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INVESTIGATION OF MICROPLASTICS PRESENCE IN THE DAMBOVITA RIVER

Cristina MARIA[1], György DEÁK[1*], Georgeta TUDOR[1], Elena HOLBAN[1], Camelia ZAMFIR[1], Alexandru Anton IVANOV[1], Gheorghe GRIGORE[1], Nurliza RAHIM[2]

[1] National Institute for Research and Development in Environmental Protection,294 Splaiul Independenței Street, Bucharest 060031, Romania
[2] Sustainable Environment Research Group (SERG), Centre of Excellence Geopolymer and Green Technology (CEGeoGTech), Universiti Malaysia Perlis, Arau 02600 Perlis, Malaysia

Abstract

In recent years, plastic pollution has been brought more and more to the attention of scientists and the general public alike by the increasing number of studies regarding the insidious presence of microplastics in every aspect of human life and in the environment. Macroplastics and large microplastics have a clear direct impact on faunal health and conservation by clogging the digestive systems of affected individuals and even acting as promoters for the introduction and long-distance transport of potential invading species of algae and molluscs. However, the behaviour and the largely unknown long-term effects of microplastics and nanoplastics, which have the ability to break the intestinal barrier and become adsorbed into the circulatory system and tissues of key ecosystem species, may pose an even greater threat to biodiversity conservation. This paper aims to identify the presence of microplastics in two of the components of the Dâmbovița River, namely in the water column and in the sediment, in order to identify and later eliminate plastic waste pollution, which would have long-term positive effects for habitat and biodiversity. The collected samples were analysed in the laboratory, and the presence of microplastics was identified in all the water and sediment samples. Also, the abundance of identified microplastics was systematically higher in sediment samples than in water samples, with the highest identified level of microplastics being almost 90 mg/kg of wet sediment and 9 mg/L of water downstream of the municipal wastewater treatment plant. FTIR analysis showed a mix of PE, PP, and PET absorption bands, and the microscopic analysis of microplastic particles retained on micro-cellulose filters has been greatly hampered by the fact that many of the separated particles have irregular shapes, very small sizes, are transparent and colourless, and, for this reason, have been more difficult to identify and quantify.

Keywords: *Microplastic; Plastic waste; Floating waste; Freshwater pollution; Sediment pollution; Microscopic analysis*

Introduction

Plastic pollution is one of the main forms of environmental aquatic pollution reported since the 1970s. Plastics represent about 60-80% of marine waste and 90% of waste floating on seas and oceans. According to the Convention on Biological Diversity (2002), more than 663 marine species are affected by the presence of plastics [1].

Microplastics (MPs) are small synthetic polymers (0.06-0.5 mm) resulting from the degradation of plastics in the environment under the influence of UV light or mechanical action. Some MPs are directly manufactured products (e.g., microspheres from personal care products,

* Corresponding author: deak.gyorgy@incdpm.org

pharmaceuticals), and others are decomposition products of macroplastics (e.g., textile microfibers, tyres, plastic packages) [2].

There are numerous adverse health effects of microplastics presence in the aquatic environment, such as the alteration of the biogeochemical cycles and dynamics of aquatic food chains, inducing physical damage due to their small size (entanglement, breathing difficulties, asphyxia, damage to the respiratory and digestive tract), the release of additives from the composition of the plastic, adsorption/absorption and release of other toxic pollutants from the environment (e.g., PCBs, PAHs, etc.), being just a few of the more direct effects [1, 3-6].

Knowing the extent of freshwater pollution by plastics is vital because these bodies of water provide drinking water for human consumption and are vectors of plastics transport to the seas and oceans. A. Lechner [3] detected in the years 2010–2012 a total abundance of plastics in the Austrian Danube of 17,349 particles, with an average ±Std.dev. = 316.8±4,664.6 particles/1000m^{-3} and estimated that the plastic contribution of the river into the Black Sea is approx. 4.2t per day [7].

There are numerous studies attesting to the presence of microplastics in all the studied freshwater ecosystems, both in rivers and lakes, from Europe, Africa, Asia, and America. The variation range of the detected microplastic concentrations is very wide; even for the same watercourse, there are significant differences in the distribution of microparticles due to the high degree of heterogeneity and the influence of hydrodynamic conditions specific to the sampling location. The density of plastic particles plays an essential role in their environmental behaviour. For example, the density of plastic particles has a major impact on whether they float on the surface or sink. Studies that have identified polyethylene and polypropylene particles in sediments, which, according to their density, should have risen to the surface, indicate an opposite effect due to the influence of interactions with the environment such as the absorption and adsorption of other substances in and on the plastic particles surface, as well as their inclusion in the local biological circuit either through ingestion or as support for anchoring or developing biota (algae, biofilm, molluscs). Even at the sediment level, the heterogeneity of the microplastics distribution can be pronounced both on the surface and in the depth profile of the sediment layer [8, 9].

