Scientific Papers. Series E. Land Reclamation, Earth Observation & Surveying, Environmental Engineering. Vol. XII, 2023
Print ISSN 2285-6064, CD-ROM ISSN 2285-6072, Online ISSN 2393-5138, ISSN-L 2285-6064

STUDY ON MICROPLASTICS OCCURRENCE IN THE LOWER DANUBE RIVER WATER

Madalina CALMUC, Valentina Andreea CALMUC, Nina Nicoleta CONDURACHE, Maxim ARSENI, Ira-Adeline SIMIONOV, Mihaela TIMOFTI, Puiu-Lucian GEORGESCU, Catalina ITICESCU

"Dunarea de Jos" University of Galati, REXDAN Research Infrastructure, 98 George Cosbuc Street, Galati, Romania

Corresponding author email: madalina.calmuc@ugal.ro

Abstract

Microplastics are considered emerging pollutants of growing concern due to their ubiquitous presence and toxic potential in the aquatic ecosystem. However, there are few studies assessing the occurrence of microplastics in freshwaters, most articles are focused rather on the marine environment. Due to the lack of standardized protocols for separating and analyzing microplastics, different methods are described in the literature data. In this paper, FT-IR spectrometry coupled with microscopy (micro-FT-IR) was applied to identify the presence of microplastics in the Predeltaic sector of the Danube River. Based on the morphological classification, the microplastics collected were fragments, films, and fibers. The results of micro-FT-IR analysis confirmed the majority presence of polyethylene and polypropylene-based microplastic particles in water.
.

***Key words**: emerging pollutant, freshwater, micro-FT-IR, Lower Danube water.*

INTRODUCTION

Microplastics (MPs) are plastic fragments smaller than 5 mm classified based on their origin into primary and secondary microplastics (Eerkes-Medrano et al., 2015; Li et al., 2018; Wagner et al., 2014).

Primary MPs are manufactured at the microscale for use in various industrial applications such as personal care products and plastic pre-production pellets.

Secondary MPs result from the degradation of larger plastic waste (meso and macro) under the influence of environmental conditions (e.g. UV radiation, high temperatures, mechanical and biological factors) (Cera et al., 2020; Horton et al., 2017).

Due to their ubiquity and toxicity in the aquatic ecosystem, MPs are considered to be emerging contaminants (Lambert and Wagner, 2018). According to Ding et al., 2021, the toxic potential of microplastics in freshwater is given by the following two behaviours:

a) Size and shape of MPs can cause physical and histophysiological injury;
b) MPs are transport vectors for other types of organic and inorganic pollutants. MPs in combination with these contaminants cause synergistic effects in organisms.

Regarding the microplastics assessment protocol in freshwaters, there are no standardized methods of sampling, isolation, identification, and quantification of microplastics. To this end, it is required to develop a standardized protocol that allows an objective comparison and evaluation of the results from various places and times (Rios Mendoza & Balcer, 2019; Razeghi et al., 2022). Although the first studies on the presence of microplastics in marine environments were published in the 1970s, research on microplastic occurrence in freshwaters began about 15 years ago (Talbot & Chang, 2022). This subject should not be ignored given that rivers are now known to play a crucial role in microplastic transport in marine ecosystems (Sarijan et al., 2021).

The main aim of this paper is to evaluate the occurrence of microplastics in the second longest river in Europe, namely the Danube River. More specifically, the Predeltaic sector of the Danube, which is the transport pathway of microplastics into the Black Sea, was investigated.

Scientific Papers. Series E. Land Reclamation, Earth Observation & Surveying, Environmental Engineering. Vol. XII, 2023
Print ISSN 2285-6064, CD-ROM ISSN 2285-6072, Online ISSN 2393-5138, ISSN-L 2285-6064

MATERIALS AND METHODS

The microplastics were taken from the following three stations located on the Romanian Lower Danube sector (Figure 1):

- P1 - the confluence of the Siret River with the Danube;
- P2 - the confluence of the Prut River with the Danube;
- P3 - the riverside sector of the city of Isaccea.

