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Investigation of Microplastic Exposure to Marine Fish in the Marine Tourism Area of Makassar City

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Abstract

Plastic waste pollution in the marine environment triggers the formation of microplastics dissolved in seawater. Microplastics are one of the nutrients for plankton and phytoplankton. Through the food chain, microplastics can accumulate in the bodies of marine biota, until they finally reach the human body. The purpose of this research is to investigate and determine the microplastic group in fish in Makassar City KWB destinations. The method applied is maceration extraction using 70% C_2H_5OH for 3 days, then extracted with N-hexane. The non-polar extracts identified the microplastic components using FTIR spectroscopy and analyzed the types of microplastics based on their absorption spectrum images. The results of the study were that all fish samples coded PS.B.1, PS.B.2, PS.B.3, were contaminated with secondary microplastics. Types of microplastics were identified, namely PP, PVC, PE, PS, PET and PC. The microplastic contaminants are thought to be the result of community activities. The public needs to be aware of the potential for microplastic accumulation in the bodies of marine fish that are consumed. Managers of Makassar City KWB destinations are advised to apply a pattern of supervision to the community to care about waste and educate the implementation of plastic waste recycling management.

Keywords: Marine fish, Pollutant, Microplastic, Maceration extraction, FTIR Spectroscopy

INTRODUCTION

Makassar City is known as one of the tourist cities which is visited by both local and foreign tourists. In addition to natural and cultural tourism, there is also marine tourism, such as marine tourism areas with small island destinations, including Samalona Island, Barrang Caddi, Barrang Lompo, Kodingareng Keke, Langkai, and several other islands (I. Marzuki et al., 2021). The presence of tourists in marine tourism destinations (KWB) is included in the Spermonde archipelago with biota of thousands of species of fish, sponges, shells, and the beauty of coral reefs, making Makassar worthy of a visit, but the potential of the KWB is predicted to put negative pressure on the quality of the marine ecosystem (Bijang, Tanasale, Kelrey, Mansur, & Azis, 2021; Ismail Marzuki et al., 2021)

Tourist visits to the Makassar City KWB area with various activities are very likely to produce domestic waste and various types of waste, especially plastic waste. Plastic waste is very likely to be wasted in the sea, so it is vulnerable as a component of pollution to marine ecosystems including the biota in it. Plastic waste in marine waters undergoes a degradation process due to interactions with high salinity seawater, currents, waves, sunlight, and various characteristics that exist in the sea (Afdal, Werorilangi, Faizal, & Tahir, 2019; Santos & Nascimento, 2015). Degradation of plastic waste produces small pieces and eventually dissociates to form dissolved particulates called secondary microplastics (Alfaro-Núñez et al., 2021; Chiu et al., 2020).

Plastic pollution in the environment is causing serious problems because of concerns about the implications it has for marine ecosystems, the ecosystem services it provides, and most importantly the health status of its penetration on human health (Germanov et al., 2019). In some coastal areas, we often see plastic waste scattered widely from the shoreline to the open sea and deep-sea bodies. In several coastal areas around the world, we often see plastic waste scattered widely from the coastline to the open sea and in marine bodies (Hasti et al., 2022). The volume of plastic waste is estimated to reach 5.8–13.6 million tons that enter the sea in 2020. This figure tends to increase from year to year, following the trend of increasing the human population. This condition is exacerbated by the increasingly varied community activities (Hantoro, Löhr, Van Belleghem, Widianarko, & Ragas, 2019; Armus et al., 2021).

Several types of waste are currently trending on a global scale and are of global concern, namely heavy metals, hydrocarbons, especially PAHs, microplastics, and pesticide residues (Ismail Marzuki, Kamaruddin, & Ahmad, 2021). The general, there are six types of microplastic waste that are known to be the most widely circulated in the environment and are most often used as containers, media, packaging, or as certain equipment, namely the types of polypropylene (PP), polystyrene (PS), polyethylene (PE), polyvinyl chloride (PVC), polycarbonate (PC) and polyethylene terephthalate (PET) (Mazur et al., 2021; Alfaro-Núñez et al., 2021).

