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Textural characteristics and abundance of microplastics in the Nethravati river estuary sediments, south-west Mangalore beach, India

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ABSTRACT

Microplastics commonly enter the world's sea through rivers and estuaries. Yet somehow, very little is known about what happens to plastic waste in estuaries. This study provides important information on the Microplastics (MP's) distribution and features in the Nethravati estuary. The present level of knowledge on microplastic trash dispersal in estuaries and their intertidal ecosystems. The MPs identified in this were classified as: source (Primary and secondary MPs), size < 1000 µm (78%), followed by >1000 µm (22%), color (coloured plastic (32%) and white plastic (68%), shape (fibre (96%), beads (3%), fragment (1%). The polymer types detected are Polyamide (60%), polyethylene (33%), followed by polypropylene (5%) and polystyrene (2%). We observed that secondary MPs were the most often recovered microplastics in 22 samples, indicating that primary microplastics had been destroyed by photo-degradation, chemical degradation, and biological degradation. According to the FTIR study, polyamide and polyethylene were the most common microplastics, followed by polystyrene and polypropylene. Future research to track MPs abundance along the Netravati estuary's shoreline can utilize the results of this study as guidelines. The best methods to prevent the abundance of MPs in estuary sediments are to manage solid wastes properly, implement laws, and spread awareness about the cause of MPs to the ecosystem.

KEY WORDS: Microplastics (MP's), FTIR, degradation, Netravati estuary, South-west coast.

INTRODUCTION

The plastic products are an excellent packaging material that is ideal for a variety of applications because of its low cost, excellent oxygen and moisture barrier properties, bio-inertness, and light weight. Globally, the amount of plastic manufactured each year has almost doubled since the 1950s, reaching 322 million metric tons in 2015. In the 1970s, a report on ocean plastic pollution was published, bringing it to the attention of the scientific community for the first time (Carpenter et al., 1972; Colton and Knapp, 1974; Coe and Rogers, 1996). About 80% of the plastic garbage is generated on land, including beach debris. Nearly 18% of the marine plastic waste found in the ocean environment comes from the fishing sector. In addition to other things created of land based resources; the aquaculture business can likewise release plastic into the ocean (Hinojosa and Thiel, 2009). MPs size ranges from 0.5 mm to 5 mm were categorised as macro or mesoplastics (Andrady, 2011; Cole et al., 2011). However, the phrases "microplastics" and "microlitter" have been interpreted differently by

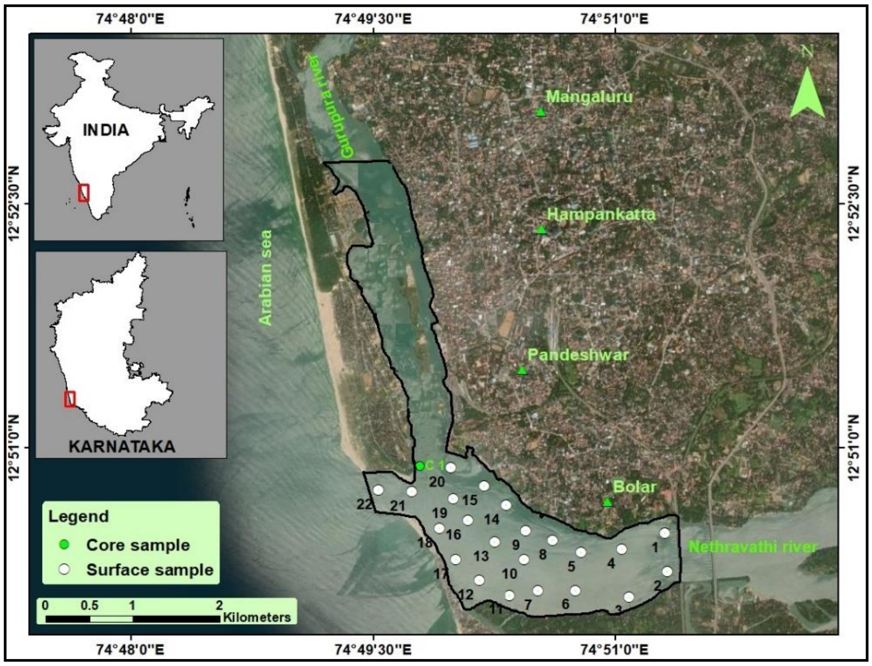


Figure 1. Map showing sample locations in the Nethravati river estuary


Figure 2. Sediment sample collection


Figure 3. Plastic wastes in the Nethravati river estuary

various academics. (Gregory and Andrady 2003) defined microplastics as particles with a diameter between a few µm to 500 µm, while microlitter was defined as practically imperceptible particles that are retained by a 67 µm sieve (≈0.06–0.5 mm in diameter). Microplastics constitute a risk to the aquatic environment due to their prolonged residence periods, tendency for biota eating, and release of hazardous components during decomposition (Andrady, 2011). The Netravati-Gurpur estuary is characterized by a mixed type of semidiurnal tides (Reddy et al., 1979). The Netravati and Gurpur Rivers deliver 12,015 x 106 m^3 and 2,822 x 106 m^3 of fresh water and 14 x 105 and 1 x 105 tons of sediment annually in to the Arabian Sea (Subramanian et al., 1987; Karnataka Irrigation Department, 1986). The mean annual rainfall in the drainage area is 3,954 mm, of which, nearly 87% is received during the southwest monsoon (Murthy et al., 1988). Therefore, currents in the river mouth are controlled by fresh water discharge during the southwest monsoon and by tides during the rest of the year (Reddy et al., 1979). For this reason, ebb flow is


