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ORIGINAL PAPER

Characteristics of microplastics in sediment of the Vaal River, South Africa: implications on bioavailability and toxicity

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Abstract

The aim of this study was to examine the physical characteristics and chemical composition of microplastics in sediments of the Vaal River, South Africa. Microplastics were detected in all samples, with abundance ranging from 29.12 to 1095.89 particles/kg dw. The physical identification of microplastics revealed dominance of small-sized particles of less than 0.5 mm, which accounted for 31.75% of the total microplastics detected in all samples. Fragments and fibres were significantly abundant compared to pellets, representing 63% and 35%, respectively. Microplastics were observed in different colours, among which blue, white and green were the most dominant. Raman analyses of microplastics showed the presence of high density polyethylene, low density polyethylene, polyurethane foam, polypropylene, polyethylene co-vinyl acetate, and poly(ethylene-co-1-hexene). Additionally, two pigments (vine black and smalt), one dye (saffron), three minerals (orthoclase, carbon, and microcline), and one additive (cis-13-docosanol) were also identified. The dominance of fragments and fibres, with the clear signs of fragmentation implied that microplastics in the Vaal River are mostly from secondary sources. The study reported the first data on microplastic pollution and characteristics in sediments of the Vaal River, thus, providing a benchmark and reference platform for relevant formulation and decision-making regarding this essential water source.

Keywords Anthropogenic activities · Microplastics · Sediment · Vaal River

Introduction

The benefits of plastic materials are undeniable; due to their lightweight, flexibility, and low-cost, they are used in various applications (Nikiema et al. 2020a, b). However, the negative impact of plastics is gradually emerging due to low recycling rates and mismanagement. Based on current production rates, it is expected that about twelve billion metric tonnes of plastic waste will be generated by 2050, which will end up in open dumps, landfills, and the natural environment (Geyer et al. 2017; Shams et al. 2021).

One of the emerging environmental concerns associated with plastic pollution is microplastics (MPs) (Maheswaran et al. 2022). MPs are categorized into primary MPs (plastics manufactured in the microscopic size) and secondary MPs (formed by the degradation of large plastic items) (Sun et al. 2019; Onoja et al. 2022). Research on MPs is rapidly evolving; recent years have seen explosive growth of studies focusing on quantitative and qualitative monitoring of microplastics in various environmental media around the world (Connors et al. 2017; Cowger et al. 2020). A variety of sampling and processing techniques are used, as well as different methods of identification, quantification, and characterization. Sampling approaches include selective, bulk, and volume-reduced sampling (Rocha-Santos and Duarte 2014). Density separation is widely used for extracting MPs from environmental samples. The most frequently used density separators are sodium iodide, sodium polytungstate (SPT), sodium chloride, and zinc chloride (Wang and Wang 2018). Digestion is also a common pre-treatment process to disintegrate the interfering organic matter in environmental samples (Avio et al.

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2015). Digestion methods include alkaline digestion, enzymatic digestion, and acid digestion (Shiye Zhao et al. 2017; Pfeiffer and Fischer 2020). Optical microscopy and scanning electron microscopy are used for visual identification of MPs, while the most common chemical identification techniques are infrared and Raman spectroscopies (Shim et al. 2017).

Despite the continuous growth in MP studies, there exist some limitations as more attention has been paid to the marine environment and to the quantification of MPs rather than physio-chemical behaviour that has a potential bearing on human health. The physicochemical properties of MPs are important to understand their behaviour in aquatic compartments. For instance, certain shapes are distributed differently in the water column, size and density also influence their mobility and transport, whereas colour may influence their ingestion by aquatic biota according to similarity with natural prey (Lorenz et al. 2019). The aim of this investigation was, therefore, to study the physical and chemical characteristics of MPs in the sediment of the Vaal River and to define their physio-chemical behaviour, sources, pathways, potential anthropogenic inputs, as well as potential health risks. The study also aimed at characterizing MPs concerning chemical constituents such as additives and their degradation products and potential release to media that they are exposed to. Ultimately, the study provides a comprehensive analysis of MP pollution in one of the most significant freshwater systems in South Africa. The Vaal River has great socio-economic value, supplying water to important sectors such as industry, agriculture, and energy (Iloms et al. 2020; Weideman et al. 2020).

