DISTRIBUTION AND OCCURRENCE OF MICROPLASTICS ALONG THE HOTSPOT BEACHES OF NORTH GOA, INDIA.

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DECLARATION BY STUDENT

I hereby declare that the data presented in this Dissertation report entitled, "Distribution and Occurrence of Microplastics Along the Hotspot Beaches of North Goa, India" is based on the findings carried out by me in the Masters of Science at the School of Earth, Ocean and Atmospheric Sciences, Applied Geology Goa University under the Supervision of Dr. Niyati Kalangutkar and the same has not been submitted elsewhere for the award of a degree or diploma by me. Further, I understand that Goa University or its authorities will be not be responsible for the correctness of observations / experimental or other findings given dissertation report.

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Place: Goa University

COMPLETION CERTIFICATE

This is to certify that the dissertation report "Distribution and Occurrence of Microplastics Along the Hotspot Beaches of North Goa, India" is a bonafide work carried out by Ms. Ashita Salgaokar under my supervision in partial fulfilment of the requirements for the award of the degree of Masters in the Discipline Applied Geology at the School of Earth, Ocean and Atmospheric Sciences, Goa University.

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GENERAL INTRODUCTION

CHAPTER-1

1.1 Microplastics:

Marine debris has been defined as 'item appearing on beaches as a result of human activity' (Marine Conservation Society, 2004). Plastic is a polymeric material that has the ability of being moulded or shaped, on the application of heat and pressure. Plastic is preferred over other material due to its durability, toughness, low price, can be moulded into desired shape and so on. Due to these properties of plastic the demand has increased therefore the production has also increased. According to a report by Statista (2024) the production of plastics has increased from 1.5 million metric tons from in 1950 to 400.3 million metric tons in the year 2022. The utilization of single use of plastics, haphazard dumping of plastic material has caused plastic pollution even at the most remote places on the planet. In almost everywhere large fragments of plastic have been seen even from the most popular beaches to remote islands (Bucci and Rochman, 2020). Plastic pollution is a global concern in today's world. The majority of plastic waste is being incinerated (burnt), dumped in landfills, and released into the environment, causing significant environmental and health problems (Wang et al., 2020). Only a tiny percentage that does not exceed 10.0% is recycled in the USA (Cessi et al., 2014). Plastic particles in the ocean have been shown to contain quite high levels of organic pollutants. Toxic chemicals, such as polychlorinated biphenyls (PCBs), nonylphenol (NP), organic pesticides, such as dichlorodiphenyltrichloroethane (DDT), polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyl ethers (PBDEs) and bisphenol A (BPA) have been found throughout oceanic plastic debris (Mato et al., 2001). Therefore, the majority of plastic waste is being incinerated, dumped in landfills, and released into the environment, causing significant environmental and health problems (Wang et al., 2020). The type of plastic found in the environment can be nanoplastics (< 5 mm), mesoplastics ($\geq 5 \text{ mm}$ to 5 cm), macroplastics (>5 to 50 cm), and megaplastics (>50 cm).

Microplastics according to the definition given by National Oceanic and Atmospheric Administration (NOAA) is small plastic pieces which are less than five millimetres in size. Microplastics come from a variety of sources, including from larger plastic (meso/macro/mega) that degrades into smaller pieces (micro/nano plastics). Microplastics, enter the environment from marine plastic junk breaking down, run-off from plumbing, domestic waste, leakage from production facilities and other sources. When microplastics are ingested by organisms such as birds, fish, mammals and plants, microplastics have both toxic and mechanical effects on them, leading to issues including reduced food intake, suffocation, behavioural changes and genetic alteration (UN Environment Programme 2022). MPs can be accumulated in the environment due to their inert nature (Wang et al., 2021). Deep layer ocean sediment surveys in China (2020) show the presence of plastics in deposition layers far older than the invention of plastics, leading to suspected underestimation of microplastics in surface sample ocean surveys (Xue et al., 2020). A study carried out in Germany in 2021 revealed the presence of microplastics in various human organs, in the placenta (Ragusa et al., 2019) and also in new born infants. The impact of hazardous chemicals from the microplastics on the physiology of both humans and marine organisms is still the beginning. The presence of microplastics (MPs) in the marine ecosystem was first investigated in 1971. In 2004, Richard Thompson, Professor of Marine Biology, was the first to describe their long-term accumulation and coin the term 'microplastics' in his landmark paper, 'Lost at Sea: Where Is All the Plastic?'. The accumulation of microplastic was also observed in regions that are far from population centres, such as polar ice, water and air (Obbard 2018) and in remote mountains, which indicates atmospheric deposition of microplastics. Winds, tides, waves and currents can carry the floating plastic debris over long distances from their original point (Thiel et al., 2013)



Figure 1.1: Conceptual diagram showing the sources, transport and fate of MPs. (Ateia et al., 2022)

1.2 Classification of Microplastics:

Based on the sources; Primary microplastics and Secondary microplastics;

• Primary Microplastics; primary microplastics are the microplastics that are produced by the industry for the production of macro sized plastic material these can be the plastic pellets also the microbeads used in cosmetic industry, micro fibres from the fishing nets or the textiles are a type of primary microplastics. The microplastic fibres present in the synthetic clothing and fragments from the disintegration of larger plastic items are the primary sources of MPs widely distributed in the marine ecosystem besides the beads present in facial cleansers, toothpaste, and scrubs (Cole et al., 2011). Discharge of primary microplastics from domestic sources can directly enter the sewage system and accumulate in the environment (Kalcikova et al., 2017). Primary plastics are produced in micro size and used as scrubbers in cosmetics, paint of machinery and boat hulls (Cesa et al., 2017; Napper and Thompson, 2016).

• Secondary microplastics; these are formed by the degradation products of larger plastic/macro plastic waste (Wang et al., 2019), which may occur in many shapes, and cover a high physical and chemical diversity (Rillig et al., 2019; Helmberger et al., 2020). They are formed by the breakdown of macro/large sized plastic particles due to the mechanical, chemical, biological or photodegradation. Such as plastic bottles, bag, food containers and so on are mismanaged. Secondary microplastics are derived from the breakdown of large plastic debris, fabric and polymeric materials from clothes (Browne et al., 2011).

Both types are recognized to persist in the environment at high levels, particularly in aquatic and marine ecosystems, where they cause water pollution. 35% of all ocean microplastics come from textiles/clothing, primarily due to the erosion of polyester, acrylic, or nylon-based clothing, often during the washing process (Resnick and Brian 2018).

<u>Based on the shape</u>; microplastics are subdivided into fibres, films, foams, fragments and pellets. As stated by NOAA, microfibers are produced by the synthetic textiles industries, fishing nets shed microfibers directly into the environment. clothes also shed these fibres, releasing them in the wash or directly into the water and air around during normal wear. Microbeads are those found in toothpastes and face scrubbers, face washes which wash down into the drains and into wastewater treatment plants, this treated water is sometimes released into the water bodies from which the plastics enter marine organisms. Plastic pellets, like those used to produce larger plastic items, directly enter the ocean and great lakes through a spill during shipping or at a manufacturing facility. Plastic fragments come from larger plastic items when they are littered or dumped, they can be transported by wind and storms, and travel directly from rivers and streams. Through exposure to winds, waves, and the sun, these larger plastics break into smaller and smaller pieces,

creating microplastics. Fibres contribute the most to the local microplastic pollution. China, Europe and North America are the major contributors of plastic (Plastics Europe, 2015). The accumulation of plastics in the ocean gyres has a greater threat to the marine environment, with 'microplastics' being one of the contributors (Thompson et al., 2004). Littering and uncontrolled disposal of discarded plastic waste threaten the environment because plastic is resistant and poorly biodegradable (Thompson et al., 2004; Geyer et al., 2017). Microplastics can float in the water column, settle in the marine sediments or be consumed by the organisms and enter the food chain.

1.3 Polymers of Plastic:

There are 7 basic types of plastic polymers. Each microplastic shape may be represented by different polymer types as manufacturers seek to produce plastics with specific properties (e.g., flexibility, roughness, resistance, and durability) (Espí et al., 2006).

- Polyethylene Terephthalate (PET or PETE): this is one of the most commonly used plastics. It lightweight, strong, typically transparent and is often used in food packaging and fabrics (polyester). Examples: beverage bottles, food bottles/jars (salad dressing, peanut butter, honey, etc.) and polyester clothing or rope.
- 2) High-Density Polyethylene (HDPE): collectively, Polyethylene is the most common plastics in the world, but it's classified into three types: High-Density, Low-Density and Linear Low-Density. High-Density Polyethylene is strong and resistant to moisture and chemicals, which makes it ideal for cartons, containers, pipes and other building materials. Examples: milk cartons, detergent bottles, cereal box liners, toys, buckets, park benches and rigid pipes.
- 3) Polyvinyl Chloride (PVC or Vinyl): this hard and rigid plastic is resistant to chemicals and weathering, making it desired for building and construction

applications; while the fact that it doesn't conduct electricity makes it common for high-tech applications, such as wires and cable. It's also widely used in medical applications because it's impermeable to germs, is easily disinfected and provides single-use applications that reduce infections in healthcare. On the flip side, we must note that PVC is the most dangerous plastic to human health, known to leach dangerous toxins throughout its entire lifecycle (e.g.: lead, dioxins, vinyl chloride). Examples: Plumbing pipes, credit cards, human and pet toys, rain gutters, teething rings, IV fluid bags and medical tubing and oxygen masks.