Figure 4. Van Veen grab sampler


Figure 5. Core sample collection

dominant during the southwest monsoon and flood flow during winter and summer. The primary goal of this study is to determine the textural characteristics and the abundance of microplastics in the Netravati River estuary sediments.

Figure 6. River flow direction towards west

STUDY AREA

Dakshina Kannada is a maritime district located in the south-western part of Karnataka state adjoining the Arabian Sea. The geographical area is 4770 sq. km the study area lies in between 12°56'12" - 12° 57' 59" N and 74° 47' 57" - 74°, 48' 09" E. The study area has a tropical climate and the maximum temperature recorded so far is 36° C. The average annual rainfall is 3954 mm out of which 87% is received during the southwest monsoon (Murthy et al., 1988). Wind speed varies from 7.2 to 9.6 km/hr. Mangalore town is the district headquarters, which is divided into five taluks viz. Bantwal, Belthangady, Mangalore, Puttur, and Sulya.

MATERIALS AND METHODS

22 sediment samples were collected using a Van Veen grab sampler and the grid sampling technique. Samples were collected from 400 to 500 m interval and one core sample was collected using PVC pipe measuring 10 feet long. Every 2 inches, the samples were marked, sliced into pieces, and sediment samples were selected randomly for the microplastics analysis. A GPS was used to confirm the sampling locations in the field after being chosen using pre-made grids (Garmin 010-00970-00 eTrex 10 Worldwide Handheld GPS Navigator). To eliminate big debris and retain particles smaller than 5 mm, the wet samples were sieved using a 5 mm screen. The sediment was put in ceramic bowls and dried at a 50° C. To get rid of the big debris and organic plant remnants, the oven dried samples were homogenised and put through a 5 mm testing sieve (Sruthy and Ramasamy, 2017). MPs were recovered from sieved sediment samples in accordance with National Oceanic and Atmospheric Administration (NOAA) guidelines (Masura et al., 2015). To get rid of the organic matter and calcareous component from the surface sediments, 30g of dried sediment was treated with a 30% hydrogen peroxide (H_2O_2) solution followed by 2N HCl. Later, the following density separation technique was used: 50cc of readymade zinc chloride solution (density: 1.58g/cm^3) was thoroughly mixed with the pre-treated estuary sediments. The mixture was filtered using a vacuum pump assembly and 0.45 m of Whatman® nitro-celluloe membrane filter paper. To improve the extraction results, the filtering process was repeated three times. To distinguish between the various polymer compositions in the microplastics, Bruker's Fourier-transform infrared spectroscopy (FTIR) technology was used in conjunction with an attenuated total reflectance (ATR) diamond crystal attachment. Using a setup of instruments and a freely accessible spectrum library, the frequency curve of the microplastic composition was found. Based on the colour, form, and composition of the materials, the recoverable microplastic was categorised using an optical stereo zoom microscope in polarising mode and an online digital camera system (Model: Leica DMC 4500). A pie chart was used to show the distribution of microplastics in terms of colour, shape, size, and composition (Excel, 2007). In order to avoid contamination, all vessels and equipment utilized during MPs extraction were rinsed with distilled water before usage. Similarly, petri dishes used to store the samples were wiped by Kimberly Clark cellulose wipe. All equipment was covered when they were not in use. In addition, the extraction process for a sample was repeated without sediment sample to test the contamination during analysis.

MICRO TEXTURAL STUDIES:

100 g of sediments were socked with H_2O_2 and HCl to remove the organic debris and carbonate coatings, respectively. The samples were sieved at 0.6-Ø interval by using the ASTM sieve setson Ro-tap mechanical sieve shaker. The sand grains of 120 ASTM size were used for the surface micro textural studies. To represent the variability present in a grain (Higgs 1979; Krinsley and Doornkamp, 1973), 3-4 quartz grains in each sample were studied. Quartz grains were examined for their surface microtextural features in Hitachi S-3400N SEM at magnification of ×5 to ×300,000. At the Department of Material science, Vijnana Bhavan, University of Mysore, Karnataka, India.

