SOURCES AND EFFECTS OF PLASTICS AND MICROPLASTICS IN ARABIAN SEA

FINAL YEAR PROJECT UG 2019

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2019

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CERTIFICATE

This is to clarify that the

Final Year Project Titled

SOURCES AND EFFECTS OF PLASTICS AND MICROPLASTICS IN ARABIAN SEA

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DEDICATION

We would like to dedicate this thesis work to our parents, siblings, teachers and friends; especially people who always put up their trust; and supported, guided and assisted us in the best and worst.

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ACKNOWLEDGEMENT

All the praise and thanks be to Allah Almighty, for the strengths and His blessings for the completion of this work.

Our special gratitude for our supervisor and mentor Dr. Nasir Ahmad, whose trust, training, and support helped us complete our project.

We would like to thank Rawal lake authority and Karachi Port Trust for this effort in helping and guiding us to get the samples from different locations.

Also, we are very thankful to all those people who put their efforts in guiding us to get the desired results.

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ABSTRACT

Plastic pollution has become one of the main issues of this era. The world is progressing day by day. Plastic industries are increasing with time and hence the plastic waste doesn't go away and end up in ocean every year. According to some reliable source, annual production of plastic has been increased to 381 million tons in 2015 and approximately 8 million metric ton of plastic end up in ocean. Plastic waste removal companies are working for the removal of plastic debris from the ocean but they only focus on the macro plastic, not on microplastic. Microplastics are very smaller in size, they are barely visible in size and they easily escape from the net. From research we came to know that microplastic are more effective to the marine environment more than macro ones. From there they are posing many risks to marine environment.

Other countries are working for the identification and removal of plastic waste from the ocean water and unfortunately there is no such research performed on the Arabian sea. We took an initiative to took step to provide the first-time data of plastics as well as microplastics on the basis of types, size distribution and color in Arabian Sea. We designed our own stainless-steel net, and tested on Rawal lake. Our other aim of testing this on Rawal lake is to compare our data of Arabian sea of that of Rawal lake. Plastic samples are collected with the help of net and stored in beaker. Further experimentation techniques are applied on the samples. First of all, samples are washed with water or alcohol, and separated according to their types. Melt flow index is applied and then FTIR and DSC techniques are applied on plastic samples.

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TABLE OF CONTENTS

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LIST OF FIGURES

`

LIST OF TABLES

`

ABBREVIATIONS

PAHs	Polycyclic aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PBDEs	Polybrominated diphenyl ethers
DDTs	Dichloro-diphenyl-trichloroethane
LDPE	Low density polyethylene
PP	Polypropylene
PET	Polyethylene terephthalate
AIO	Air induced overflow
PVC	Polyvinyl chloride

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CHAPTER 1

INTRODUCTION

1.1 OVERVIEW:

1.1.1 Defining *'plastic'*

Plastic is a subcategory of larger class of materials, called polymers. These are widely used in various fields to describe the physical properties or behavior of any materials i.e. soil or any geographical formations. Polymers are long chain molecular structure and have high average molecular weights. These long chains may consist of repeating identical units, known as homopolymer or consist of different sub-units in different sequences, known as co-polymer.

Those polymers that usually soften on heating and can be altered into various shapes are referred as *'plastic'* materials. These usually consist of single type of plastic or as a mixture of plastic with any additive to enhance the properties depending on the requirement. In addition to this marine debris also include thermoset materials. These materials consist of long chains and can't be remolded after heating i.e. epoxy resins, polyurethane foams or any other coating film.

1.1.2 Defining *'microplastic'*

In early 1970s, a scientific literature stated small pieces of plastics are floating in the surface ocean (Carpenter and Smith 1972) and later studies give the report of small fragments of plastics in birds. The term *'microplastic'* was first used Ryan and Moloney in 1990 in describing the survey result of South African Beaches.

Earlier there is no specific size definition of *microplastic*, but it is kept specific to those plastic materials that can only be seen through the aid of microscope. It is widely used to describe the size range of millimeter to sub-millimeter. Scientific definition of plastic pieces refers from nano to mega size range. However International research community has not yet proposed for adoption (Figure 1.1)

To define the size of *microplastic*, first international workshop on sources and effects of microplastics in marine debris was held in 2008. The suggested upper size limit of microplastic was 5mm. It is also identified that these particles direct to more threats than large plastic materials i.e. entanglement. In field studies, size ranges reported are forced by sampling techniques that were employed. For example, many studies show the size range based on sampling with the plankton net (mesh size = 330).

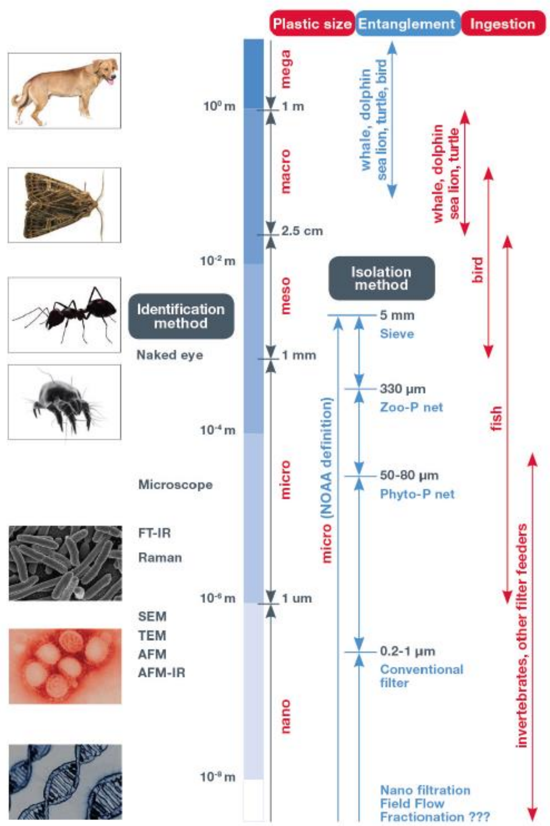

Figure 1.1: Size range of plastic particles that are found in marine water and their comparison with living materials.

Floating plastic debris are collected by using neuston net. But seriously underestimates the amount of plastic present in the sea as in the mid water or sediments. They are specified by the specific gravity. The visibility of plastic debris as jetsam requires plastics to be floatable in the sea water (specific gravity of sea water is approximately 1.25). As seen from Table 1, only few of the plastics have specific gravity less than that of sea water.

Plastic Class		Specific Gravity	Percentage production[#]	Products and typical origin
Low-density polyethylene	LDPE LLDPE	0.91–0.93	21%	Plastic bags, six-pack rings, bottles, netting, drinking straws
High-density polyethylene	HDPE	0.94	17%	Milk and juice jugs
Polypropylene	PP	0.85–0.83	24%	Rope, bottle caps, netting
Polystyrene	PS	1.05	6%	Plastic utensils, food containers
Foamed Polystyrene				Floats, bait boxes, foam cups
Nylon	PA		<3%	Netting and traps
Thermoplastic Polyester	PET	1.37	7%	Plastic beverage bottles
Poly(vinyl chloride)	PVC	1.38	19%	Plastic film, bottles, cups
Cellulose Acetate	CA			Cigarette filters

[#] Fraction of the global plastics production in 2007 after (Brien, 2007).

Table 1.1: Plastics that are commonly found in marine environment.

1.2 Primary and Secondary microplastic:

The major specification of primary and secondary microplastic is based on whether they are originally manufactured of that size which is known as primary, or they are produced by the breakdown of larger items, known as secondary. It is better to specify them to take precautionary measures to reduce their effects to the environment. Primary microplastics include plastic powders that are used in molding, spherical and cylindrical pellets, industrial scrubbers that are used in blast clean surfaces. Secondary microplastics are the result of fragmentation and degradation of large plastic materials. This happens from the phase of products of textiles, paints, tires or any item that is released into the environment.

In addition to synthetic microplastics, naturally biopolymers are also present in the marine water, but they are of less concern. The reason for this is that they are degradable and less harm to the environment. Natural biopolymers degrade into CO_2 and H_20 in the ocean.

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In sea water, microplastics are present in much larger amount than plastics. If we stop the discharge of macro-plastics in sea water today, it will take many years to degrade the microplastics totally.

1.2.1 Generation of microplastics

Plastic in marine water is exposed to solar UV radiations and it undergoes weathering degradation. Due to this surface cracks are generated, as a result they are breakdown into small fragments. Most of the secondary microplastics are produced by this method. Weathering degradation would rapidly occur on beaches and at low rate of floating debris. At low oxygen environments, the degradation is particularly slow.
To determine the rate of microplastic generation, their impact on society and particle size distribution, it is necessary to know the fragmentation rate and mechanism.

1.2.2 Weathering degradation of plastics in ocean

As discussed earlier, mostly degradation of plastics is due to solar UV radiations, which ease the degradation of polymers. In further stages of degradation, the plastic usually fades in color, become weak and brittle with time. A small force (wind, wave or any other activity) can break these degraded particles into small microplastic fragments. The degradation rate of plastics varies from plastic to plastic, due to the presence of additive which enhance the properties. For example, UV stabilizers and antioxidants often remarkedly retard light induced degradation.
The weathering of common plastic and microplastics has been studied in various environments and studies have focused on the earlier stages of degradation that directly affect the lifetime of material. Thus, there is very less information available on fragmentation and oxidation of highly weathered plastics in environment.
The effects such as temperature, mechanical impact, hydrostatic pressure, presence of pollutants (oils, fluids) and bio-fouling on weathering rates on different plastics are about unknown.

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Before long, there is no perfect methodology to determine the life of microplastic that are collected, making difficult to enquire the degradation dynamics of microplastics in sea water. It is possible to measure the extent of weathering by chemical analysis. Fourier Transform Infrared Spectroscopy (FTIR) or Raman Spectroscopy are used for this. However, the time of exposure cannot be measured from such information. Without determining the correct degradation time, developing 3-D models of microplastics abundance is unconstrained. For example, we cannot tell about particular plastic that can move great disturbance either it is in a fast current or it is in the water for a long time.

1.3 Microplastics in marine organism

Polymers containing additive chemicals and organic materials that interact with biotic and abiotic components of marine environment. In Sea water, large variety of particles are found of <100 nm in size. They usually interact with the marine organism. Due to smaller size, they are ingested and they cannot be digested nor absorbed because there is no specific enzymatic pathways to breakdown these polymers in marine organism. Thus, cause problems to marine organism. The concern is due to ability to absorb and accumulate metals and POPs, such as PAH, PCBs, PBDEs and DDTs on their surface. (Gewert, 2015). The microplastics are accumulated into sediments, where organism with non-selective deposits feeding behavior can ingest them and causes reduced enzymatic activity, oxidative stress and damage elaborated in figure 2.

