

Methodology for Sampling, Purification, Extraction and Identification of Microplastic - A Review

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Abstract: *Microplastic particles are emerging contaminants in the marine environment. This review discusses the methodology for microplastic detection. Primary and secondary microplastic serves as a source of microplastic. Discharge of wastewater effluent to the rivers and streams serves as a pathway for microplastic accumulation in the oceans and seas. We need to know about microplastic abundance and distribution to minimize the marine pollution. So various sampling method like use of Manta trawls and different sieve sizes are discussed. Purification and extraction procedure using Wet Peroxide Oxidation method also reviewed. Instrumental analyses for the Identification of microplastics and some suggestions have been discussed in this paper.*

Keywords: Microplastic, Source and transfer of microplastic, Sampling, Purification, Extraction and identification of microplastic

1. Introduction

The global production of plastic resins in recent years is about 300 MMT annually and nearly a half of the current production is in Asia (Andrady., 2017). Due to high amount of plastics produced in various sector, plastic pollution in the environment is becoming increasingly apparent (Dumichen et al., 2017). Larger plastics eventually undergo degradation and subsequent fragmentation, which leads to the formation of smaller pieces (Sul and Costa.,2013) called microplastics.

Microplastics are small plastic particles originating from the degradation of larger plastic debris (Cauwenberghe et al.,2013; Sruthy and ramasamy.,2016) or from particles originally manufactured at that size (primary) (Andersn et al.,2016) with a diameter of 5 mm or less (Costa et al.,2015). Plastic have been gaining attention in the scientific community over the past decade because they pose a pervasive threat to the marine environment (Fok and Cheung.,2015). Microplastics in the marine environment are known as global ecological problem. (Zobkov et al., 2017). Recent estimates indicating that the mass of plastic released to the marine environment may reaches 250 million metric tons by 2025 (Welden et al.,2017). Pollution has spread throughout the world's seas and ocean, into the remote and largely unknown deep sea.(Cauwenberghe et al.,2013). These microplastics can be ingested by marine organisms and end up in the human food chain (Auta et al.,2017).

So to understand the consequences of microplastic, their sampling and extraction methods are needed. There is no specific standardized method for sampling and identification of microplastic (Tagg et al.,2015).The objectives of this review are : (1) To summaries the source and transfer of microplastic to aquatic environment. (2) To review the methodology used for sampling of microplastics. (3) To discuss the purification and extraction of microplastic. (4) To review the instrumental analysis method required for identification of microplastic.

2. Sources and transfer of microplastics into the marine environment

Marine litters either directly or indirectly transferred to seas and oceans (Cole et al.,2011). Microplastics particles in the aquatic environment are made up of particles that differ in size, shape and chemical composition (Auta et al., 2017).

A direct input of primary microplastics to terrestrial environment is through personal care products and household products (Horton et al.,2017). Cosmetic products, such as facial scrubs, have been identified as a potential important primary source of microplastics to the marine environment and it is estimated that between 4594 and 94,500 micro beads could be released in a single use. (Napper et al.,2015). Polyethylene, Polypropylene granules (<5 mm) and Polystyrene (2mm) in a cosmetic product has been reported in review by Auta et al., (2017). These micro beads enter in to the wastewater treatment plants and it serves as an entrance routes to the aquatic environment which is reported in recent studies (Chang et al.,2015; Mintenig et al.,2017). More abundant in the ocean are secondary microplastic, which is a fragments of large plastic debris. It is resulting from either during use of products or weathering degradation of their litter. Input of this secondary microplastic is far more difficult to estimate (Andrady et al., 2017)

These particles then enters the wastewater treatment plant and it serves as a pathway for microplastic pollution (Mason et al.,2016). I was found that, the most of the microlitter in wastewater is removed during the pre-treatment but however treated effluent still contain microlitter particles were reported (Carr et al.,2016). Insufficient removal of from the wastewater treatment plant leads to accumulation of microplastic in to rivers and streams and later to marine environment (Estahbanati and Fahrenfeld.,2016).

