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Investigation Pollutants of Global Trends in Marine Ecosystems around Barrang Caddi Island, Spermonde Archipelago Cluster: An Ecological Approach

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Abstract: A quality marine ecosystem if it is free from GTP contaminants. Accuracy and caution are needed in the exploitation of marine resources as marine tourism destinations so that in the future, there will be no ecological hazards that cause chain effects, not only on aquatic ecosystems but also on humans. This article identifies exposure to GTP (MP, PAH, PR, HM, MW) in marine ecosystems in the MTA area and BCI waters. The combination of qualitative and quantitative analysis methods uses a combination of analytical instruments and mathematical formulas. The search results show the average total abundance of MP in seawater and fish samples (5.47 units/m^3) and (7.03 units/m^3), respectively, while in sediment and sponge samples (8.18 units/m3) and (8.32 units/m3). Based on the analysis of the polymer structure, it was identified that the dominant light group MP (PE, PP and PS), followed by PA and PC. Several PAH pollutants were identified in the samples, especially NL types found in all samples, followed by PN and AZ. BCI sea waters are suspected to be exposed to MW and PR. Pollutants of Pb^{+2} and Cu^{+2} around BCI were successfully calculated with average concentrations in seawater 0.164 mg/L and 0.294 mg/L, respectively, while in fish, 1.8110 µg/g and 2,452 µg/g, respectively. Based on these findings, the BCI area is not recommended as a marine tourism destination.

Keywords: pollutants, microplastics, heavy metals, PAH, pesticide residues, medical waste

1. Introduction

Marine ecosystems are formed by two main components, namely biotic (organic) and abiotic (inorganic) elements [1–3]. The seascape is vast and is influenced by many factors, causing the characteristics of the sea area to vary [4,5]. Each marine area has characteristics and ecosystems, such as deep-sea, poles, beaches, coasts, coral reefs, and tides [6]. The types and amounts of materials in marine ecosystems are not limited, both

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naturally occurring and due to human activities and dynamics [7,8]. Most of the human waste material can occur in all regions of the earth. Influence of ecology and gravity, garbage has the potential to end up in the sea, either intentionally or due to negligence in managing the marine environment [9-11].

Human waste materials that enter marine waters are classified as marine debris, generally containing hazardous and toxic components, such as heavy metals (HM), polycyclic aromatic hydrocarbon components (PAH), microplastics (MP), pesticide residues (PR), medical waste (MW), radioactive waste can be categorized as a global trending pollutant (GTP) [12-20]. Global trend pollutant (GTP) was introduced to the world community as a new term to describe at least five types of pollutants (MP, PAH, PR, MW and HM) which are pollutant materials that have become global environmental issues to date, especially for marine ecosystems [14, 18, 21-24].

The handling of GTP as a toxic component is a problem that has occurred for a long time, and its impacts have been felt, including contributing to these pollutants as one of the components that trigger global warming and climate change, so that it becomes a severe problem for many countries in handling and managing them [25-28]. Many countries have difficulty handling this GTP, especially developing countries with a relatively low economic level. The concern of the world's population on the massive GTP is indicated by the issuance of G20 developed countries' recommendations to reduce global carbon production [2,29]. Whether we realize it or not, these global trending pollutant inputs or GTP enter the ocean continuously and are difficult to prevent, so it is feared that the toxic components in the waste have the potential to cause anthropogenic hazards in the oceans [3,5,30].

The interaction between materials in the sea occurs continuously and produces various types of new compounds as the natural ability of the sea to maintain the sustainability of life in the ocean [31,32]. Photodegradation due to sunlight, interaction by ocean currents, mobilization of material due to differences in the waters, effects of salinity, and consequences arising from temperature differences and collisions between materials due to tidal movements in coastal areas are phenomena natural processes of the sea that occur continuously [17]. These events in marine ecosystems enrich the production of components with a diversity of marine biological and non-biological materials [33,34].

Advances in science and technology and the massive number of innovative products to meet today's human needs have indirectly triggered the birth of this global trend of toxic contaminants. Almost all scientists in the world believe and are worried by many world leaders that the dangers of this global trending pollutant can enter the anthropogenic hazard phase, adversely affecting the quality of marine ecosystems, human health and damage and threatening the safety of the world [35-37].

The effect of applying polymer technology to produce various types of industrial equipment, household appliances, and plastic-based packaging has previously been predicted to produce components that are harmful to human health and the environment, such as microplastics, but cannot be avoided due to the rapid flow of human needs [38,39]. Pesticide residue pollutants with the birth of synthetic products for activities to accelerate and increase agricultural production, fulfilment of the need for treatment with various types of synthetic drugs and medical equipment have also been studied before, which have the potential to cause negative impacts but are not able to suppress the swift pace of demand [40-42]. Estimates of the emergence of PAH-type components in petroleum processing and fossil combustion, heavy metal contaminants in mineral processing and the introduction of various metal-based equipment have all been predicted previously. However, this cannot counter the solid demand to meet human needs with reasons and pretexts of preserving life [43,44].

The GTP distribution is almost evenly distributed in many countries, and its presence is especially vulnerable in marine and coastal areas. GTP has toxic and carcinogenic properties, is generally difficult to decompose, has accumulative properties and can combine and even become part of processes that run on objects, especially metabolic

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processes [45,46]. The particle size of MP is minimal (< 5 nm), allowing it to contribute to the cell division of living things. Not least in marine ecosystems, such as fish and other marine biota and various marine biological components, which, at the end of the biogeochemical cycle, have the potential to become materials that accumulate in human foodstuffs that can be consumed by humans produced from the sea [47,48].