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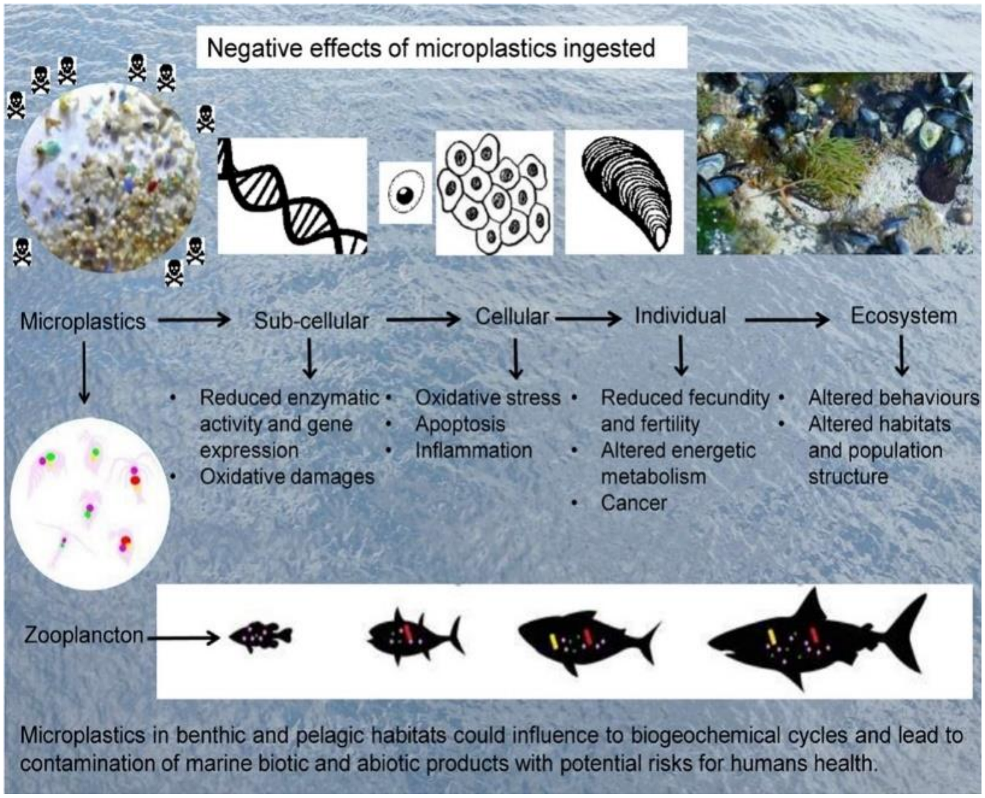

Figure 1.2: Negative effects of microplastics ingested

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CHAPTER 2

LITERATURE REVIEW

2.1 Microplastics in coastal environments of the Arabian Gulf (Abayomi, 2017)

Selected places for Sampling for microplastics were eight sandy shorelines along the coastline of Qatar and four ocean surface stations on the eastern drift, contiguous Doha Bay between December 2014 and March 2015. Microplastics, predominantly low thickness polyethylene and polypropylene, were found in all examples of silt and seawater. Blue filaments, somewhere in the range of 1 and 5 mm, were the prevailing sort of particles present. Amount of microplastics on the ocean surface differed between 4.38×10^4 and 1.46×10^6 particles/km^2, with the most noteworthy qualities being reliably discovered 10 km offshore, proposing the presence of a combination zone. No huge fleeting fluctuation was recognized for ocean surface samples. The convergence of microplastics in intertidal silt shifted somewhere in the range of 36 and 228 particles m^{-2}, with no critical contrasts among the 8 shorelines analyzed. These outcomes demonstrate the inescapability of microplastic contamination in seaside situations of the Arabian Gulf.

2.1.1 Sampling Technique:

In the initial step, focusing on low-density polymers, 1 L of saturated NaCl solution (1.2 g L^{-1}) was poured into flask containing the subsample and were shaken physically for 5 min. After settling for 5–7 hours, the supernatant was gathered and stored for further handling. A second detachment by density was finished utilizing a saturated KI solution (density = 1254 kg/m^3), for the recuperation of denser polymers. The filtrate from both division steps were homogenized, flushed, and vacuum sifted on a Whatman™

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Qualitative channel paper. Filters were oven dried at 60 °C in fixed Petri dishes and kept in a desiccator until visual arranging and measurement under a stereomicroscope. To facilitate comparisons with previous studies, abundances were expressed as m^{-2} and kg^{-1} of sediment.

Preventive measures were adopted to avoid contamination with plastic particles present in the atmosphere of the lab, garments or instruments. Procedural clear tests were run at the same time with aquarium sand, as depicted above, to check for background contaminations.

2.1.2 Results & Conclusions:

Four kinds of polymer were distinguished:

Low-density polyethylene (LDPE), polypropylene (PP), polyethylene terephthalate (PET) and PP and LDPE copolymers.

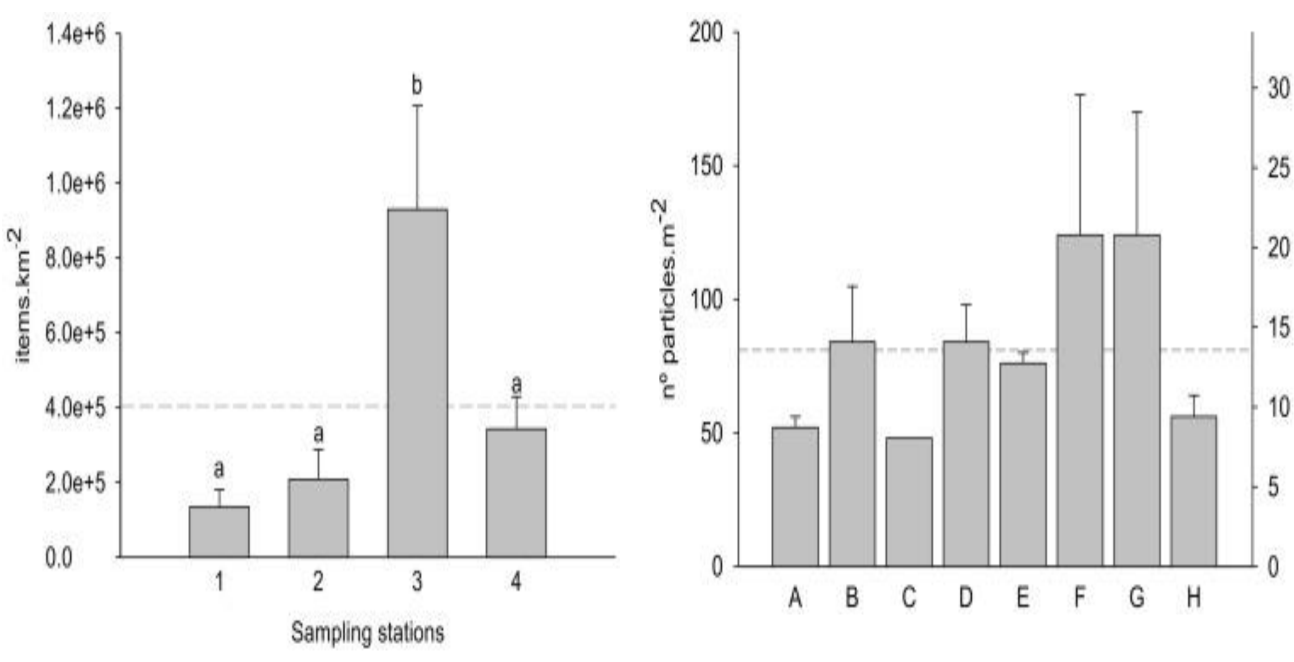

Figure 2.1: (a) Densities of floating microplastics. (b) Densities and concentration of microplastics in beach samples

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The results of the examination demonstrate that microplastics are inescapable in shoreline residue and surface seawaters along the Coast of Qatar. There were no huge contrasts in the convergence of microplastics among the eight intertidal areas examined, showing that microplastics are equitably appropriated and pervasive in the intertidal sandy shorelines of Qatar. Then again, spatial change was distinguished in surface seawater tests, with the biggest densities being reliably found at a separation of 10 km from shore. No worldly varieties were related with this sample, which proposes the presence of an assembly zone for microplastics. Low-density polyethylene and polypropylene were the prevailing polymers of microplastics detached from intertidal silt and seawater. A heterogeneous dispersion of sorts, hues and sizes of microplastics was recorded, albeit blue filaments in the size scope of 1– 5 mm were overwhelming in many examples, yet especially in surface seawater. Relinquished angling lines, nets and ropes have been distinguished as one of the principle hotspots for this kind of fiber, which is typically pervasive in close shore situations.

2.2 A new analytical approach for monitoring microplastics in marine sediments (Nuelle, 2014)

A two-step technique was developed to remove microplastics from silt. Initial, 1 kg silt was pre-separated utilizing the air induced overflow (AIO) technique, in light of fluidization in a sodium chloride (NaCl) solution. The first silt mass was decreased by up to 80%. As a result, it was conceivable to decrease the volume of sodium iodide (NaI) arrangement utilized for the ensuing buoyancy step. Recuperation of the entire system for polyethylene, polypropylene (PP), polyvinyl chloride (PVC), polyethylene terephthalate (PET), polystyrene and polyurethane with sizes of around 1 mm were somewhere in the range of 91 and 99%. In the wake of being put away for multi week in a 35% H_2O_2 arrangement, 92% of chose biogenic material had broken up totally or had lost its shading, while the tried polymers were safe. Microplastics were separated from three residue tests gathered from the North Sea island Norderney. Utilizing pyrolysis gas

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chromatography/mass spectrometry, these microplastics were distinguished as PP, PVC and PET.