3. Methodology for microplastic detection and analysis

3.1 Sampling of Microplastic

Sampling of microplastic is different for different sample type. Among these most of the studies used Manta trawl of 333µm (Free et al.,2014; Eriksen et al.,2013; Anderson et al.,2017; Zhang et al.,2017) for surface water and sea water

sampling. Commonly applied sediment sampling strategies include random sampling at several location by either excavation using shovel (Fok and cheung., 2015) or Van Veen grab sampler (Sruthy and ramasamy.,2016; Frere et al.,2017). Talvitie et al., (2017) reported that, the samples from the each unit of wastewater treatment plants (Influent, after pre-treatment, after AS and Effluent) can be obtained by using electric pump.

Table 1: Microplastic sampling method reported in various studies.

| S no | Location | Sample type | Sampling method | Reference |
|------|--|------------------------------|--|-----------------------------------|
| 1 | Hovsgol lake, Northern Mongolia. | Water | Manta trawl, 333µm (16 cm h* 61cm w) | Free et al.,2014 |
| 2 | Mangroves habitats, Singapore's coast-line | Sediment | Stainless steel spatula | Nor and obbard.,2014 |
| 3 | Laurentian Great Lake, US | Water | Manta trawl, 333µm | Eriksen et al.,2013 |
| 4 | Lake Winnipeg, Canada | Water | Manta trawl, 333µm (18 cm h* 61cm w) | Anderson et al.,2017 |
| 5 | Vembanad lake, Kerala, India | Sediment | Van Veen Grab sampler | Sruthy and Ramasamy.,2016 |
| 6 | Surface waters of Wuhan, China | Water | 12 V DC Teflon pump | Wang et al.,2016 |
| 7 | Municipal Wastewater Treatment Plant, US | Waste water effluent | Extraction pump | Mason et al.,2016 |
| 8 | Raritan river and Municipal wastewater treatment plant, Central New Jersey, US | Water and Wastewater | Plankton nets, 153µm (0.2m dia, 0.51m long) | Estahbanati and Fahrenfeld., 2016 |
| 9 | Bohai Sea, China | Sea water | Manta net, 330µm | Zhang et al.,2017 |
| 10 | Sandy beaches, Hong Cong | Sediments | Excavated using shovel (4cm depth) | Fok and cheung.,2015 |
| 11 | ----- | Facial exfoliating cleansers | Syringe extraction from cleansers (Neutrogena, clean & clear, L'Oreal Paris) | Chang.,2015 |

3.2 Purification and Extraction of microplastics

Size of microplastic particles retained is a direct influence of the mesh size used. Because no standardized microplastic monitoring methods have been established worldwide, published studies have used different types of mesh sizes (Zhang et al.,2017). Set of tyler sieves (Free et al., 2014; Eriksen et al.,2013; Mason et al.,2016) and stainless steel mesh sieves(Wang et al.,2016; Zhang et al.,2017) widely used to obtain the different sizes of microplastics were reported.

I found that highly promising technique for purification of microplastic is Wet Peroxide Oxidation (WPO) process (Anderson et al.,2017; Free et al.,2014; Sruthy and ramasamy.,2016; Estahbanati and Fahrenfeld.,2016), because it is the only applied chemical having potential impact on microplastic (Mintenig et al.,2017).Another method is Enzymatic purification, which requires considerable time and also risk of contamination is high in this, due to number of filtration steps (Mintenig et al.,2017). There is a variability in the extraction techniques applied. The densities of common plastic polymers like HDPE, LDPE, PS, PP are 0.94-0.98 g/cm³, 0.89-0.93 g/cm³, 1.04-1.1 g/cm³ and 0.83-0.92 g/cm³ respectively (Sruthy and Ramasamy.,2016).So high density chemical like NaCl (Estahbanati and Fahrenfeld.,2016; Sruthy and ramasamy.,2016) was reported in most of the studies. I was

found that NaI and ZnCl (Mintenig et al.,2017) is also best for density separation. Frere et al.,(2017) used sodium tungstate solution of density 1.56 g/cm³to extract microplastic easily from the sample.