Microplastic contaminants in the aquatic environment are a threat to the quality of marine ecosystems. The microplastic components undergo a food web cycle, where these microplastics serve as a source of nutrition for marine organisms, then the organisms are eaten by small fish, then by larger fish, and finally caught by fishermen (Arienzo, Ferrara, & Trifuoggi, 2021). Fish caught by fishermen through traders are purchased by the general public for consumption as a source of protein and other nutritional requirements (Basri, Syaputra, & Handayani, 2021). The nature of microplastics is very difficult to decompose and even form an accumulation in the body, blending with body cells through metabolic processes (Claessens, Meester, Landuyt, Clerck, & Janssen, 2011). The accumulation of microplastics in the body is very susceptible to triggering various diseases in humans (Hantoro et al., 2019).

Marine biota ecosystems include all living things in the sea, whether animals, plants, or corals which are grouped into three types based on their nature, namely planktonic, benthic, and nektonic (Izza Indah Afkarina, Sarwanto Moersidik, & Warno Utomo, 2020). Plankton can eat microplastic, then plankton is eaten by fish, finally, fish is eaten by humans. This process causes microplastics to move from marine biota to humans (Kasamesiri & Taimuangpho, 2020). The dangers of accumulation of microplastics for human health, because they can interfere with health, such as disrupting the nervous, hormonal, and immune systems, and increasing the risk of cancer (Basri et al., 2021). Microplastics interfere with the body's metabolic system because they form interactions with blood particles, being able to change important body proteins such as albumin, globulin, and fibrinogen so that they cannot function properly (Büks & Kaupenjohann, 2021). The problem of microplastics is difficult to avoid because the potential for interactions with plastic materials is very large, so a strong commitment is needed so that the environment and all living things are avoided exposure to microplastics (Chatterjee & Sharma, 2019).

The problem of microplastics has caused anxiety about the future of the environment and the degree of human health in the future, so concrete steps and efforts are needed to suppress and reduce the use of plastic products, including a series of studies that can be carried out to analyze the impact of microplastic contaminants on environmental ecosystems (Mariwy, Manuhutu, & Frans, 2021; Germanov et al., 2019). The marine area is the largest container as the estuary for almost all types of waste and waste disposal, including long-term effects on human health (Koelmans, Bakir, Burton, & Janssen, 2016). The investigation of the presence and types of microplastics in marine fish is the initial activity of a series of planned research related to microplastic contaminants in marine ecosystems (Widodo et al., 2021; Sitorus et al., 2021)

METHODOLOGY

Materials and Instrumentals

The materials used were N-hexane, ethanol, 70% C_2H_5OH p.a., Na_2SO_4 p.a., distilled water, whatman filter paper 42, aluminum foil, tissue, three fish samples each with the code PS.B.1; PS.B.2 and PS.B.3, obtained at three sampling points around Samalona Island. The main equipment used, namely the Portable Water Quality AZ-8306, pH meter, GPS, underwater camera, Shimadzu IR Prestige 21 Fourier Transform Infrared (FTIR) Spectroscopy, and a set of glassware.

Methods

The fish sampling was carried out at three different points around Samalona Island (Figure 1). During fish sampling, several physical parameters of the sampling point were measured, such as temperature, salinity, pH, TDS, and several other parameters, including morphological analysis of the sample. Measurement of sampling parameters is necessary to determine the characteristics of marine ecosystems suspected of being contaminated with microplastics (Table 1).

