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Abstract

In the present-day context, micro-plastic particles in a marine environment are increasingly ubiquitous and of considerable persistence. In line with the micro-plastic pollution, the present contribution is devoted to the investigation of micro-plastic particles (MPs) along the urban sandy beach called Marina, the renowned longest beach in India. Along the sea coast of about 5 km, the quantification of micro-plastic particles using optical microscope evidenced the granular, filamentous, filmy and tubular fragments in a total of 72 marine samples including those filtered in the marine water column (WAT; 24 samples), those found in wet sediment (WET; 24 samples) and those found in dry sand (DSS; 24 samples). The filamentous-typed plastics of 79%, 57% and 52%, respectively in WET, WAT and DSS dominated over the other granular and tubular types. The micro-plastic particles were in the range of 60 – 820 items per m^3, 60 – 1620

items per kg and 20 – 1540 items per kg for WAT, WET and DSS, respectively. The standard deviation for the microplastics abundance were 193.1, 396.6 and 364.6 for WAT, WET and DSS respectively. Upon visual inspection, the micro particles were observed in eight different colors and most of the samples were found to contain two different fragment types. Apart from the optical microscopic examination, the micro-plastics particles were studied by scanning electron microscope (SEM) coupled with elemental analysis by energy dispersive spectroscopy (EDS). The energy spectral graphs displayed that the micro-filaments and micro-tubular particles contained polyesters and fluoro-polymers. The presence of few micro-filaments of polypropylene and polyethylene was also evidenced from their atomic percentage values of carbon of about 88% and 93%, respectively. The presence of fluoro-polymers and polyesters was also confirmed by Fourier Transform Infra-Red (FTIR). Excepting the fluoro-polymers, the micro-plastics particles contained elements arising from sea water (Na, Cl, S, Mg, Ca, K). Heavy metals such as Cu, Mn, Mo, Ru and Rh were observed in micro-tubular fragments. Fe and Ti elements were detected with the highest atomic percentage of 17.19 and 19.84 in micro-tubular fragments. All the observations and analyses give a photography of the nature and the spatial distribution of MPs along this Indian beach.

Key words: *Microplastics, Microscopic quantification, SEM/EDS, FTIR*

1. Introduction

The production of plastic materials across the globe in the last seven decades was escalated to about 190 times from 2 million tons in 1950 to 380 million tons in 2015. In addition, the disposal amount also parallelly increased to about 99 million tons and expected to be tripled by 2060 (Geyer et al., 2017; Lebreton and Andrady, 2019). The plastic processing industries in India are about 30,000 units with four million employees. And about 70% of plastic packaging

items are turned into waste in a short span. Especially the largest share of plastic waste in India is contributed from chips and confectionary packets (19%) whereas bottle caps and lids (12%), PET bottles (10%), garbage bags (8%), packaging (8%) and the remaining 43% are from the other sources (AIPMA, 2019). India generated about 26,000 tons per day in 2017 – 18 (CPCB) and from which about 60% were recycled. However, the remaining went as litters on roads, in landfills or in streams. It is estimated that about eight million tons of plastic waste entered into the ocean every year and in particular the river Ganga in India alone contributed to about 115,000 tons of plastic into the ocean in 2015. Ganga is among the top 20 polluting rivers in Asia (Lebreton et al., 2017).

Next to Europe and USA, India contributes to about 5% of the global clothes production. Among the Asian countries, India is the chief producer of synthetic fibers along with China. As a consequence of the plastic waste generation with subsequent fragmentation from all possible sources, the pelagic plastic fragments smaller than 5 mm (microplastics) are destined to open oceans which include polar waters (Isobe et al., 2017), marginal seas (de Lucia et al., 2014) and coastal waters (Isobe et al., 2019). Under the class of primary micro plastics, the synthetic clothing and fabrics could release micro fibers (MFs) in wastewater and about 90% of micro-plastic particles (MPs) are retained during the wastewater treatment process (Ziajahromi et al., 2016). In line with this, studies corroborated the entry of MPs into oceans from the wastewater and undergo further breakdown in surface and deep ocean waters, deep sea sediments (Cole et al., 2011; do Sul and Costa, 2014), oceanic gyres (Cozar et al., 2014) and fauna (Taylor et al., 2016). Simultaneously, the release of non – retained and unaltered MPs into the near shore marine environment from sewage plants is also highly accountable (Grondahl et al., 2009) for the dilapidation of marine ecosystem. The contribution of primary and secondary MPs to the overall

levels in marine environments was investigated by various researchers (Essel et al., 2015; Lassen et al., 2015; Magnusson et al., 2016). Mehlhart and Blepp (2012) acknowledged that the land-based sources such as coastal populations, industry and agriculture are the major plastic transmitting sources in causing the marine plastic debris. It is likely to attribute the aeolian transport which is able to distribute small MPs that end up with the deposition on the dry and wet seashore sediments.

Cauwenberghe and Janssen (2014) reported that an average of 11,000 microplastic pieces were consumed by the shellfish. While considering similar plastic ingested sea foods by humans, many diseases such as hormonal disruption, reproductive problems, damage in nervous tissue, liver and kidney (Lamichhane, 2018), respiratory inflammation, pulmonary fibrosis and cancer (Carr, 2017) can occur. In a review report (Mishra et al., 2019), there is an estimated amount of 1.5 trillion of MFs, to date, present in the ocean and ingested by marine animals which make hazardous the lives of aquatic animals. There is a tremendous increase of about 21 times in the MFs (15 to 311 million tons) in the sediment samples of Indian Ocean in the past 50 years (Woodall et al., 2014). There are practical difficulties experienced in the filtering systems or municipal treatment plants due to the small size of MFs that are able to pass through and enter the watershed (Brannan, 2014). The presence of MPs in the stools of participants from different parts of the world revealed that an average of 20 particles quantified per 10 g of excreta (Mishra et al., 2019).

MPs act as potential vectors with the dual nature sorption and desorption of organic and inorganic contaminants. The adsorbed contaminants happen to be absolutely detrimental when the microplastics are ingested by organisms at virtually every tropic level which includes zooplanktons, mussels and lugworms, cetaceans, fish, seabirds and large sea mammals (Cho et

al., 2019; Sun et al., 2018; Koelmans et al., 2016; Scopetani et al., 2018). The low concentration of organic sorbates favors adsorption onto the surface of MPs (Hartmann et al., 2017). Fred-Ahmadu et al. (2020) detailed the factors which influence the sorption of organic contaminants onto MPs such as polymer type, crystallinity, size, pH of the medium, ionic strength, salinity, age and degree of weathering and the chemical properties of the contaminant. These MPs acting as harmful vectors are regarded as multiple stressors due to their physical and chemical impact on organisms (Rochman, 2013). As a consequence of ingested MPs into the cells by endocytosis, effects such as histological alterations, inflammatory reactions and ecotoxicological responses (at cellular, biochemical and molecular levels) and modulations of physiological functions were observed (Karami et al., 2017; Peda et al., 2016). Liu and coworkers (Liu et al., 2019) presented the results on the adsorption behavior of pristine and artificially aged microplastics and explored the higher sorption efficiency of aged PS and PVC polymers than of the pristine. Verla et al. (2019) reported a review on the quantified levels of micro-plastics with various implications to human and other living beings.

There are limited studies in view of microplastic exploration in marine samples have been surveyed. The study on beach sediments along the southeast coast covering 25 locations at a stretch of 1076 km revealed the domination of line/fibers and the FTIR evidenced the prevailing polyethylene, polypropylene and polystyrene polymers along the coastal tract (Karthik et al., 2018). In the Gulf of Mannar of Rameswaram Island, micro plastics in 20 sediment samples were visually examined along with FTIR characterization. These samples revealed the dominant polypropylene variety among the other polyethylene, polystyrene, nylon and PVC polymers as a main consequence of aeolian transportation (Vidhyasagar et al., 2018). Polyethylene was the most dominating type among the other types at three different locations

along the Indian coast (Tiwari et al., 2019). Sathish et al. (2019) quantified the microplastics in five beach sediments of Tamil Nadu and explored the dominance of polyethylene (81%) with the maximum amount of 309±184 items kg^{-1} in the sample of Marina beach. The collected yellow colored pellets from Chennai coast by Mugilarasan et al., (2017) revealed their photo oxidative damage and longevity in the marine environment and found to be more weathered which resemble the adsorption of persistent organic pollutants (POPs) from the environment.