Materials and methods

Site description

Sampling was conducted in the middle area of the river, starting from Lethabo weir up and to the Vaal River barrage (Fig. 1). This area is regarded as the hardest working region of the Vaal River, where the Eskom-Lethabo power station and Rand Water Lethabo pump station are located. Rand Water supplies water to four provinces and it is the largest water utility in South Africa, while Eskom is the largest producer of electricity in Africa (Wepener et al. 2011).

Sample collection, pre-treatment, and analysis

A 500 mL grab sampler (Van Veen) was used to collect twenty-five sediment samples from the river bed. Before analysis, samples were digested using potassium hydroxide, after which MPs were separated using sodium iodide.

Suspected MPs were physically examined using a stereomicroscope. Further, their surface morphology was examined using electron microscope (SEM).

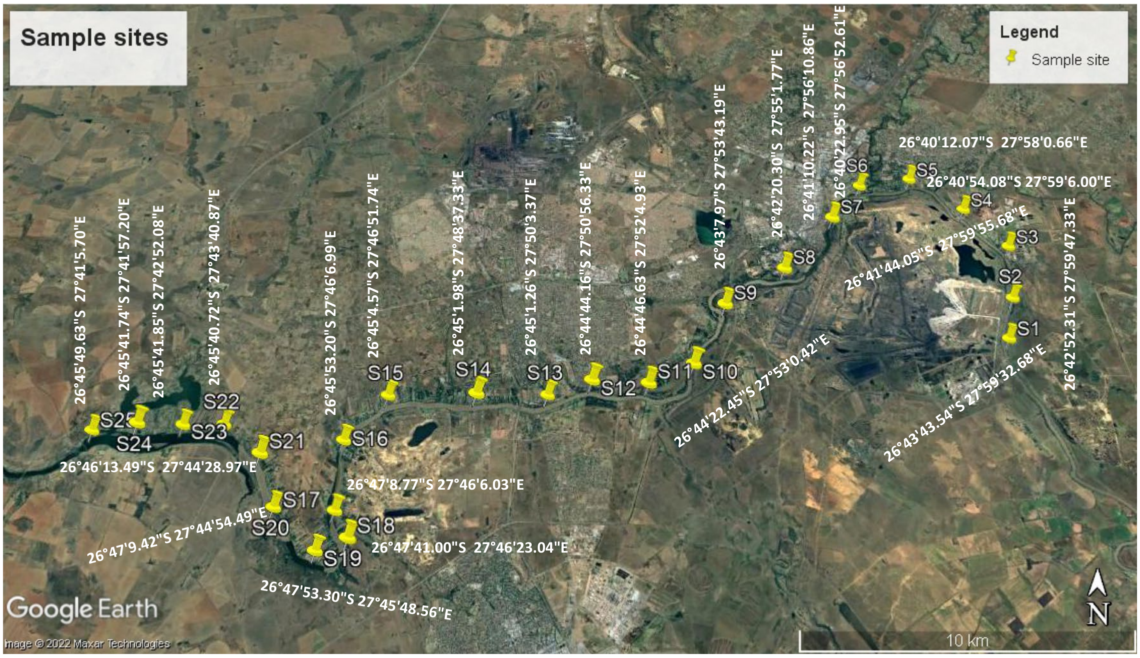


Fig. 1 Map depicting sampling locations (Google earth, 2021)

Polymers were identified using a Horiba LabRAM HR Raman spectrometer. A detailed description of the method is reported in a previous article (Saad et al. 2022a).

Quality control

Strict measures were followed to prevent procedural contamination during the fieldwork. Sample processing and analysis were conducted in a laboratory dedicated to MPs. All samples were processed in a laminar airflow cabinet. Samples were kept covered with aluminium foil and metal lids, and filtered MPs were kept in covered glass Petri dishes. All reagents were vacuum filtered on Whatman glass filters GF/A filter paper (47 mm diameter, 1.6 µm pore size). Procedural blanks were run with filtered distilled water. No particles were detected in all procedural blanks.

