QATAR UNIVERSITY

Graduate Studies

College of Arts and Sciences

INVESTIGATION OF SPATIOTEMPORAL VARIABILITY AND CONTAMINATION OF PLASTIC MARINE DEBRIS IN QATAR'S COASTAL WATERS

A Thesis in the

Department of Biological and Environmental Sciences

By

Oyebamiji Abib Abayomi

Submitted in Partial Fulfillment

of the Requirements

for the Degree of

Master of Science

June 2015

COMMITTEE PAGE

The thesis of **Oyebamiji Abib** was reviewed and approved by the following:

We, the committee members listed below accept and approve the Thesis of the student named above. To the best of this committee's knowledge, the Thesis conforms the requirements of Qatar University, and we endorse this Thesis/Dissertation for examination.

Name Dr.Radhouan Ben-Hamadou

Signature _____ Date_____

Name Dr.Saeed Hashim Al-Meer

Signature _____ Date_____

Name Dr Ipek Goktepe

Signature _____ Date_____

Name Dr. Mohammad Ahmad Al-Ghouti

Signature _____ Date_____

ABSTRACT

There has been a tremendous proliferation in plastic production in the last five decades due to its low cost and versatile applications. Plastic debris dominates the marine litter globally and has been found in the most pristine environment including the abysmal region of the ocean. Studies show that over 8 million tons of plastics are dumped in the ocean annually. Plastics are persistent in the environment and take several decades to degrade especially in the ocean. Large plastic debris can destroy the coral reefs and may cause entanglement, choking, blockage of digestive tracts when ingested by turtles, whales, sharks etc, causing several thousand deaths annually among these organisms. Microplastics are tiny plastic particles that seldom originate from fragmentation of large plastic debris or are produced to serve some specific purposes. Microplastics pose greater threats as they can be mistaken for food by filter-feeders and planktivorous fish, and can also adsorb large quantities of recalcitrant organic pollutants (OPs) which biomagnify up the marine food web, hence, explains the need for their investigation.

In the first phase of this study, the spatial and temporal distribution of microplastics was investigated in sediments and seawater respectively. Eight beaches across Qatar and four sea surface stations were surveyed between the months of December 2014 and March 2015. Microplastics were discovered in all samples and their abundance varied both in intertidal sandy beaches and sea surface. Since plastic debris are hydrophobic and easily adsorb organic pollutants the second phase of this study was targeted at investigating the concentration of PCBs and PAHs adsorbed on macroplastics in situ. Results showed that approximately all macroplastics analyzed were contaminated with PCBs and PAHs. Large piece-to-piece variations of contamination up to two orders of magnitude were discovered within sites (2 to 1,005 ng/g), although there was no significant difference in contaminant concentration among all sites for PCBs and PAHs respectively. Lastly, a field adsorption/desorption experiment was performed to investigate how pellets of different polymers and contaminated with POPs behave when placed in ambient seawater. Pellets were deployed and later retrieved at 48h, 96 h, 192 h, and 312 h respectively. The pellets were analyzed for PCBs and PAHs and undeployed pellets were also analyzed at time 0. Adsorbed PCBs and PAHs concentration showed a steady decrease with time, suggesting that contaminated pellets ending in the marine environment release their adsorbed contaminants in less contaminated seawaters revealing a complex OPs dynamic between plastics an seawater as a function of differential concentrations of pollutants.

This study is the first of its kind in Qatar and seemingly in the entire Arabian Gulf region. Marine pollution is a growing concern in Qatar coastal and offshore environment. Marine debris is of major concern due to the fact that plastic can take several decades to be fully degraded. Results from this study indicate that microplastics are ubiquitous and the fact that they are easily mistaken for food and ingested by zooplankton and smaller fishes makes them a serious threat to the marine food web. Hence, a study on the spatiotemporal distribution of microplastics is crucial in investigating the size and polymeric properties of marine debris to give policy makers an insight of the sources of the debris and proffer suggestions on how to tackle the menace using a holistic approach.

Keywords: Marine debris, microplastics, macroplastics, Organic Pollutants, ecotoxicology, Qatar marine environment

ملخص

كان هناك انتشار هائل في إنتاج البلاستيك في العقود الخمسة الماضية بسبب انخفاض تكلفتها وتطبيقاتها المتعددة. حطام البلاستيك يهيمن على النفايات البحرية على مستوى العالم، وقد تم العثور عليها في البيئة أكثر نقاء بما في ذلك المنطقة السحيقة للمحيطات. تشير الدراسات إلى أن أكثر من 8 ملايين طن من البلاستيك ملقاة في المحيط سنويا. البلاستيك هو ملوث ثابت في البيئة ويستغرق عدة عقود لتتحلل وخاصة في المحيطات. الحطام البلاستيكية الكبيرة يمكن أن تدمر الشعاب المرجانية وقد تسبب تشابك، الاختناق، انسداد القناة الهضمية عند تناولها من قبل السلاحف والحيتان وأسماك القرش وغيرها، مما تسبب في عدة آلاف حالة وفاة سنويا بين هذه الكائنات. الحطام البلاستيكية المجهرية هي جزيئات البلاستيك الصغيرة التي ما تنشأ من تفتت الحطام الكبير من البلاستيك أو يتم إنتاجها لخدمة بعض الأغراض المحددة. الحطام البلاستيكية المجهرية تشكل تهديدا أكبر لأنها يمكن أن تكون مخطئا لأغذية الأسماك ، ويمكن أيضا أن تمتز كميات كبيرة من الملوثات العضوية الثابتة التي تتضخم فى الأحياء البحرية التي تصل الشبكة الغذائية البحرية، وبالتالي ما يفسر ضرورة التحقيق فيها.

في المرحلة الأولى من هذه الدراسة، تم التحقيق في التوزيع المكاني والزماني للحطام البلاستيكية المجهرية في رسوبيات ومياه البحر. وأخذت عينات من ثمانية شواطئ في قطر وأربع محطات سطح البحر بين شهري ديسمبر 2014 ومارس 2015. الحطام البلاستيكية المجهرية تم اكتشافها في جميع العينات بوفرة متنوعة سواء في الشواطئ الرملية في منطقة المد و الزجر وسطح البحر. بما ان الحطام البلاستيك هي سهلة التمزز للملوثات العضوية استهدفت المرحلة الثانية من هذه الدراسة إلى التعرف على تركيز ثنائي الفينيل متعدد الكلور ومتعددة الحلقات بالحطام البلاستيكية الكبيرة في مواقع العينات. وأظهرت النتائج أن ما يقرب جميع الحطام البلاستيكية الكبيرة التي تم تحليلها كانت ملوثة بثنائي الفينيل متعدد الكلور ومتعددة الحلقات. تم اكتشاف ان تغيرات كبيرة من التلوث تحصل بين قطعة إلى قطعة تصل إلى اثنين من حيث الحجم داخل المواقع، رغم عدم وجود اختلاف كبير في تركيز الملوثات بين جميع المواقع. وأخيرا، تم إجراء تجربة الامتزاز / الامتزاز المضاد للتحقيق في كيفية ان كريات البوليمرات المختلفة وملوثة بملوثات عضوية ثابتة تتصرف عند وضعها في مياه البحر المحيطة. تم نشر الكريات واسترجاعها في وقت لاحق بعد 48 ساعة ، 96 ساعة و 192 ساعة، و 312 ساعة على التوالي. وقد تم تحليل الكريات لثنائي الفينيل متعدد الكلور ومتعددة الحلقات والكريات قبل نشرها في الميدان كما تم تحليلها في وقت الاصلي للتجربة. وأظهر تركيز ثنائي الفينيل متعدد الكلور و متعددة الحلقات الممتز انخفاض مع مرور الوقت، مما يوحي بأن الكريات الملوثة التي تنتهي في البيئة البحرية تطلق الملوثات الممتزة في مياه البحر الأقل تلوثا و تكشف ان مجمع الملوثات العضوية الثابتة لها ديناميكية بين البلاستيك ومياه البحر بوصفها وظيفة من تركيزات الملوثات التفاضلي.

هذه الدراسة هي الأولى من نوعها في قطر وعلى ما يبدو في منطقة الخليج العربي بأكملها. التلوث البحري هو مصدر قلق متزايد في البيئة الساحلية والبحرية بقطر. الحطام البحري يشكل مصدر قلق كبير يرجع ذلك إلى حقيقة أن البلاستيك يمكن أن يستغرق عدة عقود إلى أن يتحلل بالكامل. نتائج هذه الدراسة تشير إلى أن الحطام البلاستيكية المجهرية هي في كل مكان، و أنهم يمكن ان يتخذوا الخطأ كأغذية و يتم تناولها من قبل العوالق الحيوانية والأسماك الصغيرة مما يجعلها تشكل تهديدا خطيرا لشبكة الغذاء البحري. وبالتالي، تكون دراسة التوزيع الزماني و المكاني للحطام البلاستيكية المجهرية حاسمة في التحقيق في حجم وخصائص البوليمرية

للحطام البحري لإعطاء صانعي السياسات بصيرة من مصادر الحطام ويقدمون اقتراحات حول كيفية التعامل مع هذا التهديد باستخدام نهج شمولي

Contents

List of Tables

List of Figures

List of Abbreviations

ANA: Acenaphthene

ANTH: Anthracene

ANY: Acenaphthylene

B[a]ANTH: Benz[a]anthracene

B[b]FLAN: Benzo(b)flouranthene

B[k]FLAN: Benzo[k]fluoranthene

BP: Benzo[a]pyrene

B[ghi]PERY: Benzo[ghi]perylene

CH: Chrysene

D[a,h]AN: Dibenzo(a,h)anthracene

DCM: Dichloromethane

ECD: Electron-capture detector

EPA: Environmental Protection Agency

FL: Fluorene

FLAN: Fluoranthene

FT/IR: Fourier transform infrared spectroscopy

GC/ECD: Gas chromatography/ Electron-capture detector

GC/MS: Gas chromatography/ Mass spectrometry

GC: Gas chromatography

HDPE: High density polyethylene

I[123-cd]PY: Indeno(1,2,3-cd)pyrene

LDPE: Low density polyethylene

MRL: Maximum Residue Level

NA: Naphthalene

OPs: Organic pollutants (refers to PCBs and PAHs)

PAH: Polycyclic aromatic hydrocarbon

PCB: Polychlorinated biphenyl

PET: Polyethylene terephthalate

PP: Polypropylene

PS: Polystyrene

PY: Pyrene

uPVC: Unplasticized polyvinyl chloride

ACKNOWLEDGEMENTS

First of all, I am grateful to the Allah for the gift of life, good health and wellbeing that were necessary to complete this thesis.

I would like to express my special appreciation to my supervisor Dr. Radhoaun Ben-Hamadou, you have been a tremendous mentor for me. I would like to thank you for encouraging my research and for allowing me to grow as a research scientist. Your advice on both research as well as your financial support has been priceless. I would also like to thank my committee members, Dr. Saeed Almeer, Dr Ipek Goktepe, Dr.Mohamed Alghouti for serving as my committee members despite their several commitments. I also want to thank you for your brilliant comments and suggestions. I would like to thank the Central laboratory unit team, especially the section head, Dr Saeed Almeer for their technical assistance. I would especially like to thank the Director, Manager, Technicians, and other staffs of the Environmental Studies Center. Many thanks to Dr. Pedro for patiently correcting my thesis, encouragements and best wishes.

A special thanks to my family and friends. Words cannot express how grateful I am to you all. Your prayer for me was what sustained me thus far. Your love, support and constant patience have taught me so much about sacrifice, discipline and compromise.

Chapter 1

1.0 Introduction

The existence of plastic debris in coastal zones and open oceans has gained a global recognition due to the threats they pose to marine biota. This pressure is driven by the escalating global demand for plastics which is approximately 245 - 280 million tons annually (Andrady, 2011) and expected to grow at 4% annually until 2016 (Nor and Obbard, 2014).

Plastic has replaced conventional materials such as metal, glass, and paper due to the fact that it is relatively affordable, reusable, durable and also, an excellent material for packaging. These properties also qualify plastic materials as serious hazards to the environment. Plastics are known to comprise 60% - 80% of marine debris (Gregory and Ryan, 1997) and 10% of domestic wastes generated annually are plastics (Barnes et al., 2009). A review by Andrady (2011) corroborates the fact that plastics dominate the marine litter globally. Often times, plastics are washed from roads, garages, trash bins and landfills into drainages that are emptied into rivers and that ultimately end up in the oceans.

Although some of these plastic wastes are recycled in developed countries, the majority end up in landfills taking several decades to degrade (Moore, 2008) and generating leachates that contaminate the aquifer. Very often, they are transported over long distances and tend to accumulate in sinks such as oceans where their

extended degradation time leads to varieties of economic and environmental impacts (Thompson et al., 2009). Furthermore, approximately 10% of plastics manufactured annually end up in the ocean and cause serious ecological consequences (Thompson 2006; Gregory, 2009).

Larger plastics known as “macroplastics” are detrimental to tourism industries as they present an aesthetic issue and also have repercussions on other marine industries such as fishing, shipping, and aquaculture, which eventually affect the economy of the region (Sivan, 2011). Environmental consequences include entanglement, ingestion, injury and mortality of marine organisms. In addition, such debris can act as rafts for the colonization and transportation of invasive alien species (Derraik, 2002). It can also prevent gaseous exchange between the oxygenated overlying layers and interstitial waters, bringing about anoxia to sediments. Despite the buoyancy of plastics, Kanehiro et al. (1995) discovered that debris at the seabed of Tokyo Bay consisted of 80 – 85% plastics.