GTP is a pollutant that is very difficult to decompose, either through bio-degradation, bio-adsorption, and bioreduction methods, including destruction methods. The treatment approach using bioremediation methods for global trend pollutants is challenging to do on a large scale with a technological approach [49,50]. Bioremediator microorganisms can be carried out by Relying on natural aids of biological materials such as biosorbent plants. However, at a limited rate, they certainly cannot balance the speed of increase and increase in the volume of these pollutants entering the environment, especially in the most vulnerable marine ecosystems [51]. This condition can become a severe threat to the earth's population, especially the marine area and its ecosystems as a giant container which is the estuary for almost all types of waste disposal leftover from human activities and dynamics natural processes [52,53].

The phenomenon of tourism activities that make marine ecosystem objects a marine tourism area occurs in many countries, including Indonesia [54]. Exploiting the marine area as a tourist by presenting a variety of marine beauty, both on the surface, deep and under the sea, with various potentials, is tempting because many people are interested in it [55]. Barrang Caddi Island (BCI) is one of the islands included in the Marine Tourism Area (MTA) among five other islands, namely: Samalona Island, Kodingareng Keke, Barrang Lompo, Barrang Caddi and Langkai. These islands are designated as MTA managed by the local government of Makassar City, South Sulawesi [56]. The MTA, especially BCI, is included in a national marine conservation park and part of the Spermonde Archipelago Cluster, which is world-famous by marine sponge observers because the Spermonde Archipelago is one of the areas where tens of thousands of species and marine sponge populations live. The Spermonde Archipelago Cluster is known worldwide as a sponge study and riset laboratory [57,58].

Barrang Caddi Island (BCI) in the south is directly adjacent to Makassar City. Along the coastline, there are Soekarno Hatta seaports and fish landing ports. Still, this coastal area operates two regional and two industrial hospitals and several large and medium-sized hotels [54,55]. The beach is also full of marine tourism objects, which many domestic and foreign tourists visit. All forms of operations and services around BCI have the potential to produce waste containing GTP group contaminants. This condition contradicts the island's status as a marine tourism area, and around it live various types of sponges [59,60].

This research is exciting and essential to do, while at the same time, it has an update on the aspect of presenting data and information related to GTP contaminants in a review of seawater, sediments, fish and sponges about the dual role of BCI as MTA and the living area of various types of sponges [14-17]. The data presented is expected to be a reference in the management of BCI as an MTA, so that marine tourism activities do not add to the burden of island sustainability for the life of marine life in it, the balance of marine ecosystems is maintained, and most importantly the sustainability of the sponge population can be maintained.

2. Materials and Method

2.1 Materials and equipment

The main ingredients, namely: sediment samples, seawater, sponges, and demersal fish. Other materials, including: H_2O_2 PA (sigma) 30%, Fe(II) 0.05 M (sigma), N-hexane, PA (sigma), ethanol PA (sigma), standard analysis of PAH (anthracene) 1000 mg/L (supelco), Na_2SO_4, H2SO4, PA (sigma), NaCl, PA (sigma), HCl, PA (sigma), NaOH, PA, HNO_3, PA (sigma), $HClO_4$, PA (sigma), $Pb(NO_3)_2$ PA (sigma) (standard solution of Pb

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analysis), $CuSO_4$ (standard solution of Cu). Equipment, including Fourier Transform Infra-red (FTIR) Shimadzu IR Prestige-21, Gas Chromatography/Mass Spectrometry (GC/MS) Agilent Technologies 7890A, Atomic absorption spectroscopy (AAS) variant type AA240FS, Muffle Furnace type Thermolyne F6010, Portable Water Quality AZ 8361, a set of glassware (pyrex), plankton net (mesh size 0.4 mm), stainless steel mesh filters 5 mm and 0.3 mm, sieve shaker, density separator, vacuum pump [61-64].

2.2 Sampling

Five samples were analyzed, each obtained at three different stations around the BCI waters (Fig. 1). Physical characteristics were observed at each station, such as sampling coordinates, pH, salinity, TDS, HDL, and others (Table 1). For fish and sponge samples, morphological analysis was also carried out to determine the type or species of each sample. Sampling was carried out following standard sampling. The sample is put in a whole box in the laboratory for immediate preparation until it is ready to be analyzed using the appropriate instrument [65].

Figure 1. Barrang Caddi Island (BCI) map. The red color is the sampling station (ST)

Sediment, sponge, seawater and fish samples were obtained at three different sampling stations around BCI. This island is included in the Marine Tourism Area of Makassar City. The distance between BCI and the coast of Makassar City is ± 7.5 km. The small red circles (Fig. 1) are non-sampling which we refer to as stations, coded ST 1, ST 2 and ST 3.

Table 1. Physical characteristics of seawater sampling station, waters around BCI

Stasiun sampling	Coordinate	Depht MSL (m)	Distance from the beach (m)	pH	Temperature (^{0}C)	HDL (ds/m)	TDS (mg/L)
ST 1	S 5°5′12,48216′′ E 119°19′0,16536″	5	± 300	7,32	29,8	14,91	7,56
ST 2	S 5°5′70,1664″ E 119°19′14,20716″	6	± 350	7,30	30,4	16,69	8,12
ST 3	S 4°46′01664″ E 119°19′12,58932″	8	± 370	7,31	29,9	16,33	8,22

According to the data (Table 1), the physical characteristics of the sampling station are relatively the same as other marine areas around it, especially in the Spermonde Islands cluster. The data shows that seawater has no physical appearance as a sign that the area is exposed to one of the contaminants that fall into the GTP category.