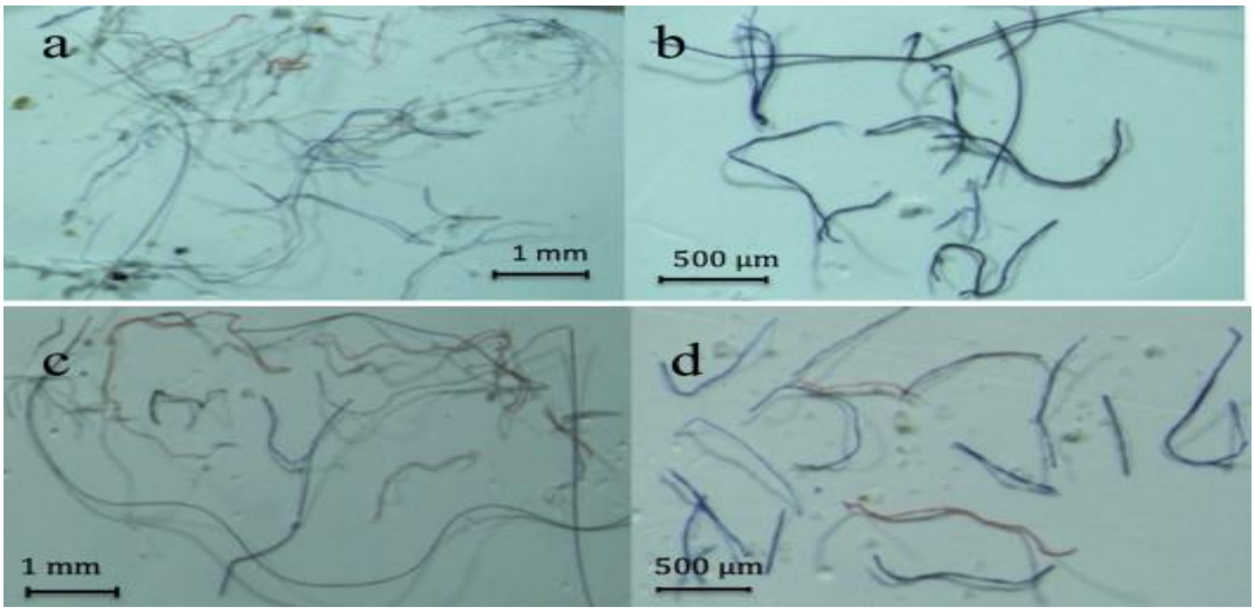

Figure 2.2: Extracted fibers from samples.

2.2.1 Sediment sampling and sample preparation:

Around 3 kg sediments were taken arbitrarily from a depth of around 3 cm and set in precleared dark colored glass bottles using stainless steel spoons. The spoons were cleaned with ocean water and lint free paper between each example. The containers were sealed and stored at room temperature in the lab until examination. Next, 2 kg wet silt from each sample was exchanged to clay bowls. The dishes were set in a drying oven at 60 °C until the silt had dried out. An aggregate of 1 kg dry residue (roughly 600 ml) was weighed out and sieved through a 1 mm mesh. The <1 mm division was additionally examined for the presence of microplastics utilizing the system of Fluidization (first extraction step) and Flotation (second extraction venture), with the special case that the sediments from Norderney did not experience treatment with H_2O_2 in light of the fact that they contained just little amounts of biogenic material.

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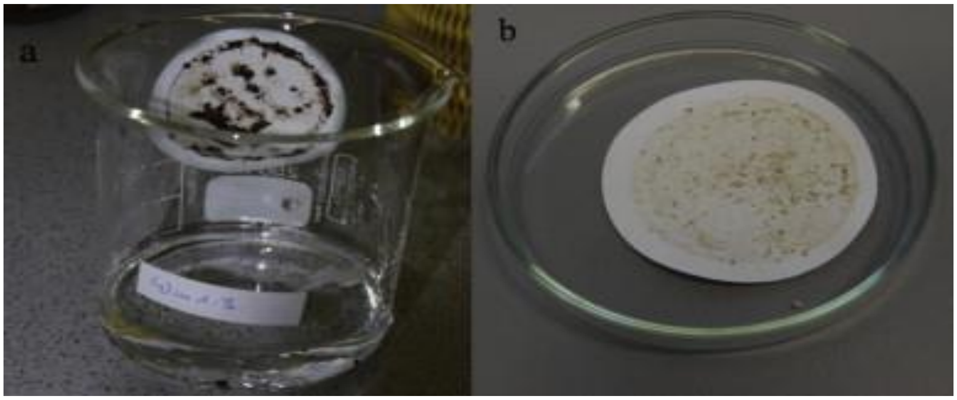

Figure 2.3: Filter of a beach sand sample before and after treatment with H_2O_2.

2.2.2 Results:

In the first place, the outcomes for the 30% H_2O_2 arrangement were exhibited regarding polymer particles >1 mm in size likewise demonstrated noticeable changes for plastic debris, which were increasingly straightforward, littler as well as slenderer after introduction. Unequivocal optical changes were additionally decided for PET (earthy shading) and LDPE (divided). For particles <1 mm, one scope of polymers was somewhat progressively straightforward, slenderer or littler (PVC, PET, PA, PUR, PP, LDPE).

Results of the tests including NaOH and HCl uncovered the optical changes to biogenic natural particles were more fragile than the response utilizing 30% H_2O_2. None of the biogenic natural particles had disintegrated totally or turned out to be completely straightforward. A solid response was just seen with 30% NaOH and 20% HCl, separately.

All silt tests gathered from Norderney contained strands with a length from about 0.5 mm to a couple of centimeters, with a diameter of under 100 μm. These samples were partitioned into colored and uncolored gatherings. Uncolored Samples contained dark, brown and beige strands as well as translucent filaments to recognize strands of a plausible common starting point from clearly colored strands – predominantly blue, red and green – where an artificial beginning was almost certain.

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2.3 First evaluation of neustonic microplastics in Black Sea waters (Aytan, 2016)

Microplastics were evaluated from zooplankton tests taken amid two travels along the southeastern bank of the Black Sea in the November of 2014 and February of 2015. In each journey, samples were gathered at 12 stations utilizing a WP2 net with 200-μm mesh. Microplastics (0.2– 5 mm) were found in 92% of the samples. The essential shapes were filaments (49.4%) trailed by plastic films (30.6%) and fragments (20%), and no micro beads were found. average microplastic concentration in November ($1.2 \pm 1.1 \times 103\ m^{-3}$) was higher than in February ($0.6 \pm 0.55 \times 103\ m^{-3}$). Expanded blending caused decreased concentrations in February. The heterogeneous spatial circulation (0.2×103–$3.3 \times 103\ m^{-3}$ for all examples) and aggregation in a few stations could be related to transport and maintenance systems connected with wind and by various sources of plastic. There were no factually noteworthy contrasts in MP fixation between sampling stations and sampling periods (t-test, $p < 0.05$). The generally high microplastic recommend that Black Sea is a hotspot for microplastic contamination and there is a urgency to comprehend their origins, transportation and consequences for marine life.

2.3.1 Sampling:

Neuston samples were collected from 12 sampling station during daylight hours (09:00–15:00), using a cylindro-conical WP2 net with 57 cm mouth diameter (0.25 m2), 260 cm long and 200-μm mesh. To determine the amount of seawater filtered, net was equipped with a digital flow meter. Net was towed horizontally for 5 min at ship speed of approximately 2 knots, in the upper 20 cm of the water column. To collect all plankton and MPs, net was washed with seawater. Then samples were transferred into the glass bottle and preserved in 4% borax-buffered formaldehyde. In the laboratory, to reduce the risk of contamination sample preparation was performed in a flow cabinet and all equipment was rinsed three times with filtered ultra-pure water. A cotton lab coat and

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nitrile gloves were worn at all times. Samples were suspended in the graduated cylinders for 48 h and MPs were separated from the samples by gravity method. MPs were visually counted using a binocular microscope and classified into three groups: fibers (from textiles and fishing nets), fragments (pieces from broken objects) and plastic films (bags, wrappings, or pieces of them). This examination of the samples was repeated twice to ensure the detection of all the smallest microplastic items.

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CHAPTER 3

EXPERIMENTAL TECHNIQUES

The main focus area of this project is Arabian Sea. Arabian Sea is the only sea that is attached to Pakistan. Why we selected this area for our project? The reason for this is that it is the only sea to Pakistan, also many other countries are researching on the sea areas near to their countries but there is no kind of research performed on Arabian that is more focused to the sources and effects of plastics and microplastics there. Hence, few researches are performed on that areas that tell about the disposal of plastics there.

Arabian Sea is the hub of the polluted water of the whole industrial area of Pakistan. All the water of Pakistan ends up in the Arabian Sea. The ratio of recycling of polluted water is very less. A research shows the figure that 95 % of the plastic pollution in the world ocean come from the overall ten rivers which hold the whole wastage directly to the sea. From that ten rivers one is the Indus River which is the largest and main river of Pakistan as well as Asia and this ends up directly in the Arabian Sea. Indus River holds the large amount of unwanted municipal, industrial as well as agricultural waste. So, the amount of plastic is very much.

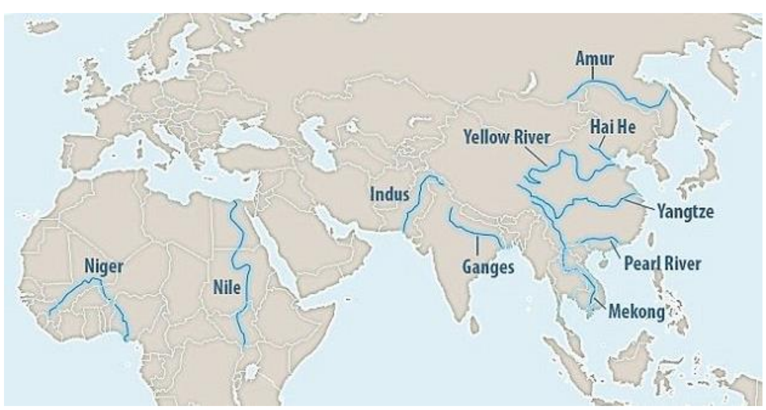

Figure 3.1: Figure shows the ten rivers, which make the 95% of plastic pollution.

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3.1 Area of Study:

- Rawal Lake
- Arabian Sea

3.1.1 Rawal Lake:

Before moving toward the Arabian Sea, we first took step to perform experimentation on the Rawal Lake. This lake is located near Islamabad territory. We also have to compare our data obtained from Rawal Lake with that of Arabian Sea and drive the conclusion about the whole plastic wastage.

Rawal lake is an artificial reservoir that provides the water to the areas of Islamabad and Rawalpindi, it has the surface area of 8.8 km^2. Different types of recreation activities are arranged there, which includes boating, sailing and diving facilities. The number of visitors is increasing every year. Due to this, every year plastic waste is increasing. Hence Water and Sanitation Agency (WASA) is working on the removal of plastic waste from water. But still there is very pollution.

Figure 3.2: Plastic pollution near water filtration plant of Rawal lake.

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3.1.2 Arabian Sea:

Pakistan covers the area of 950 km alongside Arabian Sea. It includes Indian border near Ran of Kutch in the South-East to the border of Iran near Jiwani in the North-West the Economic Zone is about 242,000 sq km. On the basis of provinces, the coastal area of Pakistan is divided into two different section, the Baluchistan coast (length: ~755 km) and Sindh coast. The Indus River Delta zone and the Karachi coast Aare part of Sindh province. With the exception of the Karachi metropolis (population over 12.1 million and industrial base over 1100 large industrial units) along the Sindh coast, major parts of the coastal areas of Pakistan are heavily populated. The area throughout Baluchistan coast have small coastal towns and developing harbors, such as Jiwani, Gwadar, Pasne, Ormaara and, Sonmiaani, which have a total population of about 1.1 million. The coastal zone of Pakistan plays an important role in national economy. The mangroove ecosystems of the Indus delta areas, Sonmiaani Bay, and Jiwani are also of important interest to Pakistan. This habitat is main source for shrimps and different species of fishes as well. In the absence of other resources, it proves to be important contributor in production of timber, charcoal and fodder for animals. The pollution issues in these areas of Pakistan have arisen mainly due to discharge of industrial waste and domestic waste.