- 4) Low-Density Polyethylene (LDPE): a softer, clearer, and more flexible version of HDPE. It's often used as a liner inside beverage cartons, and in corrosion-resistant work surfaces and other products. Examples: Plastic/cling wrap, sandwich and bread bags, bubble wrap, garbage bags, grocery bags and beverage cups.
- 5) Polypropylene (PP): this is one of the most durable types of plastic. It is more heat resistant than some others, which makes it ideal for things such as food packaging and food storage that is made to hold hot items or be heated itself. It's flexible enough to allow for mild bending, but it retains its shape and strength for a long time. Examples: Straws, bottle caps, prescription bottles, hot food containers, packaging tape, disposable diapers and DVD/CD boxes.
- 6) Polystyrene (PS or Styrofoam): better known as Styrofoam, this rigid plastic is low-cost and insulates very well, which has made it a staple in the food, packaging and construction industries. Like PVC, polystyrene is considered to be a dangerous plastic. It can easily leach harmful toxins such as styrene (a neurotoxin), which can easily then be absorbed by food and thus ingested by humans. Examples: Cups, takeout food containers, shipping and product packaging, egg cartons, cutlery and building insulation.

7) Others: This category is a catch-all for other types of plastic that don't belong in any of the other six categories or are combinations of multiple types. The most important thing here is that these plastics aren't typically recyclable. Examples: Eyeglasses, baby and sports bottles, electronics, CD/DVDs, lighting fixtures and clear plastic cutlery.

	L2 HDPE	A PVC	LDPE	♪ PP	PS	OTHER
Polyethylene Terephthalate	High Density Polyethylene	Polyvinyl Chloride	Low Density Polyethylene	Polypropylene	Polystyrene	Other
		ŌI	*		8	T I I I I I I I I I I I I I I I I I I I
Recyclable	Recyclable	Recyclable at specialist points	Recyclable at specialist points	Recycloble	Recyclable at specialist points	Not easiy recyclable

Figure 1.2: Showing plastic identification codes by Freight Center Source:<u>https://www.freightcenter.com/shipping/plastic-resins-and-polymers/</u>

1.4 Sources of Microplastic in the Environment:

- Microfibers; shed from textiles are the main contributor to microplastic pollution.
 Although only synthetic microfibers would be considered microplastics.
- ii. Vehicle tyres: make up 10 to 20% of the microplastic pollution in the environment. Tyre wear is an unavoidable consequence of their use and the rate of abrasion is influenced by the tyre composition, design, vehicle speed/acceleration, use of brakes, and road surface texture (Eunomia and ICF., 2018). Although tyres are generally thought to consist of natural rubber, the natural rubber contents in a tyre can sometimes be as little as 20% with the rest of the materials being synthetic, including plastics (Paul Quinn 2018). The total microplastics generated from the wear of automotive tyres in the European Union is around 0.5 million metric tons

(MMT) per year (Eunomia and ICF., 2018). It has been estimated that tyre wear could account for 65% (18,000 tonnes annually) of all microplastics released to UK surface waters.

- iii. City dust: which makes 10-20% of the microplastic pollution. It refers to a wide range of microplastic sources originating from urban areas - artificial turf, building paints, and industrial abrasives constitute the largest and most wellunderstood sources.
- iv. Road markings (3-5%): similarly to road covers and tyres, hot-melt paints, which are commonly used for road markings, consist of 15-25% polymer binders, which contribute to microplastic pollution when worn away. While not all road markings are plastic-based, thermoplastic bases are the most commonly used material in road markings in certain places in the Europe (Lassen, C. et al. 2015).
- Marine coatings (3.7%) many types of marine coatings applied to the hulls of marine vessels include polymers such as polyurethane, epoxy coatings, vinyl and/or lacquers, as well as other compounds such as metals (OECD 2009). When these coatings are weathered, scraped, sanded, disposed of, or spilt during the application, they contribute to microplastic load in the environment.
- vi. Personal care products and cosmetics (1-2%) Personal care products, such as exfoliants contain microbeads, which make up a relatively small but well-recognized facet of microplastic pollution.
- vii. Plastic pellets (0.3%) Plastic resin pellets (also known as 'nurdles') are used as feedstock for the manufacture of most plastic products. These pellets contribute to microplastic pollution through accidental losses occurring during transport to the converters where they are processed, and during the plastic manufacturing process (Cole, M. et al. 2011).

- viii. Fishing gear: both recreational and commercial fisheries, and aquaculture facilities directly introduce plastics into the marine environment. The commercial gears which have the potential for greatest contribution to microplastic loads are the nettings used in benthic dredges and trawls and in particular the ground ropes. This rope is dragged in contact with the sea bed for many miles, subject to abrasion from benthic sediments, or snagging and total loss. Fishing gear is made from plastic materials and fibres, which break down into microplastics when the gear is used in the water or gets lost in the ocean.
 - ix. Other sources include: Dish detergents can contain microplastics such as polyurethane particles that are used to clean surfaces and are subsequently disposed of in wastewater (Scudo, A. 2017). Plastic bio-beads used as filter media in wastewater treatment plants (WWTPs) can be unintentionally released due to accidents and leaks at plants (Cornish Plastic Pollution Coalition 2018). Other common uses for microplastics include: packaging, textile printing and automotive molding, biomedical research insulation, furniture, pillows, buoys, 3D printing, ceramics, and adhesives (European Chemicals Agency (ECHA) 2019).



Figure 1.3: Various Sources of Microplastics. (Kataria et al., 2024)

1.5 How is the plastic degraded or disintegrated?

Plastic never decomposes it only disintegrates into smaller and smaller pieces. Larger pieces of plastic in the sea or on land, such as bottles and plastic packaging, become brittle and gradually break down. This is due to sunlight, oxidation or friction, or by animals nibbling on the plastic. When the plastic or microplastic is present in the environment it is broken down by various factors that include mechanical, chemical, biological and photo degradation. Addition, various additives such as plasticizers, flame retardants, antioxidants, UV stabilizers, heat stabilizers, slip agents, curing agents, biocides, pigments and other substances added in the production process of plastics are incorporated into the plastics. Under unstable environments, such as strong shear force (Lambert et al., 2014; Paluselli et al., 2018), continuous or strong UV light irradiation (Lambert et al., 2014; Wang et al., 2020b), weathering (Lambert et al., 2014) it is easy to release these substances into the environment and cause damage to other organisms in the environment (Wang et al., 2020b; Paluselli et al., 2018). Chemical and photodegradation of plastics go hand in hand that is natural degradation of plastic begins with photodegradation, which leads to thermooxidative degradation. Ultraviolet light from the sun provides the activation energy required to initiate the incorporation of oxygen atoms into the polymer (Andrady 2011 and Raquez et al 2011). This causes the plastic to become brittle and to break into smaller and smaller pieces, until the polymer chains reach sufficiently low molecular weight (Zheng et al., 2005). Biological disintegration takes place when the plastic in the environment is broken down by biological factors such as microorganisms, algae, mushroom and bacteria. The process excretion of extracellular enzymes by the microorganism, the attachment of this enzyme to the surface of plastic and the hydrolysis of plastic to short polymer intermediates (Mohanan et al., 2020). Scientist from Japan in 2016 has discovered a species of microorganism known as Ideonella Sakaiensis capable of breaking down plastic.

1.5 Microplastic and Heavy Metals:

Microplastics are reported as carriers for heavy metals and exhibit diverse interactive effects (Liu et al., 2021). Heavy metals had been found on the MPs from North Atlantic subtropical gyre (Prunier et al., 2019), São Paulo State in southeastern Brazil (Vedolin et al., 2018), beaches in southwest England (Massos and Turner, 2017), and western Europe (Turner et al., 2019). Studies have shown that microplastic associated biofilms could affect the physical and chemical properties of microplastics and further affect the adsorption of chemical pollutants including heavy metals (Tu et al., 2020). The factors responsible for the interaction of microplastics and heavy metal include aging, temperature, pH, contact time, ionic strength, and particle size. Increase in the surface area of the microplastic can increase the absorption capacity of heavy metals on the surface of microplastic. When pH is less than a certain value, MPs will not interact with heavy metals (Tang et al., 2020). The adsorption of heavy metals by MPs is mainly controlled by the chemisorption mechanism, involving the sharing or transfer of electron pairs, and is not controlled by the material transport step, in addition to physical and chemical environmental factors, biological factors can affect the adsorption of heavy metals by MPs. The influence of microbial biofilm is one of the most concerned biological factors and it plays an important role in determining the MP surface properties. (Liu et al., 2021). Tu et al., (2020) found that biofilm formation reduced the hydrophobicity of the microplastic surface. Some studies revealed that the growth of biofilms can positively affect the adsorption of heavy metals and concentration of heavy metals on MPs will increase as the biofilm matures (Richard et al., 2019; Qi et al., 2021).