2.3 Sample preparation

Sample preparation was prepared according to the type of analysis based on the target data. Sample preparation was carried out to determine the abundance of microplastics by filtering using a plankton net (adjusted samples of fish, sponges, and sediments). The sample was dissolved and separated between organic matter and microplastic particles [66 The total abundance of microplastics was calculated in each sample (equ. 1). Microplastic polymers' structure was analyzed using micro-plastic particles collected based on differences in density, put in a cuvette, and then run using FTIR [67,68]. This instrument can produce a chromatogram as a spectrum in the form of a wavenumber that can be converted into a chemical structure in functional groups. Based on the functional groups that seem predictable, the type of MP. Seven types of MP pollutants may be present in the sample, among which the most common are polypropylene, polyethene, polystyrene, and polycarbonate [69,70].

Sample preparation for analysis of abundance and type of PAH extraction method used ethanol to extract all chemical components in the sample, then extracted using N-hexane as a solvent to separate non-polar components (PAH) [71]. Running on N-hexane extract using GC/MS [72]. The visible chromatograms were analyzed to determine the abundance and type of PAH components. Sample preparation for the analysis of the concentration of Pb^{+2} and Cu^{+2} contaminants in the sample was carried out by the dry destruction method for sediment, fish and sponge samples, while the alkaline digestion method for seawater samples. Each sample was dissolved with a concentrated acid solvent. Samples were injected into the AAS [73-75].

2.4 Sample measurement

There are five types of pollutants in the GTP category. However, those analyzed in each sample prioritized the identification of microplastic, PAH, and heavy metal contaminants, while pesticide residues and medical waste were not prioritized for limiting the publication's scope. However, these two types of contaminants can be viewed together with PAH based on GC/MS chromatogram data:

- Analysis of microplastic components, especially the parameter of total abundance of microplastics using 30% H_2O_2 solvent. Measurement of the total abundance of microplastics was carried out in triples. Analysis of polymer structure as the main characteristic of each micro-plastic using FTIR and combined with GC/MS chromatogram data [76,77];
- Analysis of the type and abundance of PAH contaminants based on GC/MS chromatogram data. Information on pesticide residue contaminants and media waste can also be obtained from the GC/MS chromatogram. However, the determination of the components is more specific because, in general, pesticide residues and several types of medical waste have chemical structures with reactive groups that should be identified using a combination of pyrolysis-GC/ MS [78,79].
- Determination of the concentration of heavy metal contaminants, particularly exposure to Lead (Pb) and Copper (Cu) ions in each sample according to AAS absorption at maximum wavelength, for Pb at λmax. 228.9 nm and Cu at λmax. 324.7 nm. The resulting uptake is plotted into the standard absorption regression equation for each metal (equa. 2), and the concentration of each metal contaminant in the sample is calculated (equa. 3), according to the American Society of Testing and Materials (ASTM) [80-82].

2.5 Data presentation and analysis

Presentation of analytical data for quantitative data, using the appropriate equation. Data on the total abundance of MP (equa. 1) and Pb and Cu ions contaminant concentrations (equa. 2, 3 and equa. 4). The qualitative analysis data is presented based on the instrument chromatogram. Analysis of polymer structure types of microplastic contaminants used FTIR chromatogram reading data, while data on PAH exposure types, including pesticide residues and medical waste contaminants in each sample, using GC/MS chromatography [83]. The data from the measurement, calculation and analysis are presented in tables and figures.

$$Total\ MP\ Abundance\ (\frac{unit}{m3}) = \frac{MP\ particle\ count\ (unit)}{V\ (m3)}, \quad \text{(equa. 1)}$$

$$y = bx \pm a, \quad \text{(equa. 2)}$$

$$b = Y.ave - b\ (X.ave) \quad \text{(equa. 3)}$$

$$Cons. Pb\ or\ Cu\ (\frac{\mu g}{g}) = \frac{sample\ rate\ (\mu\frac{g}{mL}x\ final\ vol.\ of\ solution\ (mL)}{sample\ weight\ (g)}, \quad \text{(equa. 4)}$$

Note: MP = microplastic, V = sample volume (m^3) or in units of mass (g), y = absorbance, b = Intersep a = slope, x = concentration (ppm), Y.ave = average absorbance, and X.ave = concentration average (μg/g) [84].

3. Results

Five types of pollutants fall into the GTP group, but the target of the GTP contaminant analysis is on samples of sediment, sponge, seawater and fish obtained from BCI (Makassar City MTA); the priority is on MP type pollutants, the main hydrocarbon components are PAHs and heavy metal pollutants (HM). Pesticide residue pollutants and medical waste described are limited and not detailed because of concerns that the data obtained are not significant due to the limitations of the analytical instrument, which ideally uses a combined pyrolysis-GC/MS analysis tool [85,86].

3.1. Microplastic pollutant analysis

Specific morphological analysis of fish and sponge samples is essential because each type of marine biota has a different lifestyle and habitat to respond to GTP contaminants or contaminants species (MP, PAH, PR, MW and HM) can vary. The results of the morphological analysis of fish and sponge samples obtained at each station are presented in full in Table 2.

Table 2. Fish and sponge morphology based on sampling point

Stasiun sampling	Sponges	Fishes
ST 1	*Cribrochalina olemda*	*Chrysiptera Unimaculata*
ST 2	*Clathria Reinwardtii*	*Ambhygphidodon Curacao*
ST 3	*Clathria* Sp	*Scolopsis Brenatus*

The grouping of samples by pairing sediment and sponge, seawater and fish in presenting the analysis results is based on the similarity of the media. The growth media and the habitat of sponges are more dominant using sediment, while the habitat and growth of fish are highly dependent on water media. In this condition, the type of pollutant MP in fish bodies is estimated to be relatively the same as the type of MP in water, MP in the body of a sponge, and type of MP in sediments [21,22].

