Groundwater: An Endangered Invisible Resource. Microplastic Pollution in Underground Karst Systems, from Surface Watercourses to Cave Waters

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Abstract	Microplastic (MP) pollution has been found in environments worldwide, including remote areas [e.g. Zhang in Sci Total Environ 758, 2021, Ambrosini in Environ Pollut 253:297–301, 2019, Cincinelli in Chemosphere 175:391–400, 2017]. MPs have a dimension less than 5 mm and are a global problem because they are easily transportable even at long distances, tend to adsorb and transport hazardous substances such as heavy metals, pesticides, persistent organic pollutants (POPs) and antibiotics [e.g. Li in Water Res 157:228–237, 2019, Li et al. in Environ Pollut 237:460–467, 2018;Rochman in Sci Rep 3:1–7, 2013;Selvam in J Hazard Mater 402, 2021;Zhou et al. in Sci Total Environ 694, 2019;], and pose a serious threat to living beings, ecosystem, and human health [e.g. Devereux in Mar Pollut Bull 173, 2021, Assas in Mar Pollut Bull 158, 2020].

Chapter 13
Groundwater: An Endangered Invisible Resource. Microplastic Pollution in Underground Karst Systems, from Surface Watercourses to Cave Waters

Valentina Balestra, Bartolomeo Vigna, and Rossana Bellopede

13.1 Introduction

Microplastic (MP) pollution has been found in environments worldwide, including remote areas [e.g. 1, 2, 3]. MPs have a dimension less than 5 mm and are a global problem because they are easily transportable even at long distances, tend to adsorb and transport hazardous substances such as heavy metals, pesticides, persistent organic pollutants (POPs) and antibiotics [e.g. 4, 5–8], and pose a serious threat to living beings, ecosystem, and human health [e.g. 9, 10].

Despite groundwater in karst aquifers constitutes a quarter of the global drinking water sources [11], MP pollution in karst areas and underground environments is still poorly known. This fact can be related to the invisibility of subterranean karst systems and their hard access, making them difficult to study. Being open systems, karst aquifers are vulnerable to contamination by surface pollution: MP presence in groundwater can be due to human activities, wastewater, surface waters and soil pollution, atmospheric deposition and litter. The subsoil characteristics play a fundamental role in the MP transport to groundwater: MPs deposited on the ground can be transported vertically in the subsoil throughout the soil pores and rock fractures [12, 13]. Precipitations facilitate the MP infiltration into the subsoil [14], as well as

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transport them over long distances [15]. The hydrogeology of the study area, the flow regime of streams and their seasonal variation must be taken into account too.

Karst environments have an important role in natural ecosystems and karst aquifer are a fundamental drinking water reserve, therefore, investigations and monitoring are required for understanding the system dynamics and identify potential sources of contamination. In this work, we conducted preliminary investigations on MP pollution in different water samples from a karst area of NW Italy, considering connected surface and underground (cave) waters.

13.2 Experimental

13.2.1 Materials

Bossea cave (Frabosa Soprana, Piedmont, Italy, 836 m a.s.l.), the oldest Italian show cave, was firstly explored in the first half of the nineteenth century and opened to the public in 1874. Today, it receives about 13,000 tourist/year (2021). The cavity has a single entrance and an ascending structure, developing for about 2800 m, with a vertical drop of about 200 m. It represents the final part of the karst system developing in the Maudagna-Corsaglia watershed. The cave is fed by a system with primary (precipitations infiltrating directly into the aquifer) and secondary supply (superficial water streams losses), such as Rio Roccia bianca, the main secondary supply contributing to the Bossea karst system recharge [16]. Infiltration waters feed an important collector which cross the Bossea cave for more than 1.5 km and directly gushes out in the Corsaglia River with a set of springs [17]. A series of tests using two different dyes, previously carried out in Rio Roccia bianca, highlighted that water coming from Rio Roccia bianca arrive in the collector of Bossea cave in short time and with high concentration [16]. Different discontinuities are present in the cave, characterized by low flow circulation [17, 18].