In recent years, a consistent effort towards a standardisation of microplastics nomenclature and analysis has been made by the ISO/TC 61/SC 14 committee, ISO/TR 21960:2020, which defines particles with a dimension above 5mm as macroplastics, particles with dimensions between 1 and 5mm as large microplastics, and particles between 0,001 and 1mm as microplastics [9]. Recent studies showed that the smaller microplastics are able to cross intestinal boundaries and propagate and accumulate in the ecosystem's food chains [10]. Moreover, small microplastics were identified even in human blood samples [10, 11], indicating that the careless use and disposal of artificial polymers may now pose a risk to the global conservation of biodiversity similar to the historical use of leaded fuels or freons.

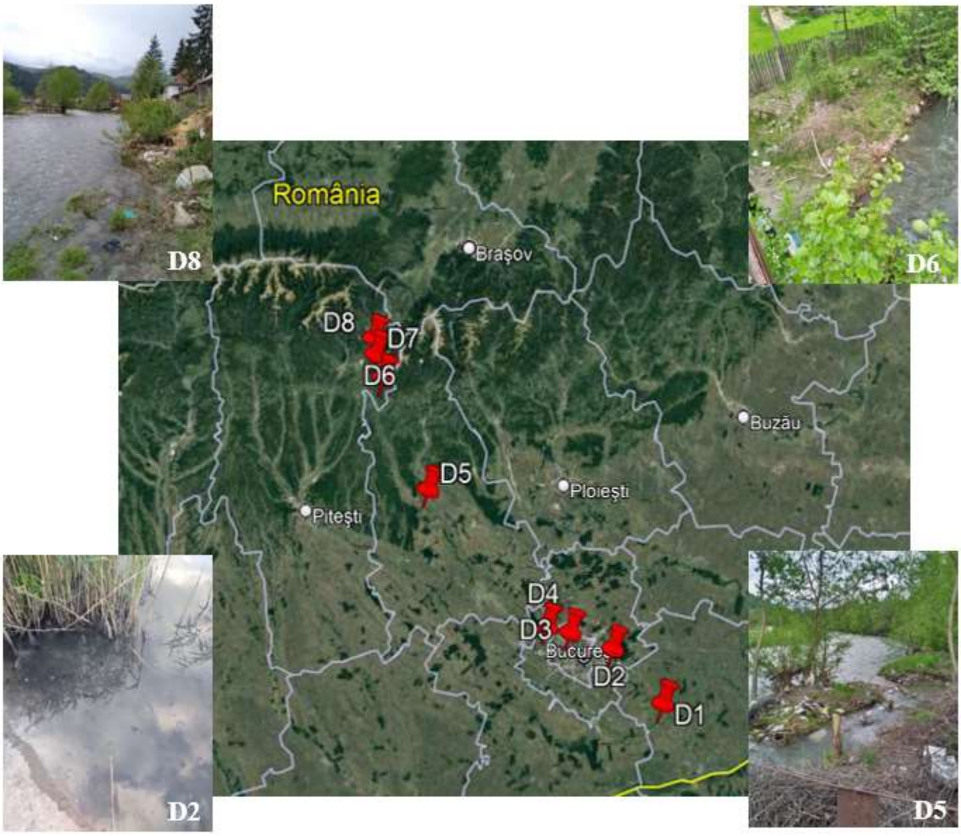
This paper aims to identify the presence of plastic and microplastic particles in two of the components of the Dâmbovița River (Romania), namely, in the water column and in the sediments. Knowing the extent of microplastic pollution is important from the perspective of identifying the sources of microplastic pollution, implementing programmes to reduce pollution at its sources, and promoting awareness programmes on the danger posed by plastics to the trofic chain and implicitly to people's health.

Experimental part

Study area and sampling

The Dâmbovița River is located in the south of Romania, in the Muntenia region, with a NW-SE orientation; it crosses the counties of Argeș, Dâmbovița, Ilfov, and Călărași, as well as the municipality of Bucharest.

In order to achieve the study objectives, water and sediment samples were taken from eight points located in the vicinity of localities with more than 2000 equivalent population. Figure 1 shows the map with the precise location of these sampling points, marked from D1 to D8. The map was created using Google Earth.



