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Groundwater in the age of plastic

Bertil Nlend[1*], Dan Lapworth[2], Michaela Cashman[3], Melissa Lenczewski[4]

[1]University of Douala [2]British Geological Survey [3]US Environment Protection Agency
[4]Northern Illinois University
*nlendbertil@yahoo.fr

@BertilNlend; @LapworthBGS; @EnviroMichaela; @geology79
@iahgroundwater

Abstract

Among the emerging contaminants, microplastics (1-5,000 µm) are becoming an important issue due to their ubiquity in the environment. However, research on this emerging contaminant has been conducted mainly in marine surface waters while microplastics (MPs) are now being found in even the most remote parts of the environment. For example, in groundwater which is the primary water source which supply the world, scientists are just starting to gather evidence on risks to groundwater and dependent ecosystems. This paper reviews the current understanding of plastic contamination in groundwater, summarizes methods that can be used for sampling and detection of plastics as well as the status of environmental regulation of plastics. From the handful of published studies, MPs origins in groundwater are mainly from wastewater effluent, road runoff, agricultural activities, and landfill leachate. The relevant nature of these contaminants are related to their high specific surface area and hydrophobicity allowing co-contamination with various hazardous chemicals such as PCBs, PAHs, BPA, PBDEs, heavy metals and antibiotics. Related to this issues of co-contamination in groundwater, there are potential risks to human health and wider ecosystems that are poorly understood and there has been almost no research undertaken on the occurrence of nanoplastics (<1 µm) in groundwater systems. MPs can potentially contribute to cardiovascular diseases, skin irritation, cancer, reproductive effects, and respiratory and digestive problems. In addition, soil and groundwater contamination can be detrimental to aquatic micro-organisms. There is an urgent need to develop a better understanding of the risks MP and associated co-

contaminants pose and advance national and regional regulations to restrict microplastic contamination of groundwater.

1. Microplastics Background

Plastic contamination in the environment is ubiquitous and we are only just starting to gather evidence on risks to groundwater and dependent ecosystems. This paper focuses on the current understanding of plastic contamination in groundwater, summarizes methods that can be used for sampling and detection of plastics as well as the status of environmental regulation of plastics.

Microplastics (MPs) are solid plastic particles between 1-5,000 µm (Danopoulos et al. 2020) while nanoplastics are plastic particles smaller than 1 µm. MPs that are intentionally produced and enter the environment directly are called primary microplastics. Most MPs are known as secondary MPs, which form when larger plastic items break down into smaller pieces through exposure to chemical, physical, and biological processes in the environment over time. MP abundance varies geographically and is largely governed by environmental and anthropogenic factors; thus, it is difficult to predict global concentrations. However, MPs are found in even the most remote and unsuspected parts of the environment (Obbard, 2018). Although research on this emerging contaminant has been conducted mainly in marine surface waters (Gola et al. 2021), MPs are everywhere, including groundwater (Figure 1).

From the handful of published studies that have quantified MPs in groundwater in countries including the United States, Canada, Australia, India, the United Kingdom, Germany, and China, various sources of these emerging contaminants have been identified: wastewater effluent, road runoff, agricultural activities, and landfill leachate (Mu et al. 2022; Patterson et al. 2023; Sanandra et al. 2022; Viaroli et al., 2022). Panno et al. (2019) confirmed the occurrence of MP fibers in karst groundwater in the US with maximum concentrations of 15.2 MP particles/L. Mintenig et al. (2019) assessed MPs in groundwater drinking water sources in a sedimentary aquifer in Germany; however, results from raw groundwater samples were inconclusive because of the relatively high contamination found in blank samples. Sanandra et al. (2022) found an average of 38 MP particles/L, with the identification of polyethylene terephthalate (PET), polypropylene (PP), polyethylene (PE), and polystyrene (PS) in shallow alluvial aquifer systems in Austria. Esfandiari et al. (2022) found low concentrations of MPs (0.1-1.3 MP/L) with the detection of PS, PE, and PET in alluvial sedimentary aquifers in Iran. Mu et al. (2022) reported a high abundance of MPs (notably PET and polyurethane) from five groundwater sites in China. Lapworth and Shockley (2022) detected MPs (predominantly PP and PE) in groundwater samples from 8 sites in alluvial and Chalk aquifers in the UK, with concentrations between 0.01 and 0.2 MP/L. Sample numbers in these published studies are relatively small; therefore, these results should be considered preliminary, but indicative of the range of MP concentrations and variety of different polymers found in groundwater.