RESULT AND DISCUSSION

COLOR CLASSIFICATION OF MICROPLASTICS

The MPs are made available to fishes due to its attractive colours, small size, and high buoyancy (Chatterjee and Sharma, 2019). The use of coloured plastic items in daily life, such as clothing, packaging, and fishing equipment, causes MP's of different colours to appear in the silt. (Wang et al., 2017; Zhang et al., 2015). However, weathering during transportation in the surface water can cause the hues to shift (Kalogerakis et al., 2017; Wu et al., 2018). The colour classification of MPs was: coloured plastic (32%) and white plastic (68%) made up the microplastic overall, in core the colour classification is as follows: coloured plastics (97%) and white plastics

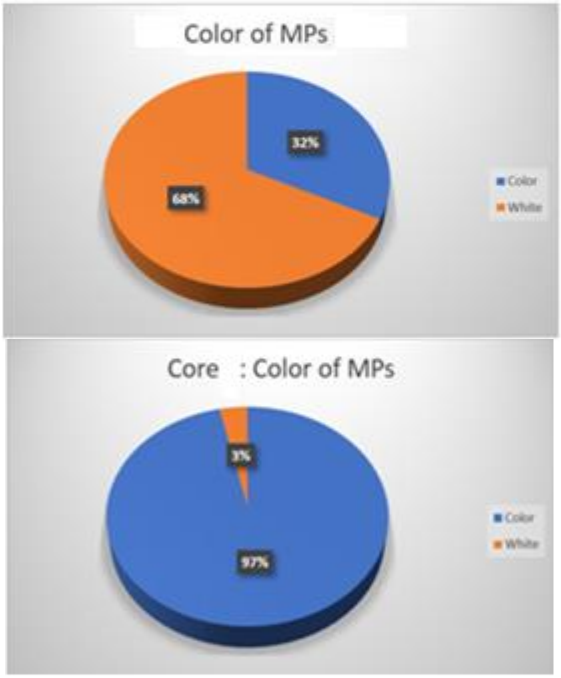


Figure. 7 Pie Chart representing the MPs color towards west

(3%). The transparent variety out numbers the white-colored variety in white plastics and the majority of the fragments were blue and white in colour (Tables 1& 3. Figure.7)

SHAPE OF MICROPLASTICS

Plastics are composed of four main categories: fibres, films, pieces, and pellets (Doyle et al., 2011; Hidalgo-Ruiz et al., 2012) Fibres are likely created by fishing gear and textiles, (Andrady, 2017) and are often poured into drainage canals of the rivers (Peng et al., 2017) both asserted that household waste from using personal care products and washing clothing is a significant contributor to fibre pollution in the environment, and larger plastic items break down in rivers due to mechanical and UV aging (Maes et al., 2017). Figure 8 and Table 1 and Table 3 show the shapes of the MPs. The shapes of MPs are classified as fibre (96%), beads (2%), fragment (1%), and film (1%). In core sediments the MPs are classified as fiber (81%) and fragment (19%) (Table 1 and Table 3; Fig. 8).

SIZE CLASSIFICATION OF MICROPLASTICS

The most popular method for quantifying microplastics is visual counting under an optical microscope, but it is labor-intensive and prone to error. MPs size and distribution are governed by UV light intensity, physical conditions, and plastics durability

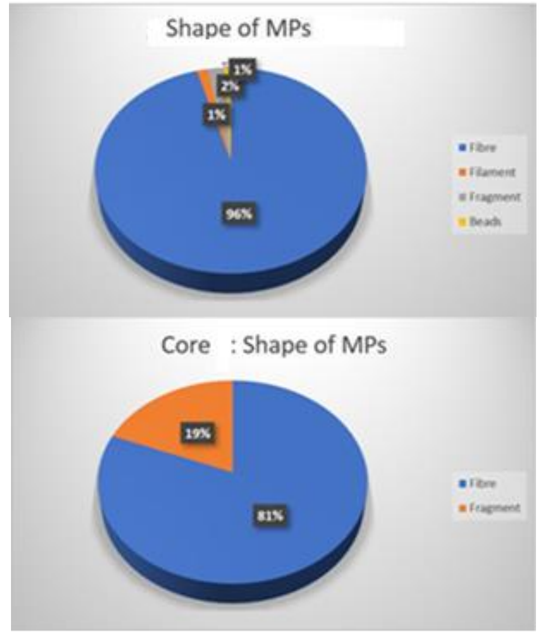


Figure 8. Pie Chart showing the shape classification

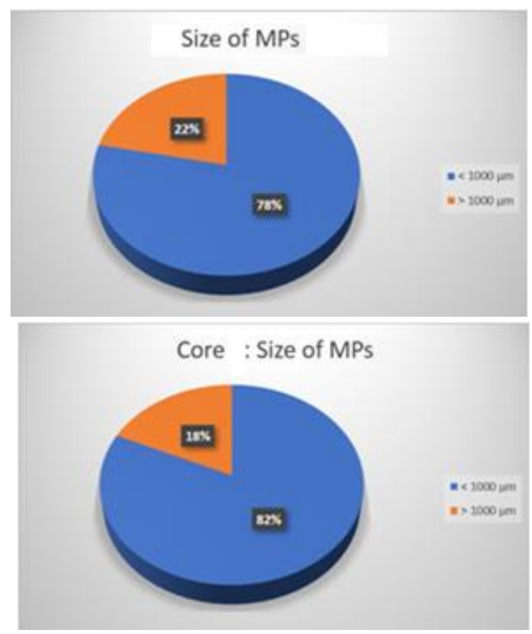


Figure 9. Size classification of MPs

(Thompson et al., 2004; Barnes et al., 2009). The size classification of MPs suggest that the majority of particles fall under < 1000 µm (78%), followed by >1000 µm (22%) in surface sediments. In core sediments MPs are <1000 µm (82%) and >1000 µm (18%). In the sediment core samples the trend of reduced trend of larger microplastics is noted, indicating the difficult vertical mobility capacity of the larger MPs (Fig. 9; Table 1 and Table 3).

