need to be specified with regard to their material structure using FTIR analysis. The spectra of materials used must be included in the library, and the particles from the samples must be compared with them.

Furthermore, larger MP particles can be damaged and even fragmented as they pass through the pump, especially when pumps with impellers are used. This may lead to an overestimation of the presence of MPs. Therefore, it is important that researchers first test the pump for the potential fragmentation of plastic particles.

Design of the field filtration system

Designing a filtration system to sample large quantities of samples in the field can be challenging, as this requires a closed filtering system to prevent contamination from the atmosphere. Direct contact between plastic materials and samples should be avoided. This can complicate the construction of the system due to the limited options for suitable materials. Although some plastics have the desired properties such as elasticity or impermeability, they can be difficult to replace and are associated with higher costs. For example, silicone hoses and stainless-steel filter cartridges are favoured over plastic hoses and pipes, and hemp threads are a better alternative to plastic thread sealants.

Among the articles reporting on water sampling using pumping systems, two emphasise the use of silicone and stainless-steel materials [112,121] and mention the use of peristaltic pumps without providing any further information. Two other studies mention PVC components for the system [2,113].

It is also crucial to monitor the pressure in a closed system, as pressure-related problems can occur due to the strength of the pump and the likelihood of filter clogging. Such problems can result in damage to the system or filter, as well as loss of samples. It is, therefore, important to monitor this parameter closely by using a pressure gauge.

To control the amount of water collected, it is necessary to use a flow meter. Typically made of plastic, the flow meter can come into contact with the sampled water. This can be prevented by using it after the water has been filtered. This approach was used by Cha et al. [121].

Determination of the sample volume

To avoid underestimating the occurrence of MPs, the recommended minimum volume of GW sampled is 500 L [119]. The same volume has also been suggested for tap water [15]. Of all the studies examined, only two adhered to the recommended minimum sample volume of 500 L [112,121]. These studies detected a lower number of particles than other studies, which contradicts their initial assumptions. Both studies were conducted with similar sampling methods in the same type of aquifer. To establish whether the lower numbers observed are due to the type of aquifer or the sampling methods, further studies using the recommended minimum sample volume need to be conducted.

Collecting a minimum of 500 L of sample water poses a certain logistical challenge, especially when it comes to transporting the sample to a laboratory for filtration in a controlled, filtered air environment. It is therefore necessary to perform in situ filtration, despite the problems that this process may entail.

Selection of the proper filters

When analysing MPs in samples, studies report that the smallest size of MPs detected corresponded to the size limitation of the filter used [109–112,115]. This suggests that the filter used may have limited the detection of smaller MP particles during sampling. However, in most of the studies analysed, filter pore size did not appear to be a limiting factor, as the size of MPs detected was generally larger than the filter pore size. Nevertheless, it is worth noting that the detection limit of the analytical methods may influence the results.

For example, Kim et al. [112] mention the use of a filter size of 20 μm due to the 20 μm detection limit of the equipment for analysis. The use of a smaller pore size would therefore not help to extend the detection range of the MP particles but rather increase the risk of filter clogging. Sometimes also membranes $>20 \mu\text{m}$ become rapidly clogged. To avoid clogging, the use of cascade filtering system is recommended.

In addition to the pore size, the material of the filters is also important. For the analysis of samples with an FTIR microscope or a Raman spectrometer, aluminium- or gold-coated polyester membranes and silicone membranes, which are suitable for analysis of particles in reflection mode, are particularly recommended. However, they have limitations in terms of pore size, which are generally too small and unable to filter large amount of water. Innovations and improvements are still needed in this area.

Purging before real sampling

The construction materials and work involved in building a well can lead to MP contamination. In addition, open-air wells can become contaminated with plastic waste or MPs due to atmospheric deposition. In order to accurately investigate the occurrence of MPs in GW through borehole sampling, it is necessary to purge the well before sampling begins. This involves pumping out two to three times the volume of the well or until the physicochemical parameters of water stabilise [132]. This standard procedure ensures that the sample is taken from the aquifer rather than the accumulated water in the well [108]. Moreover, sampling without purging yields information on the MPs present in the wells, which can provide useful information on the exposure to MPs for those using the water from that well for domestic purposes [131]. Some of the articles analysed in this study do not indicate whether purging was performed, while some of them mention purging for a specific duration, such as 5 or 30 min. Such a duration may or may not confirm the pumping of two to three times the well's volume or the stabilisation of physicochemical parameters. It may also result in inadequate purging. Therefore, it is important for studies to mention whether or not purging was performed prior to sampling as this would allow a more accurate interpretation of the results.

The importance of conducting blank sampling in the field and quality control

The difficulty of avoiding the use of plastics during in situ sampling reinforces the need to perform blank sampling for the pumping and filtration processes in the field. This is to ensure that the potential contact of the sample with plastic materials does not influence the results.