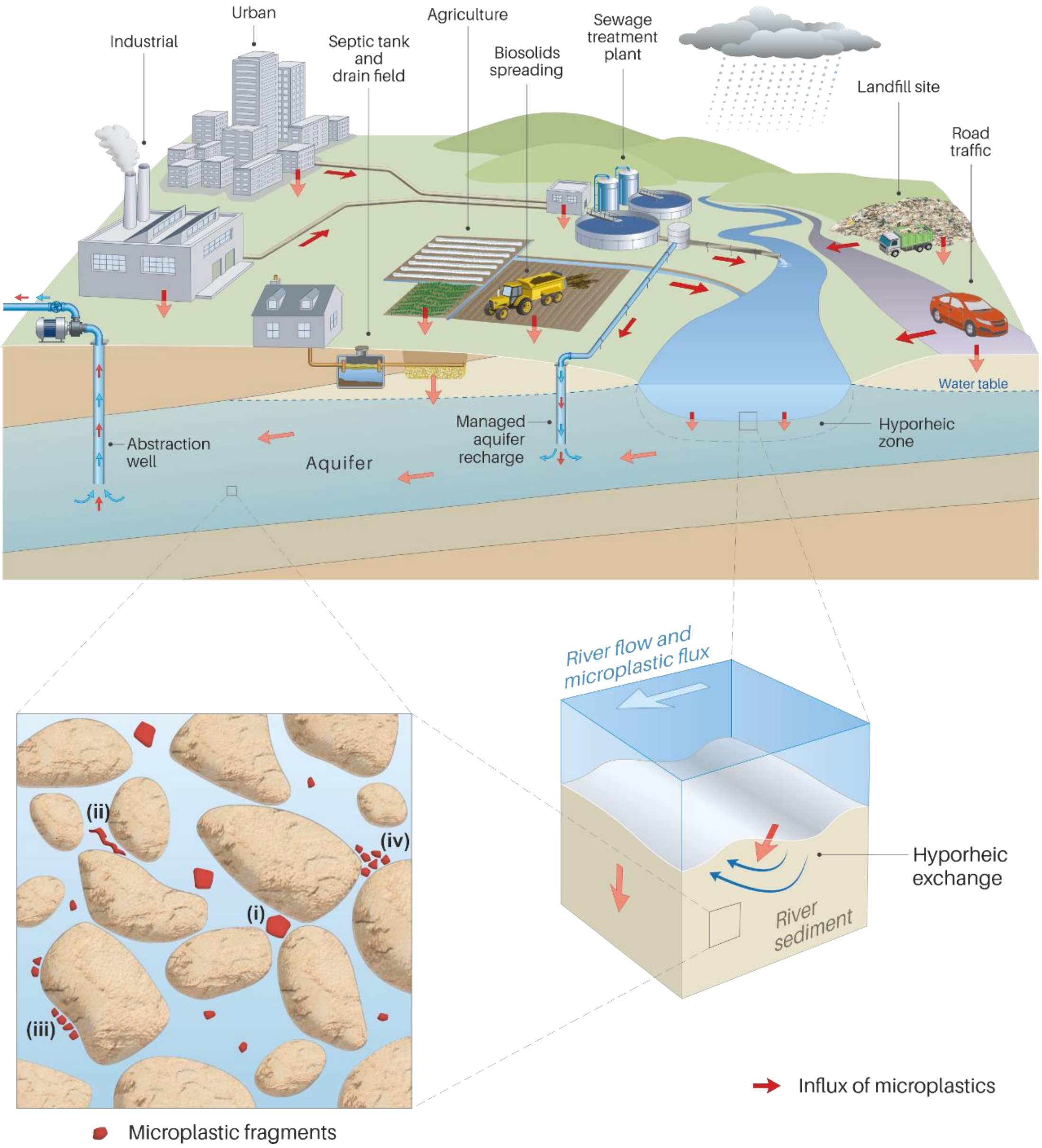

Figure 1. Sources and pathways for microplastic contamination of groundwaters. Source BGS © UKRI 2023. (i) less mobile larger MPs trapped, (ii) MP fibers trapped between grains, (iii) sorption of smaller MP to grain surfaces, (iv) smaller MPs trapped due to narrow pore space.