COMPOSITION OF MICROPLASTICS

For FTIR analysis, a total of 22 MPs were chosen. Nearly 92.6% to 97.5% of the frequency curve of the MPs composition matched a spectral library for an instrument that is easily available (Fig. 10). The FTIR results revealed that among several types of MPs in surface sediments polyamide, polyethylene, polystyrene, and polypropylene are the predominant polymers. The polymer types in decreasing order are: Polyamide (60%), polyethylene (33%), polypropylene (5%), and polystyrene (2%). Table 2. The polymers in the core samples are: Polyamide (69%) and polyethylene (13%), which are followed by polypropylene (5%) and polystyrene (13%). There are synthetic and natural polyamides. Proteins like those in wool and silk are examples of naturally occurring polyamides. Solid-phase synthesis or step-growth polymerization may be used to create synthetic polyamides, which are then utilized to create products like sodium polyaspartate, nylon, and aramids. Although ethylene may be made from renewable resources, it is often acquired from petroleum or natural gas. Ethylene is the precursor to polyethylene and can be created from these sources as well. Polystyrene have been detected in air, soil, water and sludge. Polystyrene comes from the production of Styrofoam and other products like toys, CDs and cup covers. Polypropylene are the source comes from industries such caps and closures for pallets, crates, bottles, just-in-time storage solutions, bottles and jars for packaging (condiments, detergent, and toiletries), and thin-wall containers (yoghurt cups, disposable hot beverages cups, etc.). Polypropylene is used as rigid packaging.

Figure 10. Pie Chart showing classification of MPs

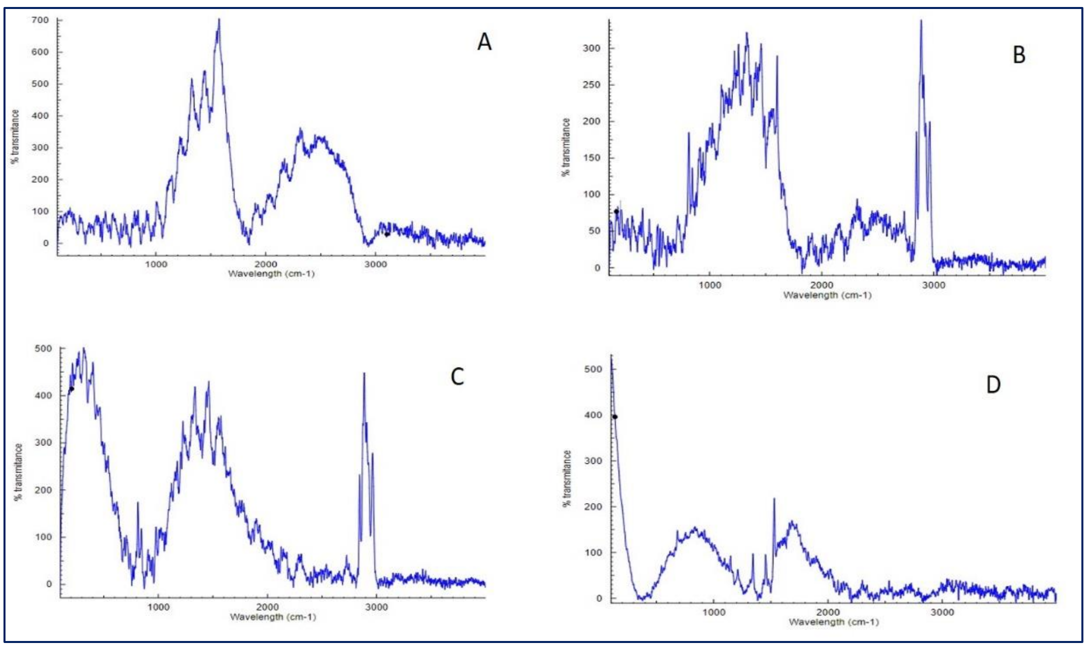


Figure 11. FTIR peaks of MPs: (A) polyamide, (B) polyethylene, (C) polypropylene, and (D) polystyrene