Karachi’s port, is one of the major sources contributing to marine pollution. Karachi generates 11,000 tons of solid waste every day, due to no proper waste management system this dump plastics ends up in Arabian sea which is the enemy for marine life.

Pollution is not only threatening marine life, fish catch and aesthetic value, but it is also causing disasters. According to scientists, Arabian Sea's tropical cyclones that are now becoming devastating, are also caused by increasing marine pollution.

In recent years, a garbage patch was found in the Indian Ocean. The increasing number of pollutions have resulted in the extinction of many fish species

3.2 SAMPLING LOCATIONS:

3.2.1 Rawal Lake:

Experiments are performed on two locations of Rawal Lake.

- One is near the boating area of lake.
- Near the spillway of Dam.

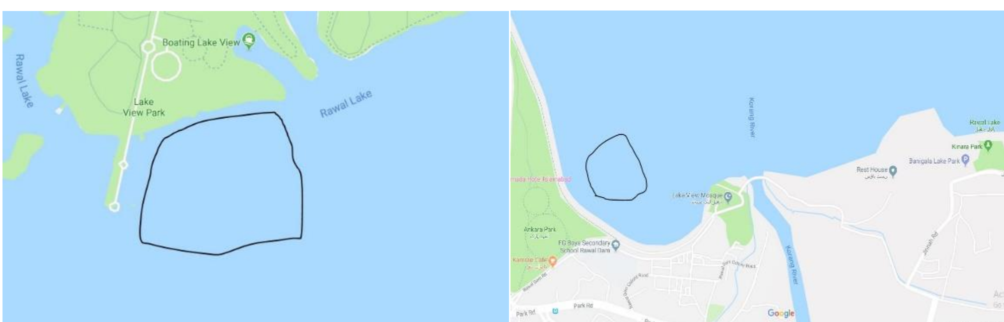

Figure 3.3: (a) boating area of lake (b) Near spillway.

3.2.2 Arabian Sea:

3.2.2.1 Manora Beach:

Manora is a small area (2.5 km²) located just near the Karachi's port. Manora beach is 11 kilometers drive away from main population of Karachi. The western side of the

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harbor is comprising of mangrove forests which border the Sandspit and Manora beach.

Manora is also a popular picnic spot for people as a lot of people visit this place o daily basis because of its sandy beaches.

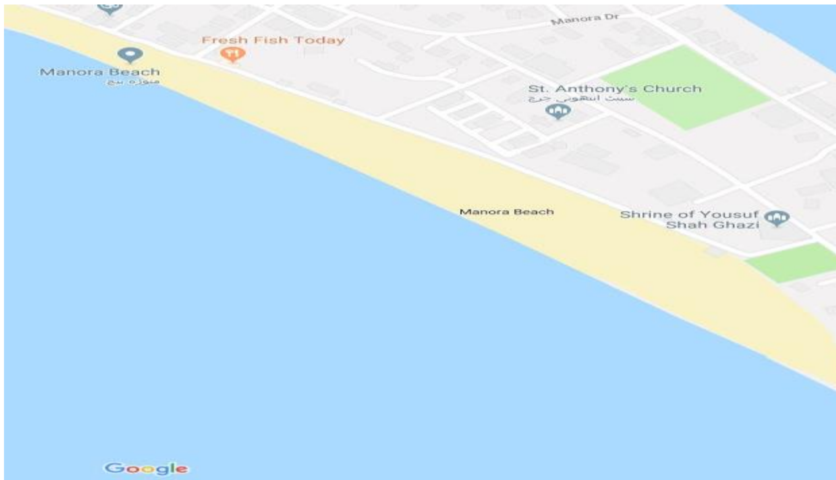

Figure 3.4: Manora Beach Location

3.2.2.2 Hawke's Bay Beach:

Hawke's Bay is located on the south west of Karachi. The routes leading to hawkes bay are maripur road and goth rakh road. The beach is named after Bladen Wilmer Hawke, who owned a house there in 1932.he occasionally used it for parties and tours.

it is an important tourist spot because of its color of water and its long sandy beaches. it is a populated tourist spot as a lot of people visit here daily

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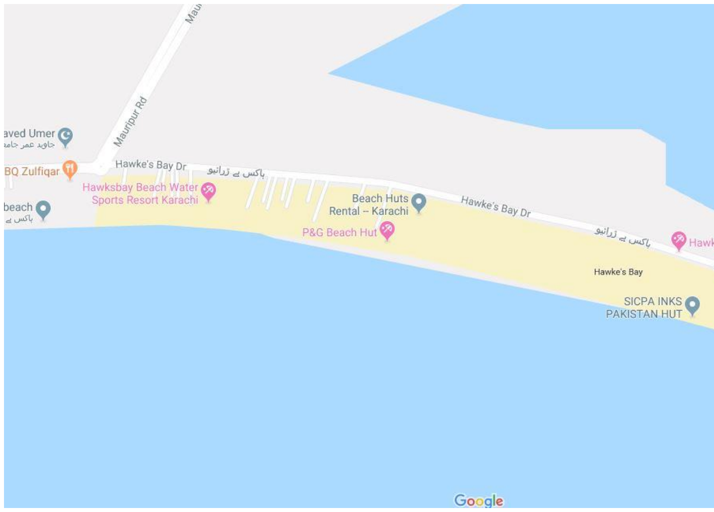

Figure 3.5: Hawke's Bay Location

3.3 Material and Methods:

Our project is to research about the plastic as well as the microplastic. So, we don't have to take any risk about our equipment in Arabian Sea. Microplastics are of size less than 5 mm. They can't be collected with the help of simple net. We have to use the net of 300 mesh size that can collect particles of size less than 5mm. For that we have different types of nets:

- Manta net
- Nylon Net
- Stainless steel net

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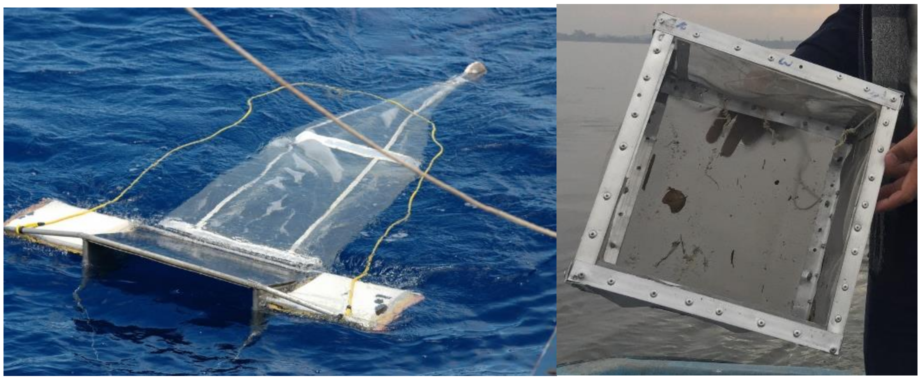

Figure 3.6 (a) Manta Net

Figure 3.6 (b) Stainless steel net

3.3.1 Stainless Steel Net:

Stainless steel net is a squared shape net and designed in SCME workshop with net of 300 mesh size. It has a stand of Aluminum which holds the net. Some allowance is set to hold the water pressure. It is fixed with the boat and moved in the water to the depth of around 0.5 ft. We have to collect the plastics and microplastics. Due to less density, particles float on the surface of water. Further experimental techniques and methods are explained further.

3.4 SAMPLING AND EXPERIMENTATION:

3.4.1 RAWAL LAKE:

The sampling method for Rawal lake is explained in steps:

- The stainless-steel net is deployed on the side of the boat. The boat is moved for around 20 minutes each trip.
- Plastics are collected in the net. (microplastics as well as macro plastics)
- All the plastic debris are separated from the net with the help of water and collected in the beakers.

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- Microplastics are investigated under microscope according to the:
- Various size range.
- Different colors.
- Types of samples (threads, filaments etc.)
- While macro plastics are separated with naked eye.
- Further Experimental characterizations are performed on the samples.

3.4.1.1 EXPERIMENTAL CONSTRAINTS FOR BOAT:

Depth	Approx. 1 ft.
Sampling time	20-30 mins
Boat Speed	2-3 knots
Temperature	Moderate (15-20 ^{0}C)

3.4.2 ARABIAN SEA:

3.4.2.1 Sampling:

Sampling can be done by using two different methods. first one is collecting plastics and microplastics from water using manta net method and the second one is collecting sand sediment method. The method preferred for Arabian sea was sand sediment method because sediments have been identified as an important place for microplastics. sediments can contain up to 4% microplastics by weight. The reaction with sunlight break plastics into microplastics and marine aggregates can reduce the buoyancy force of plastics, facilitating their movement to the seafloor which leads them to beaches. so, four samples of sand were taken from 2 beaches of Karachi named as Hawke's bay and manora beach i.e. two from each beach. each sample was comprised of 1 kg sand. after the collection of samples, the most important part was to separate the plastics and