Figure 1.4: Mechanisms of biofilm involved in the interactions between MPs and heavy metals. (Liu et al., 2021)

Contamination of microplastics and heavy metals is a global environmental problem of public health concern. Aquatic organisms can ingest MPs through direct ingestion, filtering ingestion, and food chain transfer, which can produce certain toxic effects when they accumulate at high levels in the body (Murphy and Quinn 2018). Studies showed that the combination of MPs and heavy metals can induce hippocampal oxidative damage and increase mortality, but this effect was mainly caused by heavy metals, not MPs. Yan et al., (2020). MPs can also play a role in the transport of trace metals. Guan et al., (2020) reported that the development of biofilms enhanced the role of MPs in the transport and fate of trace metals [Ni (II), Cu (II), Zn (II), and Cd (II)] in the aqueous environment.

1.6 How do microplastics circulate in the ocean?

Microplastics are likely to be transported from pollution sources to sink (open oceans) via river networks (Luo et al., 2019). freshwater and estuary systems are recognized as origins and transport pathways of plastics to the oceans (Luo et al., 2019). Large-scale gyre investigations revealed the pelagic plastic pollution accumulation in open oceans and the existence of the "Great Pacific Garbage Patch" (Andrady 2017). It has been shown

that pollution sources, anthropogenic impacts and hydrodynamics have the potential to influence the rates at which microplastics accumulate and are transported (Browne et al., 2011; Eerkes-Medrano et al., 2015; Horton et al., 2017). Freshwater systems, especially rivers, are likely to transport microplastics from land-based sources to estuaries and the open ocean. The marine environment is a primary sink when considering the life-span of microplastics. Ultimately, microplastics introduced to this environment will either accumulate at the shoreline or sink to the sediment from surface seawater (Siegfried et al., 2017; Woodall et al., 2014). In the environment, microplastics can be transported through atmospheric or aquatic currents depending on their weight and density (Law et al., 2010). Rainfall, surface runoff, and ocean circulation are the possible routes that transfer microplastics from the pedosphere to the hydrosphere. Not only can microplastics be transported from land to water, but they can also travel from water to land due to ocean circulation (Zhang et al., 2019). Heavy rainfall and surface runoff from agricultural lands and urban areas can transport microplastics to surface waters (Nizzetto et al., 2016). The transport process of floating plastics in the ocean is primarily determined by dynamic conditions, such as wind forcing and geostrophic circulation. The circulation pattern results in surface accumulation zones that are characterized by convergent particle paths, including plastic debris in subtropical gyres (Howell et al., 2012; Maximenko et al., 2012). Neutral microplastics float but are suspended in the water column, from subsurface to deep water. Several studies indicate that a mismatch exists between observed and expected plastic concentrations in surface oceanic waters (Eriksen et al., 2014; Cózar et al., 2014), which promoted research into the vertical distribution of microplastics within the water column. Kanhai et al., (2018) discovered that there was a vertical distribution of microplastics in sub-surface waters (8-4369 m) of the Arctic Central Basin, and the highest microplastic abundance was in the mixed layer. Enders et al.,

(2015). Observation and simulations have confirmed that microplastics are vertically distributed within the upper water column due to wind-induced mixing (Kukulka et al., 2012). Density difference will influence whether microplastics float in surface waters, are suspend in the water column, become beached in coastal areas, or sink to deep-sea sediment (Galgani et al., 2015). High-density microplastics are naturally non-buoyant, and usually deposited in sediments from beaches to the deep sea (Woodall et al., 2014; Zhang 2017). Microorganisms can rapidly aggregate on the surface of plastic debris and develop biofilm (Andrady 2011; Cole et al., 2013; Zhang 2017). Cózar et al., (2014) assumed that biofouling enhances microplastics densities to such an extent that particles with densities lower than the density of seawater. The transport of microplastics in ocean is mainly surface currents driven or due to the atmospheric circulation. The surface ocean currents are shown in the Figure 1.5 below with 5 major plastic patches in the sub-tropical gyres. According to NOAA ocean gyres are large systems of circulating ocean currents, kind of like slow-moving whirlpools (Figure 1.5).



Figure 1.5: Major gyres in the ocean and the amount of plastics present there (Eriksen et al., 2014).

1.7 Problem Statement and Effects of Microplastics;

Plastic pollution is of a major concern as it is found even in the most remote areas of the planet. Its distribution is affecting the marine and terrestrial environment. The toxic chemicals that come from both the ocean and runoff can be biomagnified up the food chain. Plastic has the ability to alter habitats and natural processes, reducing ecosystems' ability to adapt to climate change, directly affecting millions of people's livelihoods, food production capabilities and social well-being. Microplastics are a concern because they can harm organisms, enter the food chain, and affect human health. Microplastics are found in the oceans, mountains, air, drinking water, and human bodies. They can be ingested by animals of all sizes, including small invertebrates and large mammals. It is estimated that plastics (including microplastics) could take hundreds or even thousands of years to break down and therefore plastics debris is accumulating in our oceans year on year. Microplastics can be mistaken for food by birds and marine life and there is evidence that this can cause harm. The ingestion of microplastics has been observed in a variety of marine organisms. As the primary consumers, zooplankton can pass microplastics in the food webs and contaminate the higher consumers, including crustaceans, fish, and sea birds (Sun et al., 2018; Zhang et al., 2020; Zheng et al., 2020). Among them, bivalve molluscs are filter feeders and are more susceptible to the uptake of microplastics (Jiang et al., 2022). The increasing attention on research on plastics is attributable to their longevity, which enable long distance distribution from their source and accumulation in global waters, including polar oceans (Thompson et al., 2004; Cole et al., 2011; Van Cauwenberg et al., 2013). Polymers of plastics can release dangerous dust and vapours when they enter living organisms for example, vinyl acetate in humans may affect the heart, nervous system, and liver. Most harmful toxic chemicals found in plastic which have shown their hazardous effect on human and animals health are BPA (bisphenol), phthalates, antimony trioxide and poly fluorinated chemicals (Richa Khare and Smriti Khare 2023). These chemicals can cause endocrine disruption, which can lead to reproductive, growth, and cognitive impairment. Other negative effects include: cancer, birth defects, and impaired immunity. Some compounds leaching from polystyrene food containers have been proposed to interfere with hormone functions and are suspected human carcinogens (McRandle 2004). The rivers Yangtze, Indus, Yellow, Hai, Nile, Ganges, Pearl, Amur, Niger, and Mekong transport 88% to 95% of the global plastics into the sea (Schmidt et al., 2017). The presence of plastics, particularly microplastics, within the food chain is increasing. In the 1960s microplastics were observed in the guts of seabirds, and since then have been found in increasing concentrations (Barnes et al., 2009). Research on the environmental impacts has typically focused on the disposal phase. However, the production of plastics is also responsible for substantial environmental, health and socioeconomic impacts (Livia et al., 2021). Because of their diverse sizes, shapes, and densities, environmental microplastics are often perceived as complex (Kooi & Koelmans 2019). Most microplastics start their journey on land and are carried by rivers and wind to the ocean, where they are caught in the global ocean circulation system. Microplastics have been found on beaches around the world, even in our protected areas, and have been documented in sea ice in the Arctic and on the ocean floor. Once they enter the ocean, it can be difficult to understand where exactly these tiny plastics have come from. Once microplastics are in the ocean, they break down into even tinier particles (called nanoplastics) and accumulate in the food chain, posing a threat to fish and other marine organisms that ingest them ('Tracking Global Marine Microplastics' NOAA 2022). When microplastics are exposed in the natural environment, absorption of chemical contaminants and the formation of biofilms further enhance their complexity (Kooi & Koelmans 2019). For that matter people who live along the coast are dependent

on sea food for their diet they are affected when they consume fish. Microplastics have been found in the stomachs of many different types of wildlife, from the smallest species of plankton to large whales. Microplastics also have been found in the air, tap water, sea salt, bottled water, beer, and the fish that humans eat. The abundance of microplastics in marine environment is of major concern as 20% of the population is dependent on the sea food for their daily protein intake.

In coastal waters, the transfer and distribution patterns of MPs are directed by ocean and atmosphere dynamics (Atwood et al., 2019). Wind mixing further influences the vertical distribution of MPs in the water column (Kukulka et al., 2012). Polymer density also affects the distribution of microplastics in the water column. The denser microplastics tend to sink at the bottom of the ocean floor while the lighter polymers will float in the water column (Wright et al., 2013). Microplastic research in India has been fast evolving in recent years. However, despite being one of the major producers and consumers of plastics, marine MPs in India have been relatively unexplored compared to other countries.

Coastal areas are one of the most significant ecosystems, sustaining rich bioresources. Coastal seawaters are subjected to human interferences that lead to pollution and pose serious environmental issues (Pavithran 2021). Global attention on microplastic pollution has risen recently as the consumption and production has also increased. Plastic trash in the ocean, near the coast and on land. Tourism (UNEP, 2005), fishing, particles lost or broken off of marine vessels (Webb et al., 2009), harbour activities, industrial effluents, and land-based plastic debris migrating through river runoff (Schmidt et al., 2017) are the major sources of plastic debris in the nearshore environment. Moreover, wastewater treatment plants play a key role in the transport of microfibres (i.e., synthetic fibres) into the marine environment (Napper and Thompson, 2016). In the oceans, the decay of plastics is accelerated by four processes: photodegradation, thermo-oxidative degradation, hydrolytic degradation, and biodegradation (Webb et al., 2009). A recent study by Jambeck et al. (2015) shows that 275 million metric tons (MMT) of plastic waste was generated in 192 coastal countries in 2010, with 4.8–12.7 MMT entering the ocean. Microplastics are ubiquitous and worldwide contaminants that accumulate in estuarine, coastal and marine environment, especially on sandy beaches (S Veerasingam et al., 2016).