Table 1. Shape and color of microplastics in surface sediments

Shape of MPS	**Fibre**							**Filament**	**Fragment**					**Beads**	**Total**
Colour of (Mps) / S. NO	Transparent	White	Blue	Red	Green	Black	Pink	White	White	Blue	Orange	Pink	Black	Black	
1	2	1	5	6	1	4	0	0	0	0	0	0	0	0	**19**
2	0	1	5	3	1	0	0	0	0	2	0	0	0	0	**12**
3	1	2	9	3	0	1	0	0	0	0	0	0	0	0	**16**
4	0	4	1	4	0	0	0	0	0	0	0	0	0	0	**9**
5	0	9	2	6	1	5	1	2	1	0	0	0	0	0	**27**
6	0	5	3	4	0	0	0	0	0	0	0	0	0	0	**12**
7	0	4	9	5	0	0	0	0	0	0	0	0	0	0	**18**
8	2	5	4	3	1	1	1	2	0	0	0	0	0	2	**21**
9	0	13	5	5	1	0	0	0	0	0	0	0	0	0	**24**
10	1	4	8	5	1	1	0	0	2	0	0	0	0	0	**22**
11	0	1	5	2	1	1	1	0	0	0	0	0	0	0	**11**
12	0	3	7	2	0	2	0	0	0	0	0	0	0	0	**14**
13	1	3	1	3	0	4	3	0	0	0	0	0	0	2	**17**
14	3	0	1	1	3	2	1	0	1	0	0	0	0	0	**12**
15	3	0	4	0	0	4	0	0	2	0	0	1	0	0	**14**
16	1	0	0	4	0	4	0	1	0	0	0	0	0	0	**10**
17	1	0	1	13	1	8	0	0	0	0	0	0	0	0	**24**
18	6	0	8	3	1	1	0	0	0	0	0	0	0	0	**19**
19	6	1	3	2	0	0	0	0	0	0	0	0	0	0	**12**
20	0	0	2	1	2	4	0	0	0	0	0	0	0	0	**9**
21	0	1	1	2	7	7	0	1	0	0	0	0	0	0	**19**
22	2	0	2	5	1	0	0	0	0	0	0	0	0	0	**10**
Total	**29**	**57**	**86**	**82**	**22**	**49**	**7**	**7**	**6**	**2**	**0**	**1**	**0**	**4**	**351**

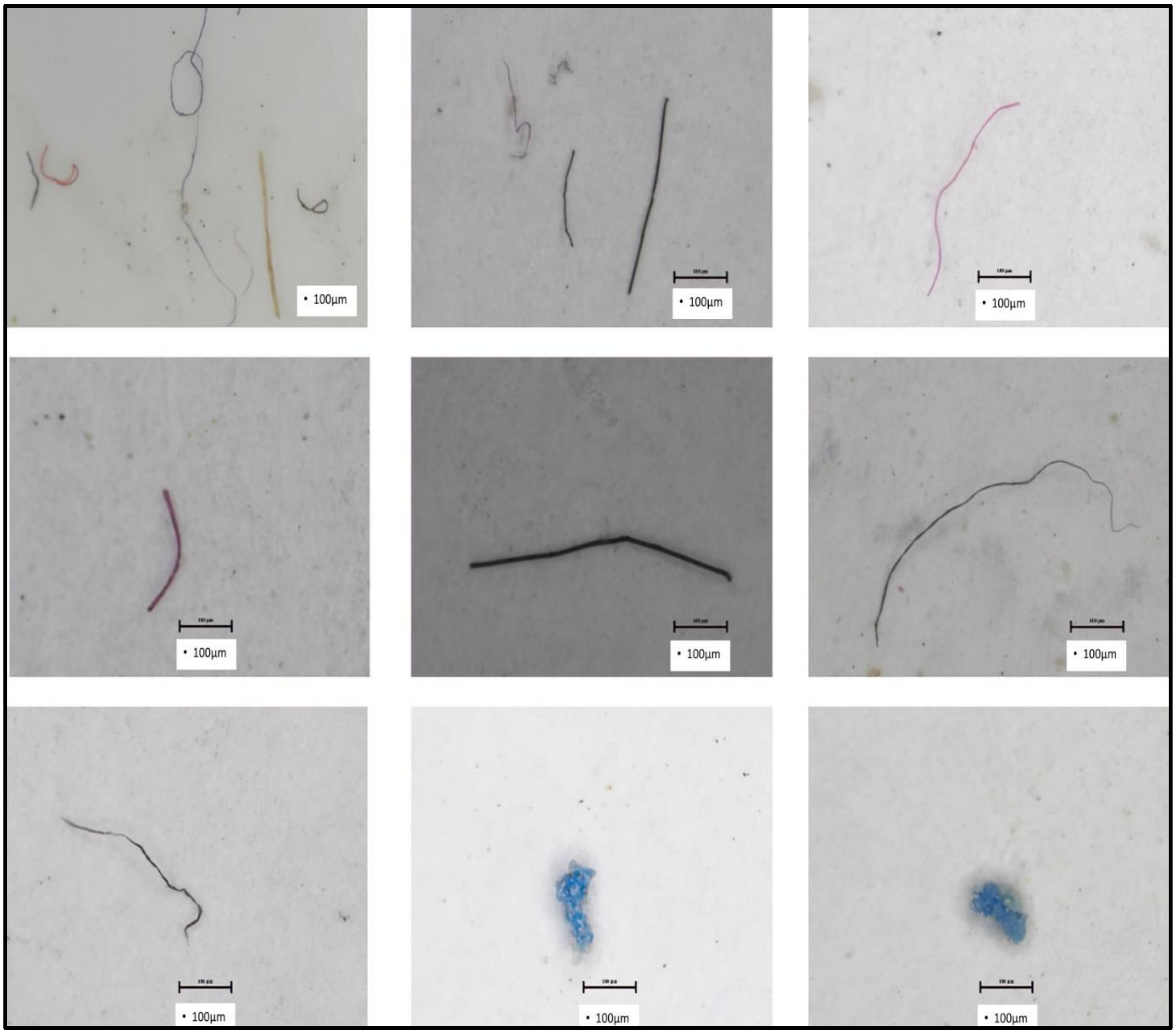


Figure 12. Fibre, filament, and fragments in the Nethravati River estuary sediments