Two parameters were analyzed for the MP pollutant in the sample: the total MP abundance (Fig. 2 and 3) and the MP type (Fig. 4 and 5).

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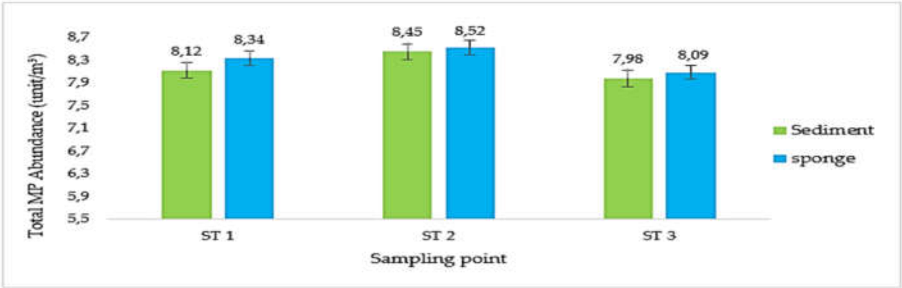

Figure 2. Total abundance of microplastic (MP) of sediment and sponge samples based sampling point

The total MP abundance in the sediment samples was relatively the same as the total MP abundance in the sponge samples (Fig. 2). These results illustrate that MP exposure in sediment samples is relatively consistent with MP contaminants in sponge samples, generally thought to be dominated by fibre and fragment types. It is based on the difference in density between the two types of MP, which have higher specific gravity than water and film type MP so that the two types of MP accumulate more on the bottom of the water. The relatively settled lifestyle of sponges in one place and how food nutrients are obtained by sucking particles from the mud and removing the dregs (filter feeder) are solid arguments for why the total abundance of MP in sediments is relatively the same in sponges [26,27,37].

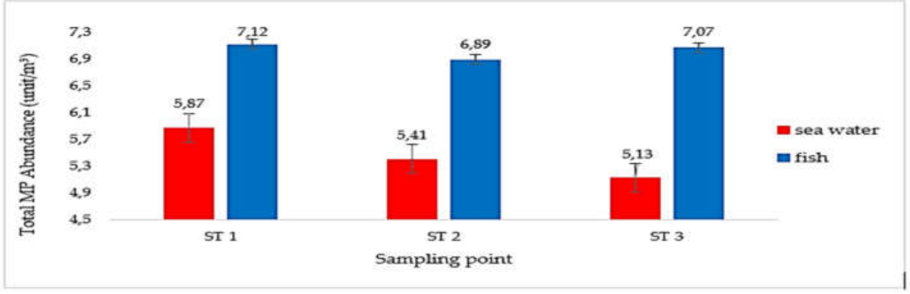

Figure 3. Total abundance of microplastic (MP) of sea water and fishes samples based sampling point

Analysis of the total MP abundance in fish samples was higher than the total MP abundance in seawater samples. This condition occurred at all three sampling points (Fig. 3). This result is entirely rational, where fish mobility is wider, so the presence of fish is not expected to always be in the zone of seawater exposed to MP. The type of exposure to MP in fish samples is also thought to be dominated by the type of film with a lower density than water. So that its presence in the waters floats in the surface zone, this condition is prone to be swallowed by fish, where the fish consider it food. The difference in the total MP abundance of fish samples between stations 1, 2 and 3 (Fig. 3) is thought to be more influenced by the different fish samples between stations (Table 2). The average total abundance of MP in the samples, namely samples of sediment (8.18 units/m^3), sponges (8.32 units/m^3), seawater (5.47 units/m^3) and fish (7.03 units/m^3) [19,22].

The type of MP pollutant is based on the polymer structure that is thought to be present in each analyzed sample by analyzing the spectrum that is read in the FTIR chromatogram. The FTIR spectrum (Fig. 4 and 5) shown for each type of sample is only the sample obtained from station 1 (ST 1), which is considered representative of the sample ST 2 and ST 3 [37,39].

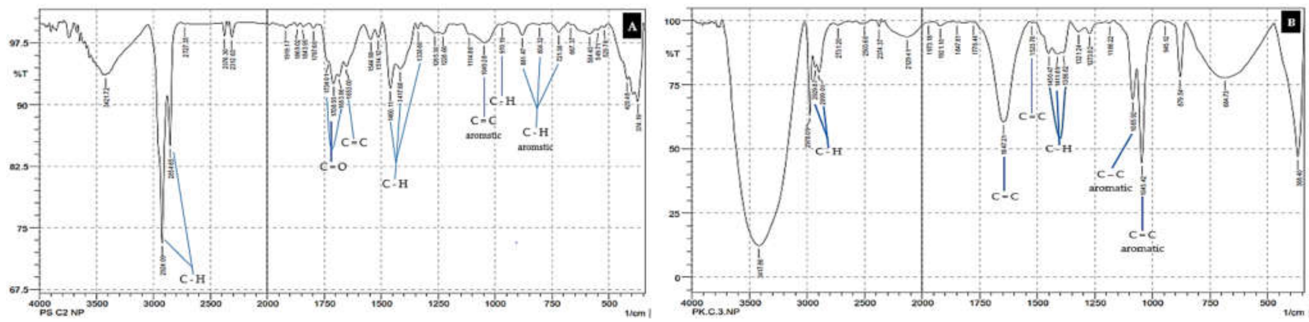

Figure 4. Identification of the type of MP pollutant in the sample based on the FTIR chromatogram. (A) sediment samples; (B) sponge sample