Results and discussion

Abundance of MPs

MPs were detected in all samples indicating widespread contamination in this region. The average abundance was 463.3 ± 284.1 particles/kg dw. The abundance per sample location is given in Fig. 2.

Physical characteristics of the detected MPs

The physical characteristics of MPs including size, colour, shape, and surface texture are essential for understanding their behaviour in the environment, as well as their bioavailability and toxicity (Saad 2023). Therefore, the findings of this study will be discussed in light of the physio-chemical properties of the identified MPs, as to provide an insightful assessment/analysis of the pollution status in the Vaal River.

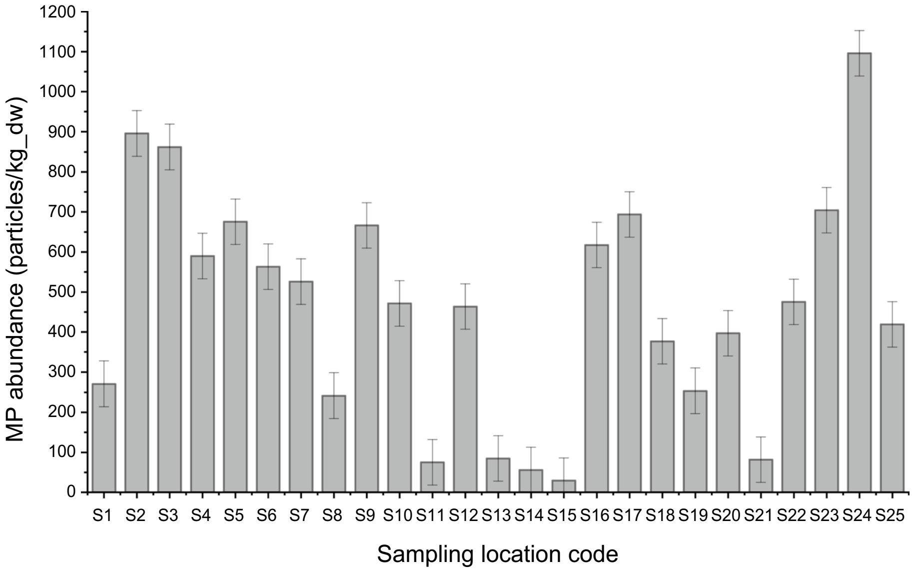
Size

MPs were grouped into six size ranges (0 to 500 µm; 500 to 1000 µm; 1000 to 2000 µm; 2000 to 3000 µm; 3000 to 4000 µm; and 4000 to 5000 µm). The majority of the MPs were observed in the 0–2000 µm range, representing around 82% of the total MPs. Among these, MPs of less than 500 µm were most prevalent, accounting for 31.8%. Figure 3a shows the size distribution of MPs in all samples.

In natural environments, MPs are susceptible to frequent fragmentation under different environmental conditions, resulting in a high abundance of small-sized MPs (Egessa et al. 2020). Gravitational forces, the magnitude of buoyancy, and the magnitude of the drag force are all influenced by the size of MPs (Shamskhany et al. 2021). Thus, influencing their dispersal in the water column as well as accumulation in sediment. Small-sized MPs sink faster when exposed to biofouling (Besseling et al. 2017; Du et al. 2021). This may explain the predominance of small MPs in the sediment of the Vaal River.

The relationship between MPs size and abundance in sediment samples was examined by Spearman correlation test as shown in Fig. 4. The results indicated a weak positive correlation with a p value of 0.03158, implying an increase in MPs abundance with the decrease in their size. This suggests that sedimentation of MPs may occur over the long term, during which they are susceptible to frequent degradation. To further confirm this, SEM analysis was performed to examine MPs surface morphology for signs of degradation and weathering, if any. SEM images revealed cracks and pores on the surface of MPs. This increases surface