D1: 44°13'55.21"N; 26°27'14.20"E D2: 44°23'46.22"N; 26°14'5.44"E
D3: 44°27'46.82"N; 25°56'40.64"E D4: 44°52'7.76"N; 25°25'4.18"E
D5: 45°11'57.84"N; 25°12'46.92"E D6: 45°16'7.82"N; 25°10'43.31"E
D7: 45°18'58.93"N; 25°10'5.87"E D8: 45°23'9.31"N; 25°10'50.25"E

Fig. 1. Location of sampling points (D1 - D8) and their GPS coordinates along the Dâmbovița River

Water was sampled from a depth of maximum 30cm below the surface using a 2.0L vessel made of stainless-steel vessel. Sediments were sampled from the bottom using a 1.0L capacity conical vessel device made of stainless steel perforated from place to place to allow water to drain. After sampling, water and sediment samples were transferred to decontaminated glass vials, sealed with plastic-free lids, and labelled. All samples were transported on the same day to the laboratory [12, 13].

Methods

The analytical method used for the microplastics analysis in surface water and sediment samples was adapted from *J. Masura et al.* [14]. In addition, a final Fourier Transform Infrared (FTIR) spectroscopic analysis step was added to this method in order to precisely identify their polymer composition and validate the visual identification results.

This analytical method is applied with very good results for the determination of plastics most commonly found in the environment, namely: polyethylene (PE, d = 0.91-0.97g/mL), polypropylene (PP, d = 0.85-0.94g/mL), polystyrene (PS, d = 1.04-1.1g/mL) and polyethylene terephthalate (PET, d = 1.4-1.6g/mL) [14, 15]. (d = note the density here).

Stainless steel sieves with 5 mm, 315 mm, and 125µm mesh openings and cellulose acetate filters with 0.8 µm pore sizes were used to help differentiate the separated microplastics.

This method is simple, accessible, does not require excessive costs, and involves the steps schematically presented in Figure 2.

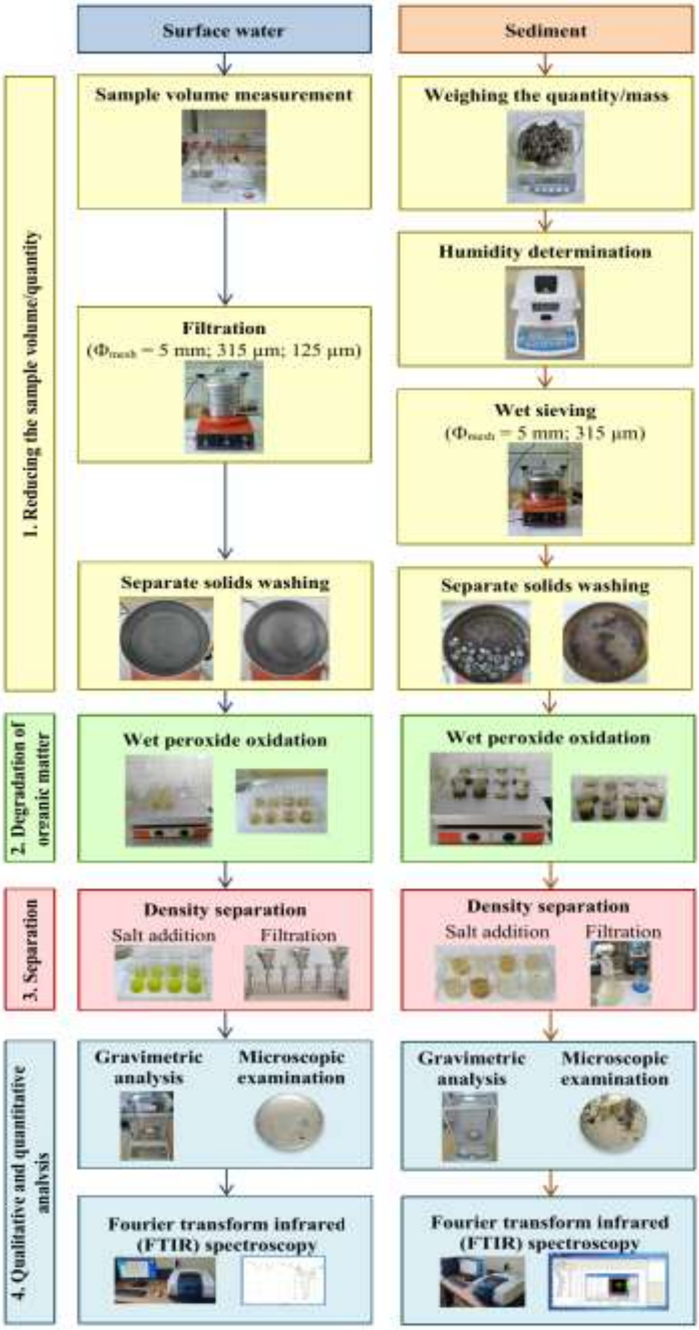


Fig. 2. Flow diagram for the microplastics analysis method of water and sediment samples