MP mobility through porous media depends on several factors. The interaction between soil and groundwater is a complex process, involving physical, chemical, and biological mechanisms that can affect the transport and transformation of MPs (Wei and Chen 2023). One study found that the ionic strength of water and aging of MPs impacted transport (Wang et al., 2022). Increased ionic strength of groundwater retained MPs more than lower ionic strength water. In addition, aged MPs with more surface charges showed higher mobility. Research using column experiments examined how flow velocity affected 10-20 µm MPs sized particles. Higher velocities increased mobility, and larger MPs were less mobile. Moreover, increased water salinity decreased mobility, again demonstrating the influence of ionic strength (Qi et al., 2022). Overall, these studies show how small particle size, aging, lower ionic strength, and higher flow velocities promote MP transport through groundwater systems. MP Retardation factors range from 1.58 to 1.75, with microfibers exhibiting the highest retardation, and spheres the lowest (Schenkel, 2022). This aligns with size exclusion principles because fibers likely encountered more strain. While retardation occurred, the retardation factors for different plastic types did not vary significantly.

2. Risks

2.1. Co-contaminants

MPs and nanoplastics with high specific surface area and hydrophobicity are more likely to favor the adhesion and sorption of various contaminants. For example, Shi et al. (2022) found antibiotics in groundwater samples, where their concentrations were significantly correlated with MP occurrences. However, the sorption of pesticides onto MP particles depends on several parameters, such as the hydrophobicity of the pesticide, the pH of the soil, the polymer type, and the degree of weathering of the MP (Hüffer et al., 2019; Seidensticker et al., 2018). Where septic effluents influence groundwater chemistry, a link has been established between machine washing synthetic fiber garments and MPs from wastewaters (Browne et al., 2011; Panno et al., 2019). MPs mixed with absorbed hazardous chemicals such as PCBs, PAHs, BPA, and PBDEs can cause endocrine disrupting effects (Halden, 2010; Smith et al., 2018). Likewise, PVC associated with toxic hydrocarbons and pharmaceuticals, including their metabolites, could become carcinogenic, mutagenic, and endocrine disruptors after uptake. Microorganisms colonizing the plastic environment are often referred to as the "plastisphere" and form biofilms (Sooriyahumar et al., 2022). Microbial habitation accelerated by biofilm formation on particulate plastics enables the movement of microorganisms, especially in the aquatic environment, and impacts the transport and toxicity of contaminants associated with these particulate plastic fragments (Sooriyahumar et al., 2022). Finally, the relationships between heavy metals (HMs, e.g. Cu, Pb, Cd) and MPs are now well documented (e.g., Ren et al., 2021). However, the key factors behind this adsorption are still not well understood. Future research is required to deepen the understanding of the transport of heavy metals and organic compounds by MPs and their interactions in the aquifer.

2.2. Human and Ecological Health

Research on the risks posed by groundwater MP contamination on human health has not been undertaken. This reveals a major gap in the research that needs to be filled in the future. However, although the direct effects of groundwater MPs on human health have not been studied, some authors have pointed out that MPs can contribute to cardiovascular diseases, skin irritation, cancer, reproductive effects, and respiratory and digestive problems (e.g., Rai et al. 2021). Indeed, toxicity may increase due to the adhesive properties of MPs, which allow the adsorption of various chemicals, additives and microorganisms. A good assessment of the effects of MPs on human health is based on their particle size. Particles smaller than 150 µm can be absorbed in the lymph, while those smaller than 100 µm can enter the portal vein, and particles smaller than 20 µm can enter organs such as the liver, lungs, kidneys, and intestine (Gouin et al., 2019; Iqbal et al.,2022; Koelmans et al., 2022; Noventa et al., 2021; Sangkham et al., 2022). At 10 µm, MPs can cause oxidative stress in cerebral human cells (Schirinzi et al. 2017).