Figure 1. Microplastic sampling stations

The samples were collected from the surface layer of the water (0-15 cm) using a sampling equipment consisting of a pump with a flow rate of 5 litres/second and a net with 125 µm mesh (Figure 2). The total volume of filtered water was 10 m^3. The main advantages of this type of sampling equipment are that samples can be taken from different depths of the water column and the filtered water volume is known.

Figure 2. Microplastics sampling equipment
(A - pump and B - net)

After the samples were taken, they were transported to the laboratory to isolate the microplastics. The organic matter was removed using KOH 10M and H_2O_2 30%. The separation from the other impurities was carried out in the separation funnel with zinc chloride ($ZnCl_2$) 60-70% (Pojar et al., 2021; Călmuc et al., 2022). The microplastic supernatant was filtered using a vacuum pump filtration system on a glass fibre filter paper with a diameter of 47 mm and pore size of 2 µm (Figure 3).

Figure 3. Collection of microplastics on filter paper

In order to identify and confirm the occurrence of the microplastics, the Spotlight 400 FT-IR Imaging System (micro-FT-IR), PerkinElmer from the Spectrometry laboratory of the REXDAN Research Infrastructure, "Dunarea de Jos" University of Galati, Romania was used (Figure 4).

The parameters of the micro-FT-IR analysis method applied in this study were as follows:

- Spectral range: 4000 -750 cm^{-1};
- Resolution: 16 cm^{-1};
- Scans per pixel: 2;
- Interferometer speed:1 cm/s;
- Pixel size: 25 µm.

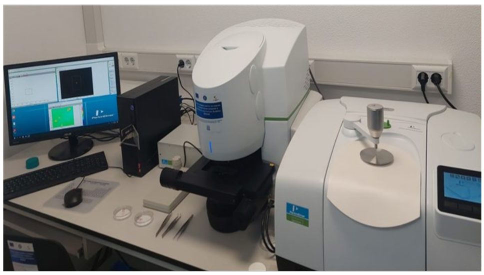

Figure 4. Micro-FT-IR analysis of microplastics

RESULTS AND DISCUSSIONS

Figures 5, 6, and 7 illustrate the microplastics isolated from the three samples collected. The abundance of microplastics in station P1 was 9 particles per 10 m^3 of which, based on the morphological characteristics (Rosal, 2021; Xu et al., 2021), 8 were fragments and one fiber (Figure 8).

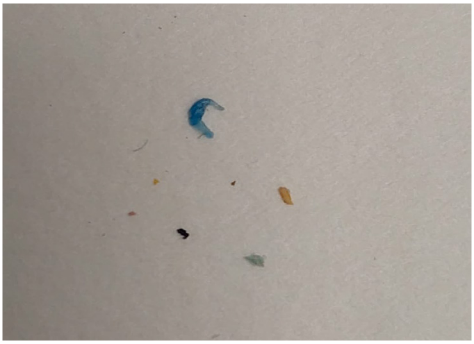

Figure 5. Microplastics collected from P1 sampling station

Most microplastics were collected from site P2, respectively 20 microplastics per 10 m^3 were extracted, the majority being fragments (15), and the rest fibers (3) and films (2). This sampling station is located at the confluence of the Prut River with the Danube, which has an important contribution to the Danube quality as it crosses many urban agglomerations on both the Romanian and Moldavian territory.

Figure 6. Microplastics collected from P2 sampling station

From station P3, 12 microplastics were sampled including 10 fragments, one film and one fiber. Information on the shape of microplastics is essential since they can suggest their origin, implicitly the sources of pollution. For example, the fragments are produced by the breakage of plastic waste in the presence of UV radiation and mechanical forces. The films are the result of the fragmentation of plastic bags and vinyl used in agriculture. Also, the fibers can be originated from de fishery field (nets and ropes) and municipal sewage discharge (laundry washing) (Kye et al., 2023).