Spot sampling were carried out in Rio Roccia bianca superficial tributary (one sample), in the Bossea cave waters (four samples), and in the Corsaglia stream, where the waters of the underground collector emerge (one sample). In the Bossea cave, two samples were collected in the speleological traits (Sifone and Polla delle anatre), as reference samples of unpolluted waters, and two in the touristic area (Uovo and Sala frane). In Sifone, in the final part of the cave, the water comes out from a siphoning tract and are collected in a lake. Polla delle anatre is a small pool of water flowing out of a fracture in the rock, entering in the inner collector [18]. Along the tourist path, in Uovo, water flows between different gours, slowing down, while, in the initial part of the cave, in Sala frane, the collector waters flow quickly before leaving the cave. Groundwater and superficial water samples were collected into 1 L glass vessels, in September 2021, under low-flow conditions, transported to the laboratory in coolers, and kept refrigerated at 6 °C until analysis.

13.2.2 *Methods*

MP samples were analysed according to the previously published method for cave sediments [see 19 for details], adapted to the liquid matrix. Glass filters were replaced to silver ones to determine MP typology using the infrared (IR) spectroscopy. MPs were detected by exploiting their fluorescence under ultraviolet (UV) light, given by Fluorescent Whitening Agents (FWAs), commonly used additives in plastic production [20, 21] (Fig. 13.1). All researchers used nitrile gloves and cotton coats. For every step, all surfaces and materials were cleaned with ethanol and distilled water to avoid external contaminations. Plastic equipment was replaced with glass or metal one.

13.2.2.1 Preparation of Samples

Water samples were filtered through a 0.8 μm pore size silver filter (GVS Life Sciences, Membrane Disk 47 mm). Filters, positioned on glass petri dishes and covered with aluminium foil, were dried in an oven at 40 °C for 2 h. The organic matter removal was carried out on dried filters through the application of 2 ml of 15% hydrogen peroxide solution, left to react for 30 min at room temperature and, finally, dried again for 1 h at 50 °C.