Factors determining the spatial distribution of plastic debris are interconnected. On a local scale, wind pattern is responsible for the distribution of plastic debris as it differentially moves or mixes debris of different densities (Kukulka et al., 2012). Over ocean basins, the spatial distribution of plastic debris is largely determined by interacting atmospheric and oceanic circulation patterns that result in high concentration of buoyant plastic debris in subtropical gyres (Maximenko et al., 2012). These conditions are also responsible for the transport of persistent organic pollutants

(OPs) and other contaminants to more pristine marine ecosystems (Zarfl and Matthies, 2010).

In view of the detrimental effects of plastic debris discussed above, this study is imperative as it focuses on filling the gap of marine debris pollution in the Arabian Gulf region by investigating the distribution, abundance and composition of microplastics in Qatar and further quantifying OPs adsorbed on macroplastics distributed on the coast of Qatar.

1.1 Aims and objectives

The coast of Qatar is susceptible to plastic debris pollution due to the fact that Qatar's population is growing rapidly and the population is concentrated at a close proximity to the sea. Furthermore, fishing, recreational, and commercial maritime activities are very common due to the rapid urbanization and industrialization of Qatar. Based on evidences of the existence of floating marine debris in samples from Qatar coastal waters, this research thesis is aimed at investigating the spatial and temporal variability of marine plastic debris in sea surface and coastal areas. Due to the fact that the abundance of larger plastic debris has been extensively assessed, this study will lay more emphasis on microscopic plastic particles in the study area.

In this study, surface seawater will be sampled from four sea surface stations and sediments from eight coastal stations to reveal and quantify plastic debris

(microplastics and macroplastics) present in these areas. Therefore, the objectives of this study were:

1. To analyze the spatial and temporal variability of microplastics in seawater and sediments, in sea surface and intertidal sandy beaches environments respectively.
2. To characterize the isolated microplastics based on size, shape, color, and type of polymer.
3. To describe macroplastics collected from beaches based on polymer type and quantify the concentration of OPs adsorbed on their surfaces.
4. To investigate the rate of adsorption of OPs on known virgin plastic pellets in a field experiment.

Chapter 2

2.0 Literature review

Microplastics in the ocean were first reported in the scientific literature in the early 1970s, however, drew little attention from researchers at the time (Carpenter and Smith, 1972; Coe and Rogers, 1996). The threats posed by plastics to marine environment were initially underestimated or ignored for a prolonged period. For instance, Ferguson (1974) stated that plastics only cause an eyesore due to their small proportion at the time and could not cause a considerable harm to the environment. Concern started growing in the scientific community about a decade later, and this was due to the ecological consequences of plastic debris which ranged from entanglement of mammals (Laist, 1997) and other species; and ingestion by turtles (Mascarenhas et al., 2004) and birds (Mallory, 2008). Rios and Moore (2007) verified that some species of marine birds such as black-footed albatross feed their chicks with plastic granules. A study done by Robards et al. (1995) revealed that plastic ingestion by marine birds increased significantly between 10 – 15 years period of study. In addition, Blight and Burger (1997) discovered plastic debris in the stomachs of eight of the eleven seabirds species caught at the North Pacific as bycatch. Furthermore, Moser and Lee (1992) proved that some seabirds mistake plastics for prey due to similarities in shape and color. Also, Carpenter et al. (1972) affirmed that certain species of fish feed selectively as they discovered white plastic spherules in their guts, which must have been mistaken for prey.

Laist (1997) claimed that 267 species of marine biota have been affected by plastic debris. However, this figure will most likely increase when smaller marine organisms are studied, besides, there are several other victims that go unnoticed in the vast ocean due to predation and sinking (Wolfe, 1987).

Microplastic beads have been used in several zooplanktons feeding experiments, indicating that such plastics fall within the size range of staple phytoplankton diet ingested by zooplanktons (Leys and Eerkes-Medrano, 2006). Hence, microplastics are more problematic than macroplastics in the lower trophic level of the marine food web as they are easily mistaken as food. Once ingested, microplastic granules with rough edges can cause internal abrasion to tissues in the digestive tract (Nor and Obbard, 2014) or accumulate in the digestive cavity and tubules (Browne et al., 2008).

2.1 Origins of microplastics

Microplastics are generated in the ocean basically by two sources:

1. Microplastics deposited in the ocean by runoffs and drainages – usually Primary microplastics. These are manufactured to be of microscopic size and are often used in cosmetics and facial-cleansers. Other applications include air-blasting technology, vector for drug delivery (in medicine; Patel et al., 2009) etc.

2. Weathering and disintegration of macro- and mesoplastic debris (Secondary microplastics) – as discussed in the previous section, long period of exposure of macro- and mesoplastics to sunlight coupled with abrasion, turbulence and wave-action leads to bond cleavage of polymer matrix (Andrady, 2011) and loss of structural integrity. The continuity of these processes makes the fragments smaller to an extent where microplastics are generated (Fendall and Sewell, 2009). Additives added to enhance durability and corrosion resistance of microplastics could be leached into the surrounding water during disintegration of large plastic debris (Talsness et al., 2009).

2.2 Plastics used in the Ocean

Sizeable amount of plastic material used in packaging are often encountered in the coastal environment (Andrady, 2003). Polyethylene and polypropylene are commonly used in the manufacture of fishing gear (Timmers et al., 2005) and some of these gears and other debris are lost, carelessly disposed in the ocean or left over by beachgoers. In 1975, an approximated 135,400 tons of plastics from fishing gear were dumped in the ocean by fishing vessels (Derraik, 2002). Hence, the fishing industry is known to be responsible for depositing 18% of plastic debris in the ocean while land based sources account for 80% of marine plastic debris (USEPA, 2011). Flash flooding, hurricanes and other cases of extreme weather facilitate the transfer of land-

based sources of plastic debris into the ocean. Lattin et al. (2004) showed that microplastics concentration ~1 km from the coast of South California increased from <1 item/m^3 to 18 item/m^3 after a storm. Sadly, disposal of plastic debris into the ocean is an incessant problem. A survey conducted five years apart in South African beaches revealed a substantial increase in the densities of plastic debris (Derraik, 2002). In addition, beaches cleaned experimentally in Panama showed a 50% increase in plastic debris after a period of three months (Derraik, 2002).

Microplastics are ubiquitous in the marine environment and have been found even in the most pristine regions including subtropical gyres, mid-ocean islands (Ivar do Sul et al., 2009) and Antarctica (Zarfl and Matthies, 2010). Nevertheless, the increased density of plastic debris in coastal waters, globally, has been attributed to high population densities along the coast. Vianello et al. (2013) documented a maximum of 2,175 particles per kg dry weight sediments in a study conducted in a coastal area of the Mediterranean Sea. Microplastics have continued to accumulate since the past four decades (Thompson et al., 2005). Microplastics in the North Sea and Northwest Atlantic during the 1980s and 1990s were much more than those in the 1960s and 1970s. According to van Franeker et al. (2011), the incidence of plastic ingestion by Fulmers (a species of bird) increased from 91% in the 1980s to 98% in 2000 and the average consumption of plastic also doubled in this period. Also in Belgium, microplastic concentration in sediments tripled from ~55 microplastics/kg (1993 –

2000), to ~156 microplastics/kg (2005 – 2008; Claessens et al., 2011), although, much smaller than the number of plastics recorded by Vianello et al. (2013).

2.3 Impacts of plastics on marine biota

Plastic debris has several detrimental physical effects on marine organisms including entanglement, ingestion leading to blockade of the digestive tract, alteration and damage of the habitat etc (Allsopp et al., 2006). According to Ryan et al. (2009), plastics were found in the gut of seabirds in the 1960s when the global annual plastic production was below 25 million tons. Further, a study carried out on Fulmars in the Netherlands revealed that 94% of the specimen had plastics in their gut, individual specimen having approximately 34 plastics (van Franeka, 2010). Most organisms might consume microplastics voluntarily, mistaking them for food. On the other hand, some organisms ingest microplastic as a result of preying on lower organisms that previously consumed microplastics (Browne et al., 2008; Fendall and Sewell, 2009).

Floating debris is often colonized and transported, thereby, increasing the risk of invasive alien species. Aside the physical harm caused to marine biota, plastic debris also serve as vectors of organic pollutants (OPs) such as polychlorinated aromatic hydrocarbons (PAHs) which they adsorb from surface water, subsurface water and sediments due to their hydrophobicity (Teuten et al., 2009). The concentration of such

compounds on meso-/microplastics is much higher than their concentration in surrounding water or sediments by several orders of magnitude. Once ingested, absorption into the body of marine organisms creates a route through which the OPs and other pollutants get into the marine food web. However, the level of bioavailability of such contaminants sorbed on microplastics to biota and the manner of bio-magnification in the marine food web is not fully understood (Moore, 2008; Teuten et al., 2007). Voparil and Mayer (2000) demonstrated that bioavailability of OPs in benthic deposit feeders is possibly facilitated by gut surfactants. Planktons with small body mass are said to be more toxicologically impacted by OPs and toxicity is greatly determined by the volume of microplastics ingested, residence time of the OPs and partition flux between the microplastics and zooplankton. Ryan et al. (1988) reported a positive correlation between the quantity of ingested contaminated plastic debris and the concentration of OPs in fatty tissues in larger marine species.

Also, “plasticisers" (e.g. phthalates, bisphenol A) used as additives during plastic manufacturing elongate the lifespan of plastics making them even harder to degrade and also capable of leaching into surrounding water and cause harm to the biota (Lithner et al., 2011). Such harm is facilitated by the large surface-area-to-volume ratio of microplastics which exposes the marine biota to the contaminants and additives after ingestion of the plastics. Polyvinyl chloride (PVC) for instance is composed of approximately 90% of plasticizers. Hence, it is denser than seawater and can be a major source of endocrine disruption to benthic biota (Talsness et al., 2009).

Phthalate is an example of an external plasticizer which is not properly bound to plastics and can easily migrate, leach out of PVCs to contaminate the ambient seawater or absorbed by biota (Heudorf and Angerer, 2007).

Impacts on marine biota may include endocrine disruption, carcinogenesis, and sexual disruption, etc. These impacts may not always be obvious but OPs surely affect marine biota once they enter the food web even at low concentrations (Mato et al., 2001).

2.4 Plastic degradation in marine environment

Degradation reduces the molecular weight of plastics leading to weakening of such polymers. Prolonged degradation leads to embrittlement of the polymer which causes it to fall apart upon handling. Hence, degradation can be classified into:

1. Photodegradation: brought about by UV rays from sunlight in an outdoor environment.
2. Thermal degradation: occurs as a result of exposure to high temperature.
3. Thermooxidative degradation: prolonged breakdown by oxygen at moderate temperature.
4. Hydrolysis: degradation induced as a result of reaction with water.
5. Biodegradation: breakdown by microbial activities.

Polymers in the marine environment usually undergo photo-oxidative degradation due to exposure to UV-B radiation. Without further exposure to UV-B radiation, the degradation process can proceed to thermo-oxidative degradation once initiated, as long as oxygen is not lost in the system. Photo-oxidative degradation is much faster as compared to other types (e.g. hydrolysis) of degradation by several orders of magnitude (Andrady, 2011). Biodegradation on the other hand is retarded especially in the marine environment due to the fact that the microbes responsible for the breakdown of high molecular weight plastics are rare in nature.

As discussed above, photo-oxidative degradation is very efficient in plastics lying on the beach or exposed in air. However, this is not the case for plastics floating in seawater as the photodegradation process is severely impeded. This is due to the fact that oxygen concentration and temperature are relatively low in seawater as compared to the beach surface.

The disparity in degradation between plastics exposed to air and those in seawater is aggravated by fouling effect. Floating plastics are usually colonized first by biofilm, next by algal mat and then invertebrates (Muthukumar et al., 2011). A study conducted by Andrady and Song (1991) in Biscayne Bay, Florida, showed the sequence of succession of plastic surface by epibionts as follows:

Bacteria ► Diatoms ► Hydroids ► Ectocarpales ► Barnacles ► Bryozoans

Water conditions and season of exposure also determines the sequence and kinetics of fouling. Fouling increases the density of the plastic up to a level that its density exceeds that of seawater and the plastic sinks below the surface water (Railkin, 2003). This is the main mechanism through which plastic debris get to the benthos (Backhurst and Cole, 2000). Lobelle and Cunliffe, (2011) described the speed at which biofouling could occur in polyethylene bags immersed in seawater at 16.2^{O} C. Visible biofilms were observed after just 7 days and at the end of the 3-weeks experiment, there was a significant increment in biofilm density causing the polymer to move below the surface and become neutrally buoyant. Similarly, study conducted by Moret-Ferguson et al. (2010) revealed that fouled microplastics (< 1mm) collected between 1991 and 2007 in western North Atlantic Ocean had greater densities than the same polymer type collected from the beach.

In a study conducted in the North Pacific gyre, Moore et al. (2001) observed that approximately 8.5% of floating plastic debris were fouled, whereas, at about 10m depth, diatoms and algae fouled a higher proportion of plastics. Hence, subsequent de-fouling due to foraging by organisms in the water column or other mechanisms reduces the density of the plastic and returns the plastic to the surface water. In addition, turbulence at the seabed resulting from a storm could re-suspend microplastics settled at the benthos (Lattin et al., 2004).

Biodegradable plastics were introduced as viable replacement of conventional plastics with the hope of curtailing the ecological consequences of the latter. Thompson et al.

(2004) however argued that they could also be a source of microplastics since they are composed of starch, vegetable oils and synthetic polymers. They may also contain specialist chemicals such as TDPA^{TM} that facilitates degradation under hot, humid and aerated conditions in composting plants (Thompson, 2006). Nonetheless, only the organic constituents such as starch will be degraded and synthetic polymers will remain after degradation. As the hot, humid, and well aerated conditions that facilitate degradation cannot be met in the ocean, bio-plastics can also be fouled, reducing UV permeation and prolonging degradation duration of even the degradable components by many folds (O'Brine and Thompson, 2010). Secondary microplastics are usually generated when such bio-plastics degrade eventually (Roy et al., 2011).