From India, based on the Scopus record, very limited number of 26 publications in the area of microplastics research are published from 2016 to 2020. Microplastics research in water, sediments, fish along the Southeast and Southwest Coasts (Vidhyasagar et al., 2018; Daniel et al., 2020), beaches (Karthik et al., 2018), lakes (Sruthy and Ramasamy, 2017) and rivers (Amrutha and Warrier, 2020) across India were reported. In view of an intense research along the seashore stretch of Marina beach, the present contribution claims to be the main deep investigation on a large beach surface. In the present work, MPs were isolated from 72 marine samples such as water, wet and dry sands at defined transects, they were quantified and observed, and then characterized for ascertaining the chemical structure of those plastic particles.

2 Materials and methods

2.1 About the study area

Marina beach is the natural urban beach along the Coramandel Coast on the Bay of Bengal which was renovated in 1880s. It is the longest of Indian beaches and the world's second longest beach which extends from the near Fort St. George in the North to Besant Nagar in the South and spans for a distance of 13 km. This sandy beach is with the average width of 300 m and the width at the widest stretch is 437 m. It is one of the most crowded beaches in India which

attracts about 20,000 people per day especially in the summer season.

2.2 Field work and sampling

Sampling of the marine samples along the coast was carried out between the stations, Dr. MGR Memorial (Triplicane) and Santhome Cathedral Basilica, (Mylapore) for a stretch of about 5 km during December 8, 2019. Seventy-two samples were collected along the seashore with the distribution of 24 samples each for WAT (sea water sample), WET (wet sand sample) and DSS (dry sand sample). The WAT and WET (line transect) sampling was done at the same point along the coast by maintaining the distance of 0.2 km between the sampling points. However, the DSS sampling was carried out along the parallel line transect which is 0.2 km away from the sampling line of WAT and WET. Each transect of 50 × 50 quadrant to a depth of 10 cm by stainless steel tweezers was made by scooping the surface sand initially with a small metal shovel. The GPS coordinates were recorded for each sample and tabulated in the supplementary section (Table S1).

2.2.1 Micro plastic extraction process

During the analytical process, due care was taken to avoid cross – contamination (Browne et al. 2011; Woodall et al. 2014). At the end of filtration process, the samples were immediately covered and/or wrapped using aluminum foil to keep them safe without contamination (Cole et al. 2014). As per the directions of Peng et al. (2017), the lab windows were closed at the time of experimental works. The reagents used for the extraction procedure were sodium iodide NaI, hydrogen peroxide H_2O_2 (30%) and iron (II) sulfate $Fe(SO_4)$ supplied by Merck, India. All solutions were made with deionized water.

A. Extraction from WAT samples

Based on the procedure (Song et al., 2018; Eo et al., 2019) with slight modifications, 100 L of water where WAT samples were isolated were passed through a wire mesh (SS 304; diameter – 8 inches; aperture – 10 µm). The filtered residues were completely transferred using a minimum volume of HPLC grade water into a glass beaker of 500 mL capacity and dried at 60°C in a drying oven until a complete drying. To these residues, 20 mL of 30% of hydrogen peroxide and 20 mL of a freshly prepared 0.05 M iron (II) sulfate solution were added and the solutions were shaken for 30 min using a water bath shaker maintained at 75 °C for the removal of organic matter. Further, some additions of H_2O_2 was made to ensure the complete oxidation of organic matter. After 30 min of shaking, the resulted mixture was allowed to cool and settle for few minutes. Then 300 mL of freshly prepared saturated solution of NaI (Crichton et al., 2017) were added to the above filtered mixture (through a wire mesh of 10 µm) and stirred for 30 min at 300 rpm and then allowed to settle for 24 h. Finally, the floating and suspended particles were subject to filtration using a Whatmann® grade GF/C filter (1.2 µm pore and 47 mm diameter) using a vacuum pump. The filtered particles were twice rinsed with deionized water.

B. Extraction from WET and DSS samples

About 500 g of the WET and DSS were collected in aluminum bags and dried at ambient temperature for two weeks. Then the sand samples were dried at 60°C for 24 h. The dried sands were sieved through a 0.3 mm sieve (NOAA, 2015).100 g of the sieved dry sand was slowly transferred into 200 mL of 30% H_2O_2 followed by 30 min of shaking in a water bath shaker at ambient temperature and the mixture was left overnight (to remove the natural organic matter). Then, the sand was dried at 60°C and after addition of 300 mL of saturated NaI solution, the mixture was stirred (~600 rpm) for 10 min (Filgueiras et al. 2019). Then the above mixture was allowed to settle for 30 min to facilitate the lighter dense materials to float in surface solution or

remain as suspension. The settled heavily dense materials at the bottom were repeated with the same procedure using 100 mL of NaI solution for another two times. The resulting supernatant was filtered as detailed for WAT samples. Finally, the filter paper was dried in a Petri dish at the ambient temperature and examined for optical microscopic and spectroscopic studies.

2.2.2 Micro plastics identification and characterization

The dried filters were inspected using the stereo microscope (MA748 + MA751 + MA730 (qty#2) + RZ-B + MA742 + RZT/LED base) supplied by Meiji Techno – RZ series, Japan which offers high resolution images at magnifications ranging from 3.75X to 300X. Scanning electron microscopy (SEM) and elemental analysis by Energy Dispersive Spectroscopy (EDS) were carried out with a Jeol JSM 6400 equipment operating at an accelerating voltage of 20 kV. Before these observations and analyses, the micro-plastic particles were coated by a thin layer of gold. The micro-plastic particles were characterized to understand the presence of various functional groups using Perkin Elmer FTIR spectrophotometer in the range of 4000 – 400 cm^{-1}.

3. Results and discussion

3.1 Consolidated profile of micro plastic particles (MPs) in the marine samples

Based on microscopic investigation (Fig. 1A), the minimum number of MPs were quantified to be 60 items each for WAT (per m^3; sample #10) and for WET (per kg; sample #14) samples, but the DSS category were recorded with a very minimum of 20 items per kg (sample #15). On the other hand, the maximum items of MPs for WAT, WET and DSS were 820 items per m^3 (sample #23), 1620 items per kg (sample #2) and 1540 items per kg (sample #21) respectively. The abundance of MPs with a standard deviation of 193.1, 396.6 and 364.6 for

WAT, WET and DSS is shown in Table – 1. The quantified MPs in wet sediments (WET) were found higher than that of dry sand samples (DSS). The average values in these marine samples along the coastal stretch of Marina were observed in the range of 248 – 402 items per m^3 or kg. The report of Tiwari et al (2019) revealed that the average micro plastics count of beach sands at Mumbai (220 ± 50 fragments per kg), Tuticorin (181 ± 60 fragments per kg) and Dhanushkodi (45 ± 12 fragments per kg) were found to be lesser than the present findings of 402 fragments per kg (WET) and 365 fragments per kg (DSS). More importantly, these dispersed microplastics at various sizes and shapes are governed by biotic and abiotic sources, debris quality, degradation type (due to UV light or other) and dynamics (exposure time) of macro plastics (Andrady, 2011), tendency of wave action/wind and the sinking rate of plastics (Critchell and Lambrechts, 2016). The abundance in microplastics in this coastal stretch was due to the maximized urbanization of the Chennai City which is one among the major metropolitan Cities in India. In pertinent to the present observation, Karthik et al., 2018 reported the possible contamination of microplastics is due to the connectivity of river mouths at the close proximity of beach sampling stations at Chennai. Most of the plastic particles belong to the filamentous type with 57% and 79% respectively in WAT and WET samples. Conspicuously, the filamentous (MFs) and granular (MGs) types of MPs in the case of DSS were closer to each other with 52% and 46% respectively. The tubular (31%) and granular (16%) types of micro fragments were observed respectively in WAT and WET samples by following the filamentous type (Fig. 2A). Unlike WAT samples, the WET and DSS were found with the micro tubular (MTs) fragments in minor percentages. Evidently, the dominance of fibers followed by granules and films in the three Indian Coastal environments (Mumbai, Tuticorin and Dhanushkodi) was explored by Tiwari et al. (2019) and the sediment samples at Palolem beach, Mumbai (Indian Ocean region) was