Figure 7. Microplastics collected from P3 sampling station

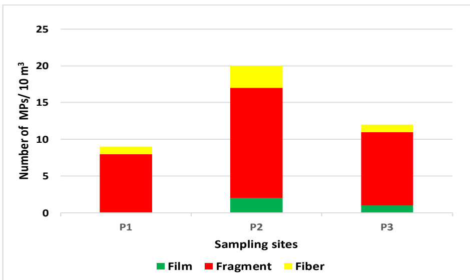

Figure 8. Abundance and morphological classification of MPs

Regarding the colour of the microplastics, they had different colours such as: blue, red, black, yellow, green, transparent. Also, the colour of microplastics can be an important indicator in terms of establishing pollution sources (Li et al., 2021).

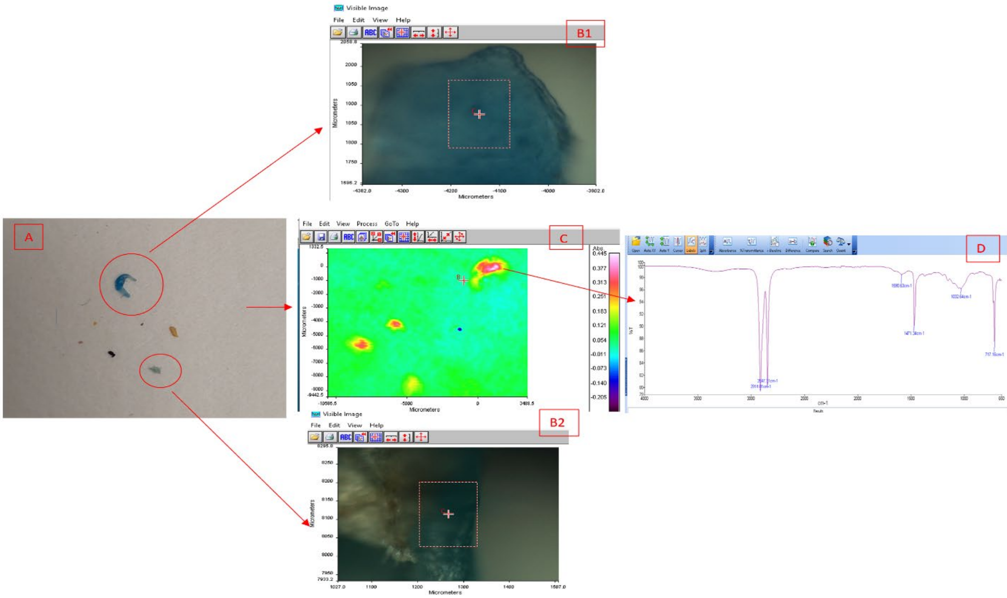

Figure 9. Micro-FT-IR microplastics analysis results (A - P1 microplastic sample, B1 and B2 - Visible images of MP, C - micro FT- IR spectral image of the sample, D - FT-IR spectrum of MP)

Figure 9 shows the diagram regarding the stages of microplastics analysis using the micro-FT-IR equipment. the filter paper with microplastics (A) was placed on microscope stage and was preliminarily investigated in the visible spectrum.

Visible images of MPs (B1 and B2) were analysed to establish the morphological characteristics such as shape, colour, size of the MP. Then, the sample was scanned in the IR range to confirm the presence of microplastics and to determine their composition. At the end of the analysis, the spectral image of the sample was obtained (C) and the IR spectra were extracted (D) for the areas where changes in absorbance were detected.

IR spectra were compared with Spectra Databases for polymers - S.T. Japan Europe GmbH to identify the type of polymers in the MPs composition (Figure 11).

Polypropylene (PE) and polyethylene (PP) polymers were mostly found in all three sampling stations (Figure 10). Sporadically, polystyrene (PS) was also identified.

The PE, PP and PS polymers are commonly used to manufacture different packaging materials (bags, bottles), films, building materials, and coatings (Andrady, 2011; Uurasjärvi et al., 2020).