Fig. 2 MPs abundance per sample



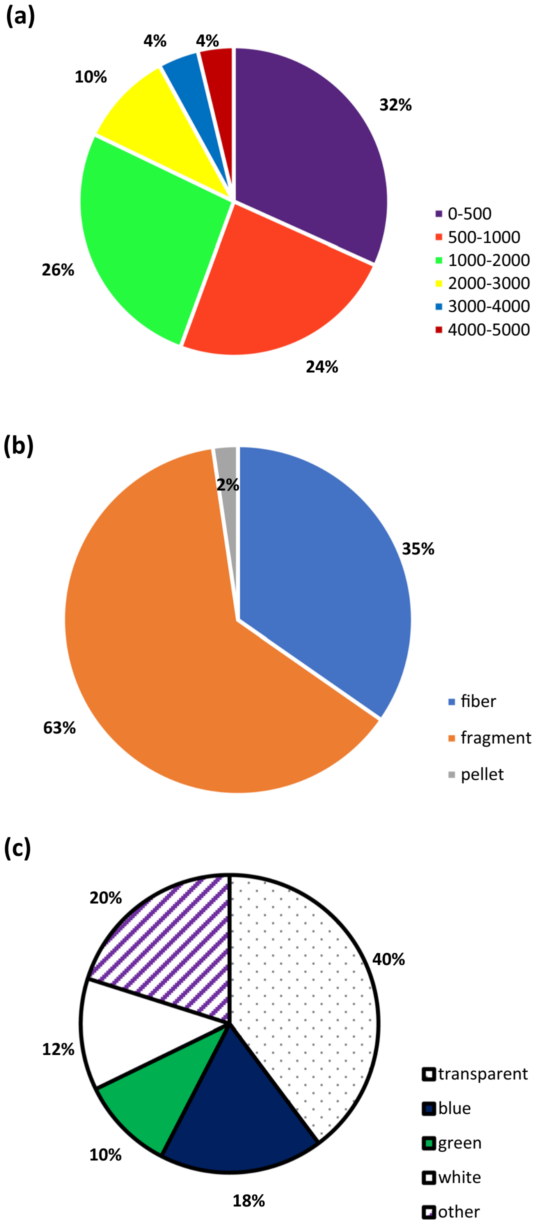


Fig. 3 Distribution of (**a**) size, (**b**) shape, and (**c**) colour

heterogeneity making MPs less hydrophobic, thus, less buoyant (Kumar et al. 2021). Consequently, the number of MPs in sediments may increase without the introduction of additional MPs (Egessa et al. 2020).

The consumption of small MPs by different organisms is well documented in several freshwater and marine studies (Collard et al. 2017; Qiao et al. 2019; Roch et al. 2020; Saad et al. 2022b). Additionally, the greater surface area of small-sized MPs makes them susceptible to the attachment of other pollutants, leading to additional health risks (Brennecke et al. 2016; Hartmann et al. 2017; Caruso 2019; Fred-Ahmadu et al. 2020; Santos et al. 2021). Consequently, smaller MPs are known to pose more hazards to aquatic biota; in the context of this study, the high fragmentation (shown by SEM images) further increases the possibility of adsorption of co-existing contaminants. Hamed et al (2022) reported the augmentation of toxicological effects of MPs with the decrease in their sizes.

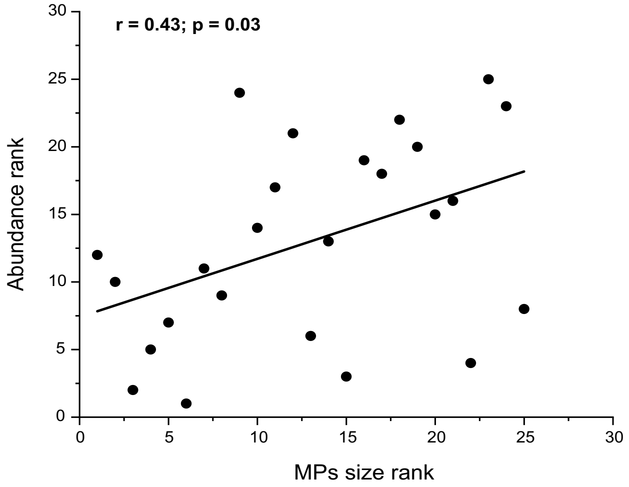


Fig. 4 Spearman correlation: Abundance vs size

Shape

MPs were identified under the microscope and classified according to their shapes. Particles with a slender and elongated appearance were defined as fibres; irregular particles were defined as fragments; and round particles with spherical shape were classified as pellets (Su et al. 2016). Fragments and fibres were dominating pellets, accounting for 63.2% and 35%, respectively, while pellets accounted for about 2% (Fig. 3b).