Figure 1. Map of fish sampling points on Samalona Island

Each sample of marine fish was cleaned, and meat was taken around the head, belly, back, and tail, each ± 3-5 g. Fish meat is mixed together and finely chopped. Macerated using 70% alcohol for 3 days with a ratio of 1:5 (1 g of fish meat and 5 mL of alcoholic extract (Mohamed Nor & Obbard, 2014). Next, the sample is filtered. The filtrate was obtained, taken as much as 10 ml, placed in a separating funnel, added 10 ml of n-hexane, shaken for ± 5 minutes, then allowed to stand and separated. Microplastic components will be extracted in n-hexane (Duplo). The lightweight microplastic components separate and are in the top layer fused with n-hexane (Claessens et al., 2011). Furthermore, the sample is ready to be analyzed to determine the presence of contaminants and the type of microplastic components specifically using FTIR spectroscopy (Zientika, Amin, & Yoswaty, 2021).

Data Analysis

The prepared microplastic sample was placed in a 20 mL vial and wrapped in aluminum foil to prevent contaminants and evaporation. The types of polymers and their abundance were obtained using FTIR Spectroscopy with the KBr pellet method. The connected software is used to read the resulting spectrum from microplastics and then matched it with a standard spectrum from a polymer database using Euclidean Distance, aiming to determine the type of polymer in the sample. Spectrum recorded over the range of 500-4000 cm^{-1} at a resolution of 2 cm^{-1} (Schwinghammer, Krause, & Schaum, 2020; Putrawan, Natan, & Syakuron, 2020). The results of the identification of the type of microplastic in the sample using FTIR Spectroscopy will be displayed in the form of a microscopic wavenumber chromatogram. The number of microplastics in the Sample is expressed in items/m^3. The types of polymers that will be identified and analyzed include the types of microplastics in the PP, PS, PE, and other groups (A. L. Lusher, McHugh, & Thompson, 2013).

RESULTS AND DISCUSSION

The types of fish that were sampled, selected the types of fish that were liked by the local community, including tourists, and also the fish population was classified as largely based on the catch of fishermen. Fish species were also randomly selected during sampling, and two types of fish were obtained, namely the sample codes PS.B.1 (ChrysipteraSpringeri), PS.B.2 (Thalassoma Lunare) and PS.B.3 (Thalassoma Lunare), according to physical details (Figure 2).

Several environmental indicators are measured as characteristics of the sampling point, including coordinates, temperature, depth of fish acquisition from the surface, salinity, total dissolved solids, electrical conductivity, method of obtaining fish samples, and the fish species (Table 1). Based on the environmental indicator data from the sampling point, it is known that the condition of the waters is fish habitat in KWB Makassar City. These conditions are relatively the same as the marine environment in general, meaning that the marine environment is conducive and of good quality for the life of various types of marine biota, especially fish as a source of protein which is very much needed by the community (Telussa, Hattu, & Sahalessy, 2022; Ismail Marzuki, Noor, Nafie, & Djide, 2018).

Figure 2. Fish sample code PS.B.1 (ChrysipteraSpringeri); PS.B.2 (ThalassomaLunare); PS.B.3 *(ThalassomaLunare).*

The type of fish selected as a physical sample and associated with habitat indicators is healthy, but of course, it is necessary to conduct a more detailed investigation related to the quality of the fish, whether it is free from material contamination that can trigger health problems in the biota itself and on human health, in particular. microplastic components (Siahaya et al., 2021; Pariatamby et al., 2020).

Table 1. Characteristics of the physical environment of fish sampling locations around The waters of Samalona Island

Analysis parameters	Sample		
	PS.B.1	PS.B.2	PS.B.3
Coordinate	S 5°6' 38, 13284'' E 119° 17'70, 75656'	S 5°6' 11, 5868'' E 119° 17'60, 05896"	S 5°6' 23, 56183" E 190° 20'27, 62424"
Sampling time (seconds)	12.25 CIT	13.15 CIT	11.10 CIT
Temperature (^{0}C)	29,44	30,01	30,12
Inside from the surface (m)	± 275	± 340	± 325
Distance of sampling point (m)	3,20	2,75	3,40
pH	7,3	7,2	7,3
Salinity (‰)	28,6	29,2	28,8
TDS (mg/L)	7,87	8,25	8,72
DHL (ds/m)	15,85	14,67	16,26
Catch method	arrow	arrow	arrow
Sample species	*Chrysiptera Springer*	*ThalassomaLunare*	*ThalassomaLunare*