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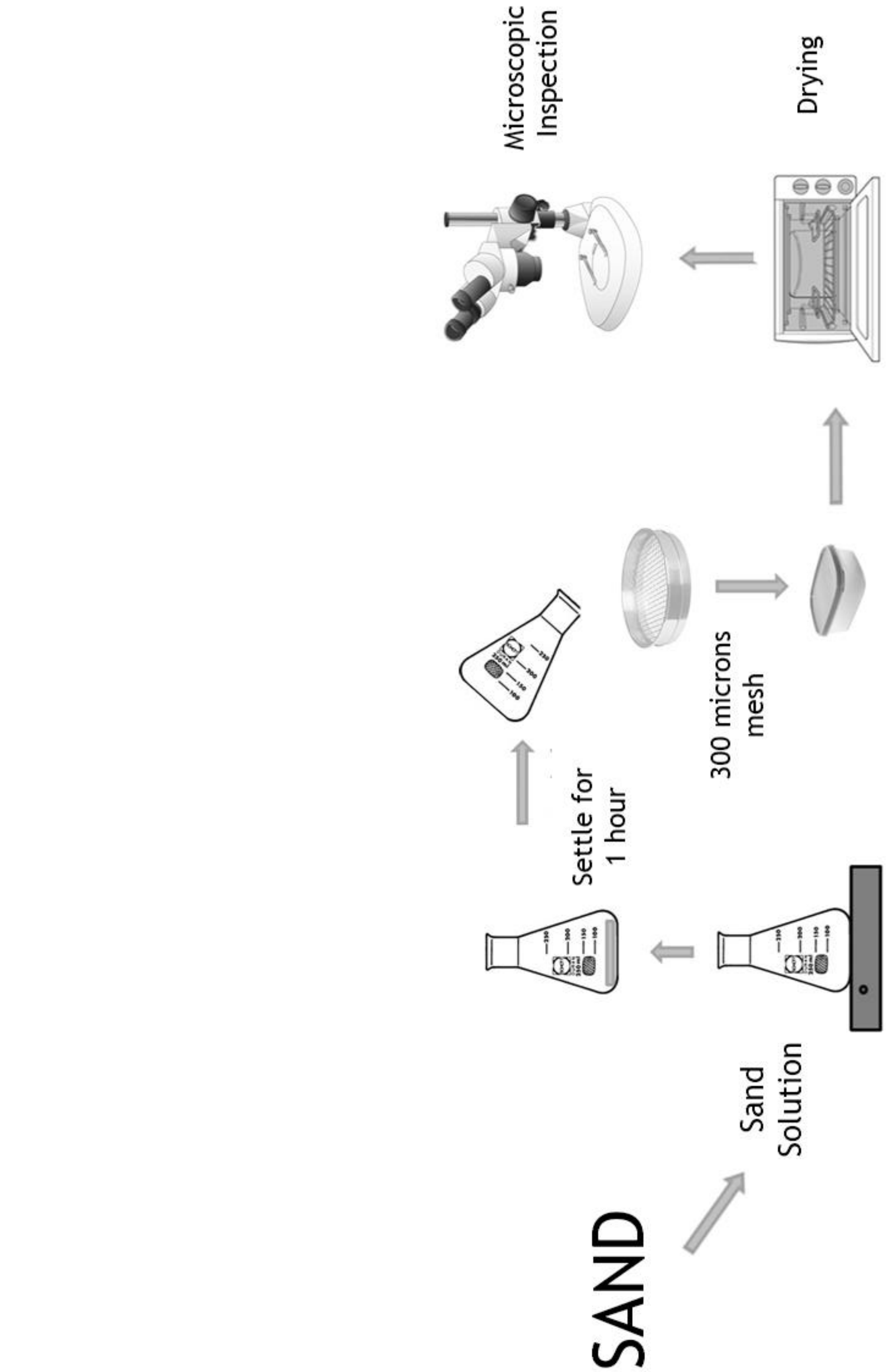
microplastics from sand for this purpose the process of density floatation was used. This process was repeated multiple times to make sure every plastic particle is separated from sand sediments.

3.4.3 Separation of microplastics from the sea surface samples:

- Pour the collected sample on the mesh with the size of 300 microns. remove the non-plastic litter from the sample by visual inspection.
- After collection of plastic litter collect the large plastic particles.
- Concentrate all remaining pieces in in one end of the petri dish.
- Now complete the microscopic examination and search for microplastic particles.
- To identify microplastics use there features i.e., no cell structure, uneven, sharp, crooked edges, uniform thickness, distinctive colors (blue, green, yellow, etc.).


SAND
Sand Solution
Settle for 1 hour
300 microns mesh
Drying
Microscopic Inspection

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CHAPTER 4

SOURCES AND EFFECTS

4.1 Influence of the Source:

The term microplastics is specified for particles having size less than 5 mm while those particles having size greater than 5mm are classified as macro plastics. Microplastics are usually produced by two methods, one by direct manufacturing of that size for some particular applications. Other method is their production by direct fragmentation or UV degradation of large plastic debris into the smaller pieces. Those smaller pieces are very large in quantity.

Microplastics particles are usually composed of six major types.

- Polyethylene
- Polypropylene
- Expanded polystyrene
- Polyvinyl chloride
- Polyamide (Nylon)
- Polyethylene terephthalate (PET)

Very few particles sink into the deep water. Most of them float on the surface due to low density. Organic and inorganic compounds or biofilms form a coating on the solid particles in the sea, by this the floating particles sink into the deep ocean.

Even if all releases of plastics in environment is stopped or ceased immediately, the number of microplastic will still continue to increase due to the fragmentation or UV degradation of large species.

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4.1.2 Distribution of Plastics in Marine Environment:

Here is a graph that show the relative search history of marine debris and litter with time. With time marine litter is increasing proportionally, shown in graph:

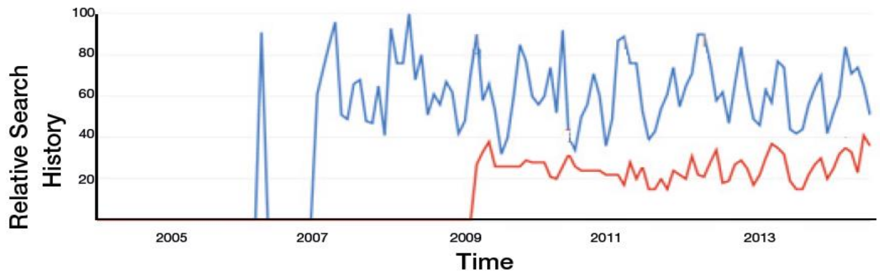

Figure 4.1: (Upper curve) Marine debris (lower curve) Marine litter

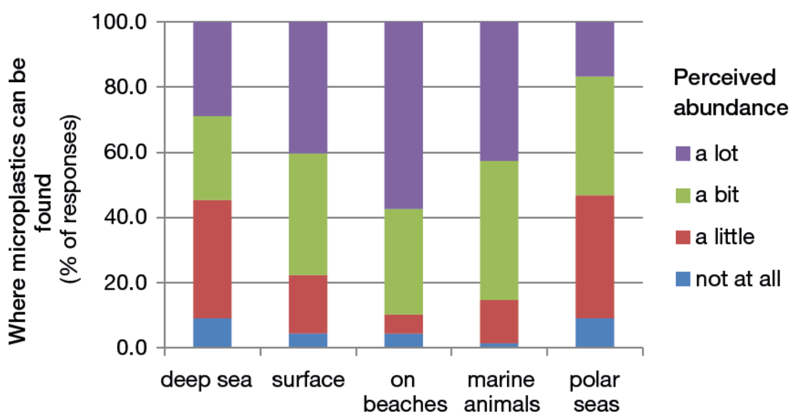

Figure 4.2 : frequency of responses about the abundance of microplastics in marine environment (GESAMP pilot survey for n=68)

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4.2 Sources of Plastics and Microplastics:

Different sources of plastics and microplastics are classified according to their various size ranges. Different size ranges vary from less than 5mm to greater than 1 m are shown here.

SIZE CATEGORIES	DIAMETER			
	Micro <5 mm	Meso <2.5 cm	Macro <1 m	Mega >1 m
SOURCES	**Primary microplastics** **Secondary microplastics** – fragmentation of larger plastic items	Direct and indirect: including fragmentation of larger plastic items	Direct: lost items from maritime activities or from rivers	Direct: abandoned gear, fishing equipment's
EXAMPLES	**Primary:** resin beads, microbeads from personal care products; **Secondary:** Textile fibers, tire dust	Bottle caps, fragments	Plastic bags, food and other packaging, fishing floats, buoys, balloons	Abandoned fishing nets and traps, rope, boat hulls, plastic films from agriculture

4.3 Observation on Occurrence of Plastic Species:

4.3.1 North Sea.

Marine species	Location	Date of study	Purpose of study	Details of ingestion	Reported impact of ingestion	Reference
North Sea						
Mytilus edulis, Blue mussel	Belgium	March 2013	Comparison of consumption mussels and wild type mussels	Microscopic fibres ranging from 200 – 1500 μm identified in mussel tissues	Not investigated	De Witte et al. 2014
Mytilus galloprovincialis, Mediterranean mussel	Belgium	March 2013	Comparison of consumption mussels and wild type mussels	Microscopic fibres ranging from 200 – 1500 μm identified in mussel tissues	Not investigated	De Witte et al. 2014
Mytilus edulis/ galloprovincialis hybrid	Belgium	March 2013	Comparison of consumption mussels and wild type mussels	Microscopic fibres ranging from 200 – 1500 μm identified in mussel tissues	Not investigated	De Witte et al. 2014
Mytilus edulis, Blue mussel	Germany	2013	Quantification of microplastic level in bivalve species reared for human consumption	Average of 0.36 ± 0.07 particles per gram tissue (ww) identified	Not investigated	Van Cauwenberghe & Janssen 2014
Clupea harengus, Herring	North Sea	July – October 2010	Quantify the occurrence, number and size of plastic particles and test the hypothesis that ingested plastic adversely affects the condition of fish	8/566 individuals contained plastic particles	No significant difference in condition factor between individuals that contained plastic and those without	Foekema et al. 2013
Gadus morhua, Cod	North Sea	July – October 2010	Quantify the occurrence, number and size of plastic particles and test the hypothesis that ingested plastic adversely affects the condition of fish	10/80 individuals contained plastic particles	No significant difference in condition factor between individuals that contained plastic and those without	Foekema et al. 2013
Merlangius merlangus, Whiting	North Sea	July – October 2010	Quantify the occurrence, number and size of plastic particles and test the hypothesis that ingested plastic adversely affects the condition of fish	6/105 individuals contained plastic particles	No significant difference in condition factor between individuals that contained plastic and those without	Foekema et al. 2013
Melanogrammus aeglefinus, Haddock	North Sea	July – October 2010	Quantify the occurrence, number and size of plastic particles and test the hypothesis that ingested plastic adversely affects the condition of fish	6/97 individuals contained plastic particles	Condition factor significantly lower in individuals that contained plastic than those without plastic. Data deemed insufficient to confirm the hypothesis	Foekema et al. 2013
Trachurus trachurus, Horse mackerel	North Sea	July – October 2010	Quantify the occurrence, number and size of plastic particles and test the hypothesis that ingested plastic adversely affects the condition of fish	1/100 individuals contained plastic particles	No significant difference in condition factor between individuals that contained plastic and those without	Foekema et al. 2013