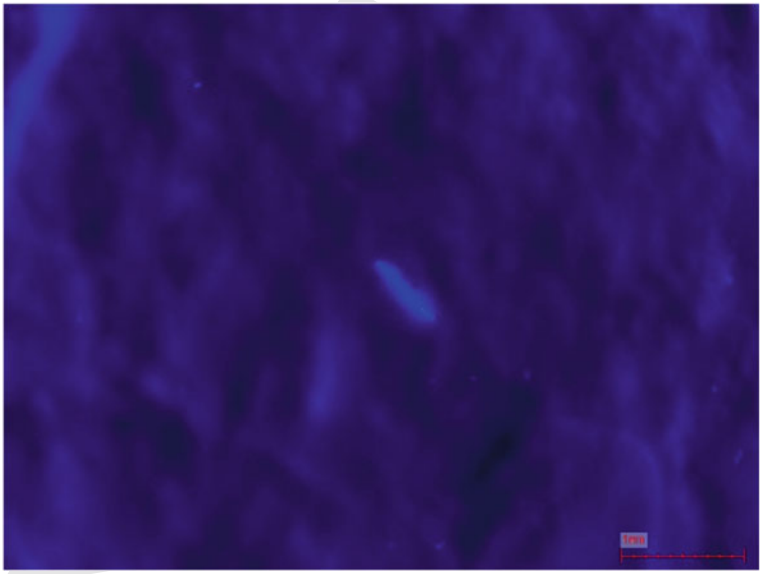

Fig. 13.1 Microplastic fibre under UV light

13.2.2.2 Analytical Techniques

Filters were observed with and without an UV flashlight (Alonefire SV10 365 nm UV flashlight 5W) under a Leitz ORTHOLUX II POL-MK microscope equipped with a DeltaPix Invenio 12EIII 12 Mpx Camera, with a 2.5x, 4x, 10 × or higher magnifications. Images of natural, artificial and synthetic fibres under microscope [e.g. 22, 23, 24] were used to compare particles observed under microscope, especially transparent fibres. The UV flashlight was positioned with an inclination of 45 °C. Visual identification was used to count MPs, according to strict selection criteria described in previous research [25–27]. A cut off of the particles smaller than 0.1 mm was made as suggested in European Commission [28]. Particles that could not be identified as MPs were not take into consideration. The counted MPs were described using the Standardised size and colour sorting system (SCS) [25].

Finally, a 10% of MPs of each filter were analysed using a micro-Fourier Transform Infrared Spectroscope (micro-FTIR) Shimadzu AIM-9000 microscope equipped with a Shimadzu IRTracer-100 spectrophotometer. Spectra were compared with the Shimadzu standard library.

13.3 Results and Discussion

13.3.1 Results

MPs were found in all water samples: 54 items/L in Sifone, 16 items/L in Sala frane, 12 items/L in Polla delle anatre, 30 items/L in Uovo, 23 items/L in Rio Roccia bianca and 29 items/L in Corsaglia River. Fibres represented the majority of the MPs present in the karst system (95.1%), followed by fragments (4.3%) and beads (0.6%). Mini-MPs accounted for 82.9% of the total MPs found in water karst system. The highest MP abundance was fluorescent under UV light (84.8%). Of the fluorescent particles, 46% were transparent, 16.5% red, 10.8% blue, 7.2% beige, and 26.7% other colours. Non-fluorescent MPs were mainly black (68%) or blue (20%). Polyethylene (51.4%) and polyvinyl alcohol (31.4%) are the main types of MPs found in the karst system waters, followed by polyester (8.9%), ethylene vinyl alcohol (2.9%), polyvinyl chloride (2.9%) and acrylic adhesive (2.9%).

13.3.2 Discussion

At the moment, a standardized method for assessing MPs do not exist. Using different methodology makes it difficult to compare the results. However, some considerations on MP amount in karst environment can be equally done. The only work detecting MP pollution in springs and wells in a karst water area has documented a maximum

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value of 15.2 MPs/L, under low-flow conditions [11], a fairly low value compared to those found in the Bossea karst system. Instead, concerning MP characteristics, the data about MPs in cave waters are similar to those described in Balestra and Bellopede [19] for Bossea cave sediments. Five sediment samples were collected along different part of the tourist path and one in the not-tourist area of the Bossea cave. Comparisons between the mean values obtained from sediment and water samples analysis inside Bossea cave are reported in Figs. 13.2, 13.3. The major part of MPs in Bossea cave waters are fluorescent, fibre-shape, and have a dimension between 0.99 and 0.1 mm, as in cave sediments (Fig. 13.2). The most of the fluorescent particles in Bossea cave waters are transparent, as in cave sediments, and the other main colours are similar too, with except of red particles, greater in water (Fig. 13.3). The non-fluorescent MPs were mainly black and blue, confirming the data found in Bossea cave sediments (Fig. 13.3). However, percentages of these data are different, as the colour of the less abundant MPs (Fig. 13.3). It could be related to different kind of biodeterioration, or to the diverse density of certainly MPs, more easily transportable in liquid medium. MPs in groundwater of Bossea karst system could be related to outside pollution, linked to the air transport of particles, soil contamination, winter activities related to the ski resorts and pollution from the near countries and could be transported especially by the main secondary supplies such as Rio Roccia bianca. The waters in the touristic part of the cave could be enriched with pollutants too, brought inside by tourists [19], which could be transported in different part of the cave and outside, in the Corsaglia river.