Replicating the properties of sampling and filtration in a field blank sample is a complex process as it is difficult to obtain a large volume of water that is free of MPs. One possible solution to this problem is to obtain a blank sample containing a smaller volume of water. For example, in a study conducted by Kim et al. [112], a blank sample of 20 L of water was collected, while the total volume of water sampled was 500 L. This approach helps to reduce friction and minimise the wear on the plastic materials in the system, although it may not exactly replicate the conditions of the target, which could potentially raise concerns about the accuracy of the results.

Given the complexity of obtaining a suitable and reliable field blank, one possible option to ensure that the materials in the sampling system do not interfere with the results is to perform an FTIR analysis of these materials. If there is a high degree of similarity between these materials and the MPs detected, as well as a match of other properties (e.g., colour and morphology), they should be excluded from the results.

4.2. Challenges Associated with Laboratory Analysis

Laboratory analysis of GW samples requires a lot of experience in the field of MP identification, as MPs are on average smaller and less colourful compared to MPs from surface water. Depending on the type of aquifer, samples may or may not need be pretreated before MP identification, which can be performed using FTIR or Raman spectroscopy. Both techniques require very experienced scientists for a good interpretation of the results.

a. Pretreatment of the samples

The process of preparing GW samples for MP analysis typically includes the following steps: filtration, digestion, and extraction. These steps, which are occasionally required to separate MPs from other particles such as sediment, organic matter, and minerals, can be challenging and may require labour-intensive sample preparation that carries the risk of contamination. Microplastics in marine environments have been extensively studied, and well-established analytical methods can be used as a reference for the pretreatment of groundwater samples if necessary. It is essential to mention that digestion steps, if necessary, should be performed before density separation, as MP particles can be entrapped in the organic material [133].

Most of the studies analysed used sample digestion to remove organic matter [2,106,107,109,110,112,113,118], as this can interfere with the analysis and lead to an overestimation of MPs, or an inflated number of particles subjected to further analyses [134]. Although this technique has been shown to be effective for the analysis of MPs [135], any treatment of the sample may result in damage or loss of the sample or involve the risk of contamination. It is therefore advisable to avoid it as much as possible. Exposure to harsh chemicals and higher temperatures than 40 °C should be minimised [133]. As GW is not expected to contain large amounts of organic matter that could interfere with the analysis of MPs, digestion is therefore not recommended.

During density separation, in order to increase the recovery rate of microplastics, solutions with densities higher than 1.7 g/cm³ are recommended [133]. For instance, sodium chloride (1.2 g/cm³) is not recommended as its low density interferes with the polymer's recovery [133]. Zinc chloride (ZnCl₂), sodium polytungstate (NaWO₄), potassium carbonate (K₂CO₃), sodium bromide (NaBr), sodium iodide (NaI), and potassium formate (HCO₂K) are commonly used density solutions [133]. The density separation process typically involves shaking for 10 min and settling for 24 h [133]. During supernatant extraction, some microplastics may stick to the container wall, which can result in sample loss. To avoid this issue, it is recommended that the container walls be washed onto the filter [136].

Validation of the effectiveness of sample preparation methods is crucial and can be achieved with the use of positive controls. In addition, the possibility of sample contamination can be controlled by using blank samples during all steps of the analysis. Of all the articles selected for this review, only two mention the use of positive controls in the laboratory [108,110].

b. Limitations of methods for MP detection and quantification

Selecting the most appropriate sampling and detection method for all sizes of MP particles, which can range from 5 mm to 1 µm, is a major challenge. Chemical characterisation of plastics with spectroscopic methods is an extension to light microscopy. Spectroscopic techniques can help to exclude the doubtful particles of bigger sizes and include smaller particles, which are difficult to recognise on the basis of morphological features. Fourier-transform infrared (FTIR) spectroscopy or Raman spectroscopy produce the sample's molecular fingerprint represented with spectra. Spectroscopic data of each particle are compared with reference spectra in the library [137]. The ATR-FTIR method enables an easy determination of the chemical composition of particles larger than 0.5 mm, and the FTIR microscope enables the determination also of particles smaller than 0.5 mm. While all FTIR techniques can easily detect larger particles, they reach their limits when detecting smaller particles (<20 µm). As the particle size decreases, the reliability of the chemical analysis results also tends to decrease. Raman spectrometry is more suitable for smaller particles and also enables the detection of particles <20 µm. Among particle size limitations, there are a few more factors that can influence the detection of MPs with spectroscopic techniques, e.g., additives, pigments, dyes, and fillers can overlay the signal of polymer, which can be seen as (i) a foreign band overlay, (ii) fluorescence, and (iii) absorbance [138].

The smaller the particles, the more difficult and time-consuming they are to detect, so complementary techniques are often required to facilitate this process. For example, in our laboratory, we work with an ATR-FTIR spectrometer for the identification of particles >0.5 mm, and with an FTIR microscope in reflection mode, we analyse particles <0.5 mm.