4.3.2 Mediterranean Sea:

Marine species	Location	Date of study	Purpose of study	Details of ingestion	Reported impact of ingestion	Reference
Mediterranean Sea						
Calonectris diomedea, Cory's shearwater	Catalan Coast, Spain	2003–2010	Opportunistic study to quantify and characterize plastics in seabirds caught as bycatch by longliner fishing vessels	47/49 individuals contained plastic particles. Average of 14.6 ± 24.0 particles per bird and 22.4 ± 48.8 mg in weight	No signficant correlation identified between mean body mass and the number or mass of ingested plastic	Codina-Garcia et al. 2013
Puffinus mauretanicus, Balearic shearwater	Catalan Coast, Spain	2003–2010	Opportunistic study to quantify and characterize plastics in seabirds caught as bycatch by longliner fishing vessels	32/46 individuals contained plastic particles. Average of 2.5 ± 2.9 particles per bird and 3.8 ± 8.4 mg in weight	No significant correlation identified between mean body mass and the number or mass of ingested plastic	Codina-Garcia et al. 2013
Puffinus yelkouan, Yelkouan shearwater	Catalan Coast, Spain	2003–2010	Opportunistic study to quantify and characterize plastics in seabirds caught as bycatch by longliner fishing vessels	22/71 individuals contained plastic particles. Average of 4.9 ± 7.3 particles per bird and 29.8 ± 86.6 mg in weight	No significant correlation identified between mean body mass and the number or mass of ingested plastic	Codina-Garcia et al. 2013
Ichthyaetus audouinii, Audouin's gull	Catalan Coast, Spain	2003–2010	Opportunistic study to quantify and characterize plastics in seabirds caught as bycatch by longliner fishing vessels	2/15 individuals contained plastic particles. Average of 9.8 ± 35.7 particles per bird and 22.7 ± 67.6 mg in weight	No significant correlation identified between mean body mass and the number or mass of ingested plastic	Codina-Garcia et al. 2013
Larus michahellis, Yellow-legged gull	Catalan Coast, Spain	2003–2010	Opportunistic study to quantify and characterize plastics in seabirds caught as bycatch by longliner fishing vessels	4/12 individuals contained plastic particles. Average of 0.9 ± 1.98 particles per bird and 1.4 ± 2.3 mg in weight	No significant correlation identified between mean body mass and the number or mass of ingested plastic	Codina-Garcia et al. 2013
Ichthyaetus melanocephalus, Mediterranean gull	Catalan Coast, Spain	2003–2010	Opportunistic study to quantify and characterize plastics in seabirds caught as bycatch by longliner fishing vessels	1/4 individuals contained plastic particles. Average of 3.7 ± 7.5 particles per bird and 12.6 ± 25.3 mg in weight	No significant correlation identified between mean body mass and the number or mass of ingested plastic	Codina-Garcia et al. 2013
Rissa tridactyla, Blacked-legged kittiwake	Catalan Coast, Spain	2003–2010	Opportunistic study to quantify and characterize plastics in seabirds caught as bycatch by longliner fishing vessels	2/4 individuals contained plastic particles. Average of 1.2 ± 1.9 particles per bird and 4.9 ± 6.7 mg in weight	No significant correlation identified between mean body mass and the number or mass of ingested plastic	Codina-Garcia et al. 2013
Morus bassanus, Gannet	Catalan Coast, Spain	2003–2010	Opportunistic study to quantify and characterize plastics in seabirds caught as bycatch by longliner fishing vessels	1/8 individuals contained plastic particles. Average of 0.1 ± 0.3 particles per bird and 0.3 ± 0.8 mg in weight	No significant correlation identified between mean body mass and the number or mass of ingested plastic	Codina-Garcia et al. 2013
Catharacta skua, Great skua	Catalan Coast, Spain	2003–2010	Opportunistic study to quantify and characterize plastics in seabirds caught as bycatch by longliner fishing vessels	1/2 individuals contained plastic particles. Average of 0.5 ± 0.7 particles per bird and 0.4 ± 0.5 mg in weight	No significant correlation identified between mean body mass and the number or mass of ingested plastic	Codina-Garcia et al. 2013

4.3.3 North Atlantic Ocean:

Marine species	Location	Date of study	Purpose of study	Details of ingestion	Reported impact of ingestion	Reference
North Atlantic Ocean						
Nephrops norvegicus, Norway lobster	Clyde Sea, UK	May – June 2009	To determine whether N. norvegicus ingests small plastic fragments in the Clyde Sea	100/120 animals contained plastic in their stomach. Predominantly monofilament	Not investigated	Murray & Cowie 2011
Crassostrea gigas, Pacific oyster	Brittany, France	2013	Quantification of microplastic level in bivalve species reared for human consumption	Average of 0.47 $\pm$ 0.16 particles per gram tissue (ww) identified	Not investigated	Van Cauwenberghe & Janssen 2014
Myoxocephalus aenus, Grubby	Long Island Sound, USA	February – May 1972	Opportunistic sampling of fish caught for analysis of power plant impacts	White, opaque polystyrene spherules ingested and found in the gut	Not investigated	Carpenter et al. 1972
Pseudopleuronectes americanus, Winter flounder	Long Island Sound, USA	February – May 1972	Opportunistic sampling of fish caught for analysis of power plant impacts	White, opaque polystyrene spherules ingested and found in the gut	Not investigated	Carpenter et al. 1972
Roccus americanus, White perch	Long Island Sound, USA	February – May 1972	Opportunistic sampling of fish caught for analysis of power plant impacts	White, opaque polystyrene spherules ingested and found in the gut	Not investigated	Carpenter et al. 1972
Menidia menidia, Silversides	Long Island Sound, USA	February – May 1972	Opportunistic sampling of fish caught for analysis of power plant impacts	White, opaque polystyrene spherules ingested and found in the gut	Not investigated	Carpenter et al. 1972
Merlangius merlangus, Whiting	Plymouth, UK	June 2010 – July 2011	Part of routine long term trawl sampling. 70–75 mm cod end mesh size	16/50 contained plastic particles	Not investigated	Lusher at al. 2013
Micromesistius poutassou, Blue whiting	Plymouth, UK	June 2010 – July 2011	Part of routine long term trawl sampling. 70–75 mm cod end mesh size	14/27 contained plastic particles	Not investigated	Lusher at al. 2013
Trachurus trachurus, Atlantic horse mackerel	Plymouth, UK	June 2010 – July 2011	Part of routine long term trawl sampling. 70–75 mm cod end mesh size	16/56 contained plastic particles	Not investigated	Lusher at al. 2013
Trisopterus minutus, Poor cod	Plymouth, UK	June 2010 – July 2011	Part of routine long term trawl sampling. 70–75 mm cod end mesh size	20/50 contained plastic particles	Not investigated	Lusher at al. 2013
Zeus faber, John dory	Plymouth, UK	June 2010 – July 2011	Part of routine long term trawl sampling. 70–75 mm cod end mesh size	20/42 contained plastic particles	Not investigated	Lusher at al. 2013
Aspitrigla cuculus, Red gurnard	Plymouth, UK	June 2010 – July 2011	Part of routine long term trawl sampling. 70–75 mm cod end mesh size	34/66 contained plastic particles	Not investigated	Lusher at al. 2013

4.3.4 South Atlantic Ocean:

Marine species	Location	Date of study	Purpose of study	Details of ingestion	Reported impact of ingestion	Reference
South Atlantic Ocean						
Pachyptila vittata, Broad-billed prion	Gough Island, Central South Atlantic Ocean	October & November 1979	Opportunistic sampling after observing plastic pellets in regurgitated skua pellets	Thirty-three plastic pellets observed with prion bones and feathers in regurgitated predatory Great skua Catharacta skua pellets	Not investigated	Bourne & Imber 1980
Puffinus gravis, Great shearwater	Gough Island, Central South Atlantic Ocean	September – October 1983	Dead birds collected for analysis and others harvested as necessary for sampling	11/13 birds contained plastic particles in their gizzards	No negative impacts identified	Furness 1985a
Pelagodroma marina, White faced storm petrel	Gough Island, Central South Atlantic Ocean	September – October 1983	Dead birds collected for analysis and others harvested as necessary for sampling	16/19 birds contained plastic particles in their gizzards	Statistically weak correlation identified between mass of ingested plastic and body mass	Furness 1985a
Pachyptila vittata, Broad-billed prion	Gough Island, Central South Atlantic Ocean	September – October 1983	Dead birds collected for analysis and others harvested as necessary for sampling	12/31 birds contained plastic particles in their gizzards	No negative impacts identified	Furness 1985a
Fregetta grallaria, White-bellied storm petrel	Gough Island, Central South Atlantic Ocean	September – October 1983	Dead birds collected for analysis and others harvested as necessary for sampling	5/13 birds contained plastic particles in their gizzards	No negative impacts identified	Furness 1985a
Garrodia nereis, Grey-backed storm petrel	Gough Island, Central South Atlantic Ocean	September – October 1983	Dead birds collected for analysis and others harvested as necessary for sampling	3/11 birds contained plastic particles in their gizzards	No negative impacts identified	Furness 1985a
Stercorarius antarcticus, Tristan skua	Gough Island, Central South Atlantic Ocean	September – October 1983	Dead birds collected for analysis and others harvested as necessary for sampling	1/11 birds contained plastic particles in their gizzards	No negative impacts identified	Furness 1985a
Puffinus assimilis, Little shearwater	Gough Island, Central South Atlantic Ocean	September – October 1983	Dead birds collected for analysis and others harvested as necessary for sampling	1/13 birds contained plastic particles in their gizzards	No negative impacts identified	Furness 1985a
Lugensa brevirostris, Kerguelen petrel	Gough Island, Central South Atlantic Ocean	September – October 1983	Dead birds collected for analysis and others harvested as necessary for sampling	1/13 birds contained plastic particles in their gizzards	No negative impacts identified	Furness 1985a
Pterodroma incerta, Atlantic petrel	Gough Island, Central South Atlantic Ocean	September – October 1983	Dead birds collected for analysis and others harvested as necessary for sampling	1/13 birds contained plastic particles in their gizzards	No negative impacts identified	Furness 1985a
Pterodroma mollis, Soft-plumaged petrel	Gough Island, Central South Atlantic Ocean	September – October 1983	Dead birds collected for analysis and others harvested as necessary for sampling	1/18 birds contained plastic particles in their gizzards	No negative impacts identified	Furness 1985a