The quantity, polymers and the morphology of the microplastics found along the coasts are of importance as they could give us their possible sources and the amount of time they are present in environment. After knowing their sources, it is possible to give mitigation measures.

1.9 Aims and Objectives of the Study:

- To study the distribution and abundance of microplastic along Vagator, Anjuna, Baga, Calangute and Candolim beaches.
- To identify the chemical composition (polymer) and delineate their origin using Fourier-Transform Infrared Spectroscopy (FTIR).
- To study the surface morphology of selected samples using Scanning Electron Microscope (SEM).

1.10 Scope of Study:

In this study, research on coastal waters along five hotspot beaches of North Goa were carried out. Total of 25 stations were selected to compare the abundance of microplastic contamination. All the water samples were collected and stored without letting them get contaminated. Laboratory analysis was conducted and the selected samples were sent for Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM) analysis for polymer detection and the study of surface morphology respectively.

<u>CHAPTER-2</u> LITERATURE REVIEW

2.1 International Scenario

Marine debris constitutes, "any persistent solid material that is manufactured or processed and directly or indirectly, intentionally or unintentionally, disposed of or abandoned into the marine environment or the Great Lakes," (UNEP, 2009). In many beaches around the world, occurrence of MPPs is frequently reported and found as real threat to those ingested by seabirds and other animals (Costa et al., 2010). Recently, global production rose 4% between 2013 and 2014, from 299 million tonnes to 311 million tonnes (Plastics Europe, 2015). The creation of plastic items from the industrial feedstock's, leaking of microbeads and plastic powders from air-blasting practices are the further sources to contribute plastic contamination in the marine habitat (Claessens et al., 2011; Sadri and Thompson, 2014). It is estimated that there are over 5.25 trillion plastic particles weighing about 2,69,000 tonnes in the world's ocean (Eriksen et al., 2014). In the year 2010 it was estimated that 4.8 to 12.7 million metric tons of plastic entered the ocean from coastal countries (Jambeck et al., 2015). The marine environment currently faces significant threats from pollution, over exploitation, habitat destruction and climate change. Microplastic ingestion has been observed in a wide variety of organisms, including zooplankton (Cole et al., 2013; Desforges et al., 2015; Setala et al., 2014), filter feeders, such as oysters and mussels (Cole and Galloway, 2015; Cauwenberghe et al., 2015; Cauwenberghe and Janssen, 2014), and fish (Lusher et al., 2013, Mazurais et al., 2015). As of 2014, it has been estimated that between 15 and 51 trillion particles, weighing up to 236,000 tons have accumulated in marine systems (Sebille et al., 2015). The majority of the anthropogenic debris found in the seas is composed of plastic material (60-80%) (Derraik 2002; Vegtner et al., 2014). Microplastics are reported as carriers for heavy metals and exhibit diverse interactive effects (Liu et al., 2021). Heavy metals had been found on the MPs from North Atlantic subtropical gyre (Prunier et al., 2019), São

Paulo State in southeastern Brazil (Vedolin et al., 2018), beaches in southwest England (Massos and Turner, 2017), and western Europe (Turner et al., 2019). The Guanabara Bay of Brazil is one of the most polluted beaches due to hydrocarbons and heavy metals the study conducted there in 2016 by Carvalho et al., showed high amount of microplastic abundance that is 12 to 1300 particles per m2, fragment was abundant followed by foam, pellets and fibres. The source of this microplastic pollution was concluded to be the rapid development of urban centres in the surrounding and the input of a large volume of untreated sewage, several accidental oil spills, and the great contribution of waste from river systems. Similarly, research in Shri Lanka carried out by Dharmadasa et al., (2021) where two national parks situated along the coast was carried out, the Bundala National Park (BNP) and Hikkaduwa Marine National Park (HNP). The most common shape and polymer type found were fragments and Polyethylene respectively. The microplastics found at both the locations were oxidised which was concluded to be there in the environment from a long period of time. Stolte et al., (2015) investigated and evaluated MP contamination along the German Baltic coast and concluded that the high microplastic concentrations in Baltic beach sediments likely originated from municipal waste, industrial and commercial activity, and tourism. Microplastic in Korean coastal waters indicated dominance of microplastic near urban areas (1051 particles/m3) then in rural areas (560 particles/m3) indicating industrial and domestic waste discharge. polypropylene and polyethylene polymers were abundant (Song et al., 2018). A study done in the northern Gulf of Mexico (Wessel et al., 2016) polypropylene and polyethylene were most abundant polymers found. all microplastic pieces found during this study were secondary microplastics (i.e. resulting from the breakdown of larger plastics) and that no plastic manufacturing pellets were found. cigarette butts, bottle caps, food wrappers, beverage bottles, grocery bags and plastic straws were found along the shoreline.

Research by Tsang et al., (2020) along the Deep Bay, Tolo Harbour, Tsing Yi and Victoria Harbour of Hong Kong on Spatial and temporal variations of coastal microplastic pollution revealed that MPs in the shape of pellets and fragments were abundant in surface waters and sediments respectively. Seasonal pattern of microplastic pollution was consistently observed in Victoria Harbour and Tsing Yi, where the number of MPs was always higher in dry season than in wet season for two consecutive years. The cause of high amount of microplastics could be the discharge of wastewater from the Sewage Treatment Works of the Victoria harbour.

In the year 2015 Fok and Cheung noted that large plastic >5mm in size and microplastic debris from 25 beaches along the Hong Kong coast, where more than 90% consisted of microplastic. Among these, expanded polystyrene (EPS) represented 92%, fragments 5% and pellets 3%. The mean abundance of microplastic was found to be 5595 items/m2 making Hong Kong hotspot of marine plastic pollution. Cai et al., (2018) found microplastics from the surface water and sediments from the pearl river the dominant type of microplastics were fibres in both water and sediments. This could be the reason for the microplastic pollution in the open sea in which it is drained as the microplastics would be carried from the source river along the course to the mouth of the river. Morgana et al., 2018 studied the residence of microplastics in the fishes and the sub surface waters of Northeast Greenland. 25% of the fishes showed the presence of microplastic in their gut and the abundance of microplastic in water ranged from 2.4+/- 0.8 items/m3. Polyethylene and polyester were the dominant polymer found. Making this region of Arctic hotspot of microplastic pollution. Microplastic pollution in the environment is closely related to the surrounding industrial and human activities (Dang et al., 2020). A quantitative analysis of microplastic pollution along the south-eastern coastline of South Africa by Nel and Froneman (2015) revealed that more than 90% of samples comprised

of blue/black fibres. Densities in the beach sediment ranged between 688.9 ± 348.2 and 3308 ± 1449 particles·m- 2, while those in the water column varied between 257.9 ± 53.36 and 1215 ± 276.7 particles·m- 3. The data indicate that the presence of microplastics were not associated with proximity to land-based sources or

population density, but rather is governed by water circulation. The abundance, and characteristics of the microplastics on the southern coast of the Black Sea were assessed (Terzi et al., 2022). Where the sediment and water samples contained 64.06 ± 8.95 particles/kg and 18.68 ± 3.01 particles/m3, respectively. The microplastics that were encountered were synthetic, Fibres and fragments abundant. PET, PE and PP dominating composition. Investigation of water and beach samples along Tarragona beach (NE Spain) revealed presence of high amount of microplastics. 1.30 items/m3 in water sample and 32.4 items/kg in sediments. Polyester fibres were dominant. Polyethylene and polypropylene dominating composition (Expósito et al., 2021). A case study in the North Coast of Surabaya, Indonesia showed presence of microplastics in water samples foam was in abundance, polystyrene composition was dominating (Cordova et al., 2019).

2.2 National Scenario

Though India has long coastline of 5,420 km along the mainland with 43 % of sandy beaches, data on litter accumulation, particularly the plastics, which are one of the most common and persistent pollutants in marine environment, are scanty (Jayasiri et al., 2013). Probably, the intense use of beaches for recreation, tourism, and religious activities has increased the potential for plastic contamination in urban beaches in Mumbai (Jayasiri et al., 2013). As indicated by Ajith et al. (2020), the research on MPs has progressed in India from 2010 onwards (represented in Fig. 1a) and requires much more comprehensive studies in this domain due to various toxicities associated with this emergent pollutant



Figure 2.1: Microplastic studies conducted in India. a. the number of studies conducted year-wise; b. percentage of studies conducted in different compartments; c. percentage of studies conducted in different regions. (Vaid et al., 2021).