2.5 Evaluating microplastic abundance

Assessing the quantity of microplastics in the ocean is challenging due to the monumental size of the ocean as compared to the quantity of plastics being assessed. This is exacerbated by the spatiotemporal variability brought about by oceanic currents and seasonal patterns (Doyle et al., 2011). So far, several sampling methods have been invented so as to ease the determination of microplastics in the marine environment. They include:

1. Beach combing – it involves the joint efforts of researchers and environmental awareness groups and requires little logistics and low cost (MCS, 2010).

According to Ryan et al. (2009), debris are collected and identified systematically and repeatedly along a specific coastline stretch over a period of time to understand the manner of accumulation of debris over time. However, this technique has been faulted as it is targeted towards macroplastics and other larger non-plastic debris. In addition, this technique does not accurately indicate plastic debris in the ocean since the debris collected include those washed by the current and also litters dropped by beach users (Cole et al., 2011) which might end up in the ocean.

2. Marine observational surveys – This is similar to beach combing as it involves observation of macroplastics by divers and/or observers on boat and submersibles over relatively large areas. Microplastics are usually left out as they are not easily visible to the naked eyes and the macroplastics observed do not undergo further evaluation (Ryan et al., 2009).
3. Biological sampling – As a sizeable number of marine species mistake microplastics for food (Tourinho et al., 2010), this technique involves investigating plastic fragments internalized by marine species. Seabirds and other marine mammals can be dissected and the content of their GIT analyzed for microplastic contents, quantified and identified (van Franeker, 2010). Cole et al. (2014) investigated the rate at which a zooplankton species *Temora longicornis* ingested fluorescent polystyrene beads and the quantity internalized overnight. Similarly, Fulmars have been used in several studies to

investigate the plenitude of plastic debris in the ocean (van Franeker et al., 2011).

4. Sediment sampling – this involves analysis of benthic materials from beaches, seafloor etc for microplastic presence (Claessens et al., 2011). Supersaturated solution of NaCl, KI, NaI etc are used to separate microplastics which are less dense, from the denser sediments. Visible microplastics could be removed using tweezers and further investigation using lipophilic dye could be done for confirmation. Fourier-Transform Infrared Spectroscopy (FT-IR) is also employed to ascertain the type of polymer identified via spectra matching and comparison (Barnes et al., 2009).
5. Marine trawls – different section of the water column require different equipment for sampling. Surface water is usually sampled using manta trawls while subsurface and seabed requires bongo trawls and benthic trawls respectively (Browne et al., 2010). Samples collected can be filtered with sieves ranging from 20 µm to 330 µm mesh size or evaporated and the residual samples investigated. The samples can then be viewed under 3D-stereo microscope to investigate the size and morphology of the microplastics. The difference in mesh size of sieves usually yield wide variation in the quantity of microplastic obtained. The quantity of microplastics obtained by KIMO Sweden using 80 µm mesh size sieve was five orders of magnitude greater than when 450 µm mesh size sieve was used (Lozano and Mouat, 2009).

Since it is recognized that microplastics are either transported as primary microplastics or generated by weathering of larger plastic debris in situ, it is imperative that plastics are removed by screening of waste water systems and collection from municipalities to prevent them from being transported to the ocean. Also, effective beach cleaning is implemented so as to mitigate microplastics generation. Hence, beach cleanup offers not just aesthetic benefit but also of great benefits to the marine ecosystem as it drastically reduces the presence of microplastics, OPs and other contaminants in the marine food web (Andrady, 2011).

In addition, several suggestions have been proffered for removing microplastics from the ocean, one of which involves large scale filtration with neuston net. For this to be feasible, it is crucial that we are well aware of the ratio of dry plastic mass to zooplankton biomass. Miriam et al. (2013) approximated based on median North Pacific Subtropical Gyre (NPSG) ratio of 1.368 that for each 1000 mg of plastic filtered, 731 mg dry zooplankton biomass would be removed. This corresponds to a significant removal of carbon content which they concluded would have significant ramification on nutrient dynamics. Hence, understanding the spatial and temporal distribution of microplastics in Qatar as this study investigates will give an insight on how to tackle the menace of plastic debris pollution in Qatar given that it is an extremely important environmental issue that requires urgent attention. Several authors devised different size ranges for

classifying microplastics. In the present study, plastic particles below 5 mm microplastics were considered microplastics. All other larger sizes (> 5 mm) were termed macroplastics.

Chapter 3

3.0 Materials and Methods

The general framework of our materials and methods is reported in the organogram provided below (Figure 1). Details are given in subsequent sections for each procedure.

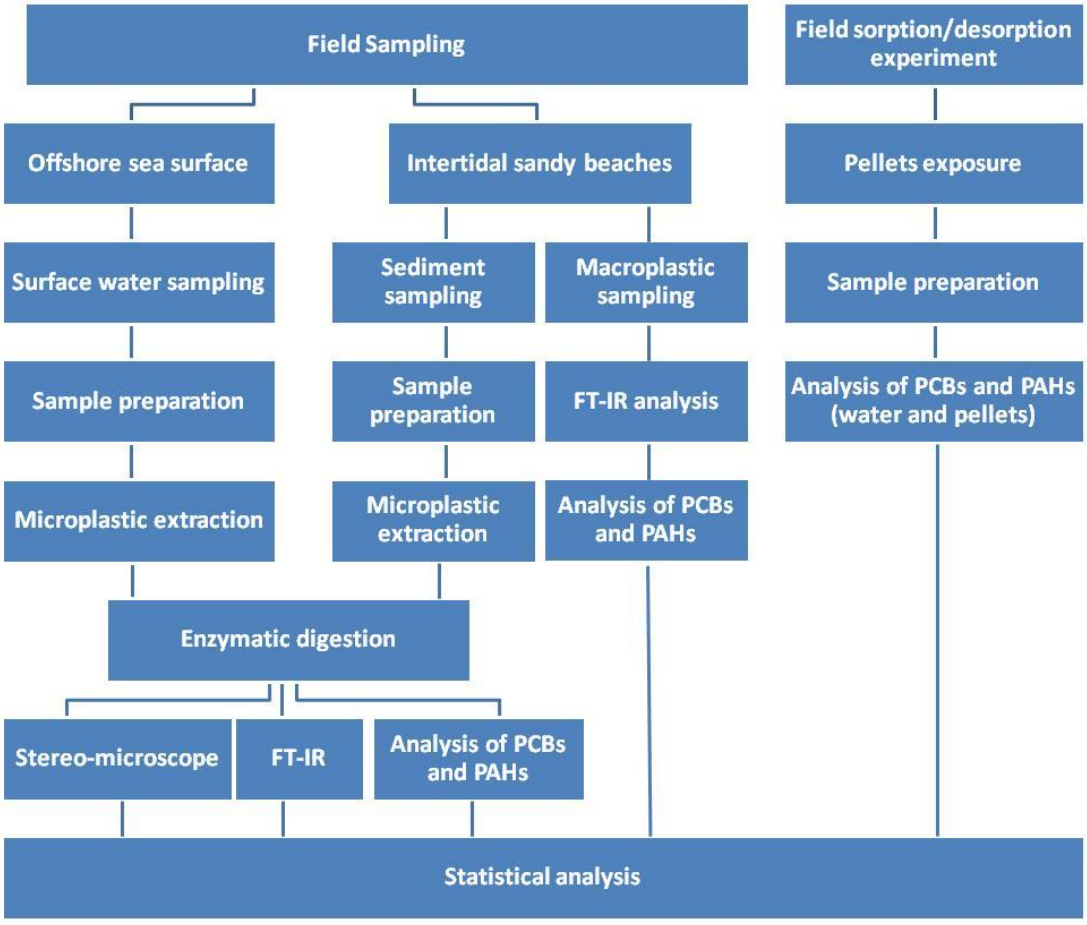


Figure 1: Organogram of field sampling and subsequent laboratory analysis carried out in this thesis

3.1

Four sea surface stations (Figure 2 and Table 1) were visited on the 7th day of January, March 3rd and March 29th 2015 using a speed boat. Station 4 is located in an area known to be used by vessels at anchor awaiting access to Doha Port and they may be source of pollution to the surrounding waters.

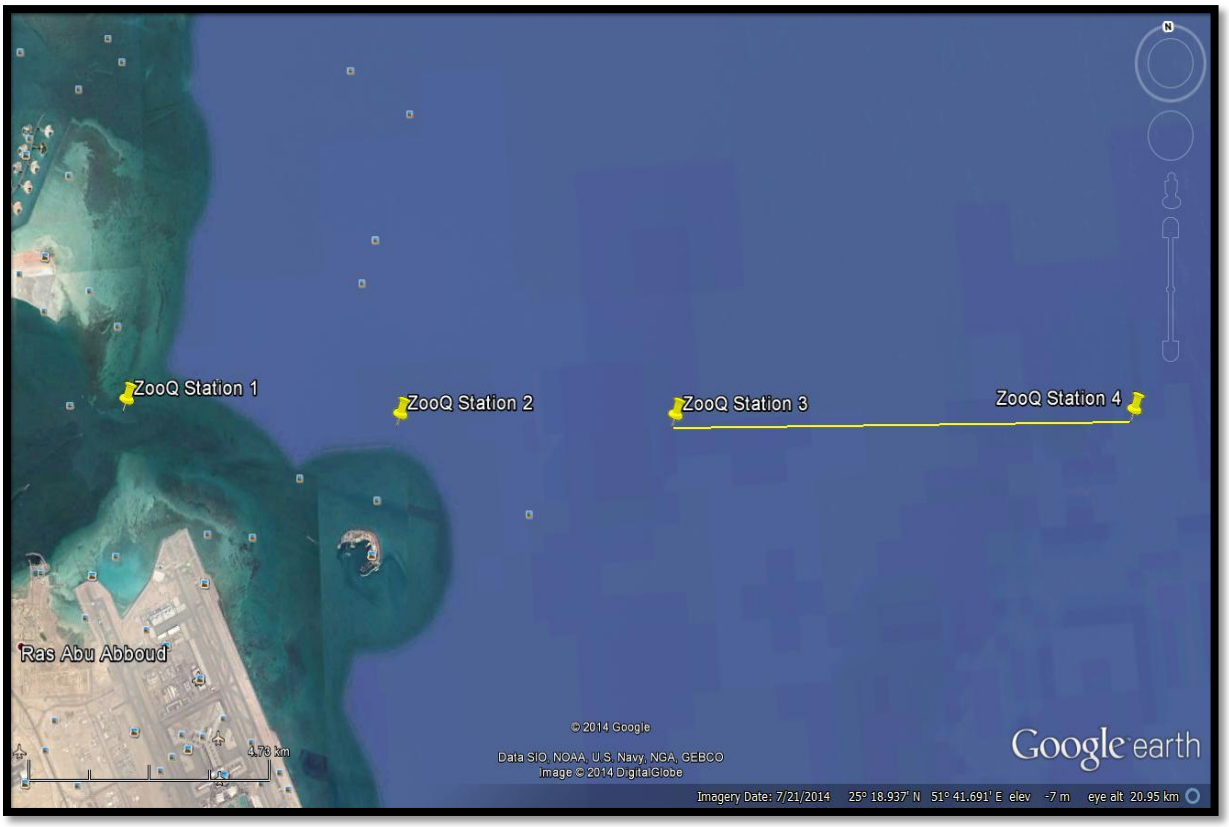


Figure 2: Map displaying sampling locations for surface seawater offshore Doha

For each sampling, seawater was collected respectively with a surface neuston net (300 µm mesh size) towed off the side of the speed boat in undisturbed water for 5 minutes at 1.5 knots (Figure 3). After retrieval from the ocean, the net was carefully

rinsed from the exterior in order to collect all debris in the cod end (Doyle et al., 2011). Next, collected materials in the cod were transferred into labeled, acid-treated insulated glass containers to prevent contamination. Microplastics concentration was given in square meters as sampling was done in two-dimensional air-sea interface. Physicochemical parameters (temperature, salinity, pH and dissolved oxygen) were measured *in-situ* and recorded at each sampling site.