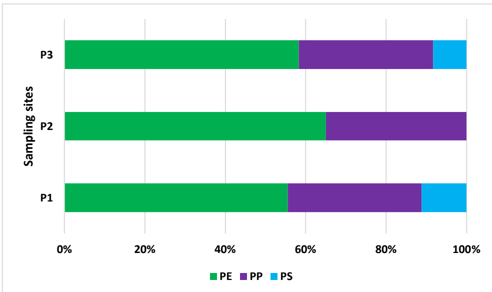

Figure 10. The type of polymers identified

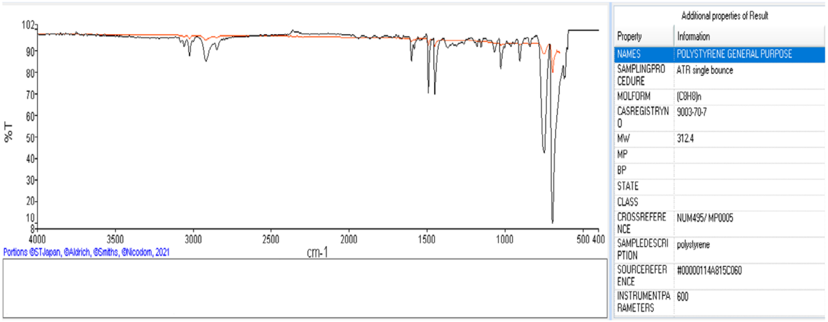

Figure 11. IR spectra of polystyrene

CONCLUSIONS

The microplastics occurrence in the Predeltaic sector of the Lower Danube was studied in this paper. A pump-type equipment was used to collect the microplastics from the surface of the water in three sampling stations.

Regarding the abundance of microplastics, most were taken from the P2 site (20 microplastic per 10 m^3), which was located at the confluence of the Prut River with the Danube River. Based on the morphological criteria, most MPs were fragments.

Micro-FT-IR spectroscopy was applied in this study to confirm the presence of microplastics and identify the type of polymers in their composition. The most identified polymers were polyethylene and polypropylene.

According to the results obtained in this study, it can be concluded that the methods applied were suitable in assessing the occurrence of microplastics in the investigated Danube sector.

ACKNOWLEDGEMENTS

The present article was supported by the project An Integrated System for the Complex Environmental Research and Monitoring in the Danube River Area, REXDAN, SMIS code 127065, co-financed by the European Regional Development Fund through the Competitiveness Operational Programme 2014-2020, contract no. 309/10.07.2021.

REFERENCES

Andrady, A.L. (2011). Microplastics in the marine environment. *Mar. Pollut. Bull., 62*, 1596–1605. https://doi.org/10.1016/j.marpolbul.2011.05.030

Călmuc, M., Călmuc, V.A., Arseni, M., Simionov, I.A., Antache, A., Apetrei, C., Georgescu, P.L., Iticescu, C. (2022). Identification and characterization of plastic particles found in the Lower Danube River. *Scientific Papers. Series E. Land Reclamation, Earth Observation & Surveying, Environmental Engineering, XI.*, *332 - 337.*

Cera, A., Cesarini, G., Scalici, M. (2020). Microplastics in Freshwater: What Is the News from the World? *Diversity, 12*, 276. https://doi.org/10.3390/d12070276

Ding, R., Tong, L., Zhang, W. (2021). Microplastics in Freshwater Environments: Sources, Fates and Toxicity. *Water. Air. Soil Pollut.*, *232*, 181. https://doi.org/10.1007/s11270-021-05081-8

Eerkes-Medrano, D., Thompson, R.C., Aldridge, D.C. (2015). Microplastics in freshwater systems: A review of the emerging threats, identification of knowledge gaps and prioritisation of research needs. *Water Res., 75*, 63–82. https://doi.org/10.1016/j.watres.2015.02.012