The country is situated between the latitude 8°4′ and 37°6′ N and the longitude 68°7′ and 97°25′ E and has a coastline of 7517 km (Kumar et al. 2006). The contamination of marine environments with MPs is dependent on several factors of natural and anthropogenic origin. Natural ones include wind currents, coastline geology, etc., while anthropogenic ones comprise mismanaged plastic debris releases, unregulated industrial discharges, etc. (Barnes et al. 2009). With this ongoing scenario of plastic debris mismanagement, it has been predicted that by the year 2050, there will be a greater number of MPs in our oceans than the total number of fishes (World Economic Forum 2016). In the study carried out by Nithin et al., (2023) the analysis of microplastic in the sediments from the coast of Tamil Nadu, India showed high abundance of fibres followed by films and fragments. LDPE (39%) and PP (35%) were dominant polymers. The source was concluded to be

domestic, industrial, and fishing wastes. A study in the north eastern coast of the Arabian Sea done by Gurjar et al., 2023 showed high presence of microplastic fibres followed by fragments. Higher abundance was found in the monsoon season. higher concentration of microplastics from catchment areas are brought to the sea during this season. Along the west coast of India (Maharashtra, Goa and Karnataka) showed a high concentration of microplastic. Highest concentration was found along Maharashtra coast followed by Karnataka and Goa. Sources were concluded to be land-based and related to nearshore plastic industries, port areas, petroleum industries (Maharana et al., 2020). Microplastic pollution estimated in water and sediment samples from selected stations along the Cochin estuary and nearby coastal areas in Kochi recorded a larger number of microplastics with a mean abundance of 751.7 ± 452.21 particles/m3 and 1340 ± 575.22 particles/kg, respectively (Suresh et al., 2020). The study area was polluted by single use plastic which could be the possible reason of microplastic pollution also the sampling site near a jetty had high abundance of microplastics. microplastics in surface seawater from the northern coast of Kerala revealed dominance of fibres and polypropylene (PP) was the prevalent polymer type also Polybutadiene (BR), a characteristic component of tyres was observed from the coastal waters. The cause of microplastic pollution was concluded to be anthropogenic activities along the coastline (Pavithran 2021). Veerasingam et al., 2018 studied the sources, distribution, surface features, polymer composition and age of the microplastic pellets (MPPs) in the sediments of Chennai coast during March 2015 (pre-Chennai flood) and November 2015 (post Chennai flood) using a stereoscopic microscope and ATR-FTIR spectroscopy. White MPPs were most abundant with a polymer composition of polyethylene and polypropylene. The abundance of MPPs was higher in November then in the month of March. Confirming that large amount of MPPs were washed from land during the flood. The polymers that were found were

Polyethylene (73.2%), polypropylene (13.8%), nylon (8.2%), polystyrene (2.8%) and polyester (2%). The recreation, religious and fishing activities are the major contributors to plastic pollution in these beaches, which is borne out by the high abundance of MPs in the study sites. Coastal water and sediment samples are analysed for microplastics from the shelf region of the central east coast of India (Sambandam et al., 2022). Stereomicroscopy, Raman spectroscopy, and micro–Fourier Transform Infra-Red Spectroscopy (FTIR) were employed for the quantification and characterization of the polymers. Fiber shaped; blue coloured, small MPs (<1 mm) are mostly common. Polyethylene and polypropylene were the dominant polymers. It was concluded from this research that riverine input is the major source of microplastics. Water samples from St. Mary's Island, Udupi Karnataka showed 0.218 particles/L. Blue fibres and white foam were abundant. LDPE, PS, PA, PP, PE and HDPE were dominating polymers (Khaleel et al., 2023).

2.3 State Scenario

Goa being famous for its tourism, fishing and other water activities have a very high chance of being contaminated by plastic. The plastic that lies near the shore in the form of fishing nets, boats, fishing trawlers in the off tourist or fishing season is attacked by waves, sand due to action of wind or the sunlight catalyses the degradation of these plastic material which convert the macro sized particles in micro or nano plastics. Also, there are many industries and housing societies located on the banks of the rivers that flow through the inland of Goa which might release the untreated or treated wastes into the rivers which eventually drain into the estuarine bodies or the open ocean. Up to 80% of plastic comes from land-based sources and the rest from the marine sources such as fishing and shipping (Jambeck et al., 2011). These low-density micro or nano plastics are then carried by waves or wind and are dumped on the shore. Due to their buoyant and persistent properties, microplastics have the potential to be widely dispersed via hydrodynamic processes and ocean currents (Carvalho et al., 2016). therefore, not always the source of the microplastic will be from the vicinity areas, it could be from the far of places. But the amount of plastic pollution is to be detected to see the level of pollution and to take suitable mitigation measures. In a study carried out by Veerasingam et al., (2016) on microplastic pellets along the coast of Goa it was concluded that white microplastic pellets (MPPs) with PE and PP polymer types are abundant in all beaches (Keri, Vagator and Calangute of north Goa, and Colva, Mobor and Galgibag of south Goa. the surface properties of MPPs collected in June were virgin MPPs with low levels of surface oxidation showing that these MPPs were fresh input with short residence time in the marine environment, derived from nearby marine sources. Talking about microplastic fibres in the marine environment could be the result of releasing untreated domestic waste into the coastal waters. This includes the microplastics from personal care products (PCPs) and twenty samples from washing machine effluents (WMEs) (Rathore et al., 2024). A study on spatial and seasonal variation in the estuarine system of river Mandovi and Zuari showed elevated abundance of MPs during the wet season than during the dry season and it was concluded that the probable source of MPs might be anthropogenic inputs and land runoff (Gupta et al., 2021). The presence of microplastics in the estuarine region is proven to be due to anthropogenic activities which was proved by Gupta et al., 2024 which showed a decline of 2 to 7 times in MP concentration was apparent from Before Isolated Pandemic (BIP) to After Isolated Pandemic (AIP) period. An assessment of micro and macroplastics along the west coast of India by Maharana et al., (2020) it was found that the abundance of microplastic particles $(43.6 \pm 1.1 - 346 \pm 2 \text{ items/m2})$ was significantly higher as compared to macroplastics $(21.6\pm3-195\pm6 \text{ items/m2})$ on the Maharashtra beaches followed by Karnataka and Goa, it was concluded that these macros

and microplastics had non-point pollution sources. Fibers and films were abundant in surface waters of Sal River, Goa (Kumar et al., 2019) it was concluded that the sources of MPs in the water could be from the textile industry, domestic plastics, fishing boats located along the river. A study carried out by Kalangutkar et al., (2023) on microplastic pollution in the Chapora River of Goa showed abundance between 0.1 to 0.47 particles/L. The dominant type of microplastic encountered was fibre followed by fragments, films and foam. Polyethylene Terephthalate followed by High Density Polyethylene were the dominant polymers.

<u>CHAPTER-3</u>

METHODOLOGY

3.1 <u>STUDY AREA</u>

Goa lies between the Northern Latitudes of 14°53′54″ and 15°40′00″ and Eastern longitudes of 73°40′33″ and 74°20′13″. Goa is India's smallest state by its geographical area and the fourth smallest by population. Physiographically Goa comprises of the Western Ghats on the east, the central plateau and the coastal plains on the west. The State has geographical area of 3702 Sq. Kms. It has a coastline of 101 km. Geologically the state constitutes the north-westerly extension of the granitoid - greenstone terrain of Karnataka, comprising rocks of Precambrian age. Tourism activity is generally promoted on the coastal areas of Goa. The Tourist season in Goa begins in late September and carries on through early March. As stated by the tourism Minister total tourist arrivals in the State in the year 2023 were estimated to be 80.48 lakh indicating an increase of 17.9 per cent over the previous year (O'Heraldo). 4.03 lakh Foreign Tourist visited Goa during January-November 2023(Press Information Bureau, Govt of India). Bardez taluka which has the beautiful Baga and Calangute beaches, had around 24,56,631 domestic tourists (Gomantak Times).

Goa state as a whole receives mean annual rainfall of about 330 cms. A study revealed that South West monsoon contributes 90% of the annual rainfall of the state. (Metri and Singh 2010). However, rainfall is more in the areas which are nearer to the Western Ghats in east parts of Goa (Tourism department of Goa). Goa receives rainfall from South West monsoon between the months of June to September. The state receives abundant of precipitation during these monsoon months. July is the wettest month of the year with more than 995 mm of rainfall. In the year 2023, highest rainfall was recorded in September which was 3,007.700 mm (CEIC data). August month received 167.1mm of rainfall. This has been possible mainly due to the extremely heavy rainfall of 1836.2 mm recorded during July in 2023.

This made July the wettest month. The mean monthly contribution of each monsoon month to the seasonal total had been: July 35.75%, June 31.28%, August 22.37% and September 10.58% (Times of India, October 2023).

The study area starts from Vagator beach. 25 water samples were collected from the 11 km stretch of North Goa coast which included; Vagator, Anjuna, Baga, Calangute and Candolim beach (Fig). These beaches are visited by lakhs of tourists every year. Along the sampling locations there were shacks, hotels, construction site present.



Figure 3.1: Study Area Map

Sampling sites were selected as per the accessibility and only few prominent locations that had higher chances of contamination were selected. Along the Vagator beach there was a lot of garbage that was seen also during the time of sampling the waves had brought a lot of waste and dumped (Figure 3.2 c & d) along the shore similar situation was with Anjuna beach there were many shacks and hotels present. At Baga beach the first location
that was the mouth of the river Baga (Figure3.4 b) here many fishing nets, boats and kayaks were kept these can contribute to microplastic pollution in a long run, also being the mouth of the river that flows 11 km from the villages that has many houses, hotels and resorts may contribute to microplastics. Calangute (Figure3.4 a, b & c) and Candolim beach at the time of sampling did not show much contamination in the surrounding and the water too, but at some places there were water bottles and polythene bags littered.