Method for the analysis of microplastics in water samples

The first step consists of reducing the sample volume by filtering through a series of stainless-steel sieves with mesh diameters of 5mm, 315µm and 125µm. The solid materials retained on the sieves with meshes of 315µm and 125µm are well washed with distilled water, and the total mass of the solids present in the sample is determined gravimetrically.

The second stage consists of the wet oxidation of the organic material present in the mass of retained solid materials with a solution of H_2O_2 (30%) in the presence of a Fe(II) catalyst at a maximum temperature of 75°C.

Then, in the third step, the mixture from the wet oxidation step is subjected to density separation with a concentrated NaCl (d = 1.2g/mL) or $ZnCl_2$ (d = 1.5-1.7g/mL) solution to isolate the plastic debris through flotation.

In the fourth stage, the mass of the plastics isolated in the previous phase is determined gravimetrically, and the plastic particles are sorted manually by direct visual examination or under a microscope.

In the last stage, the Fourier transform infrared spectroscopic analysis (FTIR) of the sorted microplastics is performed in order to determine their chemical composition.

Method for the analysis of microplastics in sediment samples

In the first stage, the sample is weighed and the sediment humidity is determined. Then the sediment sample amount is reduced by wet sieving through a series of stainless-steel sieves with mesh diameters of 5mm and 315µm.

In the second stage, the organic matter present in the solid material retained on the 315µm mesh sieve is wet oxidised with hydrogen peroxide (30%) in the presence of an Fe(II) catalyst at a maximum temperature of 75°C.

In the third stage, the flotation separation of the existing plastics in the sample takes place based on the difference in density of the concentrated NaCl (d = 1.2g/mL) or $ZnCl_2$ (d = 1.5-1.7g/mL) solution.

In the fourth stage, the gravimetric analysis of the separated plastics takes place, followed by their manual sorting by visual direct identification or under a microscope.

In the last stage, the microplastics extracted from the sediments are spectroscopically analysed (FTIR), and their chemical composition is precisely identified.

Results and discussion

A total of sixteen samples (8 water samples and 8 sediment samples) were taken along the Dâmbovița River and analysed in order to identify the presence of microplastics. The obtained results are presented separately for water and sediments, both in graphic form (Fig. 3) and as maps of the distribution of the microplastic concentrations detected along the investigated river (Fig. 4).

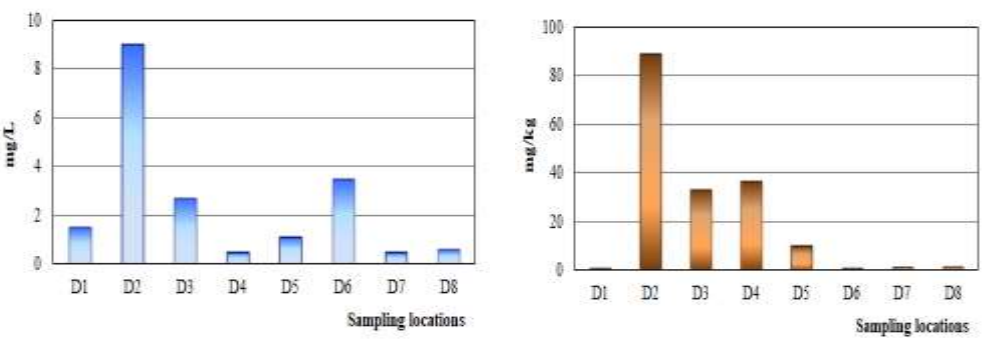
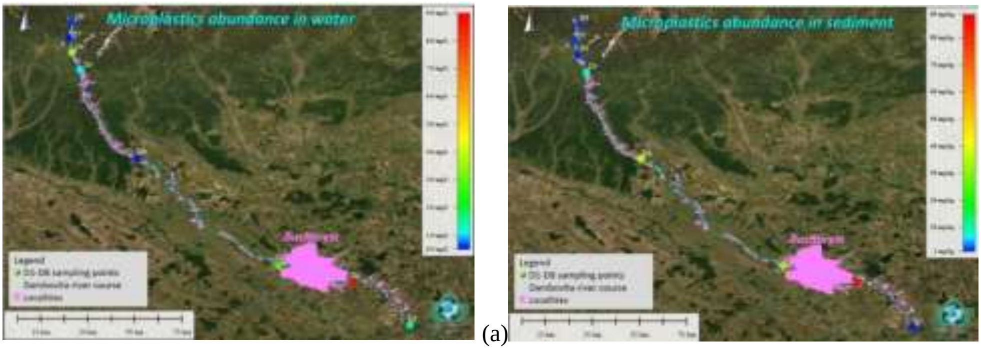