substantiated with the maximum fibers (Balasubramaniam and Phillott, 2016). The predominance of micro filaments (MFs) in the present study is corroborated with the other findings (Enders et al., 2015; Gallagher et al., 2016; Lahens et al., 2018; Zhao et al., 2019). Regular consumers of sea salt were reported to ingest about 37 filamentous particles per day apart from sea foods containing MPs. Besides, the presence of filamentous particles in honey, bear and sugar through air transportation was also reported (Singh et al., 2020). The consolidated bar chart (Fig. 1B) on the MPs of WAT, WET and DSS illustrates the higher contribution of quantified MPs by WAT for the marine samples #8, #15, #23 and #24 to the total MPs (MPs of WAT + MPs of WET + MPs of DSS). Remarkably, the dominative contribution of WET in eight samples (#1, #2, #3, #5, #6, #7, #9 and #10) and DSS in four samples (#4, #19, #20 and #21) could be evident from the bar chart. Nevertheless, in eight marine samples (#11, #12, #13, #14, #16, #17, #18 and #22), no consistent domination from a particular type of marine sample (WAT or WET or DSS) was observed. As shown in Fig. 2B, about 38%, 54% and 75% of WAT, WET and DS samples respectively were found to contain two – fragments (2F). However, the marine samples containing three – fragments (3F) were relatively decreased in WET (25%) and DSS (17%).

Marine samples containing only one type of fragment (1F) of 29%, 21% and 8% was observed in WAT, WET and DSS respectively. The fragment percentage values of WAT, WET and DSS are likely to decide the fragment combinations (1F and 2F). Presumably, the higher percentages of filamentous and tubular fragments (F – T) corroborate their combination of 38% in WAT samples. On the other hand, the dominance of 1F was envisaged more with filamentous followed by tubular fragments in WAT samples. In WET and DSS categories, the 2F combination was undoubtedly made by filamentous with granular fragments. In the case of WET

samples, only the MFs were dominated whereas in the DSS, either MFs or MGs domination was observed.

3.2 Inspection of colors in micro plastic fragments

In respect of color classification (Fig. 2C), these microplastics were identified in violet (V), blue (B), green (G), yellow (Y), red (R), pink (P), greenish blue (GB) and black (BL) colors. Mostly MPs appeared in blue, green, pink and red in the three types of marine samples. Despite these microplastics appear in many colors, the highest percentage was recorded with blue (31.4%) in WAT, green (22.6%) in WET and 25.3% in DSS. MPs colored in black, greenish blue and yellow were found absent in WAT, WET and DSS respectively, but they were present in minor percentages of 3.6 (black; WET), 2.9 (greenish blue; WAT) and 2.5 (yellow; DSS) in the marine samples. Mostly MGs appeared in blue, yellow and pink whereas MTs were in blue and white colors. Irrespective of the nature of marine samples and colors, MFs were omnipresent. Rillig, (2012) associated the washing processes of synthetic textiles with the highest abundance of filamentous type in the marine samples. The possible sources in view of the MFs are the treated or untreated domestic wastewater (Browne, 2011), carpets, discarded/weathered polypropylene materials being used in air filters, diapers, fishing materials (Naidoo et al., 2015) and airborne fibers which ultimately reach the aquatic systems (Dris et al., 2016). In addition to ingestion, chemical leaching and adsorption of plastics, the report of Carson et al. (2011) led to a perceptive insight on the altered permeability and subsurface temperatures due to plastics-contaminated sediments in beaches. The highest number of six colors appeared among 1620 fragments (per kg) in blue, pink, red, green, violet and black in a WET (#2) sample. The sample (WAT #7) was examined with 220 fragments (per m^3) in five different colors (B, P, R, V and BL). However, WET (5 samples) and DSS (4 samples) were observed to contain 60% and 75%

of B-P-R-G-V combination respectively. The major percentage of four – color (4C) combination of B-P-R-G was found to be 50%, 80% and 60% respectively of WAT (8 samples), WET (5 samples) and DSS (5 samples). The other 4C noteworthy combinations were B-P-G-V (25% in WAT), B-R-G-V (20% in WET), B-P-R-V (20% in DSS) and B-P-R-Y (20% in DSS) among the marine samples. In the case of tri – color (3C) combination from 10 marine samples of WAT and DSS, B-P-R (20% in WAT and 30% in DSS) and B-P-G (30% in WAT and 30% in DSS) were observed but no specific combination from the colors B, P, R, G and V was exhibited by WET category of marine samples. The two – color (2C) combination among MPs was mostly dominated by B-P and P-G in all categories of marine samples. Notably, the appearance of pink MPs as filaments seems to be more likely in combination with blue and green colored fragments. It was peculiar to observe a sample (#15) only with 20 blue colored MFs (per kg) in the DSS category. Especially in the three samples under WAT category, blue colored MFs (60 fragments per m^3 in sample #10 and 160 fragments per m^3 in sample #13) and, green colored MFs (40 fragments per m^3) along with MGs (40 fragments per m^3) in the sample #19 were evident from the microscopic investigations. The distribution of colors among various fragments in all the marine samples of the three categories are shown in the supplementary section (Table S2).

3.3 Micro plastic filaments (MFs), granules (MGs) and tubules (MTs) in the marine samples

The classified MPs (Fig. 3) as filaments, granules, tubules and films are generated as "secondary microplastics" as a consequence of disintegration or degradation of macroplastics due to physical, chemical or biological processes (Cole et al.,2011; Horton and Dixon, 2018). In line with this, it was succinctly reported that certain interactions among the interspecies in water column and sediment could influence the structure, stability and behavior of biofilms and

subsequently facilitate the colonization and biodegradation of microplastics (Arias-Andres et al. 2018; Pollet et al. 2018; Oberbeckmann and Labrenz 2020). In all the marine samples under WAT, WET and DSS the dominated fragements were MFs (Fig. S4). Napper and Thompson (2016) studied the ability of 6 kg of wash load of acrylic fibers to release over 700,000 fibers into the sewage treatment plants and ultimately into the aquatic environments. Mostly the MFs are typically made of nylon, polypropylene and PET (Gago et al., 2018). However, MGs in 83.3% of the DS samples were decreased to 62.5% and 54.2% respectively in WET and WAT samples. Conversely, the MTs in DS samples registered a minimum of 25% (6 out of 24 samples) but, observed with 42% and 50% in WET and WAT samples respectively.

Conspicuously, there was no detectable (minimum) value of MGs and MTs was recorded in all the categories of marine samples. On the other hand, the maximum values for MFs (1440 fragments per m^3), MGs (600 fragments per kg) and MTs (920 fragments per kg) were recorded in WET, WAT and DSS respectively. An average value of 323 MFs per kg (in WET), 172 MGs per kg (in DSS) and 90 MTs per m^3 (in WAT) was the highly recorded values among the marine samples. An average value of seven MTs per kg was recorded among the DS samples.

Although MFs dominate under all the three categories, there are marine samples under WAT category (#15, #21 and #23) where the MTs excelled about 2 – 3 times greater than that of MFs. Similarly, a WET (#13) sample with 160 MGs per kg was 2.7 times higher than the MFs. In addition, the µG fragments in the marine samples (#03, #05, #19, #20, #21 and #24) of DSS category surpassed in the range of 1.5 – 6 times than the MFs. At the same time, the MFs are equally present as that of MGs in certain marine samples under WAT (#19), WET (#10) and DSS (#01, #07 and #11) where no MT fragment was observed. Consequently, the MGs are destined to a particular shape (as beads or pellets) due to the continuous impact of sand particles

or rocks as a consequence of wave or tidal actions. The presence of micro – translucent – granules in yellow demonstrated the photo degradation by UV – light and subsequent bleaching of these MGs.