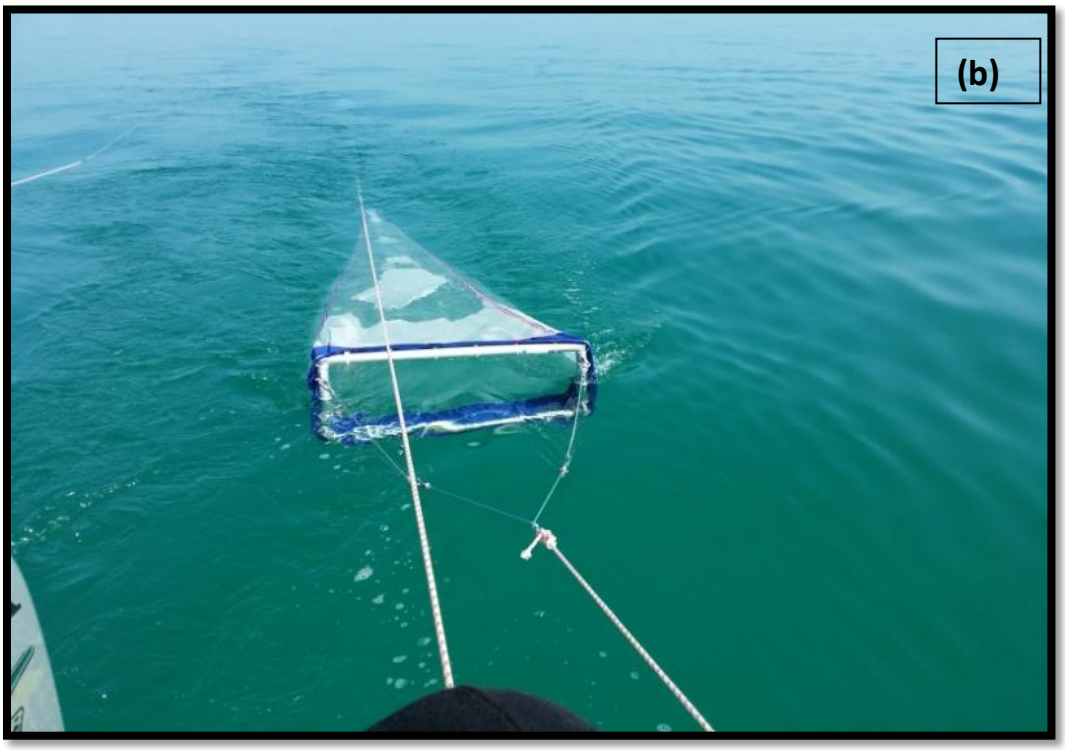


Figure 3: (a) Deployment and (b) Towing of neuston net for surface seawater sampling

Table 1: The coordinates, speed and duration of sample collection

Station #	Coordinate X	Coordinate Y	Duration Min	Speed
1	51.35818 E	25.19313 N	5	1.5knot
2	51.39103 E	25.18947 N	5	1.5knot
3	51.47792 E	25.18895 N	5	1.5knot
4	51.47146 E	25.18482 N	5	1.5knot

Table 2: Physicochemical parameters of the sampled seawater

Date	Station #	Depth (m)	Temperature (^{o}C)	Salinity %	DO %	DO mg/l
7/1/2015	1	8.0	20.5	41.9	102.9	7.2
	2	6.4	20.7	42.0	101.8	7.1
	3	16.4	21.2	41.7	101.7	7.0
	4	26.5	21.0	42.5	101.4	7.0
3/3/2015	1	3.0	20.8	44.3	111.4	10.0
	2	5.0	21.6	41.7	110.9	9.5
	3	3.0	20.8	41.0	106.0	9.6
	4	21.0	20.7	41.5	110.0	9.8
29/03/2015	1	8.0	23.9	41.7	119.3	10.2
	2	5.0	23.5	41.7	116.0	9.9
	3	15.0	22.6	41.3	114.0	9.8
	4	20.0	22.5	41.5	113.9	9.8

3.2 Sediment Sampling

Eight coastal stations (Al Dhakhira, Ras-Laffan, The Pearl, Doha Bay, Al Ruwais, Dukhan, Umm Bab, and Mesaieed) were chosen on the basis of their accessibility and being evenly distributed along Qatar coastline (Figure 4). Table 3 reports the geographic coordinates of sampled beach stations and dates of sampling. Samplings were done between 25th of December, 2014 and 5th of March 2015.

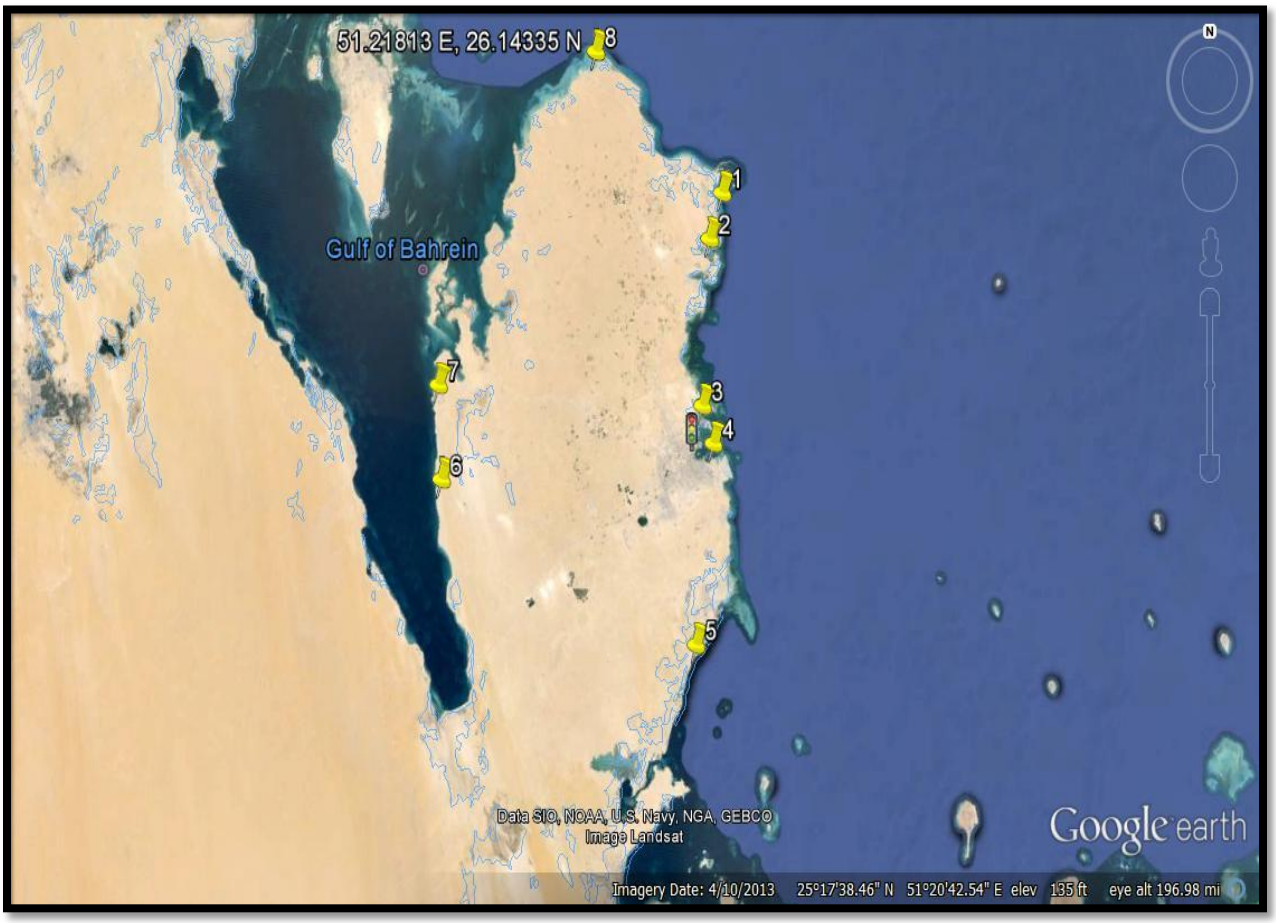


Figure 4: Map displaying the geographical location of Sediment Sampling Sites in Qatar

For each sampling, sediments from the top 2 cm were collected at the most recent high tidal mark on shore from a square area (0.5 x 0.5 m) along the shore line. Three replicate quadrats (5 meters apart) were sampled in each beach. The samples were homogenized and transferred into acid-treated glass containers to prevent contamination and transported to the laboratory for analyses.

Table 3: Sampling sites for sediments

S/N	Station	Coordinate X	Coordinate Y	Date
1	Ras Laffan	51.58865 E	25.83396 N	25/12/14
2	Al Dhakhira	51.5516 E	25.73381 N	25/12/14
3	The Pearl	51.52948 E	25.37008 N	25/12/14
4	Doha Bay	51.56122E	25.28779 N	25/12/14
5	Mesaieed	51.50943 E	24.84903 N	05/03/2015
6	Umm Bab	50.76813 E	25.20892 N	04/03/2015
7	Dukhan	50.75895 E	25.41494 N	04/03/2015
8	Al Ruwais	51.21813 E	26.14335 N	02/03/2015

3.3 Macro-plastic sampling

Larger plastic debris and pellets (≥ 5 mm) were collected into glass containers using stainless steel tweezers from five coastal stations (Al Dhakeera, Al Ruwais, Dukhan, Umm Bab and Mesaieed) within a transect of 50 to 100 meters, parallel to the water line (Figure 5). Samples were collected between 2nd and 5th of March 2015, respectively.

Figure 5: Geographical location of macro-plastics sampling sites in Qatar (yellow marks)

Plastics collected ranged from pellets, fragments to whole plastic bottles. Collections were done in wider ranges at sites where plastics were sparse and within few meters where plastics were in abundance as described by Endo et al. (2005). Figure 6 below shows images of macroplastics collected from shoreline across Qatar.

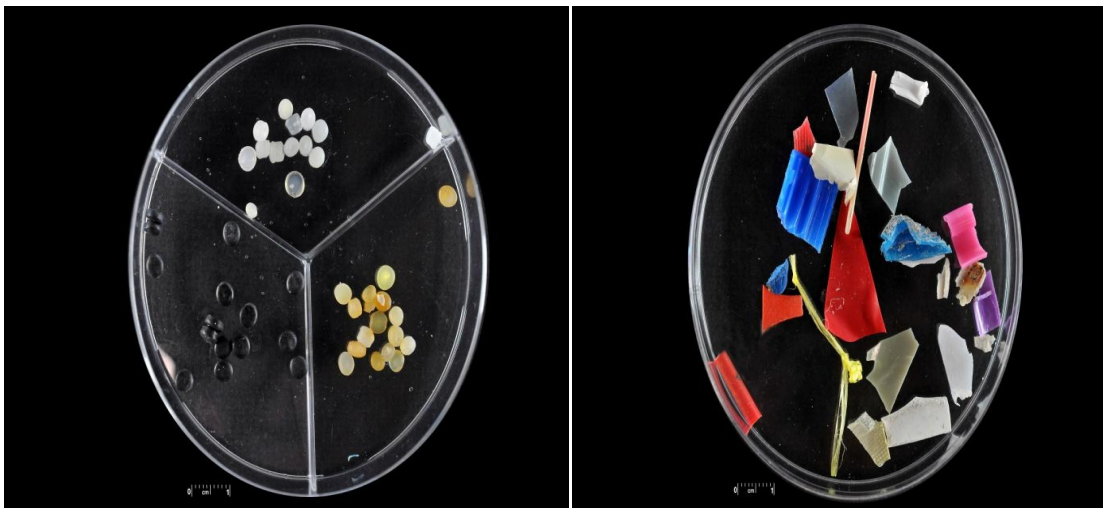


Figure 6: Photographs of pellets and plastic fragments obtained from the study areas

Five representative samples were selected from the total samples collected from each location. These samples were sent for Fourier transform infrared spectroscopy (FT-IR) analysis at the Central Laboratory Unit in Qatar university and the remaining samples were stored in the freezer at subzero temperature until further analysis of OPs.

3.4 Sample preparation

3.4.1 Surface water

In the laboratory, the neuston samples were passed through a 20 µm filter, and the retained plastics and other larger non plastic debris were rinsed with ultrapure water to remove salt and then vacuum filtered on Whatman^{TM} Qualitative filter paper. The vacuum filtered samples were transferred to sterile Petri-dishes and oven-dried at

60ºC until complete dryness and transferred to a desiccator to prevent moisture absorbance (Cole et al., 2014).

Following a 24 hours desiccation and preservation, the samples were viewed under a stereomicroscope and objects resembling microplastics were photographed and measured.

3.4.2 Sediments

Wet sediment samples were homogenized and dried in the oven at 60^{o}C for 24 hours or until completely dried (Nor and Obbard, 2014; Dekiff et al., 2014). Three replicate analyses were conducted for sediments from each location. Two-steps density separation was performed in order to separate the less dense plastic particles from the denser sediment grains. This was imperative as the densities of plastics vary depending on the type of polymer and manufacturing process. Hence, densities of polymers range between 0.8 to 1.4 g cm^{-3} while the density of sand and other sediments are approximately 2.65 g cm^{-3}.

In the first separation step, 500g of each sample was sieved through a 2 mm mesh size stainless sieve. The obtained sample was transferred into conical flasks containing 1.2 g L^{-1} saturated NaCl solution, mixed thoroughly for 5 minutes and allowed to settle and separate based on density for 5 – 7 hours. Next, the supernatant was collected and stored for further processing (Claessens et al., 2011).

The second separation step involved the recovery of denser polymers. High density

salts such as NaI, $ZnCl_2$ have been used in several literatures for this second density separation step (Claessens et al., 2013; Nuelle et al., 2014). Potassium iodide (KI) was however used in the present study due to its availability and cost effectiveness. A saturated potassium iodide solution (60% w/w) was added to the remainder of the sediments and the solution was shaken thoroughly as described in the paragraph above. After recovering the supernatant, it was then mixed with the supernatant recovered from the first extraction step and sieved with a 20 µm sieve. The retained material was subsequently rinsed thoroughly with ultrapure water (to remove salt) and the percolated sample was vacuum filtered on a Whatman™ Qualitative filter paper.

The filtered samples were transferred into a Petri dish, oven dried at 60°C until complete dryness and transferred to a desiccator (Ng and Obbard, 2006). Following desiccation, the samples were observed with a 3D- stereomicroscope and those resembling microplastics were photographed and measured.

3.5 Mitigating contamination

Microplastics can be aerosolized, carried on clothing and on laboratory equipment; hence, contamination of samples was prevented by the following measures: apparatuses used were acid-washed before usage and consumables were taken and used directly from packaging. Lab coats were worn at all times during analysis in the laboratory. All materials and reagents not in use were covered at all times and kept

away from plastics. The stereomicroscope workplace was cleaned prior analysis of target samples.

