Omni-Akuatika, 11 (2): 1–6, 2017
ISSN: 1858-3873 print / 2476-9347 online

Review

Microplastics Monitoring in Marine Environment

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Received 19 November 2017; Accepted 27 November 2017; Available online 28 November 2017

ABSTRACT

This review summarizes the need for future spatiotemporal comparisons of microplastics abundance across marine environment, through standardized methods for microplastic sampling and analysis in sea water, beach and seabed sediment and marine organism. Pretreatment of the sample prior to the elimination of organic matter should be done using appropriate reagents was also described. Extraction of microplastics from environmental matrices is based on the different density of targeted microplastics with saturated salt solutions (NaCl, NaI, $CaCl_2$, $ZnCl_2$ and lithium metatungstate). Quantification can be achieved by microscopic techniques (binocular, stereomicroscope, fluorescence microscope and scanning electron microscope) and discussion on identification methods including FTIR, Pyr-GC/MS and Raman spectroscopy will be provided. This review also endorse the important of further study regarding the fate and impact of microplastics on marine biota and human health, especially when we acknowledge that co-pollution may occur during the transport on microplastics in marine environment.

Keywords: *marine pollution, environmental chemistry, co- pollutants, microplastics, marine debris*

1. Introduction

For worldwide scientific communities, the term of “marine debris and microplastic” are rose up in last two decades but such term is relatively newly introduced in Indonesia (Dewi et al., 2015; Rochman et al., 2015; Cordoba and Wahyudi, 2016; Syakti et al., 2017). There is several definitions of microplastics including GESAMP (2016) and UNEP (2016). The most widely used definition is referred to the particles less than 5 mm in their longest dimensions. This review proposes a practical term of microplastic related with aquatic sciences. The term of “microplastics” describes plastic debris < 5 mm in size (wide, length, thickness or diameter) which can be harmful for aquatic life. In fact, plastic has been globally used as multitude of product of the different scale mainly for packaging and broad range application including automobile, medical and building materials. Annual global production continues to grow for more than 50 years and reached to 322 million tons in 2015 (PlasticEurope, 2016). Accordingly, In Indonesia**,** the total plastic waste was predicted reached 9.52 million tons in 2019 (KLHK, 2017). Using an assumption proposed by (Van Cauwenberghe et al., 2015) and a model based on Jambeck et al. (2015), 10 % plastic waste will end up in the sea by year and may results in total 187.2 millions tons accumulation of plastic waste in Indonesia marine ecosystem in 2015. Indonesia has already been actively participating in global and regional High Level Meeting in order to increase public awareness and engagement to reduce marine plastic debris by 70 % in 2020 (CMMA, 2017). Despite a wide array of commitments being made to address this emerging issue, knowledge on marine plastics, particularly

http://dx.doi.org/10.20884/1.oa.2017.13.2.430

microplastics and its impacts, still remains rather limited. So that why, assessment of marine debris and microplastic pollution, standardized methods and protocols for sampling and laboratory analysis, understanding of the microplastics pollution impact in marine organisms should be developed and standardized even thought there is still occurs methodological limitations encountered for microplastics research.

This review paper describes the essential tool for monitoring program of microplastics extraction, enumeration and identification methods. Accordingly, we aim to promote a standardized monitoring program for microplastics in Indonesia marine ecosystem. We focus on three different environmental matrices i.e. water, sediment and marine biota.

2. Microplastic Sampling and Pretreatment

2.1. Seawater

Samples can be collected from the surface, middle and bottom layer through difference trawl model with a rectangular opening and a net connected with a collecting bag (Figure 1).