3.4 Average length of MPs in the marine samples

In addition to the color and shape of MPs, the microscopic examination also revealed the lengths of various fragments of different colors as shown in Fig. S1. Despite the MPs appeared with different colors, the most dominated colored fragments were appeared in blue and pink as MFs, MGs and MTs. In particular the thin MFs ranged between the average lengths of 325 µm and 6694 µm whereas those of thick type were appeared from 1599 µm to 4794 µm. Similarly, the blue colored MFs (thin type) were found at all ranges with a maximum value of 19080 µm for a WET (#16) sample. A dark blue MFs of length 12402 µm and 11713 µm were noticed respectively in WAT and WET samples (#9). One of the DS (#8) samples exhibited a thick micro filament in blue color of 9752 µm. The MTs in pink (average lengths of 188 µm and 546 µm) and blue (average lengths of 323 µm, 697 µm and 1489 µm) were also observed predominantly in WAT samples. The blue colored MGs with an average lengths of 251 µm, 738 µm and 1295 µm were found to be high in DS samples.

3.5 Characterization of micro plastic particles

As recommended by Shin et al (2017), the characterization of microplastics needs two main ways: (i) the physical features such as size, shape and color which can be obtained by optical microscopy, and (ii) the chemical features related to the polymer type which can be established by EDS analysis during SEM observations and by FTIR.

3.5.1. Shapes observed by SEM

After consolidating the collected samples, only the selected samples, based on shape and color were observed and analyzed by SEM and EDS. Some of the investigated samples are presented in Figs. 4 and 6, and in the Supplementary section. The repartition of the shapes does not reflect what was already observed by optical microscopy. A majority of samples were MGs of size in the range 100-150 □m with rough surface far from a smooth surface analogous to the one of grains of sand. Fotopoulou and Karapanagioti (2012) showed that the marine environment is involved in the surface degradation of plastic pellets. Few samples were filamentous particles (MFs) of diameter in the range 10-20 □m and with smooth surface. No tubular sample was observed.

3.5.2. Main elements detected by EDS

The results of EDS analyses are gathered in Fig 5. Almost all the samples are characterized by three major elements, C, O and F and they belong to two class of compounds. A first class of samples contains C and O with great molar ratios C/O in the range 1.02-9.02 (28 analyses). The high content of oxygen agrees with the structure of polyester plastics such as methyl polymethacrylate, polycarbonate, polyethylene-terephthalate (PET) and ethylene vinyl acetate which have calculated molar ratios C/O of 2.5, 5.33, 2.5 and 3.0 respectively. The greatest molar ratios C/O (> 5) may be attributed to oxidized polyethylene containing polymers or to copolymers of polyethylene and polyesters. Since all the particles were not analyzed by FTIR and EDS it is not possible to attribute a right structure to all the observed particles.

The second class of compounds contains fluoride and carbon elements with molar ratios F/C in the range 0.82-1.73 (12 analyses; Fig. 6). The molar ratios agree with the structure of polyfluoride compounds, such as polyvinylidene fluoride (PVDF) or polytetrafluoroethylene (PTFE) for which the calculated molar ratio F/C are 1 or 2, respectively. PVDF and PTFE

particles are rare in micro plastic pollution but they have already been detected (Saliu et al, 2018; Zobkov et al, 2019; Cincinelli et al., 2017). The absence of simultaneous great contents of chlorine and carbon dismisses the presence of polyvinylchloride (PVC) in the analyzed particles. The absence of PVC is expected by the separation method which used NaI saturated solution for which the density does not allow the flotation of PVC particles. Low contents of chlorine were found associated with sodium as expected for a material which was impregnated by sea water.

3.5.3. Minor elements detected by EDS

Few elements were frequently detected in suspected polyester particles. The results are gathered in Table S3. These elements are Na, Cl, Mg and K. All these elements constitute the signature of the sea water origin of the analyzed micro particles. A remarkable result is that the molar Na content is generally greater than the molar Cl content, whereas the inversed contents are observed in sea water. This observation agrees with the occurrence of ester hydrolysis leading to sodium carboxylate functions. Sometimes for particles of sample 2, the molar K content is greater than the molar Cl content, showing that potassium carboxylate functions may be created. As presented in Fig. 5 (and in Table S3) the polyfluoride compounds do not contain minor elements, excepted analysis 134. The absence of minor elements in these polymers agrees with the chemical stability of this class of materials.

3.5.4. Miscellaneous elements

Few elements, especially heavy metals, were also detected: Ti, Mo, Ru, Rh, Cu and, Al, Si and Fe as well (Fig. S2 – S5). These elements may be residues of catalysts or flame retardants or UV stabilizers. All these minor elements contribute to the pollution due to the presence of micro plastic particles in sea water.

3.6 FTIR study

As for SEM study, the micro plastic particles analyzed by FTIR were arranged in four samples which contained several particles. Unfortunately, there was no identity between samples for FTIR and sample for SEM, so some conclusions are difficult to confirm. The FTIR spectra are gathered in Fig. 7. The strongest vibrations bands which were observed were the results of the behavior of the more dominant polymers.

Sample 1 appears to contain polypropylene and fluoride polymer. The presence of polypropylene (PP) is proven by the vibrations at 2950, 2922 and 2850 cm^{-1} which are attributed to asymmetric and symmetric C-H stretching vibrations, in agreement with the values given at 2952, 2918 and 2840 cm^{-1} by Kaczmarek et al, (2005), or at 2950, 2917 and 2838 cm^{-1} (Castillo et al., 2016). Additional vibrations which were observed at 1450 and 1375 cm^{-1} are given at 1456 and 1376 cm^{-1} by Kaczmarek et al, (2005) or at 1456 and 1375 cm-1 (Castillo et al., 2016). One vibration observed at 1375 cm^{-1} could belong to the polyvinylidene fluoride (PVDF) spectra. But the presence of PVDF is ruled out because the characteristic vibrations at 1176 and 874 cm^{-1} due to C-F stretching were not observed (Wei et al., 2011). The vibration at 1375 cm^{-1} is a characteristic of PP. However, the presence of polytetrafluoroethylene (PTFE) is proven by the observation of two strong vibrations at 1200 and 1150 cm^{-1} due to the asymmetric and symmetric stretching of $-CF_2$ groups, in agreement with the values given by Salapare et al, (2008) at 1224 and 1155 cm^{-1}, or 1207 and 1151 cm^{-1} (Mason et al., 2000). Additional weaker vibrations belonging to PTFE spectra were observed at 713, 645 and 550 cm^{-1} instead of 640 and 553 cm^{-1} in Salapare et al., (2008). The weak vibration observed at 1733 cm^{-1} may be attributed to the vibration of a – CF=CF – group or a carbonyl one (Cozad et al., 2010).

The broad peak around 3400 cm^{-1} could be attributed to the diffusion of water in polypropylene since such vibration is accompanied by another characteristic vibration at 1640

cm^{-1} and no vibration was observed at this wave number (Shen and Wu, 2003). Broad peaks centered at 3300-3400 cm^{-1} have been often observed for MPs as the result of aging and oxidation leading to hydroxyl groups (Xu et al., 2019; Peng et al., 2017; Corcoran et al., 2009).

