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Environmental Forensic

ANALYSIS OF MICROPLASTICS FOR ENVIRONMENTAL FORENSIC APPLICATIONS

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Introduction

The knowledge that microplastics (defined as plastics smaller than 5mm in size), a pollutant of emerging concern, can pose significant challenges to the ecosystem and human health due to its ubiquitous and persistent nature, calls for urgent measures for its control. Identifying the sources of pollutants and the extent of their contribution is one of the first steps in their management. However, the source apportionment is extremely challenging in microplastic pollution, due to diverse use of a single type of polymer, multiple manufacturing techniques, use of different additives in the same type of polymer by different industries, etc. (Kumar and Varghese 2021b). Use of robust environmental forensic techniques and protocols, both at the sampling and analysis stages can address this challenge to a great extent.

Gwinnett et. al (2021), in an earlier edition of this column had explained the different sampling methods adopted for microplastics with emphasis on the special considerations required when sampling is carried out for forensic purposes. Just as sampling for forensic purposes demands certain procedures to be followed, so does its subsequent analysis. Once the microplastic is sampled and brought to the laboratory, it goes through distinct phases of analysis, namely, drying of the samples (if the sample is wet), separating the microplastics from the matrix, classification, microscopic observations, polymer identification and interpretations regarding the sources. Brief explanations of these phases are given below for the analysis of microplastics from sand/sediment.

Drying of samples

When extracting microplastics from soil/sand/sediment samples, these matrices regularly have high moisture content and thus drying prior to microplastic separation is required. Drying is also required for preserving the samples for future analysis. Depending on how wet the sample is, the duration of drying can vary. For moderately wet beach sediment samples, 6 hrs drying at 60°C was found to be suitable (Kumar and Varghese 2021a). When the purpose of the analysis is to know the abundance of microplastics or its impact on the ecosystem, keeping the physical properties of the microplastic intact may not be important. However, when the sampling is for forensic application, this is not the case. Heating at higher temperatures is found to disfigure and change the colour of microplastic, resulting in the loss of characteristics which are vital for forensic examination.

Separating microplastics from the sand matrix

There are different techniques followed for separation of microplastics, based on the objective and the type of environmental matrix (Figure 1). The most commonly used separation technique is density separation explained in the manual by NOAA (Masura et al., 2015). A major problem with this method is the possibility to leave out the denser plastics, and also those with biofilms present on the surface. Missing a particular type of microplastic from the chain of analyses can prove costly, especially when the analyses are for forensic applications. Sieving and separating the microplastics (Hidalgo-Ruz et al. 2012) is reported to be useful in overcoming this problem when the matrix is fine beach sediments and the microplastics targeted are more than 1 mm in size (Kumar and Varghese, 2021a). Although the method is cumbersome, involving manual sorting of microplastics, it was seen to give good results for forensic applications. If the focus of study is microplastics below 1mm in size which are difficult to be handpicked, density separation followed by filtration of the supernatant and observation under a microscope is a possible technique (Windsor et al. 2019; Urban-Malinga et al. 2020). Microplastics may be freshly formed from the fragmentation of accumulated macro plastics, rather than transported to the sampling location as microplastics. Therefore, plastics above 5mm, though not considered as microplastic, should be preserved after separating it out from the matrix as they could be of use in identifying the source if a matching

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FIGURE 1: Microplastics separated out from Beypore beach, Kerala, India.

part is retrieved from the samples (Ashwini and Varghese, 2020).

Classification

After separating the microplastics from the environmental matrix, it is classified under various morphological categories to draw useful conclusions regarding its source, fate and effects. A frequently used classification scheme classifies microplastics into fragments, film and fibre (Karbalaei et al. 2019). However, this scheme of classification does not differentiate the regular 3D shaped fragments from the irregular. Regular shapes for microplastics, like spherical, cylindrical, etc., are indicative of specific sources and cannot be missed when the purpose of analysis is source apportionment. Moreover, studies have also shown that there is a significant effect for the shape on the transport of microplastics in the environment (Jahnke et al., 2017; Harrison et al., 2018). Hence, there needs to be a classification scheme which distinguishes the regular shaped 3D microplastics from the irregular shaped ones. Another criteria for classification can be the colour. Classifying microplastics based on colour may lead to sources in some cases.Kumar and Varghese (2021a) were able to use colour among other characteristics to identify the source of the polyethylene fibres sampled from the Calicut beach as fishing nets.