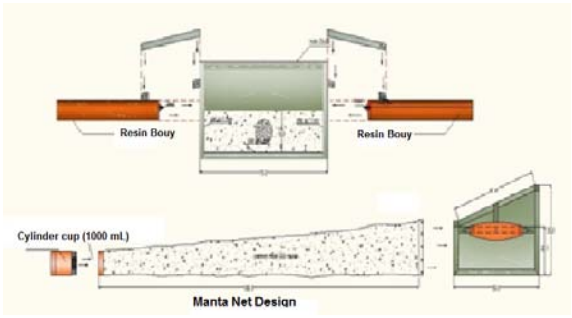

Figure 1. Mini trawl with Manta/Neuston Net type

The system can be made with 60 to 80 cm *net* diameter sizes with a rigid frame construction and buoyant aquaplanes made by a resin mixture maintain a continuous rectangular *net* opening at the surface with a maximum depth of 30 cm. Typically applied with mesh size ranged from 20-1,000 µm, the overall system called e.g. DiSalvo neuston net (DiSalvo, 1988), Manta Net (Syakti et al., 2017) and AVANI trawl (Eriksen et al., 2018).

2.2. Sediment

Sediment samples are generally taken from beach and seabed. For the beach sampling, it is recommended to collect two parallel transect lines near the high or low tide lines. The samples are taken from several 0.25 x 0.25-meter quadrat in transect lines (Wessel et al., 2016). Beach sediment samples are collected from the topmost 1 cm (Leibezeit and Dubaish, 2012), 3 cm (Manthalon and Hill, 2014), 5 cm (Corcorana et al., 2015) and 10 cm (Ng and Obbard, 2006) in each quadrat. Seabed sediment sampling can be done using a box-corer (Corconara et al., 2015; Cordoba and Wahyudi, 2016). Beach and seabed samples could be collected using non-plastic sampling tools i.e. stainless steel shovel.

After sampling, the sediment can be transported to the laboratory by using a glass or aluminum foil container and then stored at 4 °C prior to further analysis. The sediment samples are processed through a series of pre-treatment steps: drying at different temperature e.g. 50 °C and 60°C (Manthalon and Hill, 2014; Qiu et al., 2015), sieving on a successive mesh (e.g. < 5 mm, < 1 mm and < 200 µm), drying for mass at temperature below 60 °C (Osswald et al., 2006).

2.3. Marine Biota

Most studies related with ingested plastic have been recorded in fishes (Halstead et al., 2018) through direct sampling in the sea (Lusher et al., 2013) or from fish markets (Rochman et al., 2015) or even in fish larvae (Steer et al., 2017). Recently the research works also targeted other organisms such as mussels and lugworms (Van Cauwenberghe et al., 2015), crab (Watt et al., 2014), and zooplankton (Cole et al., 2013). Generally, for the fishes or macroinvertebrate, the relative data that should be recorded included their sex, length, weight, girth, etc before dissection to obtain the gastrointestinal tracts for analysis. Fish liver was also weighted to calculate the hepato-somatic index. Digestive tracts of respective biota are removed and then the stomach was flushed by shearwater to rush out any food and ingested microplastics, dried and stored before extraction. Biotic samples storages can be done by fixative technique using 4 % formaldehyde and 70 % ethanol but some polymers can be damaged, thus an alternative storage of biotic samples can be done by simple freezing (Lusher et al., 2017).

3. Microplastic Extraction

From different pretreated samples i.e. water, sediment, and biota, in order to remove organic matter remaining on the surface of the plastic and to help further identification by FTIR,

30 % of H_2O_2 should be added into the solution. Other oxidator used in microplastic research are chloride acid (HCl), nitric acid (HNO_3), potassium hydroxide (KOH) and enzymes (Nuelle et al., 2014; Cole et al., 2014). After filtering and drying, the sediment is added with high density saturated solution under quickly stirring. Typically, a saturated sodium chloride (NaCl) solution with a density of 1.202 g/mL is used for separating microplastics from sediment and sand. Sodium iodide (NaI), calcium chloride ($CaCl_2$), zinc chloride ($ZnCl_2$), and lithium metatungstate (LMT) can also be used with density 1.98 g/mL, 1.46 g/mL, 2.91 g/mL and 3.7 g/mL respectively for microplastic extraction. Table 1. showed the different density of plastic polymers and the saturated salt that can be used to float the respective plastic type and polymers.

Table 1. Density of polymers and appropriate solution for extraction.