3.3 Identification of microplastic

The composition of plastic polymers allows for a clear identification of samples to a certain polymer origin. Firstly to know the size, diameter, shape and colour of the plastic particles, Stereomicroscope (Zhang et al.,2017; Estahbanati and Fahrenfeld.,2016; Talvitie et al.,2017) is widely used in the studies due to its high resolution than light microscope (Leslie et al.,2017). Instrumental analysis methods such as Raman Spectroscopy (Frere et al.,2017) and Fourier-Transform Infrared spectroscopy (FTIR) (Zhang et al.,2017; Mintenig.,2017; Talvitie et al.,2017; Leslie et al.,2017; Fok et al.,2016; Mintenig et al.,2017) are the promising technology for the identification of microplastics reported by numerous studies. Raman Spectroscopy is a surface technique used to identify microplastic particles in different environmental samples because of its high reliability. I was found that few studies applied micro-FTIR technique to obtain the particles even less than 20µm size. (Mintenig et al.,2017).To understand the surface characteristics and chemical composition of the microplastics, samples were examined using Scanning Electron Microscope (SEM) (Eriksen et al.,2013; Anderson et al.,2017) in some studies.

Table 2: Microplastic Concentration and Polymer type reported in studies

| S.No | Sample type | Number of samples | Microplastic concentration | Polymer types | References |
|------|---------------|-------------------|--------------------------------------|---|---------------------------|
| 1 | Water | Not mentioned | 96 – 496 /m ² | HDPE, LDPE, PS, PE and PP | Sruthy and Ramasamy.,2016 |
| 3 | Water | Not mentioned | 5595 ± 27,4177 items m ⁻³ | Expanded Polystyrene, fragments and pellets | Fok and cheung., 2015 |
| 4 | Surface water | 21 | 450-450,000 km ⁻² | Acrylic, polystyrene, amino thermoset plastic, melamine. | Eriksen et al.,2013 |
| 5 | Sediment | 7 | 12-62.7 particles kg ⁻¹ | Polypropylene, PVC, Nylon. | Nor and obbard., 2014 |
| 6 | Sediment | 9 | 20,264 particles Km ⁻² | Fragments, films, foams, fibers and pellets | Free et al.,2014 |
| 7 | Water | Not mentioned | 748,000 particles km ⁻² | Not mentioned | Anderson et al.,2017 |
| 8 | Water | 11 stations | 0.33±0.34 particles m ⁻³ | Polyethylene, polypropylene, polystyrene and polyethylene terephthalate | Zhang et al.,2017 |

4. Conclusion and Suggestions

In this study, some papers investigating microplastic pollution were critically analyzed. Recent findings regarding microplastic pollution, I was found that the source control is the best way to minimize the microplastic pollution. Monitoring efforts are required to understand the distribution, abundance and ecological implications of microplastic pollution. So many sampling methods have been used in various studies. Using Manta trawl of 333µm is highly reported in the current studies, but tiny particles can be easily missed by sampler with a large mesh size, which are an important part of microplastic. Wet Peroxide Oxidation (WPO) for purification is the best method due to its best organic content removal property. After purification microplastic of lower densities can easily extract by using suitable chemicals having high densities. Use of Stereomicroscope for the detection of microplastic is highly promising and FTIR Spectroscopy and Raman Spectroscopy helps to know the composition of microplastic, which is a vital part of microplastic analysis.

There is a large range of uncertainty around the microplastic composition, diversity and volume entering the environment; it is difficult to predict the emission and still there is no standardized method for sampling, extraction and identification of microplastic in environmental samples. To improve the field of research, it is important to develop the standardized method of collecting and analyzing the samples. Such standard method has the ability to minimize the difficulty in finding the microplastic and helps in comparison between the studies

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