3.6 Procedural blank

Procedural blank tests were run simultaneously with artificial seawater samples and aquarium sand. As explained in "*Sample preparation*" above, the procedural blanks (without biogenic materials or microplastics) of both sample types (seawater samples and aquarium sand) were analyzed in the same manner as the test samples (seawater and sediments). The supernatants obtained were vacuum-filtered and observed under a magnifying lens for the presence of contaminants.

3.7 Enzymatic Digestion of biological materials

Cole et al. (2014) reported that alkaline digestion with NaOH resulted in the structural damage of Nylon fibres, change in unplasticized polyvinyl chloride (uPVC) coloration and fusion of polyethylene fragments. Similarly, conventional acid digestion was discouraged by Nakashima et al. (1988), stating that it caused compounds oxidation and molecular cleavage, and Claessens et al. (2013) iterating that it caused the destruction of low pH tolerant polymers. Hence, enzymatic digestion procedure was adopted in this study as discussed by Lindeque and Smerdon (2003).

The enzyme, Proteinase-K (250 µg mL^{-1}) was used for every 0.1g DW sample (Cole

et al., 2014). Desiccated samples were transferred into 50 mL sterile glass containers containing 15 mL homogenizing solution and were homogenized by vortexing. After incubating the homogenized solution for 15 minutes at 50^{o}C, 250 µg mL^{-1} of Proteinase-K was added and the solution was further incubated for 2 hours at 50^{o}C. Sodium perchlorate (5 M) was added next and the samples were shaken on a rotary shaker for 25 minutes at room temperature. Solutions were then physically homogenized using a vortex and the samples were incubated at 60^{o}C for 20 minutes. Post-digestion samples were vacuum-filtered, placed in Petri dishes, oven-dried and desiccated. The efficacy of digestion was determined by comparing the weight of samples + filter paper after desiccation (pre-digestion) and the weights of samples + filter paper after desiccation (post-digestion). This was done for both sediment and seawater samples (Cole et al., 2014).

3.8 Microplastics

Samples obtained from surface seawater and sediments were observed with 3D stereo microscope, measured and counted. Suspected microplastics were verified and classified using Perkin Elmer Spectrum 400 Fourier transform infrared/near infrared spectroscopy (FT-IR/FT-NIR) spectrometer (USA) in conjunction with a database as reference and OMNIC FTIR software.

3.9 Recovery efficacy

Pellets of polypropylene and low-density polyethylene obtained from the Center of Advanced Materials (CAM) in Qatar University were cut into small bits with average weight of 4.18 mg and 3.78 mg respectively and diameter < 2mm. Aquarium sand (250 g) was weighed into six conical flasks. Separated into two groups (each representing either of the polymers), 10 pellets were spiked into the aquarium sand (Nuelle et al., 2014). Sodium chloride (NaCl) solution (500 ml) was added into each flask and the mixture was shaken vigorously for 1 minute and then allowed to stand for > 30 minutes.

Next, the supernatant was collected from each flask and was vacuum filtered on Whatman filter paper 1. With the aid of a magnifying lens the recovered pellets among other impurities were counted to determine the recovery efficacy of NaCl solution. As shown in Chapter 4 below, the recovery efficacy was between 80% - 100%, hence, the experiment was not repeated with KI solution.

3.10 Analysis of OPs adsorbed on macroplastics

As it was not feasible to analyze OPs adsorbed on the surfaces of isolated microplastics due to constraint of equipment, OPs analysis was limited to macroplastics obtained from the 8 intertidal sandy beaches and virgin pellets used in the field

adsorption experiment. Between two to five samples were analyzed for each

sampling site due to scarcity of plastic debris in some sites. This was done to determine variation in concentration between individual samples from the same site and also the spatial variation among all sampled locations.

3.10.1 Ultrasonic extraction

Macroplastics were retrieved from the freezer and air-dried in the laboratory for 72 hours. Samples were weighed and transferred into glass tubes (the weight of samples ranged from 0.5 g to 2.2 g). A solution of hexane and acetone was prepared in the ratio of 1:1 and 40 ml of the solution was added into each glass tube containing individual samples. The tubes were placed into an ultrasonic bath for 35 minutes and the extract was decanted after sonication (US EPA, method 3550C). The process was repeated for a second and third time after which all extracts for each sample were collected and homogenized.

A procedural blank was run for every set containing 5 to 10 samples. In this case, equal volume of solvent was poured into the empty glass tubes and the blanks were subjected to the same extraction procedure as the rest of the samples (EPA, 2007).

3.10.2 Evaporation

Extracts were concentrated to 1 ml on a heating mantle under nitrogen stream at 45^{o}C. The concentrate was transferred into glass vials and stored until further analysis.

3.10.3 Fractionation

To ensure successful fractionation results, all cartridges used were obtained directly from the pack and used as directed by the manufacturer. Silica gel Solid-phase extraction (SPE) fractionation method was performed for sample clean-up. Twenty (20) ml dichloromethane (DCM) was added for the conditioning of the cartridges and this was followed by the addition of hexane (20 ml x3) just before the DCM got to the level of the top frit of the cartridges. Precautions were taken to ensure the cartridges were moistened during the entire fractionation process (US EPA, method 3550C).

For PCBs: One (1) ml of the samples contained in vials were decanted into individual cartridge and just as it got to the level of the top frit, 20 ml hexane was added for PCBs elution. The fraction from each cartridge was collected in a 25 ml test tube and stored for further analysis.

For PAHs: Twenty (20) ml DCM was poured into each cartridge and the fraction from each cartridge was collected in a 25 ml test tube and stored for further analysis (Endo et al., 2005).

3.10.4 Evaporation

Following fractionation, each solvent fraction was evaporated to 1 ml under nitrogen stream in a water bath at 45^{o}C. One ml concentrates were transferred into transparent and amber vials for PCBs and PAHs analyses, respectively.

3.10.5 Sample analysis

The recovery values for PCBS and PAHs ranged from 39% to 59%.

3.10.5.1 PAHs determination

Determination of aromatic hydrocarbons was performed using a gas chromatography mass spectrometry (GC/MS) (Agilent 7890A MSD 5973) equipped with a split/splitless Inlet and a 7683B auto-injector (Agilent, Santa Clara, USA). Separation was conducted using Rxi-5SILMS 30 m _ 0.25 mm _ 0.25 µm column (Agilent, Santa Clara, USA).

Analysis was executed as follows: the final temperature was set at 290^{o}C while the starting temperature was 50^{o}C at 0.5 min hold time. The temperature was raised to 250^{o}C at a rate of 25^{o} C/min, held at 0 min and then raised to the final temperature at 290^{o}C at a rate of 5^{o} C/min and held for 3.5 min (US EPA, method 8270D). The injection volume was 1 µL and the injection temperature was held at 300^{o}C. The carrier gas used was helium, at a flow rate of 1.4 ml/min, average velocity of 43.122 cm/sec, pressure at 11.747 psi, and holdup time of 1.595 min (US EPA, method 8270D).

3.10.5.2 PCBs determination

Determination of PCBs was performed using gas a chromatography equipped with electron capture detector (GC/ECD) on an Agilent 6890 N equipped with a splitless injector and a 7683 auto-injector (Agilent, Santa Clara, USA). Separation was conducted using an HP-1 30 m _ 0.25 mm _ 0.25 µm column (US EPA, method 8270D).

Analysis was executed as follows: the starting temperature was at 110^{o}C at 0.1 min hold time. The temperature was raised to 200^{o}C at a rate of 25^{o} C/min and held for 0.5 min. Next the temperature was raised to 240^{o}C at a rate of 15^{o} C/min and held for 0.5 min. Finally, the temperature was raised to 325^{o}C at a rate of 20^{o} C/min and held for 1.5 min. The injection volume was 1 µL and the injection temperature was held at 250^{o}C. The carrier gas used was helium, at a flow rate of 3.5 ml/min, average velocity of 85 cm/sec, and pressure at 20.9 psi. Nitrogen gas was used as makeup gas at pressure 60 psi (US EPA, method 8270D).

3.11 Field adsorption experiment

To study whether plastic pellets adsorb OPs from the marine environment and to determine the rate at which such adsorption occurs, a field experiment was performed. Six grams of resin pellets of different polymers; high density polyethylene, low density polyethylene, polystyrene, and polypropylene (HDPE,

LDPE, PS, and PP) were used so as to compare the rate of adsorption in each. The pellets were placed in tea balls which were subsequently placed in baskets that were attached to a rigid structure in such a way that the pellets were in full contact with the surface water of the sea (Mato et al., 2001). The pellets were harvested in the sequence of 48 hrs; 96 hrs; 192 hrs; 312 hrs, kept in a freezer at subzero temperature until chemical analyses were carried out and after 10 days, the experiment was terminated.

At the completion of the experiment, the pellets were air-dried in the laboratory and non-deployed pellets were also analyzed to ascertain the concentration of OPs on the pellets at time zero. Two grams of each pellet harvested and control pellets at 0 hrs were weighed and OPs analysis was conducted as described in Section 3:10 above.

3.12 Analysis of OPs in seawater

Seawater sample was obtained from the location of the field adsorption experiment, each time the resin pellets were harvested. This was done in order to compare the concentration of OPs in resin pellets analyzed in Section 3.11 above with the concentration of ambient water. The samples obtained were stored in the refrigerator at 4^{o}C prior to analysis. The procedures for the seawater analysis are as follows (EPA, 2007).

3.12.1 Solvent extraction

Samples were retrieved from the refrigerator and the volume of each sample was measured and recorded. Each sample was poured into a separatory funnel and 60 ml DCM was added. The funnel was shaken vigorously for 2 min and left to stand for 15 min. The tap was opened to collect the DCM at the lower part of the funnel and was closed just before the seawater escaped. The process was repeated twice but in this case, the surrogate was not added. Next, all extract was collected for each sample and 5 g of anhydrous Na_2SO_4 was added to absorb the water that must have escaped with the solvent (EPA, 2007).

Recovery was tested by spiking 5 random samples with surrogates of PCB (1 ml of 2,3-Dichlorobiphenyl) and PAHs (1 ml of 1,2-Diphenylbenzene)

3.12.2 Evaporation

The extract was transferred into a Kuderna-Danish concentrator and this was placed in a water bath at 85^{o}C and concentrated to about 30 ml. Next, the concentrate was further evaporated on a heating mantle at 45^{o}C under nitrogen stream just before dryness and the 1 ml residue was transferred into vials.

3.12.3 Fractionation

Silica gel SPE fractionation method was performed for the clean-up of the samples.

Twenty ml dichloromethane (DCM) was added for the conditioning of the cartridges and this was followed by the addition of hexane (20 ml x3) just before the DCM got to the level of the top frit of the cartridges. The cartridges were prevented from running dry during the entire fractionation process (US EPA, method 3550C).

For PCBs: One ml of the samples contained in vials were decanted into individual cartridge and just as it got to the level of the top frit, 20 ml hexane was added for PCBs elution (Ogata et al., 2009). The fraction from each cartridge was collected in a 25 ml test tube and stored for further analysis.

For PAHs: Twenty ml DCM was poured into each cartridge and the fraction from each cartridge was collected in a 25 ml test tube and stored for further analysis.

3.12.4 Evaporation

Following fractionation, each solvent fraction was evaporated to 1 ml under nitrogen stream in a water bath at 45^{o}C. 1 ml concentrates were transferred into transparent and amber vials for PCBs and PAHs respectively. Next, OPs analysis was conducted as described in Section 3.10.5 above.

3.13 Statistical analyses

Statistical analyses for microplastics, macroplastics, and field experiment data were conducted using ANOVA (Microsoft Excel 2007). One way ANOVA was used to evaluate variability of microplastics in individual location with respect to two different factors. Statistical analysis of microplastic's abundance and distribution

among sampling stations and dates, was conducted with Two-Way ANOVA. Similarly, Two-Way ANOVA was used to evaluate variation in OPs concentration with time among polymers in field experiment. The variability of microplastic's concentration in sediments was evaluated with two-factor with replication.

All multivariate analyses were done using the PRIMER-e statistical package (PRIMER-e, Plymouth Marine Laboratory).

Chapter 4

4.0 Results and Discussion

4.1 Microplastics distribution in seawater samples

Microplastics were present in all samples collected from all four stations and dates of sampling. This confirms the hypothesis that microplastics are pervasive in the top layer of the ocean (Doyle et al., 2011). The highest concentration of microplastics was in Station 3 with an average of 2.91 particles/m^2 (204 particles) and the lowest concentration was reported in Station 1 with 0.09 particles/m^2 (13 particles) respectively as shown in Table 5 below. Possible reason for the high concentration of microplastics in Station 3 is because this could be a convergence zone due to the hydrodynamics of the sea and bathymetric effect.

Statistical analysis of microplastic abundance and distribution among sampling stations and dates, was conducted with ANOVA (Two-Factor Without Replication). There were significant differences ($p \leq 0.5$) in microplastics concentration per square meter between the four stations. However, there was no significant temporal variability ($p \geq 0.5$) of microplastics found in the sea surface (Table 4).