Polymers /fibers	Density (g/mL)	Appropriate Salt Solution
PETE	1.38	NaI, $ZnCl_2$, LMT
LDPE	0.92	All salt
HDPE	0.95	All salt
PS	1.05	All salt
PP	0.87-1.01	All salt
PC	1.2	NaI, $ZnCl_2$, LMT
PVC	1.3 -1.45	$ZnCl_2$, LMT
Polyester	1.3 -1.4	$ZnCl_2$, LMT
Nylon	1.02-1.15	NaI, $CaCl_2$, $ZnCl_2$, LMT

Note. polyethylene terephthalate (PET), high-density polyethylene (HDPE), polyvinyl chloride (PVC), low-density polyethylene (LDPE), and polypropylene (PP). Sodium chloride (NaCl), sodium iodide (NaI), calcium chloride ($CaCl_2$), zinc chloride ($ZnCl_2$), and lithium metatungstate (LMT). (from different sources).

4. Microplastics Analysis

4.1. Enumeration

The most common quantification technique to determine the abundance of microplastics in different environmental matrices is generally visual counting under a dissection microscope, binocular microscope, stereomicroscope, fluorescence microscope and scanning electron microscope (SEM). With the lower cost, using binocular microscope has limitation due to poor discrimination amongst the observed microplastics. Stereomicroscope and dissected microscope can provide a moderate resolution stereoscopy with adequate discriminability. Moreover, fluorescence microscope may result in a good resolution with accurate counting. Obviously, the use of SEM even without colour appearance provide a great resolution and spectroscopy to gain the surface characterization of microplastic. The limitation of the later technique is the high cost and few laboratory in Indonesia were equipped by SEM. For instance, Eriksen et al (2013) proved that 20 % of identified plastic through ordinary microscope was later identified as aluminum silicate when identification was conducted by using SEM.

A particular attention should be made when working with muscle tissue, liver, gonad, cell, lymph system, moth, gill, and feces. To ensure material organic elimination, beside the use of an oxidant (H_2O_2), some digestion solutions are recommended such as enzyme (Trypsin, Proteinase-K and Corolase 7089), acid (HNO_3, HCl and KOH) and alkali (NaOH) (Van Cauwenberghe et al., 2015; Qiu et al., 2016).

4.2. Identification

4.2.1. Fourier Transform Infrared (FTIR) Spectroscopy

Two type of FTIR have been used for microplastic identification including micro-FTIR (Frias et al., 2010) and ATR-FTIR (Avio et al., 2015; Syakti et al., 2017). Basically, For instance, spectra can be obtained using a Thermo Electron Nexus spectrometer equipped with a diamond crystal Smart Orbit™ accessory. Spectra were recorded in attenuated total reflection (ATR) and were corrected by the ATR correction of a specific software. All the spectra were acquired between 4000 and 450 cm^{-1} with 64 accumulations and a spectral resolution of 4 cm^{-1}. Figure 2 showed an example of different polymers identification using FTIR.

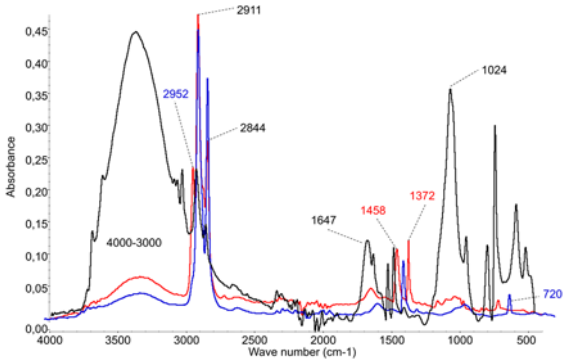

Figure 2. FTIR spectra for PP (red line), PE (blue line) and PS (black line) plastic polymers.

For instance, the peaks corresponded to the aromatic ring (C-H) stretching asymmetrical vibration (2911 and 2844 cm^{-1}) indicated

polymers PP and PE. PE can be easily identified by the 720 cm^{-1} band indicating methylene rocking in the C-H out of plane bending region (Syakti et al., 2017).