Microscopic observations

Microscopical observations of microplastics may encompass the morphological and optical properties of the samples. Many microplastic studies limit their observations to colour, size and classification of the sample set as a whole rather than fully characterizing each microplastic as seen in forensic examinations (Gwinnett et al., 2021). Much can be learnt from forensic fibre analysis, where polymer fibres are examined for their colour, width, cross-sectional shape, presence of inclusions and optical properties such as its birefringence and sign of elongation (Robertson et al., 2018). The latter can also provide an initial polymer identification (Johri and Jatar, 1979). Gwinnett et al. (2021) have proposed a new workflow for the recovery and analysis of microplastics, particularly fibres for plastic pollution monitoring using forensic approaches. This new workflow allows greater differentiation between samples and aids in source identification.

Observing degradation patterns of microplastics under an optical microscope can provide a basic idea on the resident time of microplastics in the environment (Kumar and Varghese, 2021a). Such observation will help in answering the questions if the microplastics are recently formed or are quite old. Sharp edges of a fragment indicate freshly formed microplastic when compared to a microplastic with blunt edges. Also, crack formation, loss of material from the surface, etc. are indications of longer residence time in the environment (Figure 2).

Polymer identification

One of the important steps in microplastic analysis is the identification of the polymer type. The most common polymer types noticed are polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET), the polymers of common commodity plastics used for packing, containers, carry bags, fishing nets, etc. Some plastics may have a combination of polymers like polyethylene and polypropylene. Fourier Transform Infrared Spectroscopy (FTIR) is the most widely used technique for polymer identification (Figure 3). Micro-Fourier transform infrared (μFTIR) microscopy, which is also an FTIR technique, uses a microscope to analyse smaller samples, some set-ups also automatically detect and count the microplastics of different polymer types (Li et al., 2021). A particle finder software identifies particles which is followed by the generation of IR spectra of all the identified particles. This method is suitable for smaller microplastics that do not cover the diamond aperture of the FTIR with Attenuated Total Reflection (ATR) mode in the sample holder. Not covering the diamond aperture in the instrument results in obtaining an IR spectrum with high background noise. Once the spectrum of the polymer is obtained, polymer spectral libraries can be used to match and identify the polymer analyzed. Other popular methods for polymer

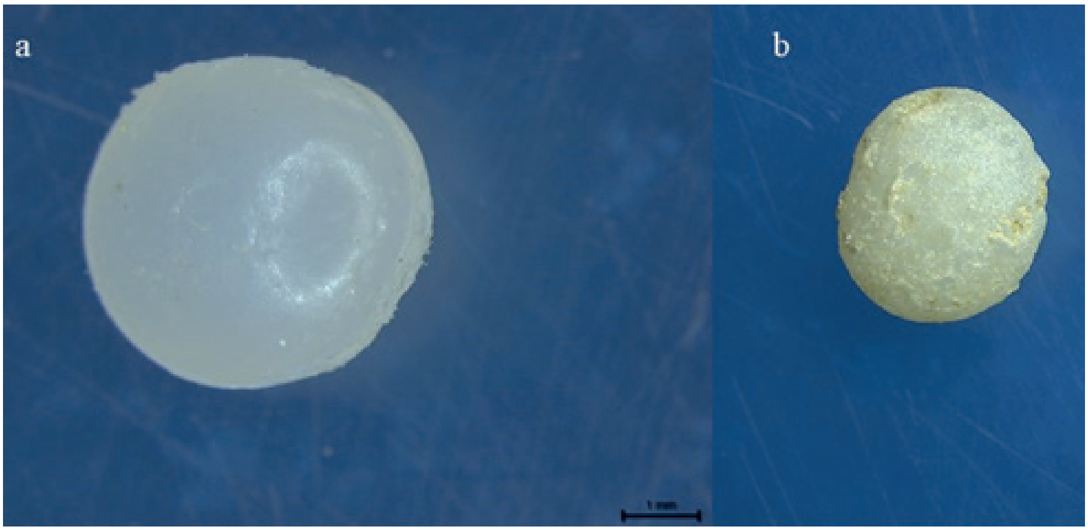

FIGURE 2: a) Low residence time plastic pellet, b) Higher residence time plastic pellet.

identification include Raman spectroscopy (Frère et al, 2016) and pyrolysis-gas chromatography with and without mass spectrometry (Jung et al, 2021).