Shu et al. [117] used an FTIR microscope to identify larger MPs, as well as a microscope with a laser Raman spectrometer to detect smaller MPs. However, using more than one technique can lead to errors in counting the samples. To improve monitoring efficiency, the sampling and detection techniques should be suitable for similar sample sizes.

4.3. Challenges Associated with Quality Assurance

There is a risk of samples being contaminated with MPs during collection, transport, and processing, which can lead to inaccurate results. The accuracy of the results obtained depends on the sampling methods used and the precautions taken to avoid contamination [15,120]. Therefore, it is essential to follow the best practices recommended by experts to obtain reliable results. To minimise the potential for cross-contamination, it is advised to use glass or metal materials for sample preparation and avoid plastic [139]. Additionally, it is recommended to clean the materials with acid and filtered water or ultrapure water [139]. All personnel involved in the sampling should wear clean white cotton lab coats. To prevent air contamination, in situ filtration with a closed device is recommended, which eliminates any air contact with the sample. It is also suggested to use glass Petri dishes for the transport and storage of filters.

It is essential to take replicates while sampling to ensure precise and accurate results. Replicates are significant in comprehending the sampling's variability and enabling the collection of trustworthy data. Therefore, it is advised to use replicates while sampling also for sampling MPs in GW. To better distinguish the sources of variability affecting the sample, it is necessary to provide information on the exact process of collecting replicate samples. However, only three studies report the use of replicates in sampling. Selvam et al. [2] report the use of two replicates, while Shu et al. [117] used three replicates, as did Samandra et al. [108], who also report that they observed no consistent trend associated with the order of sample replicates.

The difficulty and time required to sample MPs can make performing replicates a challenging task. For this reason, a sampling system in which three simultaneous samples are collected with a single pump would be ideal to save sampling time and ensure the precision of research methods. In certain situations, conducting simultaneous replicates may not be possible due to certain limitations. For instance, the pumped flow may be low in some sampling locations, which may complicate sampling and, thus, make it difficult to carry out simultaneous duplicates. Under such circumstances, using sequential replicates can be a practical alternative to ensure an appropriate sampling.

5. Conclusions

MPs present in rivers, lakes, seas, and soils can enter GW via different pathways. The articles investigating the presence of MPs in GW show different results, both in terms of the quantity, shape, and size of the MPs detected, which could be the result of differences in the investigated areas (population density, climatology, geology, land use), as well as differences in the sampling methods used in the studies.

The articles included in this review agree that the lack of standardised techniques and procedures in the monitoring of MPs can lead to discrepancies between the results of individual studies. This poses a challenge when comparing results. Therefore, there is a need to develop a standardised methodology to enable a more accurate comparison of the occurrence of MPs in GW.

The complexity of monitoring MP particles is exacerbated by their diversity and the hydrogeological conditions of the sampling sites, as well as the associated risks of contamination. Based on the analysis of twelve research articles on the presence of MPs in GW and personal experiences, the following challenges or needs in sampling MPs in GW can be highlighted:

- An accurate interpretation of the origin and pathways of MPs found in a particular sampling area requires a thorough understanding and proper documentation of the hydrogeological and hydrogeographic conditions in the area.

- When collecting borehole samples, it is important to clean the borehole by pre-pumping a certain amount of water before the actual sampling. The appropriate sampling depth to obtain representative samples of the aquifer is also important.
- To ensure representativeness of the sample, a minimum of 500 L of sample water must be collected. This requires a more complex in situ sampling system, which makes the sampling process more challenging and time-consuming.
- During in situ filtration sampling, it is often difficult to avoid the use of plastics. The sampling system used must be carefully specified, and if plastic materials are present, they should be identified and accounted for in the final results.
- Sampling pumps can physically damage or fragment plastic particles, which can lead to an overestimation of the presence of MPs in the sample. To check for plastic particle fragmentation during operation, it is important to test the pump under conditions that reflect its actual power usage.
- Given that the presence of small particles in GW is expected, the filters and size limitations of detection methods may lead to underestimations of the presence of MPs in GW. To obtain accurate results, it is therefore necessary to develop more efficient filtration systems (e.g., cascade filtration) and improve the detection methods.
- In cases where the concentration of organic matter in the GW sample is low, it is recommended to omit the digestion step during sample preparation.
- To ensure accurate monitoring of MPs in GW, it is crucial to prevent contamination during all monitoring stages. This requires the blank sampling and implementation of quality control measures.

Last but not least, understanding the transport processes of MPs through the soil, the unsaturated zone and within aquifers is important to determine the sources of MPs in GW. These questions need to be clarified through experimental work, field measurements and mathematical modelling.

Research on the presence of MPs in the environment, including GW, is advancing rapidly. Our study focused on identifying the challenges with the ultimate aim of promptly developing standardised methods that will enable comparison of the results of different studies and form the basis for the implementation of measures, including legislative measures, to curb the entry of MPs into the environment.

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