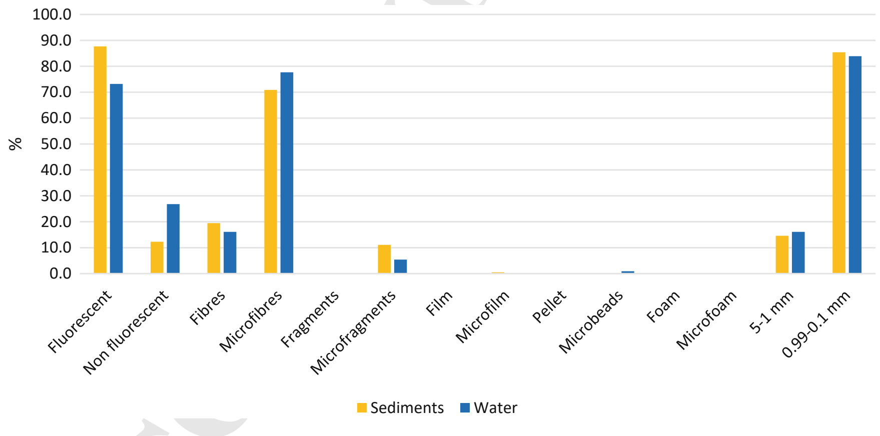

Fig. 13.2 Comparison of size, shape and fluorescence between microplastics found in Bossea cave waters and sediments

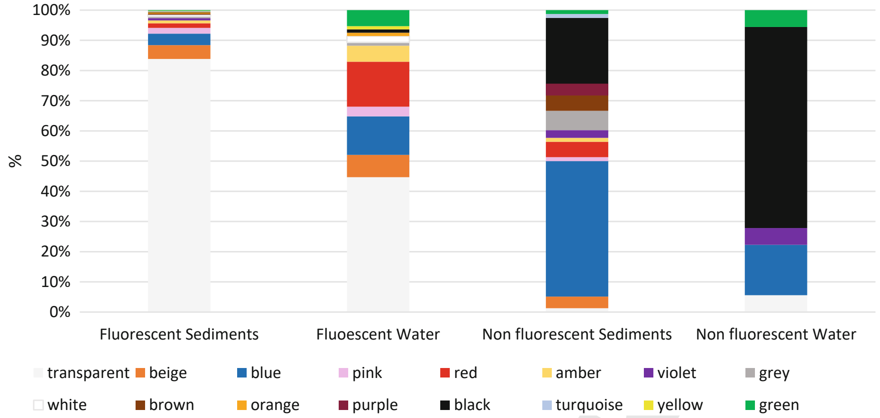

Fig. 13.3 Comparison of colours between fluorescent and non-fluorescent microplastics found in Bossea cave waters and sediments

13.4 Conclusions

This study documented the presence of microplastics in karst systems, from surface watercourses to water in cave. Microplastics with a dimension less than 1 mm and fibre shape dominate the samples and polyethylene is the main types of microplastics found in the karst system waters. Fractured aquifers may be vulnerable to microplastic pollution, contaminating waters and nearby environments, therefore, MP detection is essential to understand the pollution amount and define strategies for conservation. Moreover, karst aquifers are open systems, susceptible to pollutant contamination from surface, therefore, the above-ground areas should be monitored and protected too. Greater endeavours should be done to karst areas protection, implementing pollutants monitoring and sustainably managing important resources as water.

References

1. Zhang Y et al (2021) Microplastics in glaciers of the Tibetan Plateau: Evidence for the long-range transport of microplastics. Sci Total Environ 758:143634
2. Ambrosini R et al (2019) First evidence of microplastic contamination in the supraglacial debris of an alpine glacier. Environ Pollut 253:297–301
3. Cincinelli A et al (2017) Microplastic in the surface waters of the Ross Sea (Antarctica): occurrence, distribution and characterization by FTIR. Chemosphere 175:391–400
4. Li X et al (2019) Enhancement in adsorption potential of microplastics in sewage sludge for metal pollutants after the wastewater treatment process. Water Res 157:228–237
5. Li J, Zhang K, Zhang H (2018) Adsorption of antibiotics on microplastics. Environ Pollut 237:460–467
6. Rochman CM et al (2013) Ingested plastic transfers hazardous chemicals to fish and induces hepatic stress. Sci Rep 3(1):1–7