Pollutants analysis of several types of MP used FTIR chromatogram, based on the unique monomer structure functional groups as the main characteristic of each type of MP. It is known that seven types of MP are common and most often found in marine ecosystems, with their respective monomers: polypropylene (PP) with the molecular formula $(C_3H_6)n$; polyethene (PE) is a monomer of ethylene $(C_2H_4)n$; polystyrene (PS) $(C_8H_8)n$; polycarbonate (PC) has a carbonyl functional group (O(C=O)O)n; polyamide-nylon (PA) with monomer formula $NH_2(CH_2)_6$ $NHCO(CH_2)_4COOH$; polyvinyl chloride (PVC) with unique characteristics containing chloride (C2H3Cl)n; and acrylonitrile butadiene styrene (ABS), composed of three monomers with the formula $(C_8H_8)x(C_4H_6)y(C_3H_3N)z$ [18,19,26,27,38,64]. The results of the MP type analysis based on the FTIR spectrum display for each sample obtained at ST 1 (Fig. 4), it is suspected that MP, PP and PS types of pollutants were found in all samples. ABS type MP is found in sediment, sponge and seawater samples, while PVC is thought to be identified only in seawater samples [19,38]

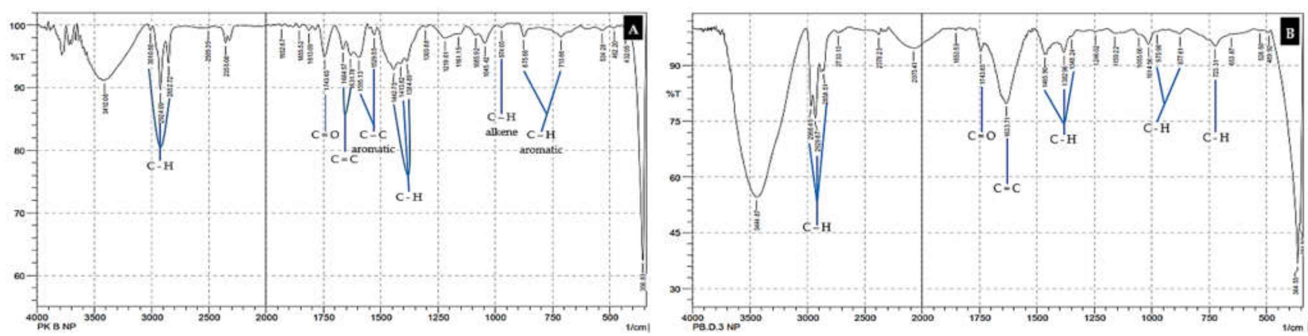

Figure 5. Identification of the type of MP pollutant in the sample based on the FTIR chromatogram. (A) sea water samples; (B) fish samples

Identifying the type of MP component in the seawater and fish samples was not much different from the type of MP identified in the sediment and sponge samples (Fig. 5). All results of the identification of MP species based on polymer structure in all types of samples obtained at three stations (ST 1, 2 and 3) shown on the FTIR chromatogram are presented more fully (Table 3).

Table 3. Type and distribution of MP pollutants in each sample

Stasiun sampling	Sample type			
	Sediment	Sponges	Sea water	Fishes
ST 1	PA, PC, PE, PP PS, ABS	PA, PE, PP, PS, ABS	PC, PE, PP, PS, PVC, ABS	PA, PE, PC, PP, PS
ST 2	PA, PC, PE, PP, PS	PA, PC, PE, PP, PS	PC, PE, PP, PS, ABS	PA, PC, PE, PP, PS

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ST 3	PA, PC, PE, PP, PS, PVC	PA, PC, PE, PS, PVC	PA, PC, PP, PS, PVC	PA, PC, PE, PS, PVC

Note: PP = polypropylene PE = polyethylene PS = polystyrene
PC = polycarbonate PA = polyamidenylon PVC = polyvinyl chloride
ABS = acrynitrile butadiene styrene

The type of MP identified in the sample obtained at the sampling point (ST 1-3) (Table 3) shows that the pollutant MP type PA was identified in all samples except seawater samples (ST 1 and 2), the type of PC was seen in most of the samples except on sponge and seawater samples (ST 1). PM type PE pollutants were also recorded in most samples, except seawater samples (ST 3). Contaminants of PP were not found in the sponges and fish (ST 3), while PS was found in all samples at each station. PVC-type pollutants were identified in all types of samples obtained in (ST 3), and ABS types were identified in sediment, sponge and seawater samples only in samples from (ST 1) [66,68].

3.2. PAH pollutant analysis

Identification of hydrocarbon pollutants, especially PAH types and other hydrocarbon components in the sample using GC/MS chromatogram data. The parameters used in determining the PAH type pollutant in the sample are based on several recorded chromatogram data units, namely peak number, retention time, peak height as a manifestation of component abundance, and content in percentage units of total PAH and component name.