Table 4: ANOVA (Two-Factor Without Replication) of spatial and temporal variability of microplastics

Source of Variation	*SS*	*Df*	*MS*	*F*	*P-value*	*F crit*
Dates	0.414614	2	0.207307	0.644444	0.557789	5.143253
Stations	4.660389	3	1.553463	4.829164	0.048507	4.757063
Error	1.930102	6	0.321684			
Total	7.005104	11				

Table 5: Incidence of microplastics in surface seawater samples

Sampling location	Sampling date	Coordinate Start	Coordinate End	Number of plastic particles				Concentr. (part./m^2)	SD	Size range (mm)	Color
				TOTAL	Fiber	Film	Frag.				
Station 1	7/1/2015	25.1931 N, 51.3581 E	25.1916 N, 51.35818 E	13	6	7	0	0.09	3.79	0.5 – 5	Blue, green, black
	3/3/2015			32	31	1	0	0.15	17.62	1 – 10	Blue, black, green
	29/03/2015			71	62	4	5	0.36	33.20	1 – 10	Blue, black, green, grey, red
Station 2	7/1/2015	25.1894 N, 51.3910 E	25.1879 N, 51.39277 E	34	30	4	0	0.301	16.29	0.5 – 10	Grey, blue, red, black
	3/3/2015			75	66	9	0	0.670	35.79	1 – 10	Blue, black, red
	29/03/2015			39	38	0	1	0.170	21.66	1 – 10	Blue, red
Station 3	7/1/2015	25.1889 N, 51.4779 E	25.1863 N, 51.42444 E	228	222	4	2	1.52	126.44	1 – 10	Green, colorless, blue, red
	3/3/2015			204	156	3	1	2.914	88.92	0.5 – 10	Green, black, blue, red
	29/03/2015			164	158	6	0	0.982	89.54	1 – 10	Green, black, blue, red
Station 4	7/1/2015	25.1848 N, 51.4714 E	25.1835 N, 51.47086 E	83	74	8	1	0.651	40.28	≤ 0.5 – 10	Blue, red, grey, green, black
	3/3/2015			49	35	5	3	0.37	17.93	0.5 – 10	Blue, black, grey, green, red
	29/03/2015			120	119	0	1	0.976	68.42	1 – 10	Blue, black, brown, red

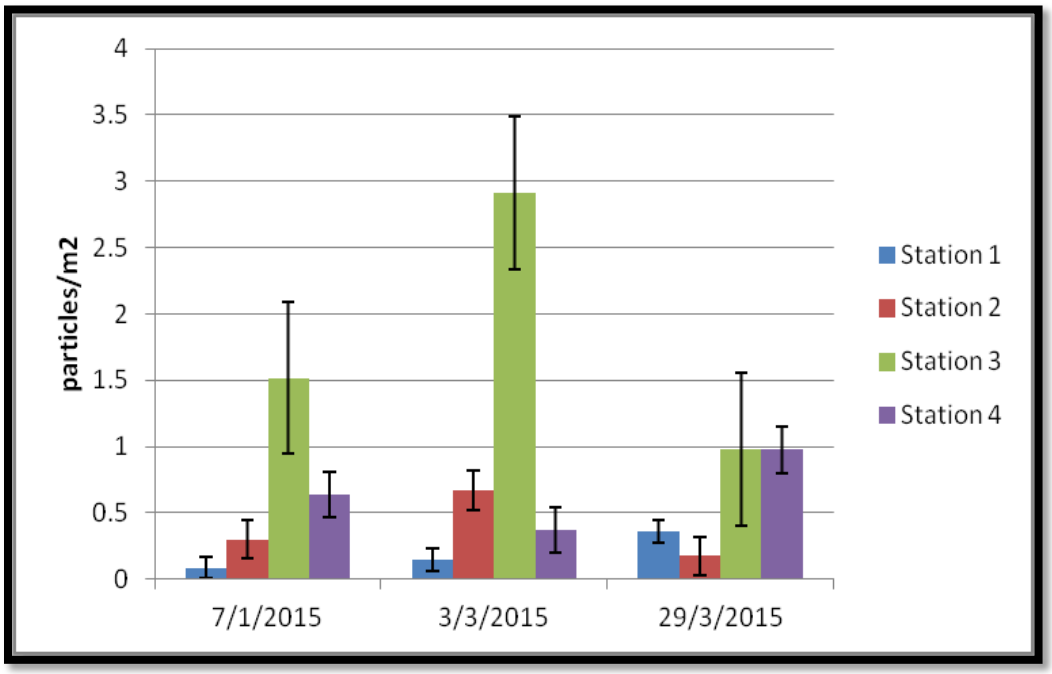


Figure 7: Spatial and temporal variability of microplastic densities in surface seawater

From figure 7 above, the abundance of plastic particles differed between sites with Station 3 consistently showing the highest density of microplastic debris possibly because it is a convergence zone.

4.1.1 Spatiotemporal variability of particle shapes in seawater

ANOVA (Two-Factor Without Replication) showed that the concentration of "fibers" among the four offshore stations differed significantly ($p \leq 0.05$), however, there was no significant difference ($p \geq 0.05$) in "fibers" concentration between sampling dates (Table 6). Distribution of film particles on a spatial and temporal scale showed no

significant differences. The concentration of fragments was not tested, due to its negligible values.

Figure 8, below, shows microplastic concentrations of "fiber" particles with respect to stations and sampling dates.

Table 6: ANOVA (Two-Factor Without Replication) of concentration of different plastic shapes

Plastic shape	***Source of Variation***	***SS***	***Df***	***MS***	***F***	***P-value***	***F crit***
Fiber	Dates	0.374902	2	0.187451	0.594557	0.581337	5.143253
	Stations	4.579708	3	1.526569	4.841974	0.048248	4.757063
	Error	1.89167	6	0.315278			
	Total	6.84628	11				
Film	Dates	0.002407	2	0.001204	1.693754	0.261098	5.143253
	Stations	0.000463	3	0.000154	0.216985	0.881222	4.757063
	Error	0.004264	6	0.000711			
	Total	0.007133	11				

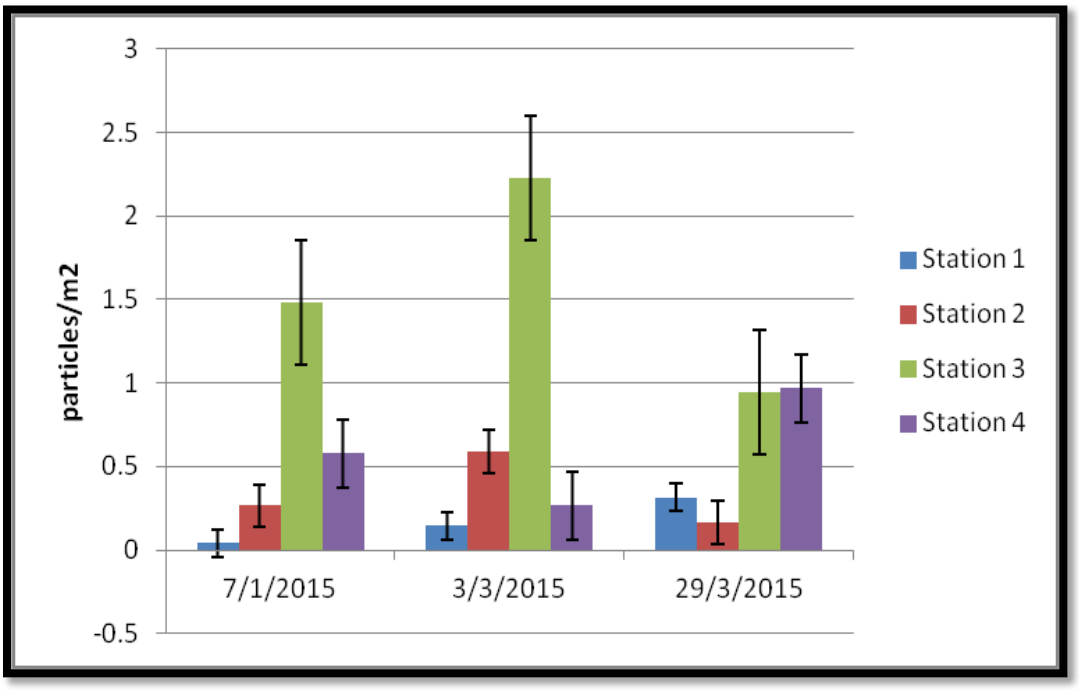


Figure 8: Spatiotemporal variability of microplastic fibers in surface seawater

4.1.2 Spatiotemporal variability of particle sizes in seawater

As shown in figure 9 below, microplastics within the range of 1 – 5 mm were dominant in all four stations and at different sampling dates. For microplastics in size range > 5 mm, their spatial variability was significant ($p \leq 0.02$). All other size classes showed no significant difference ($p \geq 0.05$) in spatiotemporal variability.

Table 7: ANOVA (Two-Factor Without Replication) of concentration of various size classes

Size class	*Source of Variation*	*SS*	*Df*	*MS*	*F*	*P-value*	*F crit*
>5 mm	Dates	0.063873	2	0.031937	0.831257	0.480109	5.143253
	Location	0.89415	3	0.29805	7.75772	0.017323	4.757063
	Error	0.230519	6	0.03842			
	Total	1.188542	11				
1 – 5 mm	Dates	0.155226	2	0.077613	0.532458	0.612538	5.143253
	Location	1.512873	3	0.504291	3.459657	0.091472	4.757063
	Error	0.87458	6	0.145763			
	Total	2.542679	11				
0.5 – 1 mm	Dates	0.000921	2	0.000461	3.575986	0.094947	5.143253
	Location	0.000392	3	0.000131	1.015427	0.448996	4.757063
	Error	0.000773	6	0.000129			
	Total	0.002086	11				

The size range of microplastics in the open ocean is of significance as it determines its bioavailability to biota (Nor and Obbard, 2014) and also determines the concentration of OPs that can be adsorbed on their surfaces. Microplastics < 0.1 mm are suitable for ingestion by a wide range of neuston organisms (Tourinho et al., 2010; Nor and Obbard, 2014)

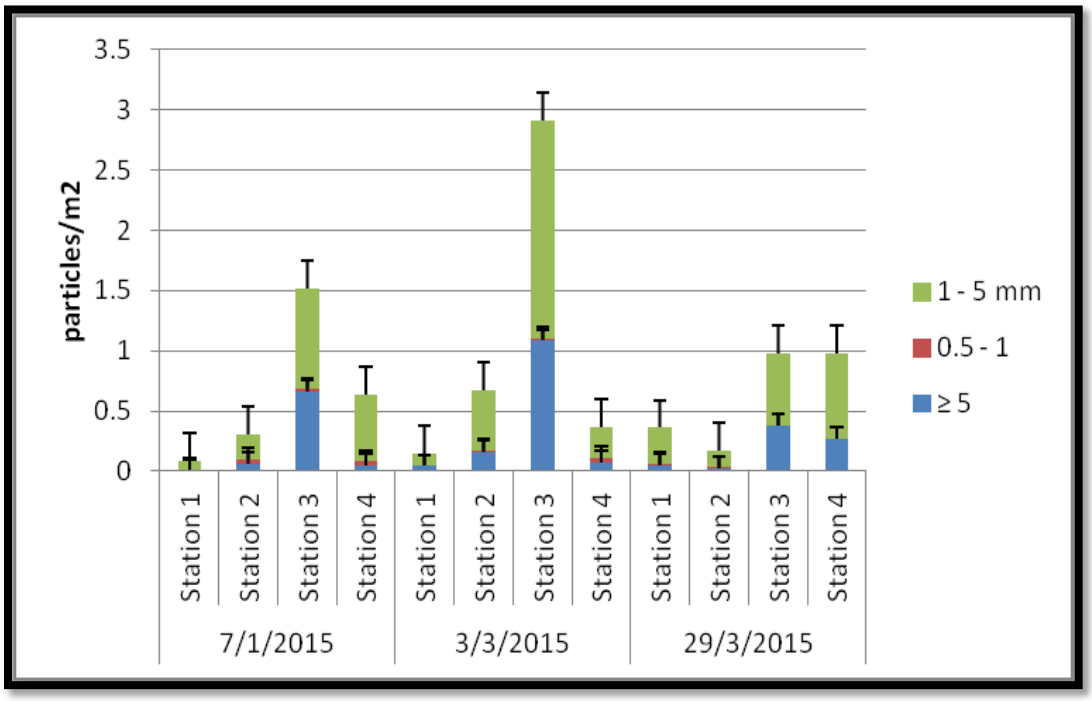


Figure 9: Microplastic concentration of various size classes in surface seawater

4.2 Microplastics in sediment samples

As both enzymatic and alkali digestion were not very efficient in digesting biogenic materials, the following criteria were adopted to differentiate suspected microplastics from other materials as described by Noren (2007) and Nor et al. (2014).

- Organic and cellular structures were not apparent.
- Particles are distinctly and evenly colored.
- All parts of fibre are equally thick, do not dwindle at the end and do not appear segmented.

Hence, microplastics were present in all sites sampled as shown in the table below and the average concentration of plastic particles in all intertidal sampling sites was

6.7 particles per 500 g (i.e. 13.5 particles/kg dry sediments) which is much less than the quantity reported in Belgium and Italy (Claessens et al., 2011; Vianello et al., 2013). Figure 17 below shows images of some microplastics (fiber, pellet, and fragment) isolated from sediments.