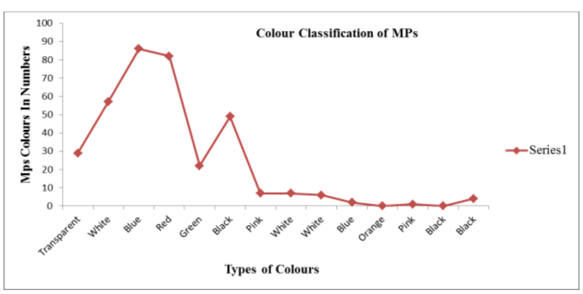


Figure 13. Color versus abundance of MPs

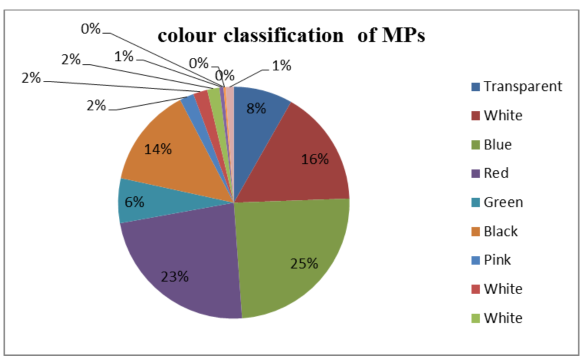


Figure 14. Pie chart showing various colors of MPs

Table 2. Shape and color of microplastics identified in core sediments

Shape of (Mps) / Colour of (Mps) / S. NO	Depth in Inch	**FIBER**					**FRAG MENT**	**Microplastics count in numbers**
		Transparent	Red	Blue	Green	Black	Blue	
1	3.6	5	2	1	0	8	1	**17**
3	10.9	0	0	0	0	3	9	**12**
5	18.15	0	0	0	0	6	7	**13**
7	25.41	0	0	0	0	3	5	**8**
9	32.67	0	3	5	0	7	5	**20**
11	39,93	0	0	3	0	4	0	**7**
13	47.19	0	6	3	2	9	0	**20**
15	54.45	0	2	2	0	5	0	**9**
17	61.71	0	2	1	1	3	0	**7**
19	68.97	0	5	2	0	3	0	**10**
21	76.23	0	2	0	0	2	0	**4**
23	83.49	0	3	0	0	1	0	**4**
25	90.75	0	2	0	0	1	0	**3**
27	98.01	0	1	0	0	0	0	**1**
29	105.27	0	2	0	0	0	0	**2**
31	112.53	0	1	0	0	2	0	**3**
33	119.79	0	2	1	0	0	0	**3**
Total		**5**	**33**	**18**	**3**	**57**	**27**	**143**

MICROTEXTURAL FEATURES OF SAND GRAINS

Quartz, being a common rock-forming mineral, which is resistant to weathering. The sediment grain transportation and depositional processes are reflected by the type of microtextures preserved on quartz grain surfaces (Margolis and Kennett, 1971; Krinsley and Doornkamp, 1973). The mechanical and chemical processes affect sediments during transport and thus the grain surfaces are modified (Al-Saleh and Khalaf, 1982; Armstrong-Altrin, 2020; Armstrong-Altrin et al., 2021, 2022). The quartz surface microstructure of sand grain reflects the depositional environment and differentiates the fluvial, marine, aeolian and glacial environments (Chakroun et al. 2009; Newsome and Ladd 1999). Geologically, Netravathi River basin consists of gneisses, charnockites, felsic and mafic dykes, meta sediments, laterites, alluvium and sand deposits of marine and fluvial origin (CGWB, 2012). Different types of microtextures with mechanical, chemical, and morphological characteristics were identified in this study.