Table 4. Types and abundance of PAH in samples at ST 1 station based on GC/MS chromatogram

Sample type	Peak number	Retention time	Peak Height	Quality (%)	Abudance (%)	Compound name
Sediment	4	9.167	2027937	91	66,386	NL
	6	15.550	68138	90	2.324	AZ
	9	17.788	26924	85	0.786	PH
	12	19.023	31894	87	1.278	PN
Sponge	2	9.168	2565156	91	76.539	NL
	6	19.023	28386	93	2.410	PN
	7	26.736	62698	87	11.672	BZ
Sea water	1	9.168	1581333	91	78.456	NL
	3	15.550	87843	91	3.045	AZ
Fish	2	9.167	2134672	91	74.456	NL
	6	26.736	54789	88	8.192	BZ

Note: the compounds taken are those that have a level of similarity (quality) reaching ≥ 85 %.
NL = Naphthalene group AZ = Azulene class PH = Phenyl group
PN = Pyrene group BZ = Benzene group

According to the source (ST 1 – 3), each sample's complete details of PAH-type hydrocarbon pollutants are presented in tabular form (Table 4 – 6). As shown in (tables 4 – 6), the peak numbers are not sequential, and it is known that each peak is identical to one component [87,88]. The peak number not included in the table is due to several reasons: first, the peak that appears is not a PAH component. Second, it is a PAH component, but the level of similarity with the comparison component (library instrument) does not reach the minimum standard of 85%. Third, the components that appear are PAH derivatives. The type of PAH identified in the four samples obtained from ST 1 (Table 4) indicates that the component is naphthalene (NL). The abundance of PAH components in the samples was NL BZ AZ PR PH, respectively. The peak numbers of the recorded GS/MS chromatograms are sequential according to the number of components [9]. However, there are peak numbers that are not included in the data (Table 1), indicating

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that the peak number is considered not to be a PAH component or maybe a derivative component of one type of PAH, but the level of similarity with the standard library on the instrument did not reach 85% [89,90].

Table 5. Types and abundance of compound hydrocarbon and PAH in samples at ST 2 station based on GC/MS chromatogram

Sample type	Peak number	Retention time	Peak Height	Quality (%)	Abudance (%)	Compound name
Sediment	1	9.168	1125323	91	84.221	NL
	2	13.205	20184	96	1.186	PD
	3	15.549	54212	85	3.643	AZ
	4	17.788	18406	85	1.369	PH
	6	19.023	62311	89	3.409	PN
	8	26.735	71925	86	5.357	BZ
Sponge	3	9.167	3219575	91	86.046	NL
	4	13.206	44603	97	0.978	PD
	6	16.283	14355	86	0.696	PT
	8	19.023	31674	87	1.312	PN
Sea water	3	9.168	860498	91	63.945	NL
	4	13.205	20327	96	1.204	PD
	9	19.023	138767	96	10.165	PN
Fish	2	9.168	4322267	87	89.859	NL
	4	19.023	12458	92	3.146	PN

Note: the compounds taken are those that have a level of similarity (quality) reaching ≥ 85 %.
NL = naphthalene group; AZ = Azulene class; PT = Penantrene
PN = Pyrene group; BZ = Benzene group; PH = Phenyl group
PD = Pentadecana

The results of the identification of PAH pollutant samples obtained at ST 2 were relatively not different at ST 1. PAH pollutant types NL and PN were found in all samples. The abundance of components in each sample was NL PN PD, while AZ, BZ and PH were identified only in sediment samples and PT in sponge samples (Table 5).

Table 6. Types and abundance of PAH in samples at ST 3 station based on GC/MS chromatogram

Sample type	Peak number	Retention time	Peak Height	Quality (%)	Abudance (%)	Compound name
Sediment	2	9.168	1222751	91	82.356	NL
	4	15.549	88566	90	3.087	AZ
	5	16.283	22123	86	1.126	PT
	7	19.023	99864	88	4.106	PN
	9	26.734	67854	86	2.123	BZ
Sponge	2	9.167	2423789	91	78.127	NL
	4	15.550	65832	85	3.983	AZ
	6	16.283	16732	86	0.883	PT
	8	19.023	34376	87	1.515	PN
Sea water	2	9.168	1222751	91	82.356	NL
	4	16.283	21874	86	1.083	PT
	6	19.023	64357	88	2.982	PN
Fish	3	9.168	1111244	91	64.362	NL
	5	19.023	13318	87	0.734	PN

Note: the compounds taken are those that have a level of similarity (quality) reaching ≥ 85 %.
NL = Naphthalene group AZ = Azulene class PT = penantrene
PN = Pyrene group BZ = Benzene group

The analysis of PAH pollutants obtained at ST 3 (Table 6) is also relatively the same as the PAH types identified in samples ST 1 and 2. NL and PR were found in the four types of samples, while PT types were identified in sediment, sponge and water samples. Sea. AZ PAH pollutants were identified in sediment and sponge samples, while BZ was only found in sediment samples (Table 6). The abundance of components in a row NL PN PT. Comparing the variation of PAH components identified at all sampling stations (Table 4 – 6), the types of PAHs in sediment samples are more varied, followed by sponge samples, then seawater samples and fish samples [14]. The types of PAH pollutants in each sample showed that the PAHs contained in sediment samples were relatively similar in sponge samples, and seawater samples were more similar to fish samples [91,92]. This result is quite rational if we compare that the habitat and growth of sponges tend to settle on the bottom of the water (sediment) and the dominant habitat and growth of fish in water media.

3.3. Pesticide residue pollutant analysis and Medical waste

Pesticide residues and medical waste are suspected of contaminating marine waters around BCI. The indication was based on the GC/MS chromatogram, which identified several types of organic compounds in the acid group (phenol, arsenous acid, sulfurous acid), the carboxylic acid (Hexadecanoic, benzoic acid), halogen group (chloridanthene, Fluoranthene, blomidanthene), phosphate, cyclopentasiloxane, thiophene, Silicic acid, Ben-zo[h]quinolone, Cyclotrisiloxane. These compounds are thought to be derived components of pesticide residues and medical waste that change during their stay in the aquatic environment. This assumption is confirmed by the GC/MS chromatogram [77,93,94].