4.3.5 North Pacific Ocean:

Marine species	Location	Date of study	Purpose of study	Details of ingestion	Reported impact of ingestion	Reference
North Pacific						
Fulmarus glacialis, Northern fulmar	Alaska	1988–1990	Targetted sampling of seabirds for feeding ecology studies	16/19 birds had ingested plastic particles (mainly pellets)	Not investigated	Robards et al. 1995
Puffinus tenuirostris, Short-tailed shearwater	Alaska	1988–1990	Targetted sampling of seabirds for feeding ecology studies	4/5 birds had ingested plastic particles (mainly pellets)	Not investigated	Robards et al. 1995
Oceanodroma furcata, Fork-tailed storm petrel	Alaska	1988–1990	Targetted sampling of seabirds for feeding ecology studies	18/19 birds had ingested plastic particles (mainly pellets)	Not investigated	Robards et al. 1995
Oceanodroma leucorhoa, Leach's storm petrel	Alaska	1988–1990	Targetted sampling of seabirds for feeding ecology studies	31/64 birds had ingested plastic particles (mainly pellets)	Not investigated	Robards et al. 1995
Phalacrocorax pelagicus, Pelagic cormorant	Alaska	1988–1990	Targetted sampling of seabirds for feeding ecology studies	2/10 birds had ingested plastic particles (mainly pellets)	Not investigated	Robards et al. 1995
Larus canus, Mew gull	Alaska	1988–1990	Targetted sampling of seabirds for feeding ecology studies	1/4 birds had ingested plastic particles (mainly pellets)	Not investigated	Robards et al. 1995
Rissa tridactyla, Black-legged kittiwake	Alaska	1988–1990	Targetted sampling of seabirds for feeding ecology studies	20/256 birds had ingested plastic particles (mainly pellets)	Not investigated	Robards et al. 1995
Rissa brevirostris, Red-legged kittiwake	Alaska	1988–1990	Targetted sampling of seabirds for feeding ecology studies	4/15 birds had ingested plastic particles (mainly pellets)	Not investigated	Robards et al. 1995
Uria aalge, Common guillemot	Alaska	1988–1990	Targetted sampling of seabirds for feeding ecology studies	1/134 birds had ingested plastic particles (mainly pellets)	Not investigated	Robards et al. 1995
Ptychoramphus aleuticus, Cassin's auklet	Alaska	1988–1990	Targetted sampling of seabirds for feeding ecology studies	4/35 birds had ingested plastic particles (mainly pellets)	Not investigated	Robards et al. 1995
Aethia psittacula, Parakeet auklet	Alaska	1988–1990	Targetted sampling of seabirds for feeding ecology studies	195/208 birds had ingested plastic particles (mainly pellets)	Not investigated	Robards et al. 1995
Aethia cristatella, Crested auklet	Alaska	1988–1990	Targetted sampling of seabirds for feeding ecology studies	1/40 birds had ingested plastic particles (mainly pellets)	Not investigated	Robards et al. 1995
Cepphus columba, Pigeon guillemot	Alaska	1988–1990	Targetted sampling of seabirds for feeding ecology studies	1/43 birds had ingested plastic particles (mainly pellets)	Not investigated	Robards et al. 1995
Fratercula corniculata, Horned puffin	Alaska	1988–1990	Targetted sampling of seabirds for feeding ecology studies	44/120 birds had ingested plastic particles (mainly pellets)	Not investigated	Robards et al. 1995
Fratercula cirrhata, Tufted puffin	Alaska	1988–1990	Targetted sampling of seabirds for feeding ecology studies	120/489 birds had ingested plastic particles (mainly pellets)	Not investigated	Robards et al. 1995

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4.4 Effects of plastics:

Everybody is aware of drastic effects of plastics in marine environment. All the marine animals are being injured and killed by plastic pollution, and its it thought that 600 species could go extinct because of it. According to current stats 360 species are affected by plastics till now which includes 83% of sea turtle species, 45% of all seabird species

and 47% of all marine mammal species. The main reason for death of these animals are entanglement and ingestion of plastics. current stats show that one out of every three marine mammals are caught up in any of the plastic litter the main sources of these plastics are the fishing gear, nets and shopping bags for example - and that over 91% of seabirds have pieces of plastics in their bellies. seabirds actually feed on the seafloors and the plastics. One study found that 98% of chicks sampled contained plastics, and that the quantity of plastic being ingested was increasing over time. There are several accounts of various whale species found dead after plastic consumption, such as in 2002 when a Minke whale was found with 800 kg of plastic bags in its stomach or in 2004 when a Cuvier's Beaked whale was found with tightly packed black plastic bags blocking the entrance to its stomach. The obvious point is that along with overfishing, pollution is contributing to the decimation of fish stocks. Any further

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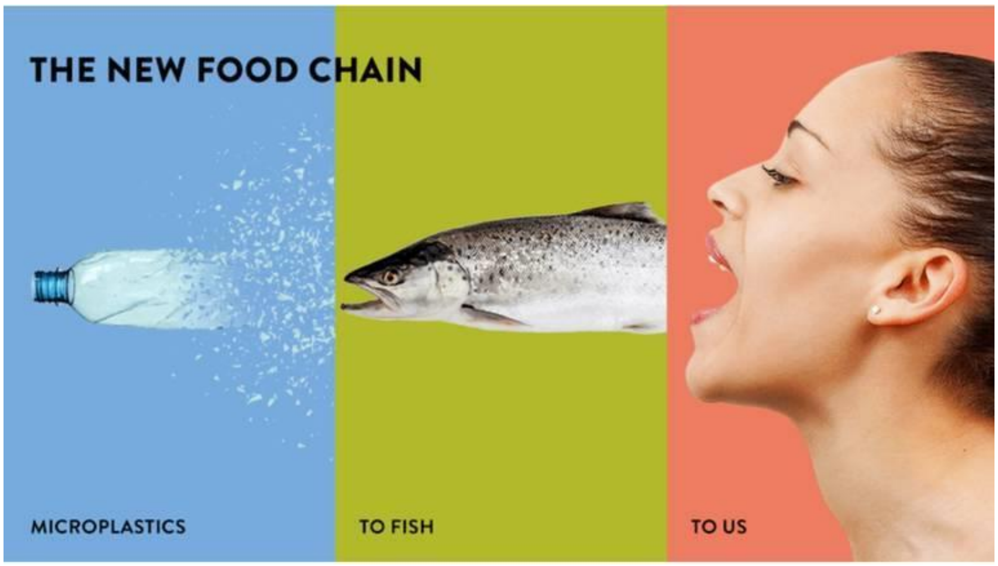
pressure on fish populations is likely to lead to a collapse, resulting in a shortage of food for humans. Just as concerning, however, is how the existing seafood we are consuming now might be impacting our physical wellbeing. We tend to think that marine debris is unsightly but ultimately not a direct threat to our health. Now we are starting to realize the connection between plastic debris, water quality, and seafood quality. Plastics are now proven to soak up and absorb pollutants containing chemicals such as bisphenol A (BPA), Ps oligomer, polychlorinated biphenyls (PCBs), and even DDT.



These toxins are released both in the ocean and in the marine animals who consume them. They are known to cause liver problems, hormonal disruption, immune system problems, and childhood development issues. Recent studies have found that more than a quarter of all fish now contain plastic, including those that we consume as seafood. We already know elements like mercury can build their way up the food chain and it is an existing concern for large fish such as tuna. Plastics and plastic related chemicals are no different.

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CHAPTER 5

RESULTS AND CONCLUSION

The microplastics were extracted from the samples using 300-micron mesh size net. These samples were collected from Rawal Lake and Arabian Sea. The samples for the Rawal Lake were collected from the surface of the water body while the samples for the Arabian Sea were collected from sand of different location on the Arabian Sea.

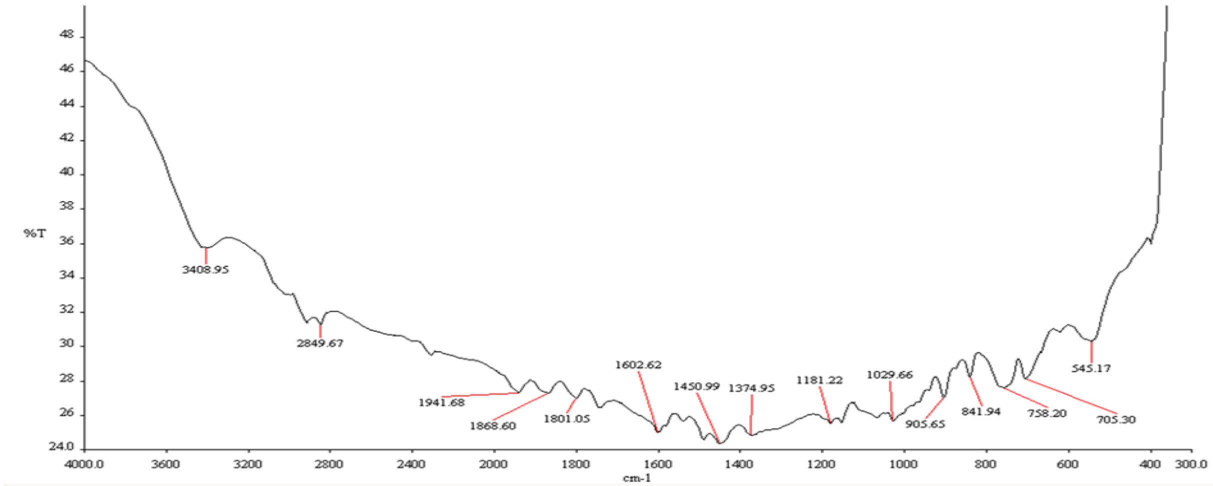
For Rawal Lake, the weight of microplastics extracted per km of surface of sampling area was 16-17 grams. Particles of the white and blue colors were abundant in the plastic debris and microplastics.

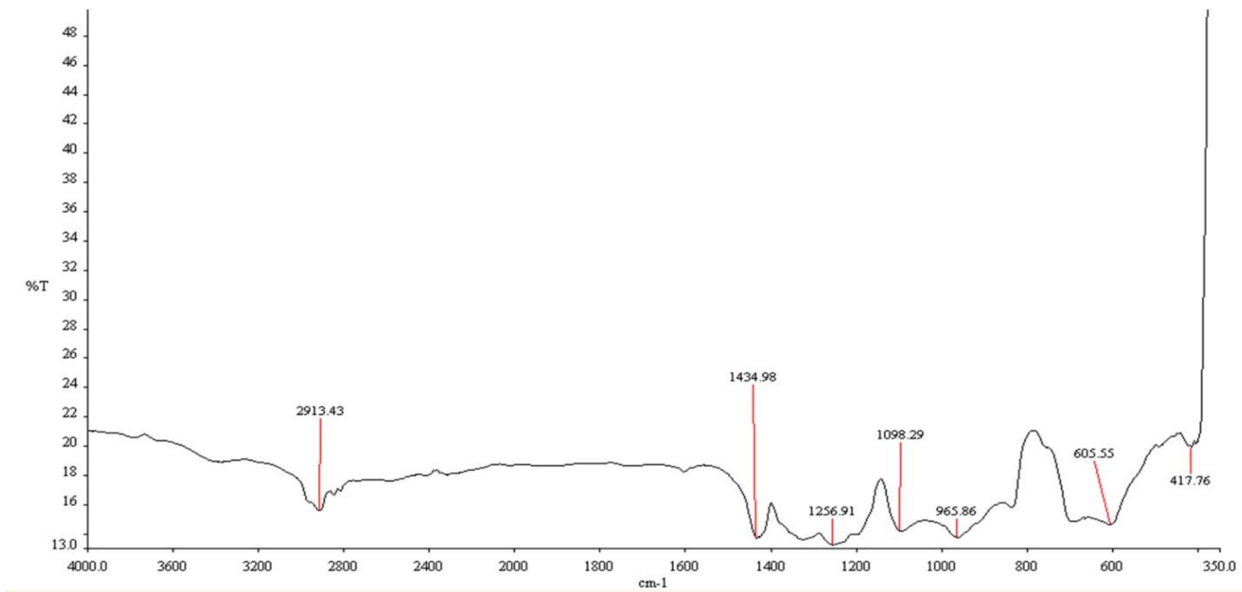
For Arabian Sea, the microplastics extracted from per kilogram of sand were approximately 12 gm. Black and light blue particles were abundant.