4.2.2. Pyr-GC/MS

Nuelle et al. (2014) demonstrated the use of Pyrolysis-GC/MS (Pyr-GC/MS) by analyzing the thermal degradation product after pyrolysis at 700 °Cfor 60 s and then transferred into GC/MS at 350 °C. The identification will be based on comparison with common standard polymer and their degradation product. This technique is not only good indication for a specific plastic polymers but also can detect interference from organic plastic additives (Fries et al., 2013). The disadvantage by using this method is destruction of the analyzed materials.

4.2.3. Raman Spectroscopy

Lenz et al (2015) clearly demonstrated misidentification problems in the visual microscopic analysis of small microplastic can be resolved by using Raman spectroscopy. Raman spectroscopy reveals the chemical and structural composition of samples. They concluded that visual identification alone is inappropriate for studies on small microplastics. Sixty-eight percent of visually counted microplastics (n = 1279) were spectroscopically confirmed being plastic. The percentage varied with type, colour and size of the microplastics. Fibres had a higher success rate (75%) than particles (64%). Similar to the more widely known IR spectroscopy (Song et al., 2015), because of Raman scattering occurs when the monochromatic light source, such as a laser interacts with molecular vibrations, Raman spectroscopy can also identify varying additive chemical composition, degradation state and organic matter coating.

5. Microplastic research in Indonesia

Indonesia has a national action plan for combating Marine Plastic Debris (2017-2025) under the coordination of the Ministry of Maritime Affairs. However, microplastic research has not yet become a national priority. While the government focuses on marine debris management, several agencies such as the Indonesian Institute of Science (LIPI), Bogor Agricultural University (IPB), Jenderal Soedirman University (UNSOED), Raja Ali Haji Maritime University (UMRAH), Mulawarman University (UNMUL), Padjajaran University (UNPAD) and the Agency for the Assessment and Application Technology (BPPT) have been conducting plastic research and monitoring. LIPI recently completed its microplastic sampling programme (2015-2017) with microplastics sampled from over 10 stations nationwide, and in 2016 published a paper on microplastics in deep-sea sediment (Cordova and Wahyudi, 2016). IPB and UNMUL have conducted the study on sediment microplastics respectively at Jakarta Bay (Manalu e al., 2017) and Muara Badak, Kutai Kartanegara (Dewi et al., 2015). The University Hasanuddin Makassar reported a study of microplastic debris, conducted in 2015 (Rochman et al., 2015), in fish and bivalves sold for human consumption while the Padjajaran University is conducting microplastics study at Seribu Islands, South of Java, Banten and North Java. In Cilacap water, UNSOED, UMRAH and Aix Marseille Univesity (France) conducted a joint research program and focused on five main aspects, including beach macro-litter monitoring, microplastic monitoring (Syakti et al., 2017); co-pollutions occurrence (such as polycyclic aromatic hydrocarbons-PAHs, polychlorinated biphenyls-PCBs and heavy metals) (Frias et al., 2010; Syakti et al., 2013); ingested plastic by fish; and community empowerment programme on re-use of plastic litter.

6. Concluding Remarks and Future Trends

To conclude, we started with a fundamental question, Do microplastic pose a significant threat to our marine ecosystem? To better answer that we must first understand the composition, the extent and the transformation of plastic during weathering or human-impacted process. Globally our analytical methods are evolving but Indonesian scientists still have a large gap due to the inadequate research infrastructures and our knowledge in this subject. Enumeration methods using binocular microscopes is time-consuming and might introduce large errors due to difficulties to distinguish between microplastics and other small particle materials.

Further research should be developed more particularly in relation to bioaccumulation and biomagnifications occurrence. Ingested microplastics can be transferred from lower trophic level to the higher trophic levels. Such a risk may become greater when co-pollution from other pollutant agents e.g. polycyclic aromatic hydrocarbons-PAHs, polychlorinated biphenyls-PCBs and heavy metals adsorbed onto plastic surface polymers.

Acknowledgement
The author thanks for the financial support from DIPA UNSOED (DIPA/023.04.2. 189899.2014)
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