It is important to investigate the microplastic content in the fish that live around the Makassar City KWB, considering that these tourist destinations are vulnerable to exposure to plastic waste, but on the other hand, it is known that the KWB is a habitat for several types of fish that are liked by the community (Ismail Marzuki, Kamaruddin, et al., 2021). This microplastic contamination investigation was carried out to provide data and ensure that fish for public consumption is free from contamination with hazardous materials and is safe for consumption. The selection of the infrared detector is based on the ability to generate a voltage that responds to the incoming interferogram through the sample forming analog, sending it to the data system, so that it is recorded in the recorder (Wang, Zheng, & Li, 2018). When the IR radiation passes through the sample, the sample molecules absorb energy through it with various frequencies which are indicated by the number of radiation waves that are passed through the sample. Infrared light is absorbed by the sample functional groups at different frequencies and can be identified based on the resulting spectrum. The spectrum is identical to the content of microplastics, where this pollutant material is very difficult to decompose (Selvam, Jesuraja, Venkatramanan, Roy, & Jeyanthi Kumari, 2021).

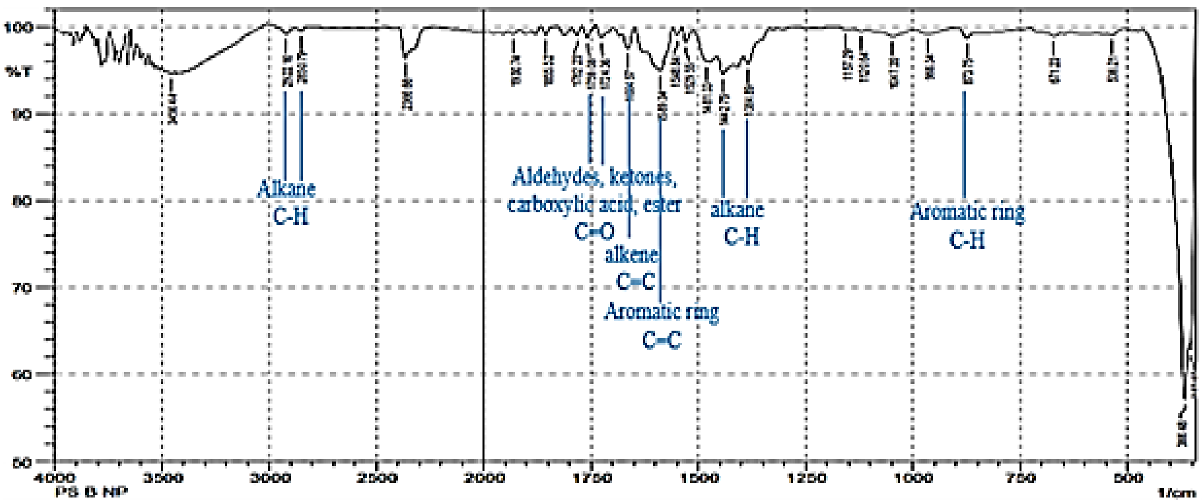

Figure 3. FTIR chromatogram of fish sample code PS.B.1, or station 1, obtained from Samalona Island

The information in Figure 3 above shows the presence of compounds that are included in the microplastic group according to the instructions contained in the Principle of Instrumental Analysis (Li et al., 2021). There is three information on the presence of organic compounds according to the FTIR chromatogram, based on the absorption peak region in the range of 4000-2500 cm^{-1}, ranges 2992.16 and 2850.79 cm^{-1}, showing the image of alkane-type compounds, characterized by the C-H functional group. The absorption peak region in the range of 2000-1500 cm^{-1}, ranges 1759.08 and 1724.36 cm^{-1}, also shows images of the presence of ketones and esters, indicated by the C=O functional group, while the absorption ranges of 1664.57 and 1589.34 cm^{-1} indicate the presence of alkenes and aromatic ring functional group, indicated by the functional group C=C (Parton et al., 2020).