Table 3. Size and polymer types of MPs in surface sediments							
S.No	**< 1000 µm**	**> 1000 µm**	**(PA) polyamide**	**(PP) polypropylene**	**(PE) polyethylene**	**(PP) polypropylene**	**Total**
1	15	4	13	1	5	0	**19**
2	9	3	8	1	3	0	**12**
3	12	4	11	0	5	0	**16**
4	8	1	7	0	2	0	**9**
5	22	5	15	2	9	1	**27**
6	8	4	8	0	3	1	**12**
7	13	5	8	2	7	1	**18**
8	17	4	11	2	7	1	**21**
9	19	5	12	1	11	0	**24**
10	18	4	15	0	7	0	**22**
11	8	3	6	1	4	0	**11**
12	11	3	8	2	4	0	**14**
13	13	4	11	1	5	0	**17**
14	11	1	7	1	5	0	**12**
15	10	4	10	0	4	0	**14**
16	9	1	8	1	1	0	**10**
17	20	4	12	3	7	2	**24**
18	11	8	9	2	7	0	**19**
19	10	2	6	1	5	0	**12**
20	7	2	5	0	4	0	**9**
21	14	5	11	1	7	0	**19**
22	7	3	8	0	2	0	**10**
Total	**272**	**79**	**209**	**22**	**114**	**6**	**351**

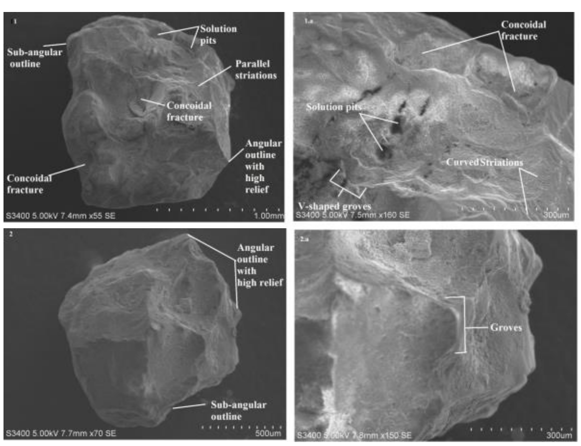
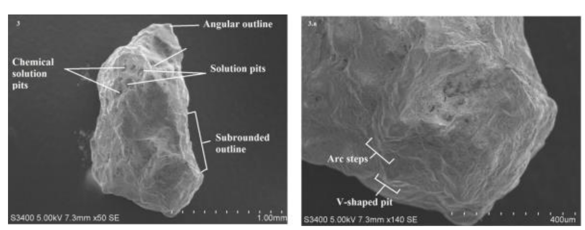
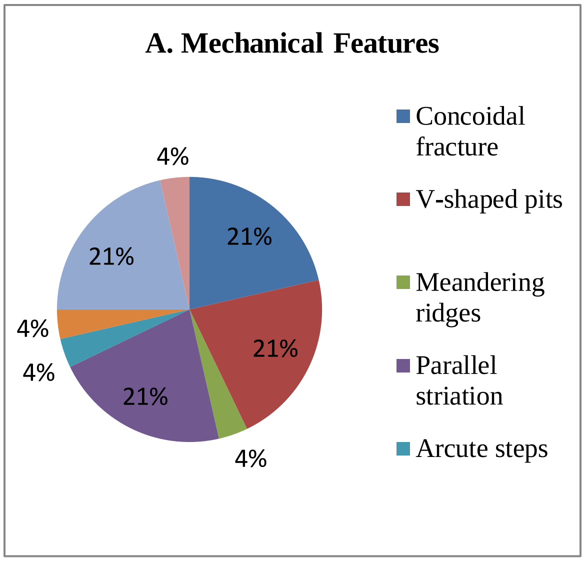
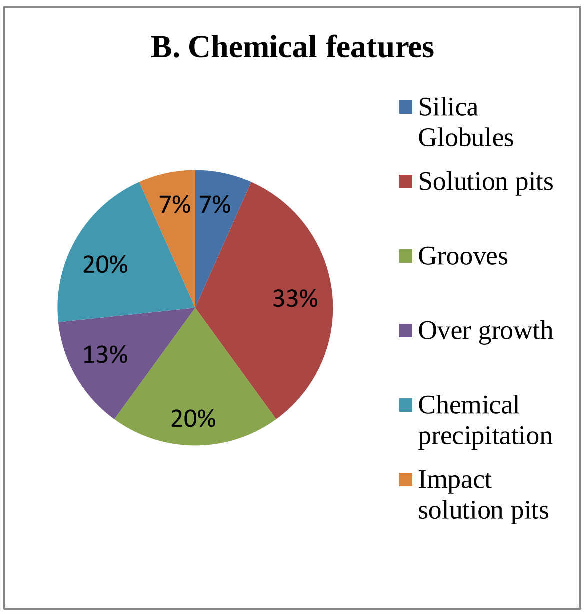


Figure 15. 1 and 1a) Surface micro textures of sand grains showing sub-angular outline, solution pits, parallel striations, and conchoidal fracture. 2) Angular out line with high relief and curved striations. 2a) V-shaped grooves. 3) Angular outline with high relief, sub-angular outline, grooves, chemical solution pit, angular out line, solution pit, sub-rounded outline. 3a) arc shaped steps and V-shaped pit.