Horton, A.A., Walton, A., Spurgeon, D.J., Lahive, E., Svendsen, C. (2017). Microplastics in freshwater and terrestrial environments: Evaluating the current understanding to identify the knowledge gaps and future research priorities. *Sci. Total Environ., 586*, 127–141. https://doi.org/10.1016/j.scitotenv.2017.01.190

Kye, H., Kim, J., Ju, S., Lee, J., Lim, C., Yoon, Y. (2023). Microplastics in water systems: A review of their impacts on the environment and their potential hazards. *Heliyon, 9*, e14359. https://doi.org/10.1016/j.heliyon.2023.e14359

Lambert, S., Wagner, M. (2018). Microplastics Are Contaminants of Emerging Concern in Freshwater Environments: An Overview, in: Wagner, M., Lambert, S. (Eds.), Freshwater Microplastics, The Handbook of Environmental Chemistry. Springer International Publishing, Cham, pp. 1–23. https://doi.org/10.1007/978-3-319-61615-5_1

Li, C., Gan, Y., Zhang, C., He, H., Fang, J., Wang, L., Wang, Y., Liu, J. (2021). "Microplastic communities" in different environments: Differences, links, and role of diversity index in source analysis. *Water Res., 188*, 116574. https://doi.org/10.1016/j.watres.2020.116574

Li, J., Liu, H., Paul Chen, J. (2018). Microplastics in freshwater systems: A review on occurrence, environmental effects, and methods for microplastics detection. *Water Res., 137*, 362–374. https://doi.org/10.1016/j.watres.2017.12.056

Pojar, I., Kochleus, C., Dierkes, G., Ehlers, S.M., Reifferscheid, G., Stock, F. (2021). Quantitative and qualitative evaluation of plastic particles in surface waters of the Western Black Sea. Environ. *Pollut., 268*, 115724. https://doi.org/10.1016/j.envpol.2020.115724

Razeghi, N., Hamidian, A.H., Mirzajani, A., Abbasi, S., Wu, C., Zhang, Y., Yang, M. (2022). Sample preparation methods for the analysis of microplastics in freshwater ecosystems: a review. *Environ. Chem. Lett., 20*, 417–443. https://doi.org/10.1007/s10311-021-01341-5

Rios Mendoza, L.M., Balcer, M. (2019). Microplastics in freshwater environments: A review of quantification assessment. T*rAC Trends Anal. Chem., 113*, 402–408. https://doi.org/10.1016/j.trac.2018.10.020

Rosal, R. (2021). Morphological description of microplastic particles for environmental fate studies. *Mar. Pollut. Bull., 171*, 112716. https://doi.org/10.1016/j.marpolbul.2021.112716

Talbot, R., Chang, H. (2022). Microplastics in freshwater: A global review of factors affecting spatial and temporal variations. *Environ. Pollut., 292*, 118393. https://doi.org/10.1016/j.envpol.2021.11839.

Uurasjärvi, E., Hartikainen, S., Setälä, O., Lehtiniemi, M., Koistinen, A. (2020). Microplastic concentrations, size distribution, and polymer types in the surface waters of a northern European lake. *Water Environ. Res., 92*, 149–156. https://doi.org/10.1002/wer.1229

Wagner, M., Scherer, C., Alvarez-Muñoz, D., Brennholt, N., Bourrain, X., Buchinger, S., Fries, E., Grosbois, C., Klasmeier, J., Marti, T., Rodriguez-Mozaz, S., Urbatzka, R., Vethaak, A.D., Winther-Nielsen, M., Reifferscheid, G. (2014). Microplastics in freshwater ecosystems: what we know and what we need to know. *Environ. Sci. Eur., 26*, 12. https://doi.org/10.1186/s12302-014-0012-7

Xu, X., Zhang, L., Xue, Y., Gao, Y., Wang, L., Peng, M.,Jiang, S., Zhang, Q. (2021). Microplastic pollution characteristic in surface water and freshwater fish of Gehu Lake, China. *Environ. Sci. Pollut. Res., 28*, 67203–67213. https://doi.org/10.1007/s11356-021-15338-8