The absorption peak with a range of 1500 to 400 cm^{-1} in the range of 1442.75 and 1384.89 cm^{-1}, indicated the presence of alkane-type compounds, presumably alkane group compounds with a C-H functional group, and an absorption range of 873.75 cm^{-1}, indicating the presence of an aromatic ring compound characterized by the presence of a C-H functional group (Li et al., 2021). The absorption that shows the image of alkane compounds, alkenes, and aromatic rings, is predicted in the fish sample PS.B.1 (Chrysiptera Springeri), or station 1 on Samalona Island, is indicated by the spectral image of the C-H functional group. In the PS.B.1 sample (Figure 3), it is also suspected to contain components of microplastic types polycarbonate (PC) and polyethylene terephthalate (PET), based on the spectral image of the C=C functional group, aromatic ring, C=O, including the alleged polystyrene (PS) content, which shows an alkene functional group and an aromatic ring (Choudhury et al., 2018).

The absorption region with peaks in the range of 4000-2500 cm^{-1} in the range 2924.09 and 2854.65 cm^{-1} shows a spectral image indicating the presence of alkane-type compounds, indicated by the C-H functional group (Figure 4). The absorption peak in the range of 2000-1500 cm^{-1}, in the range 1734.01 to 1683.86 cm^{-1}, indicates the presence of ketone and ester-type organic compounds, characterized as carbonyl functional groups (C=O). Spectrum range 1653.00 cm^{-1}, showing the image of the spectrum of alkene and aromatic ring compounds, based on the absorption that appears as the C=C functional group (Lusher, Holman, & Mendoza-Hill, 2017). Spectrum with absorption peaks in the range of 1500-400 cm^{-1}, the range of 1460.11-1338.60 cm^{-1}, indicated the presence of organic compounds from the alkane group, indicated by the presence of the C-H functional group (Yusuf, Nafie, & Dali, 2016).

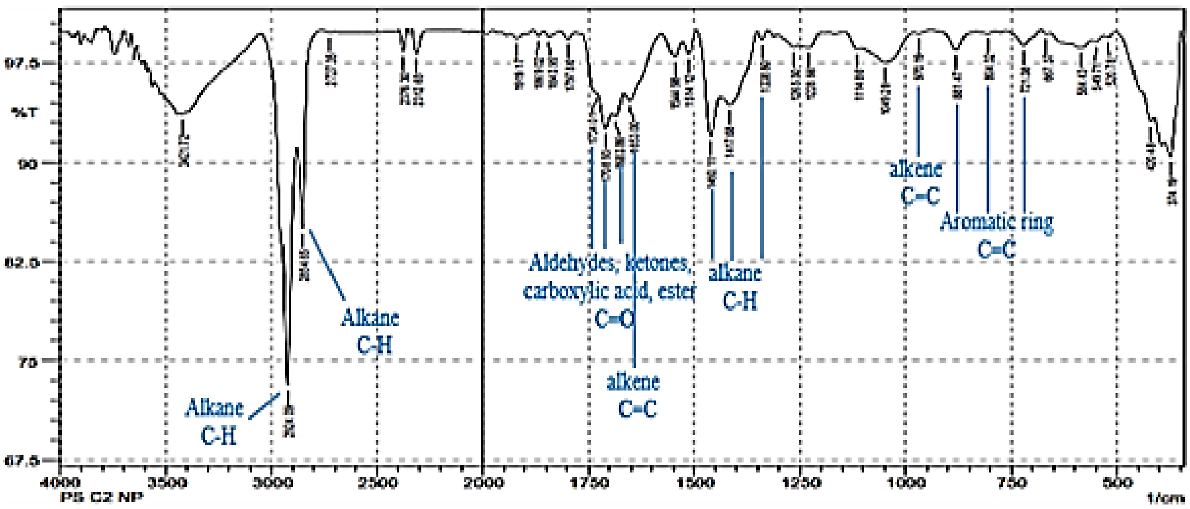

Figure 4. FTIR chromatogram of fish sample code PS.B.2, or station 2, obtained from Samalona Island