NAME OF BEACH	SAMPLE NAME	COORDINATES
Vagator	Vag 01	15°36'22" N 73°43'58" E
	Vag 02	15°36'14" N 73°44'00" E
	Vag 03	15°36'08" N 73°44'02" E
	Vag 04 & HT	15°36'02" N 73°44'01" E
Anjuna	Anj 01	15°35'09" N 73°44'12" E
	Anj 02 & HT	15°34'42" N 73°44'20" E
	Anj 03	15°34'36" N 73°44'23" E
	Anj 04	15°34'30" N 73°44'26" E
Baga	Bag 01 & HT	15°33'43" N 73°44'52" E
	Bag 02	15°33'38" N 73°44'55" E
	Bag 03	15°33'33" N 73°45'00" E
	Bag 04	15°33'27" N 73°45'01" E
Calangute	Cal 01	15°32'44" N 73°45'15" E
	Cal 02 & HT	15°32'43" N 73°45'16" E
	Cal 03	15°32'36" N 73°45'17" E
	Cal 04	15°32'31" N 73°45'19" E
Candolim	Can 01	15°30'59" N 73°45'48" E
	Can 02	15°30'53" N 73°45'49" E
	Can 03	15°30'46" N 73°45'51" E
	Can 04 & HT	15°30'40" N 73°45'53" E

Table 3.1: Coordinates (Latitude and Longitudes) of Sampling Location.



Figure 3.2 (a to d): Vagator beach at the time of sampling. a; covered boats, b; dustbins near the beach & c; garbage dumped on the shore by waves.



Figure 3.3 (a to c): Anjuna beach at the time of sampling. a; shacks along the beach, b; dump of waste and construction material & c; fibres (transparent).



Figure 3.4 (a to c): Baga beach at the time of sampling. a; mouth of Baga River, b; fishing boats and nets & c; waste brought by waves, fishing boats and kayaks.



Figure 3.5 (a to c): Calangute beach at the time of sampling. a; fishing boats, b; Calangute beach & c; dustbins kept at Calangute beach.



Figure 3.6 (a & b): Candolim Beach at the time of sampling. a; abandoned huts & b; smaller fibres (transparent).

3.2 <u>PRE FIELD-STUDIES:</u>

After doing the literature survey, the area selection for studies was done by visiting the beaches and prominent sites which could have been affected by anthropogenic activities and were accessible to collect the samples were chosen. The entire stretch from Vagator to Candolim beach was investigated using Google Earth. Out of the whole 12 km stretch of the coastline, only the prominent areas which were accessible and were used by locals and tourists were selected for sampling. The location was chosen keeping in mind to those which were more accessible to public and had high chances of plastic pollution. 20 locations were selected and pre field visit was carried out to finalize the sampling locations.

3.3 <u>SAMPLING:</u>

The sampling was carried out during the month of August and September (monsoon period). The samples were collected in a 10 L stainless steel bucket and was poured on sieves of size 5mm and 0.25 mm. Total of 100 L of water was poured. The particle from mesh 5mm was discarded and the residue on mesh 0.25mm was collected in a HDPE container which was labelled with the sample name. The time of sample collection, the weather and the description about the surrounding area was noted down. After getting the samples from the field they were kept in the refrigerator to avoid growth of any algae.







Figure 3.7: Collection of Sample. (A; sample collected in stainless steel bucket, B; sieves of size 5mm and 0.25mm, C; litter collected in smaller sieve, D; collected sample in HDPE container)

3.4 LABORATORY ANALYSIS:

The extraction of microplastics from the water samples was carried out by using the standard procedure that is outlined by National Ocean and Atmospheric Administration, (NOAA). The water sample from the containers was transferred into glass beakers which were covered by aluminium foil and kept in oven to dry and reduce the amount of water. For the digestion of organic matter Wet Peroxide Oxidation (WPO) method was used. Fenton's Method; is one of the most widely accepted methods used for organic matter treatment which includes hydrogen per- oxide and Fe2+ reagent (FeSO4.7H20). Fe (II) solution was prepared and used.

Wet Peroxide Method; for the digestion of organic matter, samples were treated using 30% H2O2 and Aqueous Fe (II) solution. This mixture was allowed to rest for a while and was heated to catalyse the reaction and dissolve the organic matter. If the organic matter is not fully dissolved more hydrogen peroxide was added. After this the sample

was kept for 12 hours so that the reaction could take place and all the organic matter was dissolved.

After WPO Density separation was done, here for every 20 ml of sample 6 gm ZnCl2 was added, the reaction was exothermic i: e heat was released hence till the mixture came to room temperature it was allowed to stand. There after the samples were transferred into separating funnels, covered with aluminium foil and kept for 24 hours for separation. After 24 hours the floating solids and settled solids were collected into different beakers. The floating solids were later sieved using standard sieve of size 1mm and 0.3mm, the solids were transferred from the sieve into two separate labelled petri dishes and oven dried. After the drying, microscope examination was done.







Figure 3.8: Laboratory Analysis, (A; dissolving organic matter, B; density separation setup, & C oven drying of petri dishes

3.5 <u>MICROSCOPE EXAMINATION:</u>

- Counting of the microplastics under stereozoom microscope was done using Olympus SZ61 stereo microscope (stereozoom) under 40x magnification. The microplastics were identified using the hot needle test and were counted based on the shapes and colours. After counting the selected microplastics were sent for fourier transform infrared spectroscopy (FTIR) analysis.
- Bruker Alpha II; was used for fourier transform infrared spectroscopy (FTIR) analysis. This technique is used to determine the chemical composition of unknown plastics (polymers) such as fillers, paints, rubber, coatings and so on. Each sample was scanned 20 times (>25 seconds measurement time) and the data was collected between 4000 cm-1 to 400 cm-1. The transmittance of the sample was measured. FTIR analysis measures the range of wavelengths in the infrared region that are absorbed by a material. Fourier Transform Infrared Spectroscopy Analysis can be used to identify unknown materials, additives within polymers, surface contamination on a material, and more. In our study the transmissivity of the sample was measured and the peak values were compared on an online library spectrum
- Scanning Electron Microscope JSM-6360LV/LA (SEM) was used to acquire highly focused images of selected microplastics to study their surface morphology. The SEM is a microscope that uses electrons instead of light to form an image. An electron gun at the top of the microscope produces a beam of electrons. The beam travels through electromagnetic fields and lenses, which focus the beam down toward the sample. When the beam hits the sample, electrons and X-rays are ejected from the sample, there are detectors that collect these Xrays and produced a highly magnified image of the sample on the system. For the

study of microplastics, the selected microplastic particle is first placed on the stub that has a carbon tape the stub was then kept for coating the sample was coated with platinum for 80 seconds after this the stub was kept on the SEM stage for the analysis

• Stereozoom Nikon SMZ745T with camera of 5MP was used to click pictures of the microplastics.



Figure 3.9: Instruments Used in Microscope Examination. (A & B; Stereozoom Microscope, C; Scanning Electron Microscope, D; Interferometer).

<u>CHAPTER-4</u>

RESULTS AND DISCUSSION

Out of the 25 samples that were collected from 20 locations along the 5 selected beaches from the North Goa district was analysed and observed. The abundance of microplastics varied between 1.12 to 0.1 particles/litre. Discussing below the results of microplastics found at every beach.

4.1 Abundance of Microplastics at Each Beach



1) Microplastics at Vagator Beach:

Figure 4.1: Graph showing abundance of MPs at Vagator beach.

The abundance of microplastics at station 01 was found to be 0.26 particles/litre at this station there were boats which were kept covered by plastic sheets (Figure3.2 a) which might be a source of microplastics. Station 02 (0.16 particles/litre) and 03 (0.19particles/litre) has comparatively lower abundance but there were traces of plastics seen along the shoreline also, there were dustbins kept (Figure3.2 b). 04 and 04 (HT) was the high 0.72 and 0.64 particles/litre respectively as it was seen at the time of sampling that there was garbage dumped by the hotel premises and also waves had brought a lot of waste along with it and dumped at the shore (Figure3.2 c & d). Within these two stations

the high tide showed less abundance compared to the abundance at low tide this could be due to the dilution effect that is the volume of water increased while the number of microplastics remained less in the water column.



Figure 4.2: Graph showing type of MPs at Vagator beach.



Figure 4.3: Chart showing type of MPs at Vagator Beach.

The graphs (Figure 4.2 & 4.3) show the abundance (particles/litre) and the percentage of the different shapes of microplastics found at Vagator beach. It was seen that the fibres were

dominant type (1.02 particles/litre) followed by foam (0.43 particles/litre), fragment (0.23 particles/litre), film (0.11 particles/litre) and then pellet (0.02 particles/litre).



Figure 4.4: Graph showing colour variation in MPs at Vagator beach.

Various colours of microplastics were encountered at Vagator, in fibres white and transparent were in equal quantities other colours such as red, yellow, green and black were also found. In film white colour was abundant followed by green. Foam had the highest percentage of white colour similarly for fragment also the highest percentage was of white colour followed by transparent. In the entire study only three pellets were found at Vagator beach, out of which two were blue in colour and one was yellow in colour.