The microplastic shape has a great effect on their behaviour and distribution in different environmental compartments. For instance, sedimentary records have shown variation based on the shape (Kowalski et al. 2016; Kooi et al. 2017; Khatmullina and Isachenko 2017). Further, several aquatic biota have been reported to preferentially ingest MPs of certain shapes (Schessl et al. 2019). This means that the shape of MPs has great implications for their bioavailability to aquatic organisms. Nonetheless, biotic factors such as, in this case, feeding habits, are to count for such preference towards certain shapes.

MPs of different shapes have different retention times and may cause different physical damage, thus, having different toxicological effects. (Gray and Weinstein 2017). Several studies reported stronger toxicity of fibres in grass shrimp, amphipods, and zebrafish (Blarer and Burkhardt-Holm 2016; Gray and Weinstein 2017; Qiao et al. 2019).

The prevalence of fibrous MPs in this study, therefore, has serious toxicological implications for aquatic organisms in the Vaal River. Ultimately, they could be consumed by humans.

Colour

Colour distribution in sediment samples is presented in Fig. 3c. MPs of different colours were found to be more abundant representing 60.3% of the total particles' number, while transparent particles represented the remaining 49.7%. The most abundant colours were blue, white, and green, accounting for 18%, 12%, and 10%, respectively. Other colours including yellow, black, brown, pink, and grey were observed in minor percentages, contributing 20% altogether.

The predominance of coloured MPs in this study is of additional concern, and aquatic biota are thought to consume MPs that resemble their natural prey in terms of colour (Roch et al. 2020). However, the concern about coloured MPs is not limited to their preferential ingestion by aquatic biota, but also due to the toxicity associated with colouring agents such as pigments and dyes (Onoja et al. 2022). This means that organisms in the Vaal are exposed to a variety of toxic chemicals associated with MPs.

Surface texture

SEM images of MPs showed signs of fragmentation and weathering on the surfaces of the MPs (Fig. 5). Exposure to different environmental conditions in the Vaal River, such as mechanical abrasion, phyto, chemical, and biological degradation, could have resulted in the reported observations.

The observed fragmentation signs may result in an ongoing increase in surface area, which expedites the adsorption of other pollutants such as metals and persistent organics (Yu et al. 2019; Fred-Ahmadu et al. 2020; Hanslik et al. 2022; Iqbal et al. 2022). Consequently, MPs may become a "cocktail" of pollutants with varying toxicological effects (Saad 2023).

Chemical identification

Polyethylene (PE) (high and low density), poly(ethylene-co-1-hexene) (PEH), polypropylene (PP), polyurethane foam (PU), and poly(ethylene-co-vinyl acetate) (PEVA) were identified. The resulting spectra of the analysed MPs are shown in red while corresponding reference spectra are plotted in blue and black (Fig. S1).

PE and PP were observed most frequently, which is consistent with other studies. This could be attributed to their intensive use in a wide range of applications due to their efficiency and cost-effectiveness (Horton et al. 2017).

The presence of PE and PP as low density polymers in the sediment samples could be explained by the impact of environmental processes such as biofouling leading to the sedimentation of low density particles that are known to be buoyant. (Kooi et al. 2017; Joo et al. 2021).

However, it is important to note that different environmental conditions including daily discharge, flow velocity, and anthropogenic activities affect sediment mobility and can mobilize settled particles, thus, altering the profile of MPs from time to time (Ballent et al. 2016; Naden et al. 2016).