7. Selvam S et al (2021) Hazardous microplastic characteristics and its role as a vector of heavy metal in groundwater and surface water of coastal south India. J Hazard Mater 402:123786
8. Zhou Y, Liu X, Wang J (2019) Characterization of microplastics and the association of heavy metals with microplastics in suburban soil of central China. Sci Total Environ 694:133798
9. Devereux R et al (2021) The abundance of microplastics in cnidaria and ctenophora in the North Sea. Mar Pollut Bull 173:112992
10. Assas M et al (2020) Bioaccumulation and reproductive effects of fluorescent microplastics in medaka fish. Mar Pollut Bull 158:111446
11. Panno SV et al (2019) Microplastic contamination in karst groundwater systems. Groundwater 57(2):189–196
12. Chia RW, et al. (2021) Microplastic pollution in soil and groundwater: a review. Environmental Chemistry Letters, 1–14
13. Wanner P (2021) Plastic in agricultural soils–a global risk for groundwater systems and drinking water supplies?–a review. Chemosphere 264:128453
14. Zhou Y et al (2021) Microplastic contamination is ubiquitous in riparian soils and strongly related to elevation, precipitation and population density. J Hazard Mater 411:125178
15. Allen S et al (2019) Atmospheric transport and deposition of microplastics in a remote mountain catchment. Nat Geosci 12(5):339–344
16. Vigna, B (2020) Assetto geologico ed idrogeologico del Sistema carsico di Bossea (SW Piemonte, Italy), in Atti del Convegno Nazionale "L'uomo domanda, la grotta risponde". Cinquantesimo anniversario del Laboratorio Carsologico Sotterraneo di Bossea, Frabosa Soprana (CN), Italy. p 283–300
17. Vigna B, (2021) Vadose Zone Hydrogeology In The Bossea Cave System (Southern Piedmont, Northern Italy), in Proceedings of the 17th International Congress of Speleology, Sidney. p 222–225
18. Balestra V, Fiorucci A, Vigna B (2022) Study of the trends of chemical-physical parameters in different karst aquifers: some examples from italian alps. Water 14(3):441
19. Balestra V, Bellopede R (2022) Microplastic pollution in show cave sediments: First evidence and detection technique. Environ Pollut 292:118261
20. Ehlers SM, Maxein J, Koop JH (2020) Low-cost microplastic visualization in feeding experiments using an ultraviolet light-emitting flashlight. Ecol Res 35(1):265–273
21. Klein M, Fischer EK (2019) Microplastic abundance in atmospheric deposition within the Metropolitan area of Hamburg. Germany. Sci. Total Environ. 685:96–103
22. Houck MM (2009) Identification of textile fibers
23. Khan A, et al. (2017) A review paper on Textile Fiber Identification. IOSR Journal of Polymer and Textile Engineering (IOSR-JPTE) 4, 14–20
24. Zhang, X (2014) Fundamentals of fiber science
25. Crawford CB, Quinn B (2016) Microplastic pollutants, Amsterdam
26. Noren F (2007) Small plastic particles in coastal swedish waters, in n-research report, commissioned by KIMO, Sweden
27. Hidalgo-Ruz V et al (2012) Microplastics in the marine environment: a review of the methods used for identification and quantification. Environ Sci Technol 46(6):3060–3075
28. European Commission: Guidance on monitoring of marine litter in European seas. A guidance document within the common implementation strategy for the Marine Strategy Framework Directive. Ispra: European Commission, Joint Research Centre, MSFD Technical Subgroup on Marine Litter. p 126 (2013)