The data in Figure 4 also shows the presence of an aromatic ring functional group. This assumption is based on the presence of an absorption peak in the range 881.47 – 721.38, which shows the image of the C-H functional group. Estimates of the presence of alkanes, alkenes, ketones, esters, and aromatic rings in the fish sample code SP.B.2 (Thalassoma Lunare), indicate that the sample is contaminated with polycarbonate and polyethylene terephthalate (PET) microplastic components which are indicated by the presence of an absorption spectrum image of the group carbonyl function (C=C), showing an aromatic ring, C=O. The type of polystyrene (PS) is characterized by the presence of an alkene functional group and an aromatic ring. In sample PS.B.2 (Figure 4) is also suspected to be contaminated with microplastic types of polypropylene (PP), polyethylene (PE), and polyvinyl chloride (PVC), this is in accordance with the indications by the presence of absorption images as the C-H functional group (Lozano & Rillig, 2020; Llorca et al., 2020). These results indicate that in the sample code PS.B.2, which is the sampling point for station 2, microplastic contamination is identified, the type and type are relatively the same as the type of exposure to microplastics in the code sample PS.B.1.

The absorption peak in the range of 4000-2500 cm^{-1} in the range of 2924.09 and 2771.71 cm^{-1}, it is suspected that there are compounds of the type of alkane, based on the spectral image that appears as the C-H functional group. The absorption peak area in the range of 2000-1500 cm^{-1}, in the range of 17388.01 and 1755.22 cm^{-1}, indicates the presence of ketone and ester type compounds, based on the spectrum image as a C=O group. The absorption ranges of 1633.71 and 1650.77, indicated the presence of alkene-type compounds. Absorption with a range of 1510.26, indicating the presence of an aromatic ring, based on the visible spectrum image, identified as a C=C functional group. The absorption peak region in the range of 1500-400 cm^{-1} in the range of 1415.75 cm^{-1}, indicates the presence of alkane-type organic compounds, according to the spectrum image that appears to indicate the C-H functional group. The absorption peaks were in the range of 875.68 and 707.88 cm^{-1} , indicating the presence of compounds containing an aromatic ring functional group, indicated by the presence of C-H bonds (Arienzo et al., 2021).

The allegation of the presence of alkanes, alkenes, ketones, esters, and compounds with aromatic ring functional groups (Figure 5), indicates that the fish sample code PS.B.3 *(Thalassoma Lunare)* was obtained from the waters around Samalona Island, a marine tourism destination. Makassar City is suspected to have been exposed to PP, PE, and PVC microplastic materials, as indicated by the spectral image that appears as the CH functional group (Alfaro-Núñez et al., 2021). The sample was also identified as contaminated with PC and PET microplastics, indicated by the presence of a spectrum image indicated as functional groups C=C, and C=O, while the PS type indicated the presence of aromatic ring functional group. The FTIR chromatogram shown by the three fish samples as an embodiment of the presence of relatively microplastic components gave the same pattern as polymers or macromolecular compounds (Büks & Kaupenjohann, 2021).