Identification of other compounds

Besides their potential health risks, concerns about MPs include the hazard associated with their constituent additives (Leslie et al. 2017; Onoja et al. 2022). Further, MPs have the potential to act as micro-vectors for toxic elements

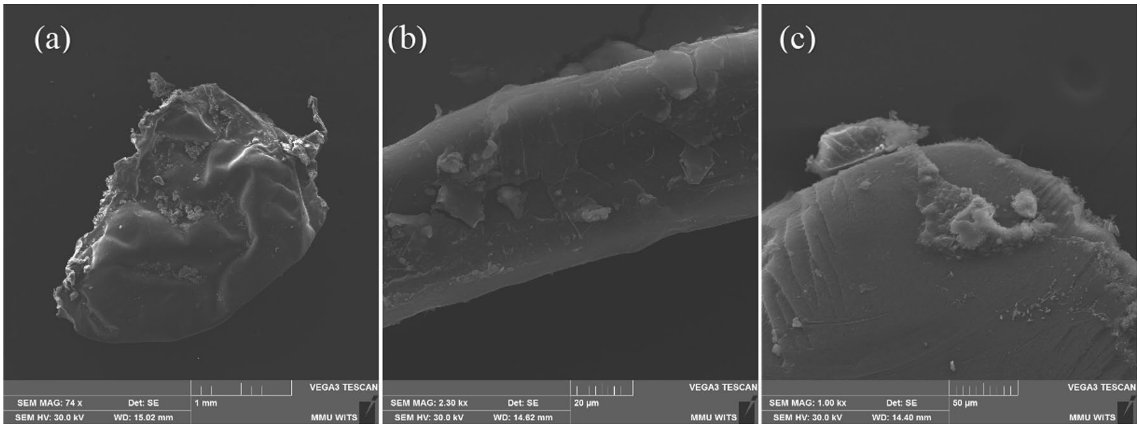


Fig. 5 SEM images: (**a**) fragment, (**b**) fibre, and (**c**) pellet

and organic contaminants, adsorbing and desorbing them depending on the prevailing environmental conditions (Onoja et al. 2022). This capability varies depending on the chemical structure of the plastic/polymer (Saad et al. 2022c). It is therefore expected that other compounds associated with MPs to be detected when analysing MPs. In this study, in addition to the six polymers presented above, three minerals (orthoclase, carbon, and microcline), two pigments (vine black and smalt), one dye (saffron), and one additive (cis-13-docosanol) were identified, according to Raman spectra (Fig. S2).

Carbon (Fig. S2a) was detected in samples collected from the upstream area of the river (S1 to S5). This sampling area is nearby Lethabo Power Station, the station burns about 50,000 tonnes of coal and produces approximately 23,000 tonnes of ash per day (Eskom 2022). The detection of carbon in these samples could be due to the MPs being coated with carbonaceous matter.

Cis-13-docosanol is found in a variety of consumer, industrial, and pharmaceutical products. It is reported to show environmental persistence and bioaccumulation properties, being thus considered an aquatic toxicant (USEPA, 2020).

Saffron is a natural dye that is used for colouring textile fabrics, fabric rugs, and sometimes is used in painting. Fabrics that are dyed using saffron tend to have good colour fastness, especially if pre-treated with neem oil and α-amylase and trypsin (Bathaie et al. 2014; El-Khatib et al. 2020).

Possible leaching of these additives from MPs is of additional concern owing to their potential toxicity (Koelmans et al. 2013; Leslie et al. 2017; Onoja et al. 2022).

Conclusion

Our findings revealed high prevalence of MPs that can potentially harm the ecosystem of the Vaal River. Further, the properties of the detected MPs pose additional concerns, considering the implication of these properties on their bioavailability and toxicity. Fragmented/small-sized, coloured, and fibrous MPs that were mostly detected are easily transported and consumed by aquatic biota, which threatens the aquatic species in the Vaal. Additionally, the productivity and profitability of the different sectors that rely on the Vaal River are highly vulnerable to plastic and MP pollution. The government of South Africa, therefore, needs to address MP pollution within its environmental management frameworks, and improve waste management practices and develop effective waste management strategies. However, effective mitigation requires collective efforts of all stakeholders (consumers, suppliers, authorities, and the scientific community). Legislative interventions and economic instruments such as tax on plastic bags and enforcement of policies to reduce illegal dumping and encourage recycling are also essential to complement these efforts. Simultaneously, the scientific community should play its role in raising awareness about MP pollution and its implications on the environment and human health.

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Declarations

Conflict of interest The authors have no relevant financial or non-financial interests to disclose.

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