Procedural Contamination Prevention

It is standard practice in forensic examinations to include strict anti-contamination protocols when handling small particulates. This is also true for microplastic analysis although many studies still only report crude or limited procedures far less comprehensive than those that would be used in criminal investigations. The potential for contamination of samples is high though, therefore protocols which limit exposure of the sample to the air and sources of plastic should be incorporated in all of the stages described above. Prata et al. (2021) describe the protocols that should be in place during the analysis stages of microplastic studies, these include; comprehensive washing of equipment before and between samples, controlled air flow in the laboratory and wearing of non-synthetic clothing during analysis. Protocols adapted from those used

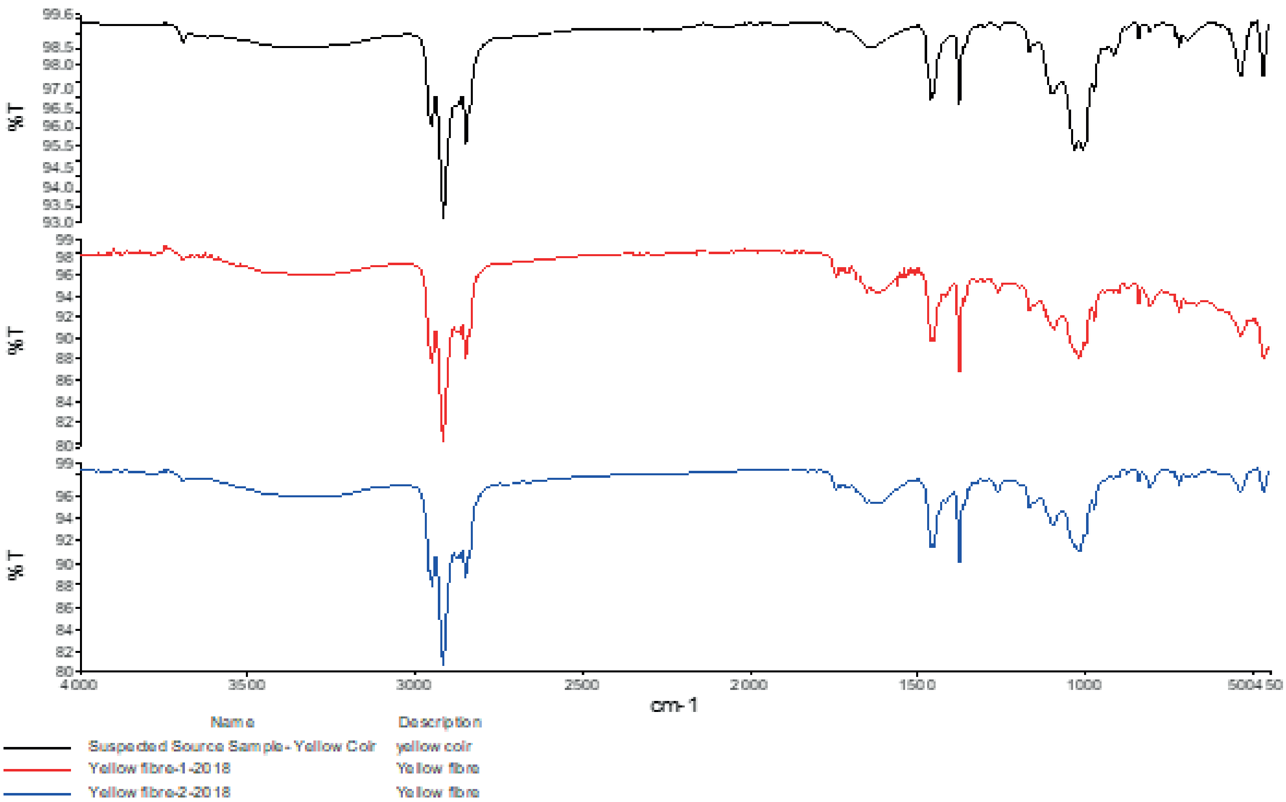

FIGURE 3: Example of FTIR spectra of suspected source and sample.

for the forensic examination of fibres, such as those developed by Woodall et al. (2015), are likely to be the most effective as they must stand up to the scrutiny of the courts.

Interpreting source

This is the phase in forensic analysis, where the information generated in the previous phases are used to identify the possible sources and pathways of the microplastics sampled from the site. Along with analysis data, information collected during sampling such as geographical features, proximity of harbor, influence of river, type of beach activities, etc. (Lippiatt et al.,2013) are also used to identify the source. Kumar and Varghese (2020) have proposed a forensic framework for the source apportionment of microplastic in beach sediments that utilizes the information collected during the sampling and the data generated in the various stages of analyses. The framework was used to reach different levels of conclusion regarding the source of microplastics; in some cases it was possible to identify the exact source, whereas in other cases only the pathway through which the microplastic reached the marine environment could be identified.

Concluding Remarks

Environmental forensic investigations leading to the identification of the source of contamination requires robust protocols starting from the sampling stage to the analysis stage. Based on the information acquired during sampling and analyses, different degrees of confirmation about the source of microplastics are possible. Though the scientific literature is scarce on the analysis of microplastics for environmental forensic applications, the current understanding is that analyses for forensic applications demand special considerations such as those mentioned above. More studies are needed and the ultimate aim of such studies should be the development of a comprehensive forensic analysis protocol for microplastics.

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