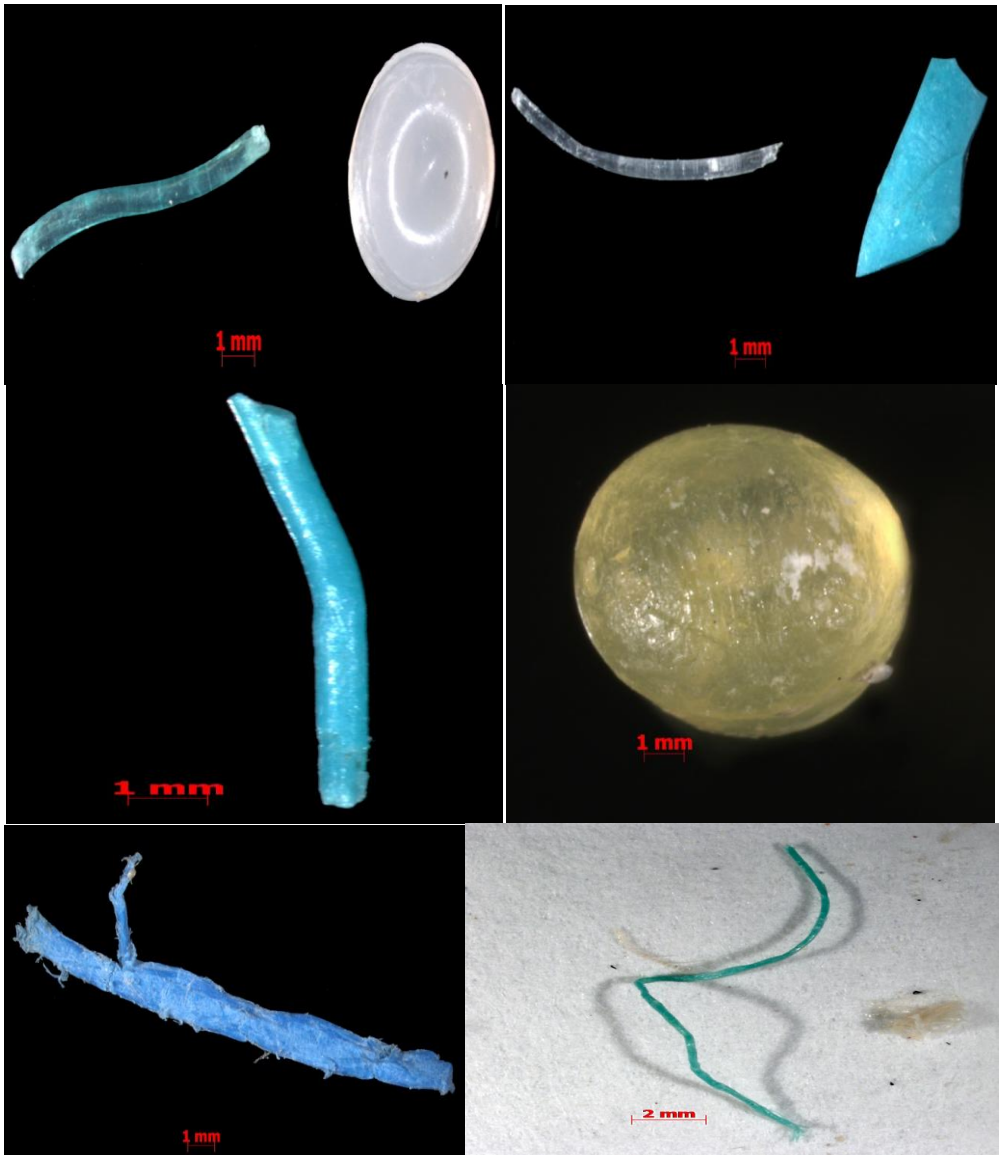


Figure 10: : Images of some plastic fibres, fragments and pellets isolated from sediments

Figure 11 below gives a representation of the average concentration of microplastic across 8 intertidal sandy beaches. The error bar used was derived from the standard error. There was no significant difference ($p \geq 0.05$) in average concentration of microplastics among all 8 locations sampled. This indicates that microplastic are evenly distributed in intertidal sandy beaches around Qatar.

Table 8: ANOVA (Single Factor) to test for the difference in average concentration of microplastics among 8 locations

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Location	131.1667	7	18.7381	1.284898	0.318243	2.657197
Replicate	233.3333	16	14.58333			
Total	364.5	23				

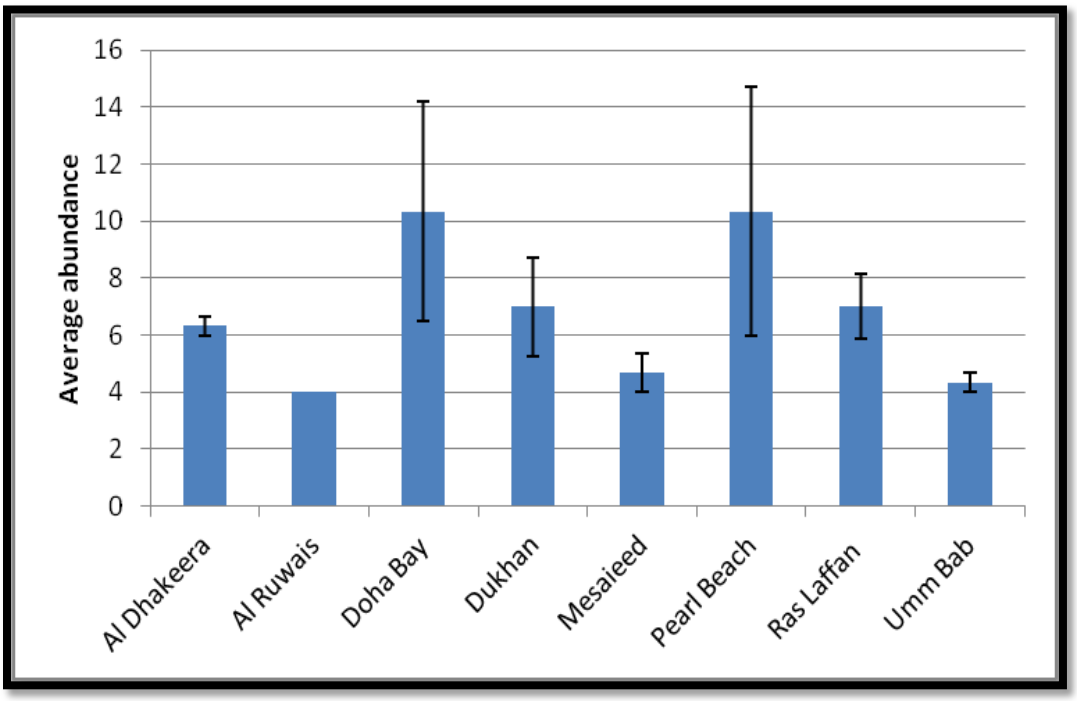


Figure 11: Average concentration of microplastics per 500 g dry sediments in 8 intertidal sandy beaches around the coast of Qatar

4.2.1 Spatial variability of different particle shapes in sediments

Single Factor ANOVA was used in comparing the 8 location in terms of abundances of different microplastic shapes. The results obtained showed no significant differences (Table 9).

Table 9: ANOVA (Single Factor) to test for differences among locations for 3 types of microplastic shapes

Plastic shape	*Source of Variation*	*SS*	*Df*	*MS*	*F*	*P-value*	*F crit*
Fiber	Locations	46.95833	7	6.708333	0.993827	0.470027	2.657197
	Replicates	108	16	6.75			
	Total	154.9583	23				
Fragment	Locations	12.29167	7	1.755952	0.916149	0.51918	2.657197
	Replicates	30.66667	16	1.916667			
	Total	42.95833	23				
Film	Locations	33.83333	7	4.833333	2	0.11888	2.657197
	Replicates	38.66667	16	2.416667			
	Total	72.5	23				

Similarly, there were no significant differences among locations for either of the size classes considered (Table 10).

Table 10: ANOVA (Single factor) to test for differences among locations for each of the 4 size-classes of microplastic considered

Size class	*Source of Variation*	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
<0.5	Location	8.5	7	1.214286	1.079365	0.420105	2.657197
	Replicate	18	16	1.125			
	Total	26.5	23				
0.5 - 1	Location	14.66666667	7	2.095238	0.824356	0.581605	2.657197
	Replicate	40.66666667	16	2.541667			
	Total	55.33333333	23				
1 - 5	Location	43.83333333	7	6.261905	1.353925	0.289457	2.657197
	Replicate	74	16	4.625			
	Total	117.8333333	23				
>5	Location	1.166666667	7	0.166667	0.8	0.598869	2.657197
	Replicate	3.333333333	16	0.208333			
	Total	4.5	23				

A recent study in Italy by Vianello et al. (2013) reported microplastic concentration of 2175 particles/kg dry sediments, which is two orders of magnitude greater than what was reported in the present study. However, Dekiff et al. (2014) reported the average microplastics concentration in sediments to be 1.0 – 2.0 particles/kg and this is considerably less than the concentration reported in the present study. The reason for high variability in concentration may be due to the methodological differences adopted by different researchers (Dekiff et al., 2014).

The incidence of these plastic particles was highest in samples obtained from the Pearl and Doha Bay with an average of 10.3 particles per 500 g (i.e. 20.6 particles/kg dry sediments). This could be attributed to the fact that these two areas are densely populated as compared to other sampling area. Hence, waste generation is highest in these two sites, though the beaches were not littered with marine debris during sample collection due to effective beach cleaning exercised in these locations. Furthermore, high concentration of microplastics in Doha Bay can be attributed to boating activities in nearby Doha sailing club.

Al Ruwais had the lowest concentration of microplastics with an average of 4 particles per 500 g (i.e. 8 particles/kg dry sediments), although this beach was, heavily littered by marine debris. This observation does not agree with the assumption by Nor and Obbard (2014) that high concentration of plastic debris is associated with high microplastic incidence in sediments. Debris found in this location comprised of plastic bottles, resin pellets, bottle caps, food wrappers, ghost nets etc. The high concentration of resin pellets could have been as a result of

transportation by ocean currents from neighboring region since there is absence of plastic industry in the area. Therefore, the possibility of transport by runoffs is ruled out. Al Ruwais is a remote location at the northernmost part of Qatar with few human population and little commercial activities. The high presence of debris is believed to have accumulated over the years due to absence of beach cleaning of the area and the low concentration of microplastic is probably due to the fact that plastics take several decades to fragment into microscopic sizes (Andrady, 2011).

The size range of microplastic is important as it determines to a large extent, its impact on marine biota. By far, the most prevalent size of microplastics in this study is in the range of 1 – 5 mm. Hence, these particles can serve as rafts for organism that become invasive in their new locations (Derraik, 2002). In addition, they can be easily mistaken for food by zooplanktons and other neuston organisms, thereby causing blockage of the digestive system and internal injuries of such organisms.

Fibers were the dominant type of particles found in this study and this supports the claim about fiber's dominance, made in Singapore (Nor and Obbard 2014), the UK (Thompson et al., 2004) and Belgium (Claessens et al., 2011). Furthermore, these fibers are believed to have been generated from secondary origins which have fragmented in the marine environment over the years.

Plastic particles visible to the naked eye and removable by stainless steel tweezer were analyzed using a Perkin Elmer Spectrum 400 FT-IR/FT-NIR spectrometer. In all samples, 13 particles isolated from sediments and 5 samples isolated from seawater were analyzed. Table 11 below shows the type of polymer of each particle analyzed.

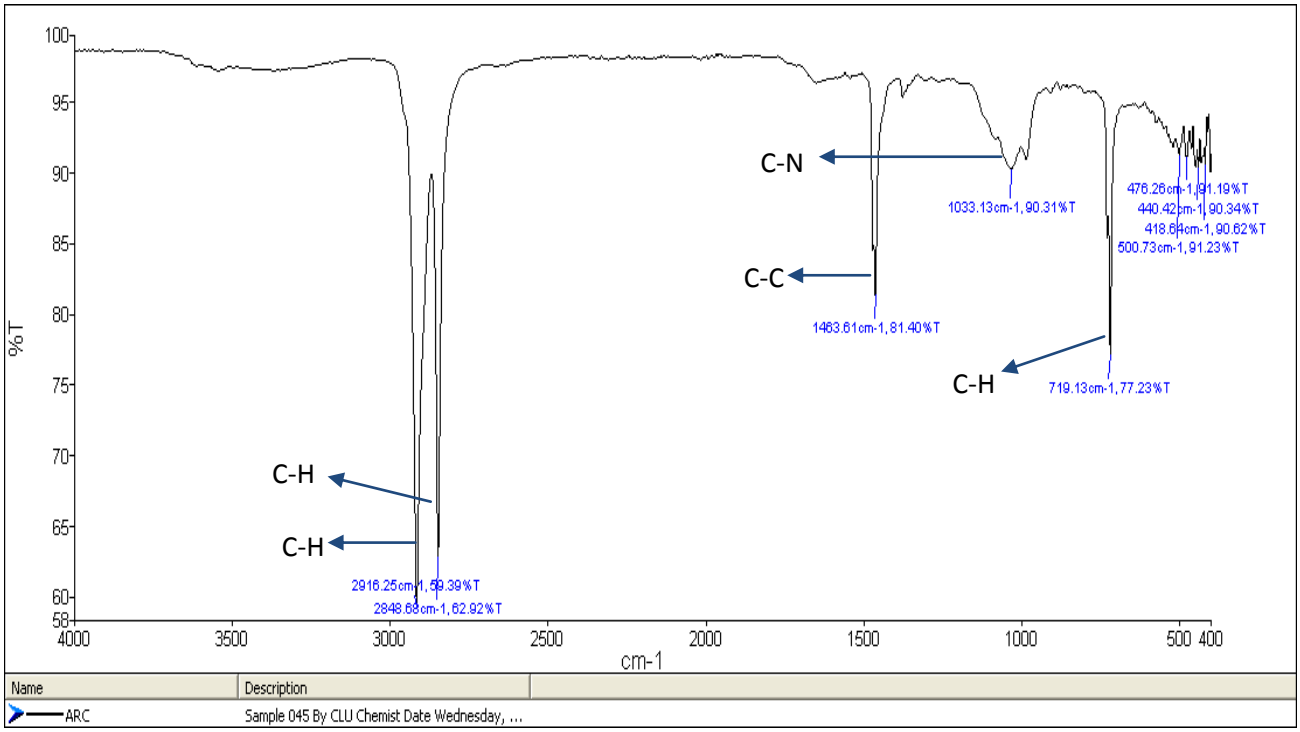
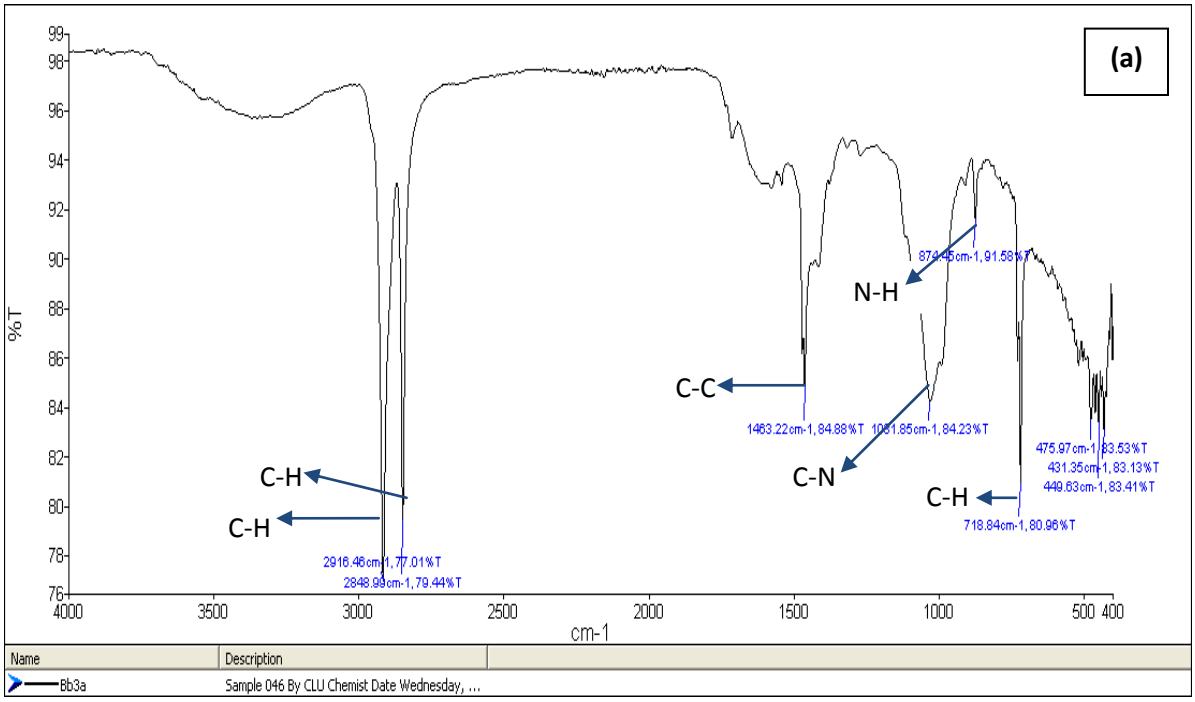