Components of pesticide residues and medical waste as above are not presented significantly in tabular form. The abundance of chromatogram peaks is due to the similarity or suitability of components with reference references in the tool library, which are less than 80%—determining a component based on the GS/MS measurement that is considered valid if it has a similarity level or quality of 80%, as was done for the hydrocarbon and PAH components [95-97]. Ideally, for the analysis of pesticide residues and medical waste in samples obtained in marine ecosystems such as fish, sponges, seawater and sediments, the preparation of these samples is carried out using a combination of pyrolysis-GC/MS instruments [78,79,98].

3.4. Heavy metal pollutant analysis

Many heavy metal pollutants are thought to enter the marine ecosystem. However, only Lead (Pb) and Copper (Cu) ions were identified in this research. Observations made in the Makassar City MTA area concluded that the two types of pollutants are the most vulnerable as components of pollution in marine areas, especially around BCI, the Spermonde Islands group.

Based on the quality standard according to KLH RI Num. 51/2004, the average heavy metals Pb^{+2} and Cu^{+2} in seawater is a maximum of 0.008 mg/L. Comparing the concentration of the measurement results (Table 7) with seawater quality standards shows that the contaminants Pb^{+2} and Cu^{+2}, about BCI, are 20 times and 25 times higher, respectively [99]. The maximum threshold value for heavy metal contaminants in fish, Pb^{+2} = 2 μg/g and Cu^{+2} = 20 μg/g, by Dirjen BPOM No 03725/B/SK/VII/89 [100].

Table 7. Heavy metal pollutant (HM) concentration analysis

Type of	Sampling	Pollutant concentration

pollutant	station	Sediment (µg/g)	Sponge (µg/g)	Sea water (mg/L)	Fish (µg/kg)
Lead ion (Pb^{+2})	ST 1	4.0414	3,8710	0.1038	2.4517
	ST 2	4.6763	3.7252	0.2508	1.6560
	ST 3	4.6435	3.8134	0.1365	1.3264
Average		4.4340	3.8031	0.1641	1.8110
Copper ion (Cu^{+2})	ST 1	9.2791	6.1658	0.3192	4.8221
	ST 2	8.8431	5.5672	0.2858	4.4742
	ST 3	7.9202	5.4742	0.2754	3.8206
Average		8.6808	5.7357	0.2935	4.3723

The average concentration of the two types of heavy metal pollutants (Table 7) shows that exposure to Pb^{+2} and Cu^{+2} is still below the threshold value. However, using the Australian and New Zealand Environment and Conservation Council (ANZECC) standard with a tolerance value of the smaller the maximum threshold, it was concluded that the two types of pollutants found in fish around BCI had exceeded the standard [101,102] The exposure concentration of Pb^{+2} in fish obtained from ST 1 (2.4517 g/g) was found to have exceeded the maximum threshold [103]. It is understandable and quite rational because consumption patterns, activities, and dynamics in each type of marine fish vary greatly. Fish samples were obtained for analysis at different stations (Table 2). The type of fish sampled at ST 1 (*Chrysiptera unimaculata*) differed from the fish sample at ST 2 and ST 3 [104,105].

4. Discussion

Physical observation of the waters around BCI did not find plastic waste, media waste or oil spills. This observation is by the physical characteristics of Barrang Caddi waters (HDL, TDS, pH, temperature) and other parameters (Table 1) are relatively the same as other surrounding marine waters [106]. It is known that the contaminants of the GTP group are invisible. Demographically, the distance between BCI and Makassar City is ± 11.5 km, the land area is ± 45,000 m², and the population is ± 3,000 people (612 families) (Fig. 1). The residents' livelihoods are generally fishers; some have vegetable gardens and traditional household processing, generally burning [107,108]. Such conditions have ecological relationships and have the potential to contribute to exposure to GTP contaminants [109].

The morphology of fish and sponges obtained at each station differed (Table 2). Overview of aspects of marine ecosystems, fish, interact with seawater as a growth medium throughout their lives, and the dominant sponges interact more with sediment (Fig. 2 – 5). Those factors cause differences in life patterns, the dynamics that occur between each type of fish and sponges, as well as the nutritional patterns of the two types of marine biota (fish and sponges) both in terms of their growth media and level of preference for types of nutrients and their tolerance limits to contaminants GTP contaminants [110,111]

The total abundance of MP for each type of sample analyzed (Fig. 2 and 3) showed that the waters around BCI were exposed to MP pollutants. The type of MP contaminant based on the density (film, fibre, fragment) contained in each sample type was analyzed further. However, the suspected type of MP based on the polymer structure could be distinguished by measurement and analysis using the difference spectrum seen on the FTIR chromatogram (Fig. 4 and 5) [77]. These observations show that the marine ecosystem around BCI waters is exposed to almost all types of MP contaminants [34,112]. The dominant MP exposure found in all samples was the mild MP group (PE, PP, PS), followed by the heavy group (PA and PC) and few PVC and ABS types were found (Table 3) [26,42]. The data illustrates that the dominant source of MP contaminants comes from community activities, both in industry, services and household activities. This type of MP is widely used in packaging applications, such as plastic bags, clothes, ropes, colouring, and recycling containers. , various types of plastic caps, bottles, disposable tableware, optical discs (CD) and other types. Almost all the use of this type of MP is identical to the daily activities of society and industry [113-114].

Other GTP contaminants analyzed are hydrocarbon components, especially PAHs. The searches carried out on all types of samples from three different stations (Table 4 – 6) identified eight types of PAH. Types of low-toxic PAHs, the NL type, were identified in all samples. NL is a simple aromatic hydrocarbon [9,38,115]. Naphthalene-based products such as camphor are thought to have come from household activities, for example, the use to eradicate insects and absorb odours in bathroom toilets. Another source can come from the distillation of coal tar. The nature of NL is volatile and carcinogenic [14,116].