2) Microplastics as Anjun Beach:



Figure 4.5: Graph showing abundance of MPs at Anjuna beach.

The abundance of microplastics at station 01 was 0.31 particles/litre, there was construction going on at this site hence there were cement bags, polythene bags dumped. Station 03 had lower abundance of microplastics (0.14 particles/litre). Now comparing station 02 (LT) and 02 (HT) it is seen that the low tide sample has lower abundance (0.13 particles/litre) as compared to the high tide (0.54 particles/litre) sample this is very evident because during the high tide the water entered beyond the high tide line and carried the garbage and the construction material (Figure 3.3 b) that was dumped along with it, this continuous process could have led to breaking down of macroplastics into microplastic hence the higher abundance. Station 04 had highest abundance (1.12 particles/litre) and the possible reason for this are the shacks that are present at this location (Figure 3.3 a) which had dumped waste nearby which was attacked by the waves and might have led to the microplastics in beach waters.



Figure 4.6: Graph showing type of MPs at Anjuna Beach.



Figure 4.7: Chart showing types of MPs at Anjuna beach.

The figures show the abundance and percentage of shapes of microplastics at Anjuna beach which varied from 1.81 to 0.01 particles/litre. Fibres were the most dominating type (87%) followed by foam 7%), fragment (5%) and films (1%). The source of fibres at Anjuna could be from the scaffolding nets and the plastic sheets used to cover the construction sites and shacks respectively which was seen at the time of sampling. Foam

and fragments could have possibly come from the equipments used in the water sports activity.



Figure 4.8: Graph showing colour variation in MPs at Anjuna beach.

Figure 4.8 shows the colour variations in microplastics at Anjuna beach. The most dominating colours in fibres was transparent other colours included white, red, yellow, green and black. The films that were encountered were only black in colour which might have come from the black plastic sheets used to cover the shacks and construction material during the time of monsoon. Foam was dominated by white colour (80%). Fragments had colours such as white, green and black.



Figure 4.9: Graph showing abundance of MPs at Baga beach.

At Baga beach station 01 showed highest abundance of microplastics (1.08 particles/litre) this was the most prominent location as the sample was collected where Baga River meets the beach (Figure3.4 a) and this is the location where there are fishing boats, nets and the water sports equipments such as the kayaks, boats, jackets (Figure3.4 b & c) and so on are kept keeping all these sources of microplastics in mind also to be considered is the river that might get the microplastics from inland which has resorts and hotels situated all along the banks. Station 01 (HT) having less microplastics abundance could be again due to the dilution effect or due to the increase in water movement that must have dispersed the microplastics in the water column. Station 02, 03 and 04 had abundance of 0.43, 0.15 and 0.56 particles/litre respectively the conditions at all these locations was similar there was very less litter and less tourism activity at the time of sampling.



Figure 4.10: Graph showing type of MPs at Baga beach.



Figure 4.11: Chart showing type of MPs at Baga beach.

As seen in the figures 4.10 & 4.11 abundance of fibres at Baga beach was found to be the highest (2.36 particles/litre) as compared to any other beach, this is because of the fishing nets that were kept at the shore which is the direct source of microplastic fibres in the environment. Next films were abundant these come from the coating done on the boats to keep away rust or growth of marine organisms. Foam was in negligible amount. Pellets were absent.



Figure 4.12: Graph showing colour variation in MPs at Baga beach

Fi 4.12 shows the variation in colours of microplastics along the Baga beach. In fibres transparent colour was dominant but one striking difference that was observed at this location was that there were yellow-coloured fibres were present in high quantity which could have fishing nets as a source during the time of sampling yellow nets were encountered (as seen at location 01). In films white colour was dominating followed by transparent carry bags could be the source of the films. Foam and Fragment showed presence of colours such as blue, green and brown.



Figure 4.13: Graph showing abundance of MPs at Calangute beach.

At Calangute beach station 01 and 02 showed similar abundance of microplastics that is 0.09, and 0.07 particles/litre respectively the conditions at the time of sampling around the station were similar. Comparing the high tide and the low tide values the abundance at high tide was more at Calangute beach as compared to the values shown by the previous beaches the possible reason for this is the increased tourism activity at the time of high tide. At low tide when the sample was collected there was not activity (Figure3.5 a) seen but at high tide there were many tourists seen this could have added to the microplastics from the synthetic clothes, footwear and so on. Station 03 had highest abundance among all (0.16 particles/litre) this is because it was seen at the time of sampling that there were small fibres that had come along with the waves. Station 04 had an abundance of 0.1 particles/litre and here there was no prominent observation that was seen.



Figure 4.14: Graph showing type of MPs at Calangute beach.



Figure 4.15: Chart showing type of MPs at Calangute beach.

The type of microplastics found at Calangute beach varied almost equally between fibre, film and foam. The percent of fibres were more (37%) followed by foam (30%) and films (30%). Fragments were present in a very less quantity (9%). The fibres here have been contributed by the deposition of waves hence it can have a foreign source.



Figure 4.16: Colour variation in MPs at Calangute beach.

Colours seen in fibres were white, transparent and red. In films and foam white was dominating colour. Also red coloured foam was present. Fragments found were transparent (majority) and white in colour.



Figure 4.17: Abundance of MPs at Candolim beach.

Station 01 from Candolim beach showed the highest abundance of microplastics (0.14 particles/litre) as there were small huts present at this particular location which were covered by plastic sheets (Figure3.6 a & b) that might have contributed to the microplastics in the environment. Station 02, 04 and 04 (HT) showed the same value of abundance that is 0.1 particles/litre at the time of sampling while taking the traverse there were no contributors for microplastics seen except for at one location there were small transparent plastic fibres that were encountered (Figure3.6 b). The condition at station 03 was similar to station 01 and may have same sources of pollution.



Figure 4.18: Graph showing type of MPs at Candolim beach.



Figure 4.19: Chart showing type of MPs at Candolim beach.

The only type of microplastic found at Candolim were fibres. No other type of microplastic was found. The source of these fibres can be the plastic sheet which were used to cover the huts present near the beach as shown in the figure 4.18 & 4.19.



Figure 4.20: Colour variation in MPs at Candolim beach.

The colours that were found in fibres were white (most abundant), transparent and some green fibres were also present.



4.2 Abundance of Microplastics in North Goa:

Figure 4.21: Abundance of MPs in North Goa.

The 25 samples that were collected from 20 locations along the 5 selected beaches from the north goa district were analysed and observed. The identified microplastics varied between 1.12 to 0.1 particles/litre. The relatively high concentration is due to the anthropogenic activities at these locations such as hotels, shacks, fishing activity, infrastructure development and tourism. The highest concentration was found at Anjuna 04 station (1.12 particles/litre) as there are many hotels along the beach line and during the time of sampling it was seen that there was garbage dumped in the open space. The second highest abundance of microplastic was found at Baga 01 (1.08 particles/litre) this station is the mouth of Baga river, at this station there were fishing nets, fishing boats and also water sports activity equipments which were kept. The lowest concentration was found at Calangute 02 with 0.07 particles/litre, the possible explanation for this could be as this is one of the most visited beaches the officials has taken proper mitigation measures so that there is minimal waste that is littered on the beach and also it was noted that there were dustbins kept at frequent intervals (Figure 3.5 c). Also to be noted is the location Vagator 04 and Vagator HT (High Tide) were the same sampling site the concentration was high during the low tide (0.72 items/litres) and lower during high tide (0.64 items/litres) the high abundance of these particles overall is due to the presence of hotels around and during the time of sampling it was seen that the waves had bought a lot of waste along with it and dumped on the shore. From the graph of abundance of MPs in North Goa (Figure 4.21) it is seen that the abundance of microplastics have declined that is from station Cal 01 to Can 04 (HT) which is unexpected as these beaches being most visited have shown less amount of microplastics which is a good sign as there are mitigation measures taken by the authorities which were seen at the time of sampling around near the stations.

4.3 Size, shape and colours of MPs:

The microplastics were observed under the microscope and were differentiated based on the size, shape and colours.



Figure 4.22: Graph showing sieve size variation in MPs.

In this study microplastics were classified into 2 sizes, ranging from 5mm to 1mm and 1mm to 0.3mm. The highest concentration of microplastics in the surface water was found in the size range of 1mm to 0.3mm (61.46% of the total MPs found). Followed by the sieve 5mm to 1mm (38.53%). The sieve 1mm to 0.3mm showed higher abundance of fibres 89.51% this could be possibly because massive numbers of textiles micro fibres are released in the environment through laundering via sewage as stated by Acharya et al., 2021 in this study we can relate it as, there are numerous hotels present along the coasts the sewage from the laundering process must be released directly into the open water body, also tourism activities at the beach must have led to the release of these fibres. The high concentration of foam was found in the 5mm to 1mm sized sieve (16.05%). The possible explanation for the bigger size of foam, fragment and films is that these particles must have formed recently and have not gone considerable breakdown therefore they must be larger compared to the fibres in size.



Figure 4.23: Colour variation in MPs in North Goa.

63



Figure 4.24: Percentage of colours of MPs in North Goa.