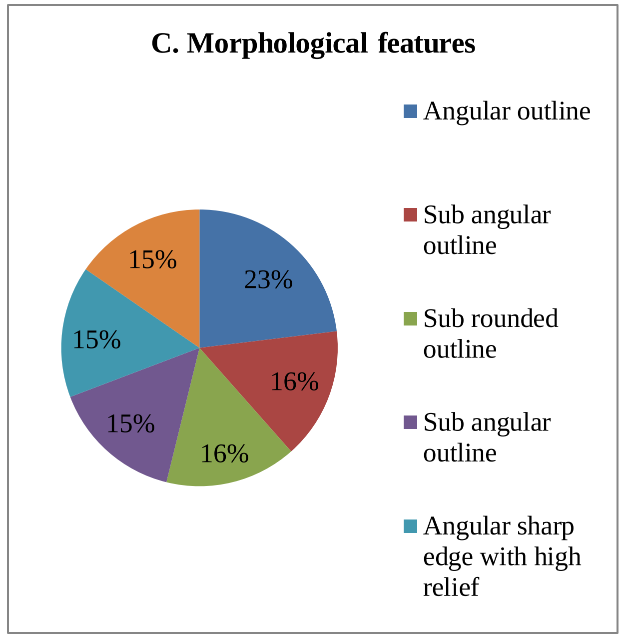


Figure 16. Microtexture types and morphology of quartz grains. A) Mechanical features, B) chemical features, and C) morphological features

MECHANICAL FEATURES

The mechanical features like conchoidal fractures, V-shaped pits, meandering ridges, parallel straight, V-shaped striations, linear fracture line, curved arcuate, arc-shaped and irregular-stepped furrows are recognized on quartz grain surfaces. These features are formed during erosion or weathering processes, grain to grain abrasion and collision during transportation of sediments from their source to the depositional basin. Irregular steeped furrows and meandering ridges are derived from the crystalline source rocks, particularly the straight scratches produced by the high energy environment (Krinsley and Margolis, 1969; Krinsley and Doornkamp, 1973; Krinsley and Marshall, 1987). The V-shaped features are formed by the grain-to-grain collision (Manickam and Barbaroux, 1987) and parallel orientation of groove features might have been caused by collision between two grains during transportation (Krinsley and Donahue 1968; Armstrong-Altrin, 2020). The abundance and size of the V-shaped pits are attributed for long duration with high intensity of subaqueous agitation (Manickam and Barbaroux, 1987). These features are associated with straight and curved scratches suggesting that quartz grains are transported by the fluvial environment (Krinsley and Takahshi, 1962; Krinsley et al., 1964; Madhavaraju et al., 2022) (Fig. 15 and Fig. 16a).

CHEMICAL FEATURES

The chemical precipitation features are associated with silica globules in the sand and are formed by the precipitation of silica from chemical solution due to the long residence of sediments in the depositional basin (Udayaganeshan et al., 2011) under a silica saturated environment (Armstrong-Altrin and Natalhy-Pineda, 2014). The sands of variable grain size with rounded and sub-rounded shapes are attributed to the influence of contaminated sea water (Krinsley and Doornkamp, 1973; Armstrong-Altrin and Natalhy-Pineda 2014). The parallel- grooves on quartz grains are formed by a chemical process at reduced water velocity (Joshi 2009). Over growth, chemical Precipitation features and impact solution pits are derived from the source rock by an action of weathering process (Bull 1977; Bull et al., 1980; Orr and Folk, 1983; Ramos-Vázquez and Armstrong-Altrin, 2020, 2021) (Fig. 15 and Fig. 16b).

MORPHOLOGICAL FEATURES

The quartz grains are showing angular and sub-angular outlines (Fig. 15). Showing angular sharp edges with high relief arcuate steps suggest that the sediments have undergone short transportation and rapid deposition, as a result of which, angular outline is gradually decreased by the action of transportation resulting in downstream rounding of quartz grains.

SOURCE OF MICROPLASTICS

The two main categories of microplastics are microscopic commercially produced particles, including those found in cosmetics, and fibres shed from garments and other materials like fishing nets. Due to the breakdown of larger plastic objects such as water bottles, secondary MPs are created. The primary cause of this breakdown is exposure to external factors, particularly sun radiation. In the present study, all the samples were secondary MPs, indicating that the MPs are the degraded remains of primary microplastics through various degradation processes such as photo-degradation, chemical-degradation, and biological degradation.

CONCLUSIONS

White colored MP's are most common in Nethravati estuary. In core sediments, the shape classification of MPs indicates that the dominant shape is fibre followed by fragment in core. The abundance of fibre indicates the degradation of fishing nets and long transport due to its morphology and the hydrodynamics of the estuary. The size classification of the MPs denotes that the smaller MPs are dominant (<1000 µm) compare to larger MPs. This is due to the greater accumulation capacity of the smaller MPs in the interstitial spaces of a sandy substrate than the inefficiency of the larger microplastics to accommodate them. Polyamide and polyethylene are the most abundant polymer types, followed by polystyrene and polypropylene. Samples numbers 5 and 9 have a greater number of microplastics; in 30 g of sediments, there are 24 to 27 MPs are identified, which is due to fishing and industrial operations. The proximity of metropolitan areas and the sampling location distance from the coast contributed MPs in sediments. The best way to solve this issue is to manage solid waste properly, implement laws that may be adopted, and create an awareness about the defect of MPs to the ecosystem.

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