5.1 Rawal Lake:

5.1.1 Results:

From the samples collected from the Rawal Lake, Plastic debris and microplastics were collected from the net and separated. The plastic debris was further examined for evaluation of types and colors of the debris. The plastic debris was then categorized into fibers, beads etc. After the categorization of the plastics debris, the microplastics were dried and then a blend of these microplastics was obtained using MFI for the ease of FT-IR characterization. For FT-IR, the pellets of the blend were made in KBr and then tested for the functional groups. Following results were obtained for the samples.





5.1.2 Disscusion:

As the blends of the microplastics were characterized, the FT-IR results had stretches of many functional groups present making it quite difficult to determine the tpe of polymers of microplastics. So, from the observation of Plastic debris, the dominating type of polymers present were PolyEthylene (PE), Polyethylene Terephthalate (PET) and PolyStyrene (PS) with others being in minor quantities.

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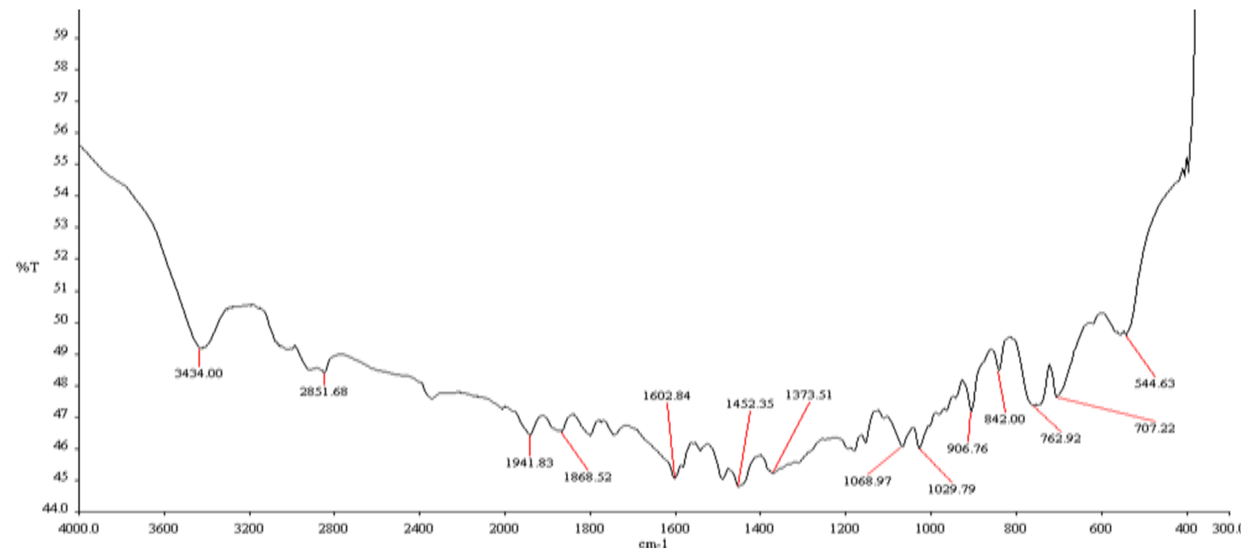
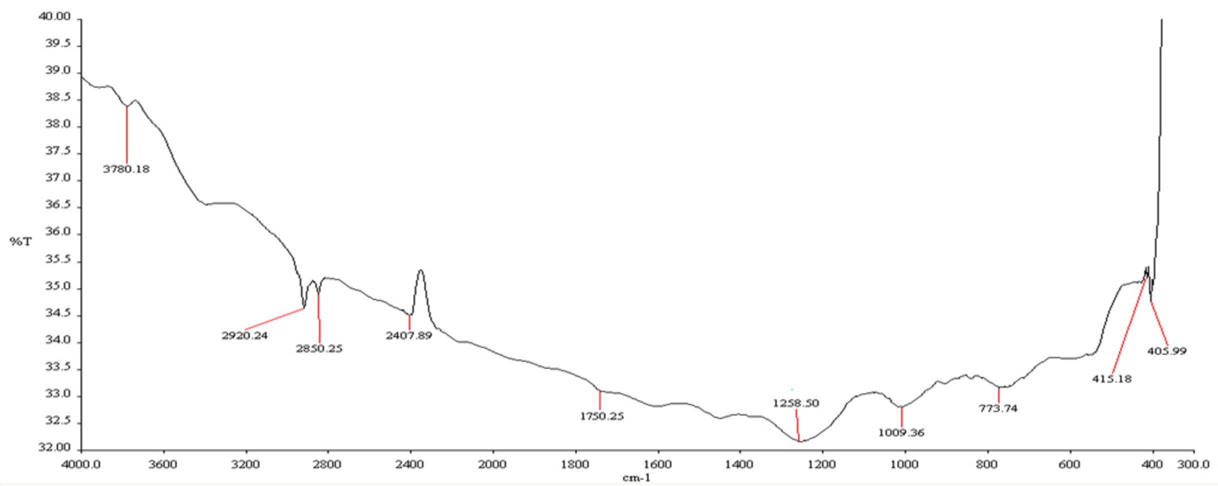
5.2 Arabian Sea:

5.2.1 Results:

The sampling from Arabian Sea was conducted using sediment method, extracting plastics and microplastics from sand sediments. To avoid the problems occurring in characterizations of blends, the microplastics were separated in particles that were very dominant in all the samples. These particles were then stored and dried for their characterization with FT-IR. FT-IR results are as follows.





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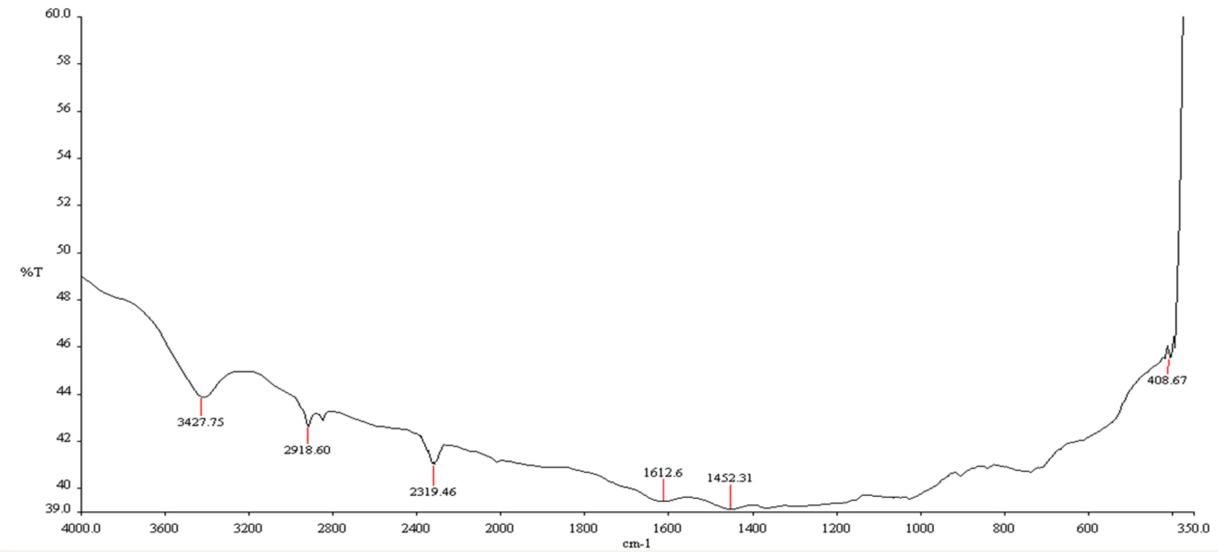

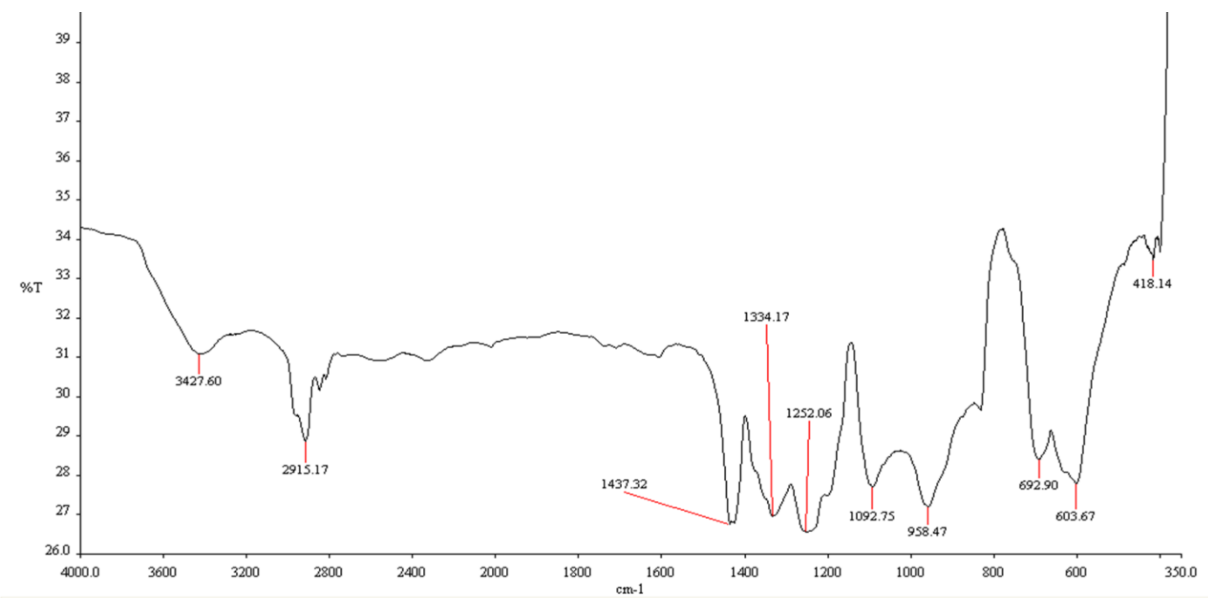

5.2.2 Discussion:

The above graphs obtained from FT-IR showed result quite similar to some polymers being used for the plastic manufacturing. From the unique functional group setup for every graph, it was determined that dominant types of Microplastics in the Arabian Sea

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are Polyvinyl Chloride (PVC), Polyethylene (PE), Polystyrene (PS), and Polyethylene terephthalate (PET).

5.3 Future Challenges:

- Identify the main sources and categories of plastics and microplastics entering the ocean
- Utilizes end-of-life plastic as a valuable resource rather than a waste product
- promote greater awareness of the impacts of plastics and microplastics in the marine environment
- include particles in the nanosized range in future assessments of the impact of plastics in the ocean
- evaluate the potential significance of plastics and microplastics as a vector for marine life in future assessments
- future assessments should address the chemical risk posed by ingested microplastics in greater depth.

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