Fig. 3. Microplastics abundance identified in water (left) and sediment (right) samples taken from the Dâmbovița River



(a) (b)

Fig. 4. Map of the microplastic abundance detected in the surface layer of the water column: (a) and in sediments (b) along the Dâmbovița River

The presence of microplastics was detected in all the analysed samples. The average microplastic load of the Dâmbovița River varied greatly from one sampling location to another. The abundances of plastic particles identified were systematically higher in sediment samples (1.1 - 88.7mg/kg) than in water samples (0.5 - 9.0mg/L). Also, in each sampling location, there is a proportionality between the loads of microplastics detected in the two types of analysed samples (water and sediments).

The maximum concentrations of microplastics were detected downstream of the city of Bucharest, more precisely, after the discharge of the wastewater treatment plant effluent, both in water and in sediments. The concentrations of microplastics detected upstream of the wastewater treatment plant (location D3 - Dragomirești Deal - 2.7mg/L in water and 33.0mg/kg in sediments) were significantly lower than those detected downstream of the wastewater treatment plant (location D2 - Glina - 9mg/L in water and 88.7 mg/kg in sediments), which proves that microplastics transit the wastewater treatment plant without being completely removed.

The lowest concentrations of microplastics were detected in sampling locations D4 (Viișoara - 0.5mg/L) and D7 (Valea Hotarului - 0.5mg/L) for the water column, and in locations D1 (Budești - 1.1mg/kg) and D6 (Slobozia - 1.1mg/kg) for sediments.

The concentrated NaCl solution, used for the separation of microplastics by flotation, has been shown to be appropriate for extracting low-density microplastics such as polyethylene (PE), polypropylene (PP), and polystyrene (PS). For the extraction of denser microplastics, such as polyvinyl chloride (PVC, d = 1.3-1.7g/mL) and polyethylene terephthalate (PET, d = 1.4-1.6g/mL), a saturated solution of $ZnCl_2$ (d = 1.5-1.7g/mL) was used.

Over 40% of the separated microplastics were fragments, 10-20% were fibres, and 5-10% were pellets or granules. The remainder of the microplastics were difficult to categorise due to their small size, irregular shapes, and lack of colour. The wet oxidation step employed may have altered the aspect and colour of some microplastics, but it is needed to eliminate the other organic sample constituents and even the biological films that often develop on the surface of microplastics in water environments.

All samples analysed by Fourier transform infrared spectrometry (FTIR) showed specific absorption bands for PE, PP, and PET polymers.

The average concentrations of microplastics extracted from the samples taken from the Dâmbovița River were 2.4mg/L from the water and 21.7mg/kg from the wet sediments.

Conclusions

In this work, the abundance of microplastics (size range 125µm - 5mm) was evaluated in the surface layer of the water column and in the sediments of the Dâmbovița River, along a section of approx. 200km between the towns of Rucăr and Budești (upstream of the confluence with the Argeş River).

The microplastics abundance reached a maximum in the metropolitan area of Bucharest downstream of the city wastewater treatment plant effluent discharge (D2 sample location), both in the water column and in the sediments.

Most of the microplastics separated from water and sediments were in the form of single-use packaging fragments, fibres, and granules of various shapes, sizes, and colours.

In general, there is a significant loading of the Dâmbovița River with microplastics (an average of 2.4mg/L in water and 21.7mg/kg in wet sediments), which requires appropriate measures to be taken by the competent authorities because the water is indispensable to life and the efficient management of existing water resources has a direct influence on the population and ecosystems/environment health.

Maintenance and conservation of ecosystem services and the efficient use of water resources in economic activities have now become the most important challenges facing humanity because water quality and availability influence energy production, agriculture, and food security.

Acknowledgments

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