There is a lack of studies on the exposure assessment of MPs on groundwater biodiversity. Groundwater is home to biodiversity called stygofauna, crustaceans such as copepods, isopods, amphipods, decapods, fungi, worms, snails, and amphibians (Hérivaux et al. 2013). Lapworth and Shockley (2022) assessed MP detections in stygofauna from Chalk boreholes in the UK from a small sample of sites (n=2 with 35 and 80 *N. Kochianus* individuals, respectively). No MPs were detected above the method blank for the stygobites samples. Two MPs were detected in the stygobite method blank, and two MPs were detected in one of the stylolite samples. Belkhiri et al. (2022) reported that MPs would result in the same effects as in surface waters *i.e*: decreased growth rate, decreased reproduction, inhibition of mobility, and increased mortality of aquatic microorganisms. In addition, soil and groundwater contamination can be detrimental to root systems that draw water (Ebere et al. 2019; Yang et al. 2021). The knowledge of such ecological effects should be better understood. Nevertheless, experiments in soils have shown that ecological disturbances are reflected in carbon allocation and biomass production after adding either polyvinyl chloride and/or PE or polythene MPs (Chia et al. 2021).

3. Current Techniques/Regulation

3.1. Sampling and Sample Preparation

The first step in sampling is to identify the research questions and analysis methods. Sampling and extraction method selection will inherently bias the sizes, densities, and shapes of MPs recovered in each sample (Cashman et al., 2020). Typically, water samples have comparatively low MP concentrations and require larger sample volumes. Therefore, volume reduction methods using sieving or filtration (Figure 2) may be advantageous (Razeghi et al., 2021; Lapworth and Shockley 2022).

Figure 2 Filtering groundwaters for quantifying microplastics (D Lapworth BGS © UKRI 2022) (*left and right*).

The most important aspect of sampling is to ensure an appropriate quality assurance plan to minimize accidental MP contamination. This may require field sampling personnel to wear clothing made from natural fibers, eliminating plastic from sampling equipment, and using lab spaces without plastics, when possible. Other recommendations include using sample blanks and spikes to estimate quality assurance (Primpke et al. 2020; de Rujter et al. 2020). Figure 3 shows for instance the protocol deployed on the field for microplastics sampling.

Figure 3 Sampling landfill monitoring borehole for microplastics (D Lapworth BGS © UKRI 2022) (*left and right*).

3.2. Methods of detection

There are no universally accepted methods for the characterization of MPs. A tiered monitoring framework presented by Coffin et al. (2023) considers the following three levels of MP identification: total particles, total MPs and chemical ID. These identification levels increase in specificity and difficulty.

Total particle analysis (e.g. Light scattering or visual spectroscopy) is the most basic assessment of potential MP abundance. Methods such as light scattering or visual spectroscopy identify the quantity of particles in a sample extract. The benefit of such methods is that they are cost-efficient and can be extrapolated to estimate the upper thresholds of MP abundance. However, these methods overestimate MP abundance because they also quantify inorganic and organic suspended solids and non-plastic particles. However, total particle analysis is often the first step in estimating MP abundance.

Total microplastic methods (e.g. Nile red fluorescence or hot needle) identify whether particles are composed of plastic but do not give any information on the polymer type. These methods rule out inorganic or non-plastic particles (e.g. quartz, silt, cotton, and chitin) but do not specify the properties of the plastic. They are more cost-efficient than chemical ID and give more accurate results than total particle analysis.

Chemical identification (e.g. Fourier Transform Infrared, Pyrolysis Gas Chromatography, and Raman spectroscopy) is the most time and labor-intensive type of MP identification. It relies on spectral analysis to identify the chemical fingerprints of individual particles. The spectrometers are expensive compared to other methods and there is significant data processing required which necessitates more extensive training. The advantage of chemical identification is the amount of data associated with each particle. Chemical identification can provide information on the polymer composition, shape characteristics and associated additives. Some chemical ID techniques can also provide mass-based concentrations. These properties play a significant role in estimating environmental risk and can provide valuable information on sources.

3.3. Global regulatory status

Many countries have taken steps to restrict MPs, especially in cosmetics and personal care products, but broader regulations, especially in drinking water or groundwater, are still limited or developing. The European Commission formally adopted a restriction on intentionally added MPs in various products in 2023 (ECHA, 2023). This restriction will ban the use of microplastics in products such as cosmetics, detergents, fertilizers, and more by 2026. In the USA, there are currently no federal regulations specifically targeting microplastics. However, some states such as California have passed legislation to phase out the use of microplastics in cosmetics and personal care products. California is the first state to try to tackle MP in drinking water (California Water Boards, n.d.) by adopting a policy handbook establishing a standard method of testing and reporting MPs in drinking water. The EA in England and Drinking Water Inspectorate has recently commissioned pilot studies to develop methods to assess risks from MP contamination in groundwater drinking water sources in the UK (Lapworth and Shockley. 2022).

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