Sample 2 seems to contain polyethylene and polyester compounds. The presence of polyethylene is proven by strong vibrations at 2920 and 2850 cm^{-1} which agree with the vibrations observed at 2916 and 2848 cm^{-1} by Favaro et al., (2007) or 2019 and 2851 cm^{-1} by Gulmine et al., (2002). One additional vibration at 1455 cm^{-1} which belongs to the polyethylene spectra was observed at 1463 cm^{-1} by Favaro et al., (2007). Sample 2 does not show a broad peak at 3300-3400 cm^{-1} which could be the result of oxidation and attributable to hydroxyl functions. The strong vibration at 1740 cm^{-1} must be attributed to an ester carbonyl (Artham et al., 2009) and its presence proves that sample 2 contained a polyester. Sample 3 seems to contain a Nylon compound (polyamide) in agreement with the published spectra by Jung et al. (2018). The vibration at 3250 cm^{-1} attributed the stretching of N – H bonds. Additional vibrations which were observed at 2925, 2850, 1640, 1540, 1460 and 1375 cm^{-1} agree with literature values at 2932, 2858, 1634, 1538 1464 and 1372 cm^{-1} (Jung et al., 2018). The weak vibration at 3100 cm^{-1} was observed at 3086 cm^{-1} by Lee et al., (2008) and was attributed to an NH fermi resonance. The carbonyl vibration at 1740 cm^{-1} is very weak and may be the result of an oxidation of the micro particles. The vibrations at 1200 and 1150 cm^{-1} prove that sample 3 also contained particles of PTFE. Sample 4 also contained polyethylene as proven by two strong vibrations at 2920 and 2850 cm^{-1} and additional vibration at 1460 cm^{-1}, is in good agreement with literature values. As for samples 1 and 3, the vibrations at 1200 and 1150 cm^{-1} prove that sample 4 also contained particles of PTFE. The vibration at 1740 cm^{-1} must be attributed to an ester carbonyl (Artham et al., 2009) and it proves that sample 2 also contains a polyester. The FTIR study of MPs which

were gathered in samples 1 – 4 confirms the result of EDS analyses regarding the presence of polyesters and fluoropolymers and it makes clear that the fluoropolymer detected by FTIR is PTFE.

4. Conclusions

This study reports the micro-plastic pollution on 0.92 km^2 of a long beach in the Tamil Nadu. Seventy-two samples have been isolated from the water, wet sand and dry sand. The micro-plastic particles were more abundant in wet sand than in water or dry sand. Three kinds of analysis have been carried out. The first one is a visual observation which gives the localization, the shape and the color of the micro-plastics. Filamentous particles (MFs) and blue and pink fragments were the more abundant isolated micro-particles. The second kind of analysis was elemental ones performed by EDS during SEM observations. The results suggested that micro-plastics were mainly polyesters and polyfluoride compounds. The EDS analysis of minor elements agreed with a contamination with ionic components of sea water. The excess of Na over Cl, which was generally observed for polyester materials, was explained by a hydrolysis reaction. The third kind of analysis were FTIR characterizations which confirmed that the isolated particles contained PTFE, polyesters, polyethylene, polypropylene and Nylon. Hydroxyl functions which were detected by their vibration on FTIR spectra confirmed that the hydrolysis or oxidation of micro-plastics occurred in sea water.

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Table 1. Descriptive statistics of the micro plastic particles for the marine samples

Sample	Minimum	Maximum	Mean	SE	SD
WAT	60	820	231.7	39.4	193.1
WET	60	1620	365.8	80.9	396.6
DSS	20	1540	330.8	74.4	364.6

SE – Standard Error; SD – Standard Deviation

Fig. 1 Optical microscopic images (A) Quantified data (B) of the micro plastic particles in the marine samples (The quantified results are expressed in items/m^3 (WAT) and items/kg (WET and DSS)

(WAT – Sea water samples; WET – Wet sand samples; DSS – Dry sand samples)

Fig. 2 Types of micro plastic particles (A) Number of plastic fragments in marine samples (B) Colors based discrimination in micro plastics (C)

(WAT – Sea water samples; WET – Wet sand samples; DSS – Dry sand samples)

Fig. 3 Distribution of MPs in WAT (A), WET (B) and DSS (C) categories

(WAT – Sea water samples; WET – Wet sand samples; DSS – Dry sand samples; MFs – Micro Filaments; MGs – Micro Granules; MTs – Micro Tubules)

Fig. 4 SEM pictures of MPs. Sample 1 (A – C), Sample 2 (A – C), Sample 3 (A – C) and Sample 4 (A – C)

Fig. 5 Energy Dispersive X – ray Spectroscopic (EDS) analysis of MPs in the marine samples *Spectral sites:*

***MPs-1**: #101 – #107; **MPs-2:** #108 – #116; **MPs-3:** #117 - #129; **MPs-4:** #130 - #146*

Fig 6 Energy Dispersive X – ray Spectroscopic (EDS) analysis of fluoro-polymers in MPs of the marine samples

Fig. 7 Fourier Transform Infra – Red spectra of MPs – sample 1 (A), sample 2 (B), sample 3 (C) and sample 4 (D)

Declaration of competing interests

☐ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Prof. V. Sivasankar

Credit Author Statement

T.G. Sunitha – Formal Analysis

V. Monisha – Investigation

S. Sivanesan – Investigation

M. Vasanthy – Resources

M. Prabhakaran – Formal Analysis

K. Omine – Supervision

V. Sivasankar – Conceptualization, Writing – Review & Editing

A. Darchen – Writing – Review & Editing

Graphical abstract

Highlights

- Microplastic particles (MPs) were collected on a beach surface of 0.92 km^2
- Three kinds of MPs were isolated from water, sediment and dry sand
- The quantification of MPs was carried out thanks to their shape and color
- MPs were analyzed by Energy Dispersive Spectroscopy (EDS) and FTIR spectroscopy
- EDS and FTIR showed a notable presence of ester and fluoride polymers

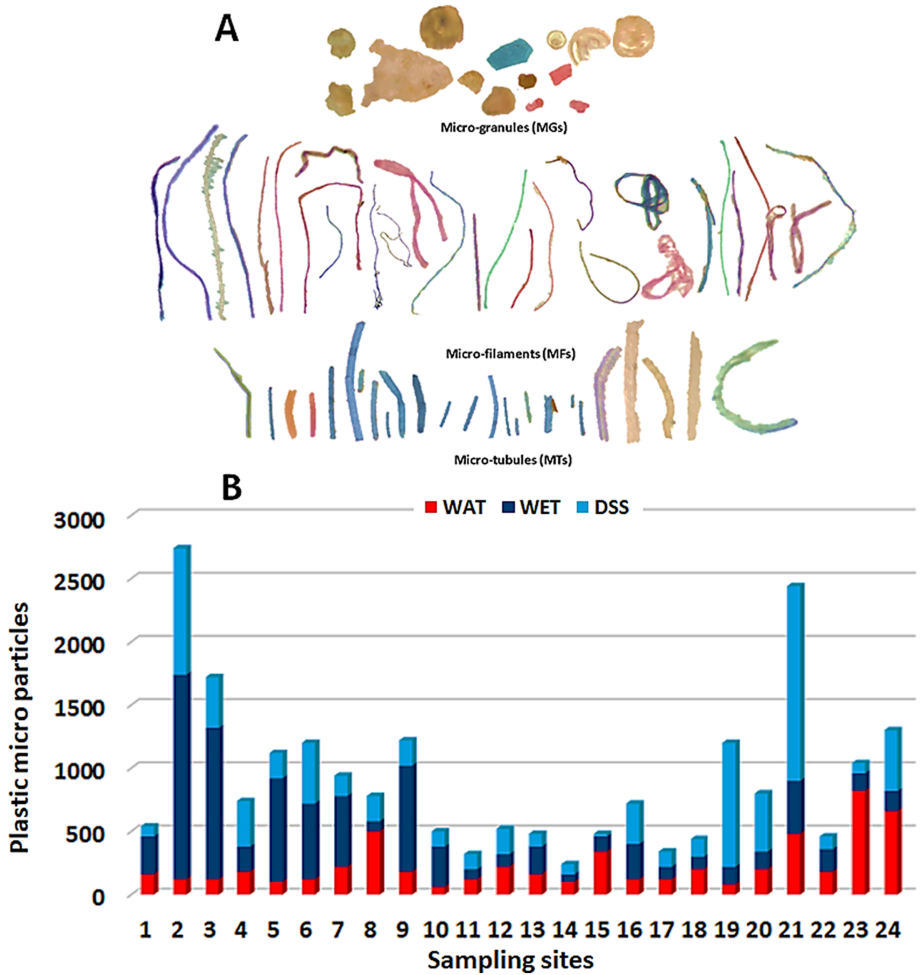
A
Micro-granules (MGs)
Micro-filaments (MFs)
Micro-tubules (MTs)
B
WAT
WET
DSS
Plastic micro particles
3000
2500
2000
1500
1000
500
0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
Sampling sites