Colour of microplastics is an important factor in the assessment of fate of pollutants as the colour of microplastic may potentially affect their injection by aquatic organisms (Zhao et al., 2022). The colours can also help in identifying the sources of plastic contamination without initially studying the polymers and can help in implementing mitigation measures. From all the samples the highest concentration was of fibres followed by foam, fragment, films and then pellets. The colours that were in abundance overall were transparent, white and yellow. In fibres transparent colour was dominating and in film, foam and fragments white colour was dominating. Only 3 pellets in total were found, out of which two were blue in colour and one was yellow in colour.

4.4 Comparing High Tide and Low Tide:



Figure 4.25: Graph showing variation in MPs during tides.

A total of 5 locations were selected to study the variation during high tide and low tide. Overall, the higher concentration of MPs was seen during the low tide, the possible reason could be that the water recedes back during low tide and the microplastics that were present in the whole water column becomes more concentrated in the shallow areas including the intertidal zone. And the lower concentration of MPs during the high tide could possibly be due to the dilution effect as during high tide the volume of water increases, leading to dilution of microplastics in the water column also another possibility could be that during high tide stronger water currents and wave action can disperse and transport microplastics away from the shoreline. During low tide fibres were found in abundance and foam and fragment was abundant during high tide. 4.5 Images of Microplastics under Stereozoom:





B











Figure 4.26: Images of MPs under Stereozoom Microscope

The microplastics when viewed under stereozoom microscope with a camera of 5 megapixels were captured, the images are shown in Figure 4.25 A to F and the description is given in table 4.1.

Figure No:4.25	Type of Microplastic
А	White fibre
В	Transparent film
С	Transparent fragment
D	White foam
Е	Blue fragment
F	Cluster of fibres

Table 4.1: Description of images of Microplastics

4.6 Polymer Composition of Microplastics:

5 microplastics (pellet, fragment, foam and two fibres) were selected from size range 5mm to 1mm for FTIR analysis this is because most of the samples were in the size range of 1mm to 0.3mm and were difficult to see by naked eye. Interpretation was done through online reference library. The result of the polymer detection is mentioned below in the table (Table 4.2):

Sr No.	MPs Type	Type of Polymer	
01	Blue Pellet (VAG 03)	Polytetra fluoroethylene	
02	White Fragment (VAG HT)	Polyethylene terephthalate	
03	White Foam (VAG HT)	Polystyrene	
04	White Fibre (ANJ 04)	HDPE	
05	Yellow Fibre (ANJ 04)	HDPE	

Table 4.2:	Polymer	compositio	on of MPs






Figure 4.27: The Infrared spectra of the recognized polymers

The figures (4.27) show the compositional spectra of microplastics that were detected. The white spectrum is the selected reference library and the red coloured spectrum is the one that was identified. The polymers that were detected are; the blue pellet was identified to be a Polytetrafluoroethylene which is commonly known as Teflon used in various applications such as coating of pans, electrical appliances, processing of equipments and so on. This might have entered the beach waters through the sewage system or by the waste dumped along the shore. The next microplastic that was fragment was identified to be Polyethylene terephthalate (PET) this is a strong and resistant polymer used in food packaging, carbonated water bottles which may have come in the environment by dumping of such things during picnics. Foam was identified to be having polymer composition of polystyrene which is used making buoys, floating docks, and life jackets which might have released these microplastic foam in the waters. Bothe the fibres showed composition of High-Density Polyethylene (HDPE) which are used in fishing nets and could have come in the environment through these fishing nets which were seen at the time of sampling.



4.7 <u>Surface Morphology of Microplastics:</u>

A



В







D



Figure 4.28 (A to D): shows surface features of microplastics. A-Fibre, B-Film, C-Foam, D-Fragment & E-Cluster of Fibres

The study of surface morphology of microplastics is important as it helps in understanding environmental impact of microplastics, help us study surface morphology which tells us about the fate and extent of weathering the microplastic has gone through (Zhou et al., 2018). This weathering can lead to the leaching of additives or chemicals from the MPs affecting the aquatic and terrestrial organisms. Rough surfaces may provide more sites for chemical adsorption. All the samples showed different surface features which indicates varying degree of surface abrasion. The figures below show the SEM images of the MPs.

All the microplastics showed different surface features which indicates varying degrees of weathering. The surface morphology of the fibre (Figure 4.27 A) is twisted and tangled also, as seen in the image the fibre looks frayed which must have resulted due to the wear and tear of the fibre in the water indicating to be in the environment for a long period of time. Film (Figure 4.27 B) has cracks formed on the surface which can be due to the hitting of the film to another hard surface, Due to UV radiation or heat. Foam (Figure 4.27 C) is showing a typical porous structure which are varying in size and are rough which indicates that is has been in the environment for quite a long period of time and has undergone significant environment degradation. The fragment's (Figure 4.27 D) top surface is comparatively smooth (indicates that it has undergone extensive abrasion, tumbling and transport) with respect to corners which are rough and indicates some degrees of weathering, fragments being tough take time to weather. The Figure 4.27 E is an image of cluster of fibres which are entangled and intertwined also, the surface of the indivisual fibre is frayed and is rough in appearance this indicated that the fibres have been in the environment from a long period of time and has been entangled during the time of its movement in the water column.

CHAPTER -5

CONCLUSION

After following the standard procedures and identifying the microplastics under microscope 'Olympus SZ61' from the 25 samples across the 5 hotspot beaches of North Goa it was concluded that the surface water showed presence of microplastics that indicates the water is contaminated. The highest abundance was found at Baga beach, followed by Anjuna and then beach the possible reason for this are the sources that contributes to the microplastics such as at Baga beach there are fishing boats and nets kept throughout the year that leads to the degradation of the nets under influence of sunlight, waves, wind and moisture (during monsoon) leads to the breakdown of these items additionally Baga river having length of almost 10 km that originates from the forests of Assagao and drains into the Arabian sea through Baga beach has paddy fields and many hotels/resorts situated on its banks which may contribute to the microplastics as stated by Luo et al., 2019 that open ocean can act as sink when rivers transport pollutants into them. At Anjuna beach the high abundance could be due to the hotels and shacks present along the beach and also many ongoing constructions going on which might have led to the contribution of microplastics. Vagator beach had similar sources as Anjuna that led to high abundance here additionally the waves had brought waste along and dumped on the shore. Contradicting this, at Calangute and Candolim beach the abundance was very less than expected compared to the other beaches. These being the most visited beaches by the tourists and having hotels, water sports activities present showed less percentage of microplastics. The possible reason for this is because at the time of sampling it was seen that there are mitigation measures taken to reduce the amount of waste disposal along the beach there were dustbins kept at frequent interval (as shown in Figure 3.5 c), clean up drives are also held by the official authorities in collaboration with NGOs and local people, CCTVs are also installed to monitor violators (if any). Multi coloured microplastics were encountered which had high presence of transparent, white

and yellow colours. The type of microplastic abundant were fibres followed by foam, fragment, films and then pellets. This result indicates that the major microplastics are derived from the secondary sources as pellets were least in number. FTIR spectroscopy indicated the fibres had High Density Polyethylene (HDPE) composition, foam was Polystyrene (PS), Fragment had composition of Polyethylene Terephthalate (PETE) and pellet had composition of Polyethylene terephthalate (PTFE). Surface morphology of most of the microplastics indicated that they are in the environment from a long period of time as they had rough surface morphology.

As all the plastic items are discarded carelessly in the open environment that leads to the degradation and breakdown of these macro particles into meso/micro/nano particles which become difficult to handle as they enter the soil, water and air. These then eventually end up in the open ocean which acts as a sink for the waste produced in the terrestrial environment. These particles release dangerous elements enter the food chain and cause harmful effects.

This study of microplastics along the beaches of North Goa revealed that there is quite a high amount of microplastic pollution in the surface waters and highlights the significant impact of plastic particles on the beach ecosystem in Goa. Understanding the pathways of microplastics in the coastal area of Goa is very important to control their occurrence and transport. This can be achieved through proper monitoring of the plastic waste around the coast, limiting the usage of plastic products or using biodegradable plastics which should be started at indivisual level. Local administration should impose different techniques such as beach cleaning, installing dustbins, impose penalty to those who litter the place. And most importantly educate and spread awareness among the people about the harmful effects of plastics.

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DISTRIBUTION AND OCCURRENCE OF MICROPLASTICS ALONG THE HOTSPOT BEACHES OF NORTH GOA, INDIA.

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Seal of the School

DECLARATION BY STUDENT

I hereby declare that the data presented in this Dissertation report entitled, "**Distribution and Occurrence of Microplastics Along the Hotspot Beaches of North Goa, India**" is based on the findings carried out by me in the Masters of Science at the School of Earth, Ocean and Atmospheric Sciences, Applied Geology Goa University under the Supervision of Dr. Niyati Kalangutkar and the same has not been submitted elsewhere for the award of a degree or diploma by me. Further, I understand that Goa University or its authorities will be not be responsible for the correctness of observations / experimental or other findings given dissertation report.

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Date:

Place: Goa University

COMPLETION CERTIFICATE

This is to certify that the dissertation report "**Distribution and Occurrence of Microplastics Along the Hotspot Beaches of North Goa, India**" is a bonafide work carried out by Ms. Ashita Salgaokar under my supervision in partial fulfilment of the requirements for the award of the degree of Masters in the Discipline Applied Geology at the School of Earth, Ocean and Atmospheric Sciences, Goa University.

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