Pyrene is the second-order PAH that has been identified in several samples. PN is a group of highly toxic and carcinogenic PAHs. The presence of PR in the sample is thought to have come from the transportation activities of petroleum carriers. This assumption is reinforced by identifying PAH type AZ, where the PAH type is a characteristic of petroleum and some of its derivative products, including those from coal processing [9,83,117]. This allegation is quite reasonable because BCI operates three ports: container port, passenger port, and fish landing port. Other PAHs, such as PT, PH and BZ, are derivative products resulting from chemical reactions, such as oxidation reactions that produce these derivatives or community waste burning activities [71,118]

Pesticide residues and medical waste are strongly suspected as one the pollutants exposed in the marine ecosystem around BCI. This assumption is based on GC/MS chromatogram peaks with varying abundances and recorded GC/MS chromatogram peaks identified with PR and MW components and observed in the PAH chromatogram data (Table 4 – 6), where the peak numbers not listed in the table are the peaks of the PR component or maybe residual MW. This assumption is based on a search that two hospitals are operating around the coast of Makassar City, which is adjacent to BCI [51,119]. Allegations of the presence of pollutant types PR and MW in samples of fish, seawater, sponges and sediments around the marine waters of BCI can also come from the activities of the people who inhabit BCI or due to biological activities, where these pollutants experience dynamics and eventually empties into the sea [55,78].

Heavy metal (HM) pollutants, especially Pb^{+2} and Cu^{+2}, were identified in all samples obtained from three different stations (Table 7). These results indicate that it is still within the tolerable concentration limits for marine biota and is not dangerous according to Indonesian KLH standards but is already in the category of worrying based on ANZECC standards [62]. Pb^{+2} and Cu^{+2} pollutants in marine ecosystems around BCI are also thought to be due to natural and anthropogenic activities [120,121].

The combination of all types of GTP identified in the waters around BCI can be in alert status, not only for the quality and sustainability of the marine ecosystem around BCI but also for the people who inhabit the tourists visiting this island. The combination of all types of GTP identified in the waters around BCI can be in alert status, not only for the quality and sustainability of the marine ecosystem around BCI but also for the people who inhabit the tourists visiting this island. Including the survival of sponges known to have primary and secondary metabolic content for raw materials for medicinal products, food concentrates and beauty products [62,122].

Exposure to contaminants from the GTP group around BCI is estimated to increase in the future due to the island's status as one of the Marine Tourism Area (MTA) islands, meaning that it is visited by many tourists and is seen as one of the potential factors contributing to the pollutant component, especially pollutant types MP and PAH [65,69]. BCI is adjacent to the city of Makassar, where the city has a beach length of ± 7.5 km. Anthropogenic sources of pollutants are thought to be heavily contributed to this sector. Along the coast, there are hotels, hospitals, industrial operations, culinary areas and residential housing that are very densely populated, and community activities occur every day for almost 24 hours [7,10]. This situation is thought to be the main factor in exposure to pollutants of the MP, MW type that has been happening so far. The vicinity of BCI is also adjacent to Soekarno Hatta Port, a fish landing port. Thus there are many transportation activities for various types of ships. This picture significantly contributes to exposure to pollutants, especially pollutants of PAH, HM, and MP types [13,46].

The Makassar City MTA manager should use this data as material for consideration in MTA operations so that the managed marine tourism does not cause an increase in one of the pollutants in the GTP category [3,47]. It is even expected to be able to wisely manage the tourist area by increasing the population of marine biota, especially sponges, through the transplant method, where sponges are known as biota that has the function of biodegradation, bioabsorption and bioremediation of several types of pollutants such as PAHs, microplastics and heavy metals [20,120]. Sponges can be used as bioindicators and biomonitoring of PAH and HM contamination [44,73]. Another effort that can be made is that along the shoreline of BCI, and it is recommended that plants that have a biofilter function against pollutants, such as mangroves, be planted [123]. Makassar City MTA managers are also advised to carry out socialization, education and advocacy to the community to be aware and care about waste so that their household waste can be appropriately managed and not enter sea waters.

5. Conclusions

This article reviews microplastic pollutants, PAHs, pesticide residues, heavy metals, and medical waste, which in this case, we call global trending pollutants (GTP) in marine ecosystems around BCI's MTA waters. The average total MP abundance in seawater samples (5.47 units/m^3), in fish (7.03 units/m^3), while sediment samples (8.18 units/m^3) and sponges (8.32 units/m^3). There are seven types of MP identified in the BCI aquatic ecosystem, dominated by the mild category of MP, PE, PP and PS, followed by PA and PC. The marine ecosystem around BCI was contaminated with PAH type pollutants, especially NL type found in all samples, followed by PN and AZ. BCI waters are also suspected of being exposed to pesticide residues and media waste. Heavy metal pollutants Pb^{+2} and Cu^{+2} were also identified in the marine waters around BCI, especially fish and seawater. The average concentrations of Pb^{+2} and Cu^{+2} in seawater are 0.164 mg/L and 0.294 mg/L, while the average concentrations of these two types of heavy metal pollutants are 1.8110 μg/g and 2,452 μg/g, respectively.

Five types of pollutants identified in the marine ecosystem around BCI illustrate that this MTA is not conducive as a recommended marine tourism destination. It is estimated concentration of these pollutants will increase, given the status of BCI as one of the islands in the MTA area. Suppose the BCI is maintained as a marine tourism area. In that case, it is feared that it will experience an ecological hazard status to the ecosystem and have a chain effect not only on the aquatic ecosystem around the BCI but can also affect the problem of sponge populations, fish status unfit for consumption, and can even cause health problems for the community. The health of surrounding humans and consumers of marine products from BCI waters.

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