Figure 1

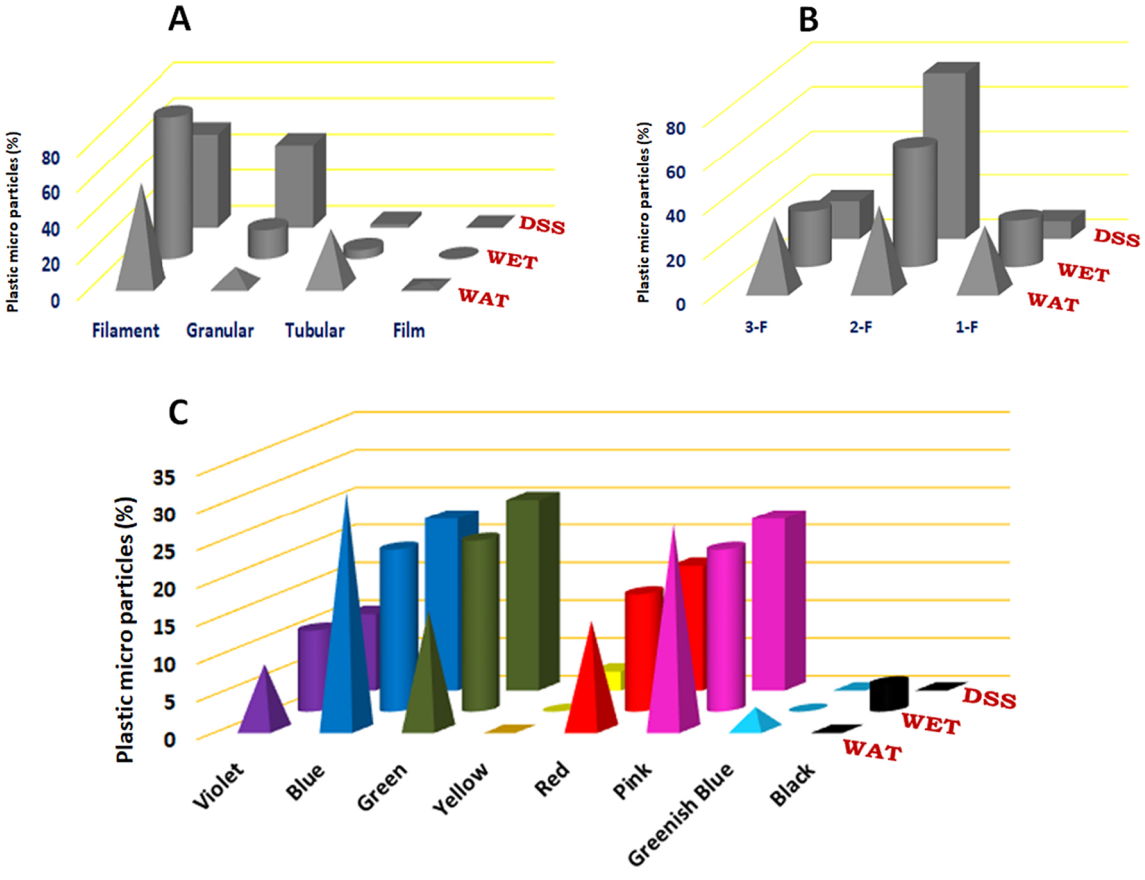
A
Plastic micro particles (%)
0
20
40
60
80
Filament
Granular
Tubular
Film
DSS
WET
WAT
B
Plastic micro particles (%)
0
20
40
60
80
3-F
2-F
1-F
DSS
WET
WAT
C
Plastic micro particles (%)
0
5
10
15
20
25
30
35
Violet
Blue
Green
Yellow
Red
Pink
Greenish Blue
Black
DSS
WET
WAT

Figure 2

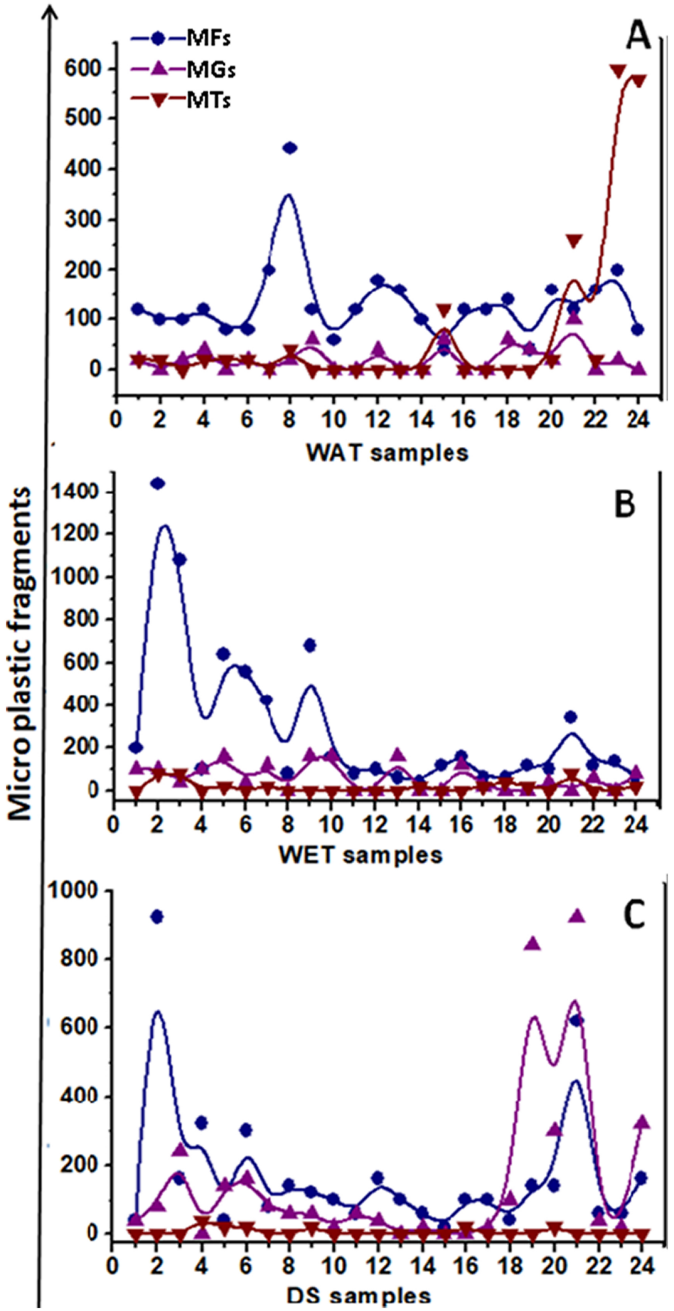
MFs
MGs
MTs
A
B
C
Microplastic fragments
WAT samples
WET samples
DS samples