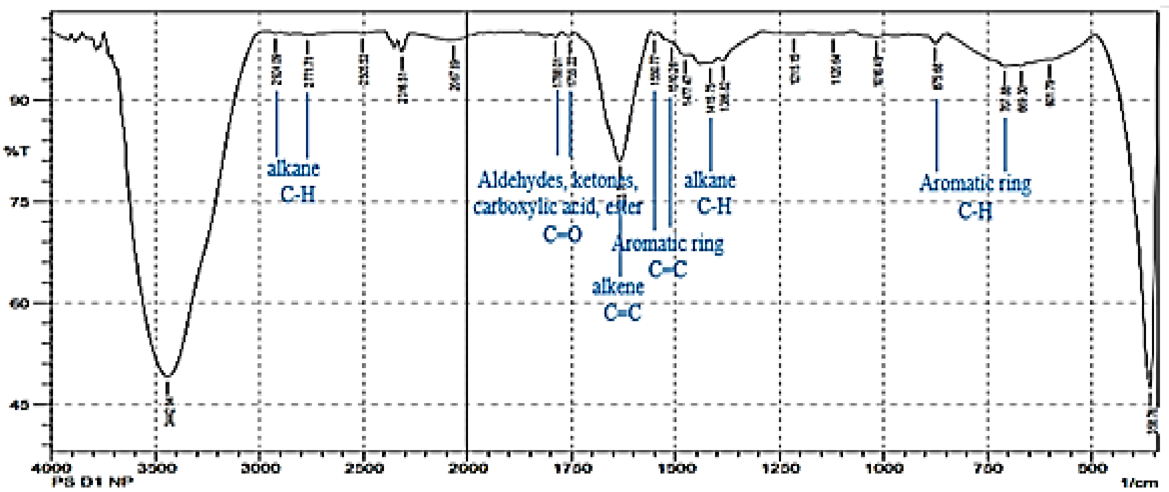

Figure 5. FTIR chromatogram of fish sample code PS.B.3, or station 3, obtained from Samalona Island

Three kinds of fish samples each coded PS.B.1, PS.B.2, and PS.B.3, according to the FTIR chromatogram (Figure 3, 4 and 5) obtained from the waters around Samalona Island, KWB area of Makassar City, strongly suspected of being contaminated with microplastic types PP, PVC, PE, PS, PET, and PC. The presence of microplastics in foodstuffs such as fish that live in the area of the KWB tourist destination is a warning to all of us, that fish caught around these waters are not safe for consumption freely (Lie et al., 2018).

The content of microplastics in fish that live in the Makassar City KWB tourist destination is a warning so that all of us can make efforts and efforts and care for the environment by not littering, especially plastic-type waste, because the waste is not degraded (Chaerul, Gusty, Marzuki, & Nur, 2021). All types of microplastic contaminants identified in the three fish samples obtained from the waters around Samalona Island are secondary microplastics or microplastics originating from human activities. (Kamaruddin, Marzuki, Burhan, & Ahmad, 2021).

Microplastics are polymers that have long chain functional groups, and are very difficult to decompose, forming accumulations for a long time. The accumulation of microplastics in certain body parts can be trapped in cells, so food contaminated with microplastics is recommended to be avoided and not consumed (Ismail Marzuki, Gusty, et al., 2021). Some types of microplastics such as Polyethylene Terephthalate and Polycarbonate have aldehyde, ketone, carboxylic acid, and ester functional groups. If one of the polymer bonds is broken, it can metamorphose into small parts, dissolved in water, as microplastics (Soo, Sabana, Chen, & Hii, 2021).

CONCLUSION

Important points were concluded based on the results of this study, including: (1) All fish samples coded PS.B.1, PS.B.2, and PS.B.3, which were obtained around the waters of Samalona Island were contaminated with secondary microplastics. (2) Parameters indicating exposure to microplastics in the studied fish samples were based on FTIR spectrum images which showed the presence of alkanes, alkenes, aldehydes, ketones, carboxylic acids, esters, and aromatic rings. (3) The types of microplastics contained in fish samples, namely polypropylene (PP), polystyrene (PS), polyethylene (PE), polyvinyl chloride (PVC), and polycarbonate (PC) an impact on community activities. (4) The public needs to be aware of the potential for microplastic accumulation in the bodies of marine fish that are consumed. Attention to the public, that there is a tendency to increase the volume of plastic waste in Makassar City KWB, so it is recommended that Makassar City KWB destination managers can apply a monitoring pattern to every tourist and surrounding community to care about waste and educate the implementation of waste recycling management.

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