Figure 3

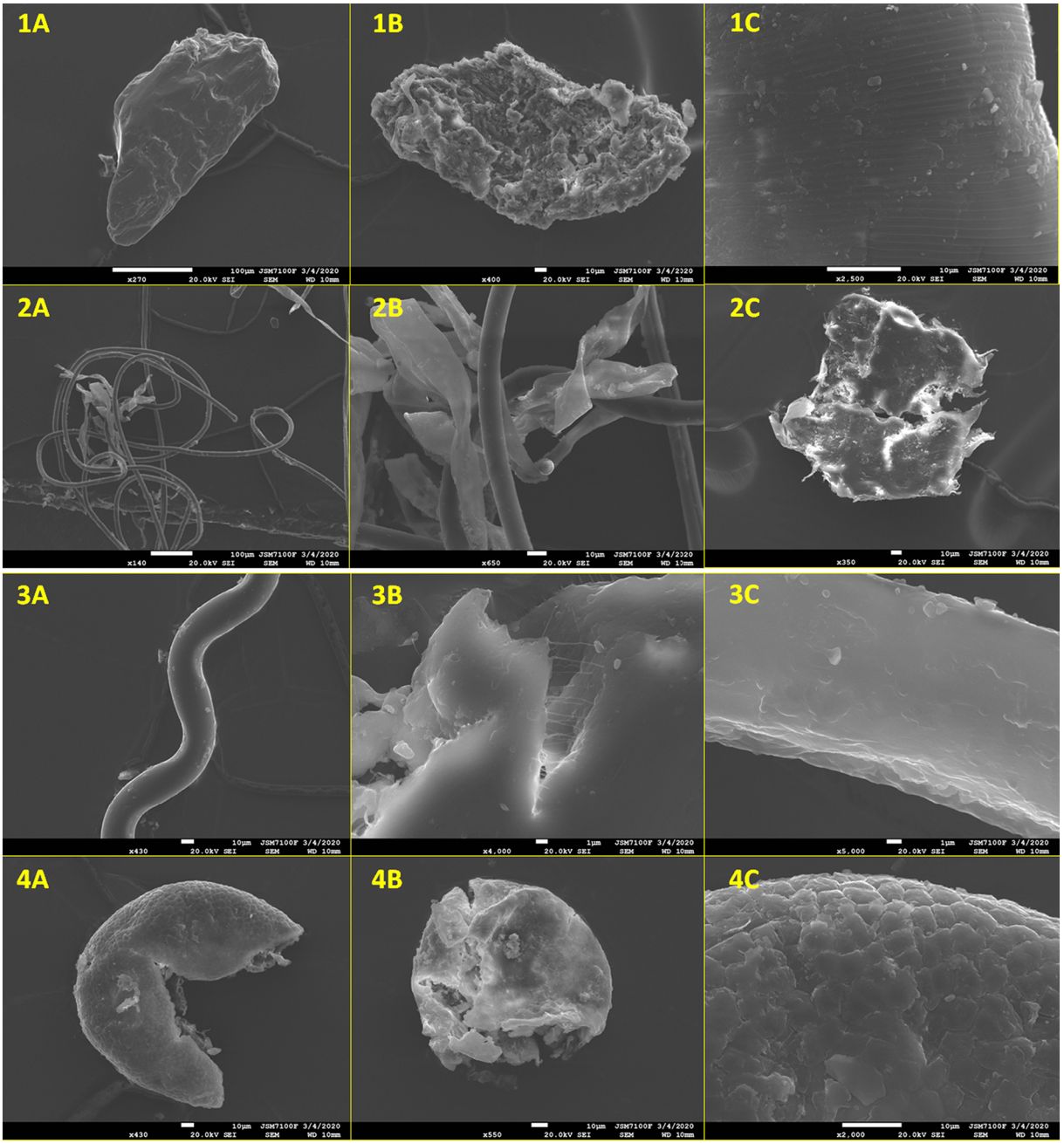
1A
100µm JSM7100F 3/4/2020
x270 20.0kV SEI SEM WD 10mm
1B
10µm JSM7100F 3/4/2020
x400 20.0kV SEI SEM WD 17mm
1C
10µm JSM7100F 3/4/2020
x2,500 20.0kV SEI SEM WD 10mm
2A
100µm JSM7100F 3/4/2020
x140 20.0kV SEI SEM WD 10mm
2B
10µm JSM7100F 3/4/2020
x650 20.0kV SEI SEM WD 17mm
2C
10µm JSM7100F 3/4/2020
x350 20.0kV SEI SEM WD 10mm
3A
10µm JSM7100F 3/4/2020
x430 20.0kV SEI SEM WD 10mm
3B
1µm JSM7100F 3/4/2020
x4,000 20.0kV SEI SEM WD 10mm
3C
1µm JSM7100F 3/4/2020
x5,000 20.0kV SEI SEM WD 10mm
4A
10µm JSM7100F 3/4/2020
x430 20.0kV SEI SEM WD 10mm
4B
10µm JSM7100F 3/4/2020
x550 20.0kV SEI SEM WD 10mm
4C
10µm JSM7100F 3/4/2020
x2,000 20.0kV SEI SEM WD 10mm

Figure 4

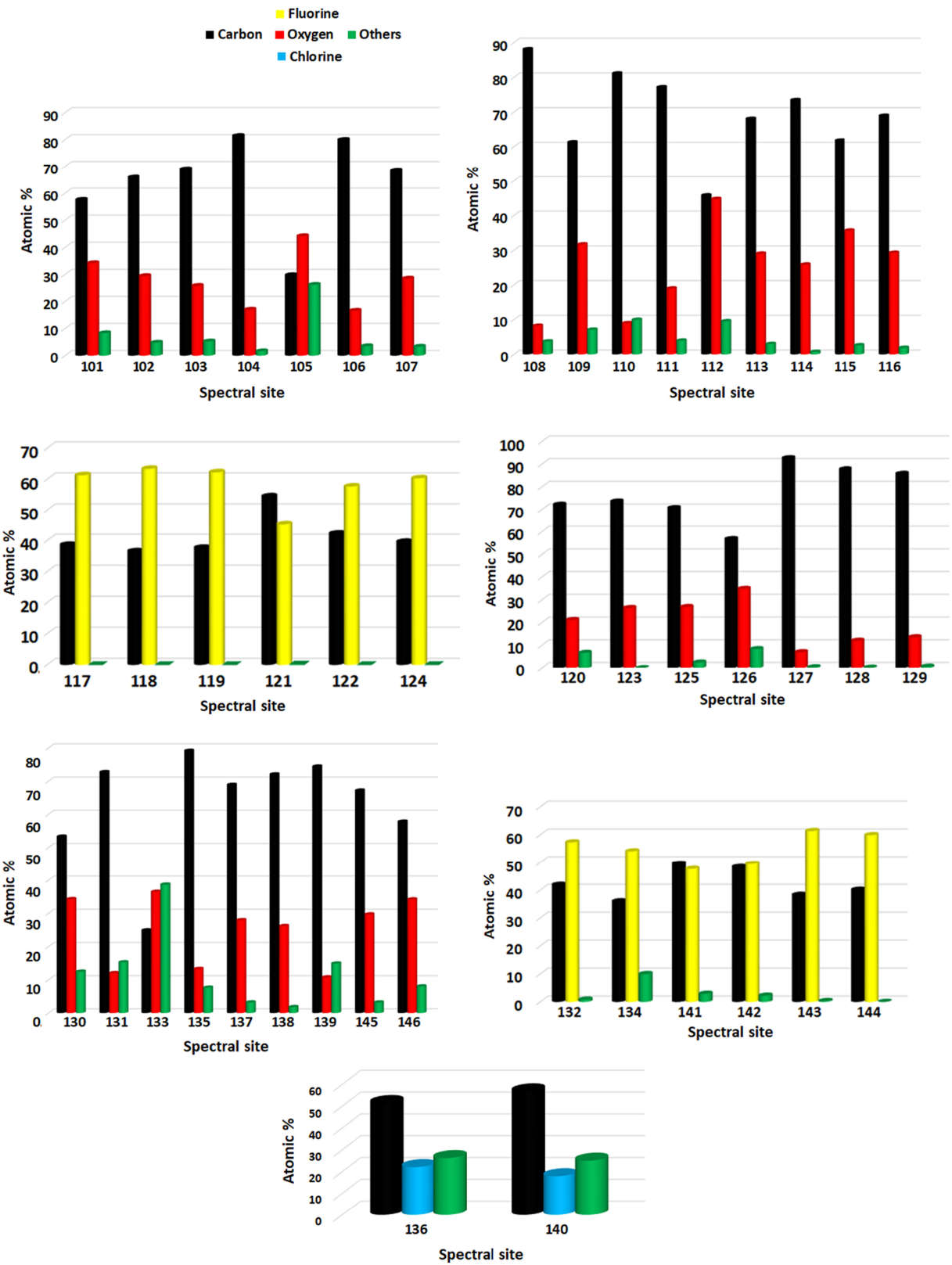
Fluorine
Carbon
Oxygen
Others
Chlorine
Atomic %
Spectral site
101
102
103
104
105
106
107
108
109
110
111
112
113
114
115
116
117
118
119
121
122
124
120
123
125
126
127
128
129
130
131
133
135
137
138
139
145
146
132
134
141
142
143
144
136
140

Figure 5

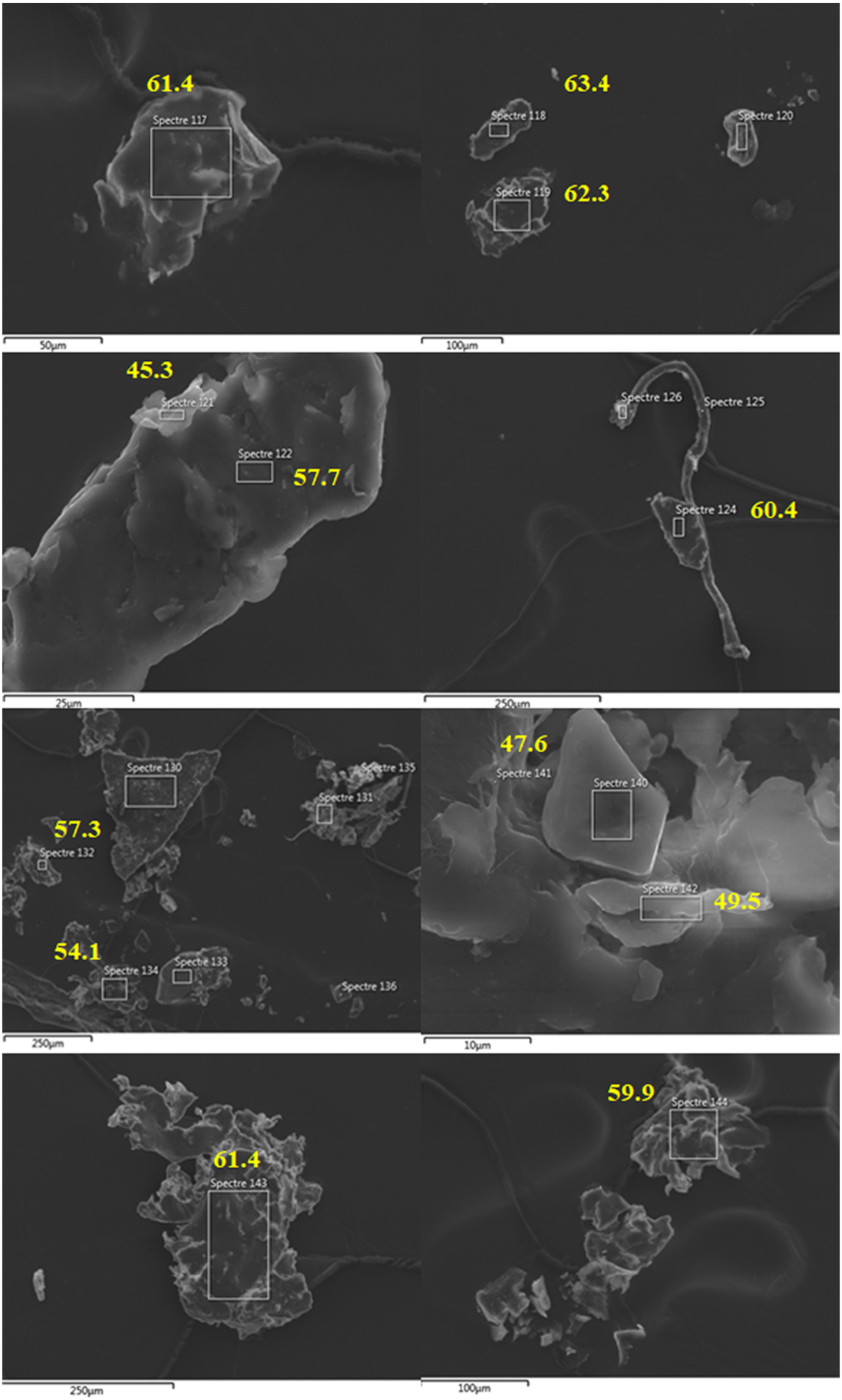
61.4
Spectre 117
50µm
63.4
Spectre 118
Spectre 120
Spectre 119
62.3
100µm
45.3
Spectre 121
Spectre 122
57.7
25µm
Spectre 126
Spectre 125
Spectre 124
60.4
250µm
Spectre 130
Spectre 135
Spectre 131
57.3
Spectre 132
54.1
Spectre 134
Spectre 133
Spectre 136
250µm
47.6
Spectre 141
Spectre 140
Spectre 142
49.5
10µm
61.4
Spectre 143
250µm
59.9
Spectre 144
100µm

Figure 6

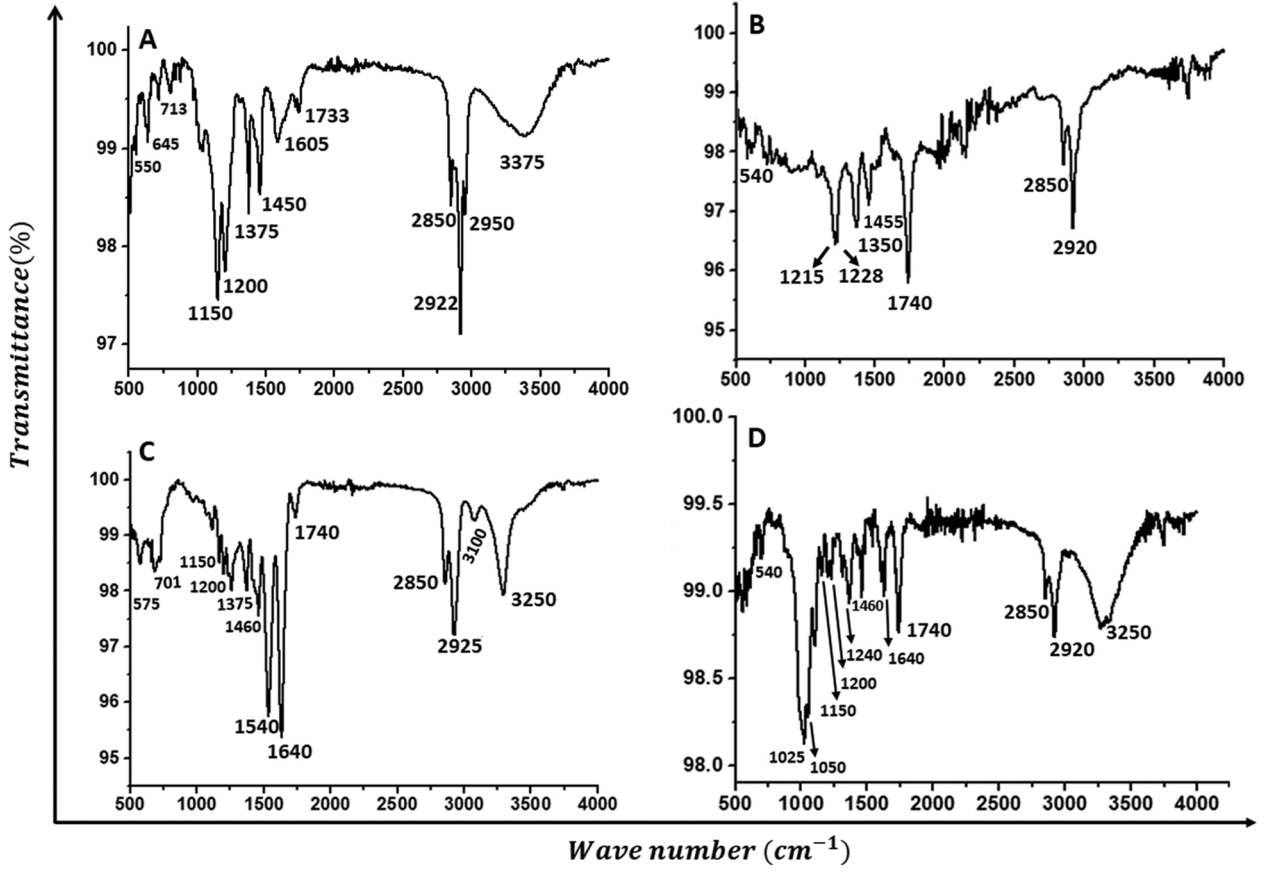
A
713
645
550
1733
1605
1450
1375
1200
1150
2850
2950
2922
3375
B
540
1455
1350
1215
1228
1740
2850
2920
C
701
1150
1200
1375
1460
575
1740
2850
3100
2925
3250
1540
1640
D
540
1460
1740
1240
1640
1200
1150
1025
1050
2850
2920
3250
Transmittance(%)
Wave number (cm^{-1})

Figure 7