Figure 12: FT-IR spectrum showing LDPE microplastic isolated from sediments in Al Ruwais

Figure 12 above shows peaks at wave numbers 2916 cm^{-1}, 2848 cm^{-1}, 1463 cm^{-1}, and 719 cm^{-1} respectively, which is typical of LDPE FT-IR spectrum. A further confirmation was done using OMNIC FT-IR software which compares peaks of samples with the database available in its library.

A fiber from Doha Bay and a fragment from The Pearl could not be identified successfully after comparing their spectra with the library and further identification with OMNIC FT-IR software, hence they were classified as "other". This could be as a result of signal interferences in the spectrum that is probably brought about by micron size range of naturally occurring organic materials due to the prolong residence time such plastic debris remained on the beach (Nor and Obbard, 2014).

Hence, a more sophisticated analysis such as X-ray diffraction, X-ray photoelectron spectroscopy (XPS) is required to ascertain the actual polymer of the unidentified particles. Figure 13 below shows the FT-IR spectrum of the polymer from Doha Bay (a) and The Pearl (b).



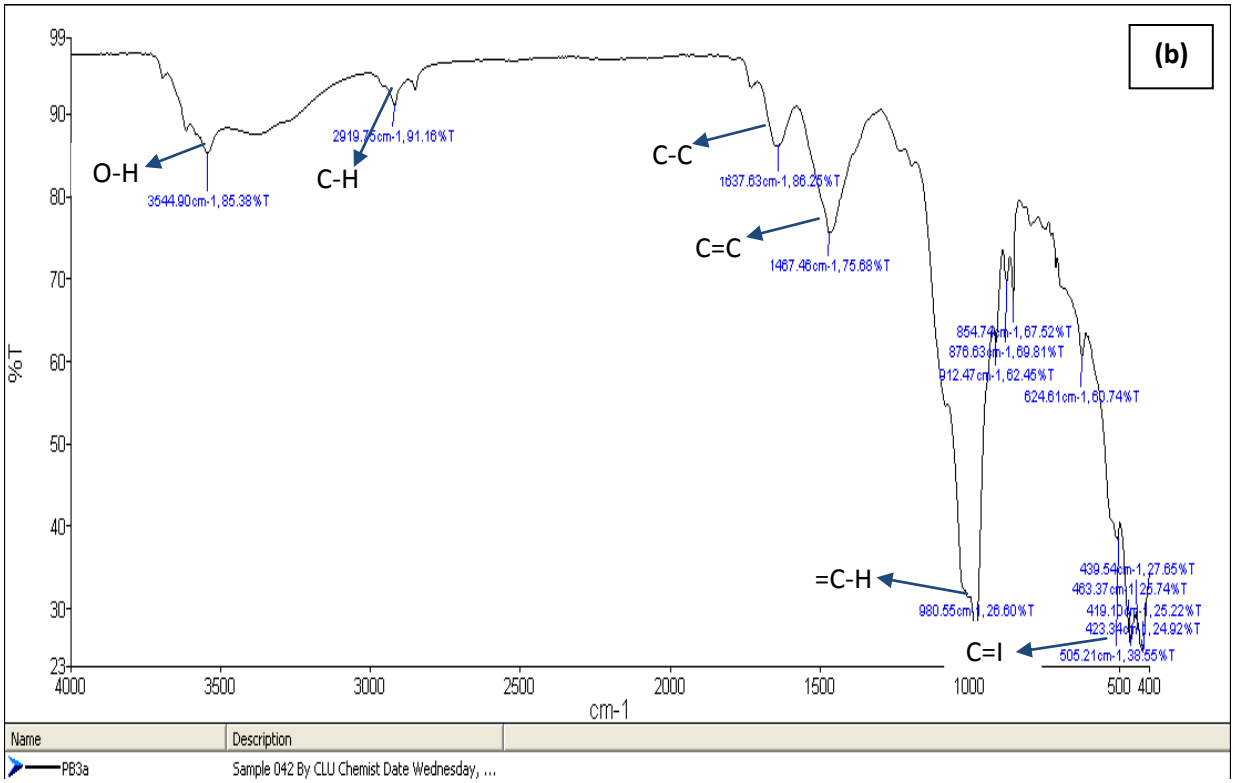


Figure 13: FT-IR spectrum of an unidentified plastic fragment isolated from Doha Bay (a) and The Pearl (b)

Table 11: Polymer type of plastic particles isolated from sediments and seawater

Sample location	Size range	Sample type	Polymer type
Al Ruwais	4 – 5 mm	Fiber (2), Pellet (s)	PP + PE (Co-polymer) (3), LDPE (1)
Doha Bay	1 – 8 mm	Fiber (4), Film (1)	LDPE (2), PP (2), PP + PE (Co-polymer) (1), Other (1)
The Pearl	2 mm	Fragment (2)	PP + PE (Co-polymer) (1), Other (1)
Umm Bab	10 mm	Fiber	PP (1)
Seawater			
Station 2	1 – 3 mm	Fiber (1), Fragment (2)	PP + PE (Co-polymer) (1), LDPE (2)
Station 3	3 mm	Fiber	Other (1)
Station 4	4 mm	Fiber	PET (1)

Note: PP - Polypropylene, LDPE - Low Density Polyethylene, PE – Polyethylene, PET – Polyethylene Terephthalate

4.3 Background contamination

Five of the six filter papers had materials with similar appearance of microplastics on them. However, there is no certainty that this was as a result of background contamination from ambient air in the laboratory as all necessary precautions were taken to avoid contamination of the samples during analysis. Hence, it can be deduced that such particles/materials were present in the aquarium sand prior to arrival in the laboratory and could have been introduced accidentally by the manufacturer during production and packaging.

4.4 Recovery study

The result from recovery study for microplastic extraction is shown in table below. The recovery efficacy of NaCl solution ranged from 80% to 100%. This is slightly higher than the recovery rate reported by Thompson et al. (2004) which ranged between 68.8% and 97.5% with slight modifications.

Table 12: Recovery study of virgin polypropylene and low-density polyethylene pellets

Polymer type	Recovery rate %		
	1	**2**	**3**
PP	90	100	100
LDPE	100	90	80

4.5 Characterization of macroplastics

Table 13 below shows the result of the physical and FT-IR characterization of macroplastics collected from 8 intertidal sandy beaches around Qatar**.**

Table 13: Characteristics of macro-plastics collected from 8 intertidal sandy beaches around Qatar

Sample location	Color	Size range	Sample type	Polymer type
Al Ruwais	Blue, Black, Discolored, White	4 – 14 mm	Bottle cap (1), Pellet (3), Rope (1)	PP (1), LDPE (4)
Doha Bay	White, Black, Colorless	6 – 50 mm	Fragment (2), Film (1)	LDPE (2), Other (1)
Al Dhakeera	Red, White, Blue	6 – 25 mm	Fragment (3), Bottle cap (2)	PP (1), PVC (1), PE (2), PS (1)
Dukhan	White, Pink, Purple, Red, Discolored	10 – 30 mm	Fragment (5)	PET (2), PS (1), PVC + Ethylene (2)
Umm Bab	Grey, Discolored, Blue, White	9 – 18 mm	Fragment (4), Fiber (1)	LDPE, PVC + Ethylene (1), PS (2), PE + PP (1)
Mesaieed	Yellow, White, Orange, Discolored, Red	12 – 25 mm	Fiber (1), Fragment (3), Film (1)	PP (1), LDPE (2), PVC (1), PP + PE (1)
The Pearl	Green, White, Orange	20 – 30 mm	Bottle cap (2), Fragment (2)	PS (1), PP (3)
Ras Laffan	Discolored Green Red Blue	25 – 50 mm	Fragment (3), Fiber (1)	LDPE (3), PP (1), other (1)

4.6 Variability of OPs concentrations and relationship with characteristics of the macroplastics

Of the 40 representative samples of macroplastics prepared for chemical analysis, 34 were analyzed individually for PAHs and PCBs due to insufficient weight of 6 samples. PAHs were detected in all samples with a wide concentrations range. Conversely, PCBs were not detected in some samples as total PCBs in other samples was as high as 1,005 ng/g. Similarly, a wide range of piece-to-piece variation in concentration (with 2 orders of

magnitude) was reported in macroplastics collected from Al Ruwais. However, Endo et al. (2005) explained that piece-to-piece variation is influenced by several factors such as surface area, type of polymer, plastic additives and residence time of plastics at the sea. In this case, the most probable source of high piece-to-piece variation is organic plastic additives (OPAs).

Statistical analysis by ANOVA (Single Factor) indicated that there was no significant difference between sample locations for total PCBs and PAHs respectively (Table 14). The highest PCB concentration was detected in black LDPE resin pellets obtained from Al Ruwais (1,005 ng/g) and the lowest was detected in a green bottle cap of PS obtained from The Pearl (3.53 ng/g). The variability between sites corresponds with a report by Endo et al, (2005). Spatial variability in their study was 6–18,700 ng/g. Conversely, the black resin pellets had a relatively low total PAHs concentration. However, this is not consistent with reports elsewhere. Frias et al. (2010) reported the highest concentration diversity for PCBs and PAHs in black and aged pellets. A simple explanation for the inverse correlation in PCBs and PAHs concentration is that contaminants are incorporated on plastic surfaces via two plausible routes. In the first mechanism, hydrophobic contaminants (PCBs) are adsorbed from ambient seawater due to the low polarity of plastic surfaces (Rice et al., 1984), and adsorption rate is dependent on many factors as stated earlier on. Alternatively, plastics are manufactured to serve specific purposes and hence incorporated with organic additives. These chemicals are added so as to fulfill a perceived purpose and, thus, give the plastics unique properties. Hence, different plastic products have different additives (Mato et al.,

2001).

Table 14: Single factor ANOVA for total concentrations of PCBs and PAHs in macroplastic debris among locations

	Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
PCBs	Location	350837.5	7	50119.65	1.132168	0.373896	2.388314
	Within Groups	1150987	26	44268.75			
	Total	1501825	33				
PAHs	Location	1.09E+09	7	1.55E+08	0.888484	0.529428	2.388314
	Within Groups	4.54E+09	26	1.75E+08			
	Total	5.62E+09	33				

4.6.1 Multivariate analyses of PAHs compounds in intertidal macroplastic debris

Two samples that could not be characterized in terms of the dominant type of plastic polymer were excluded from further analyses. A correlation matrix was used to pick out strongly correlated PAHs compounds (coefficient > 0.9) in intertidal macroplastic debris collected in 8 sandy beaches around Qatar. When these collinear compounds were of the same densities (Appendix A), they were treated as only one variable and their concentrations summed. The new correlation matrix with summed concentrations still shows some strongly correlated compounds (Appendix B) but, given that these were of different densities, no further

grouping was done.

The Principal Components Analysis (PCA) showed large variations among samples collected at the same locations (Figure 21). Two samples, one from Dukhan and one from Doha bay showed larger concentrations of most PAH compounds, relative to other samples, which largely determined the ordination pattern. No particular association was discernible between type of polymer, type and size of particle and PAH compounds grouped by density.

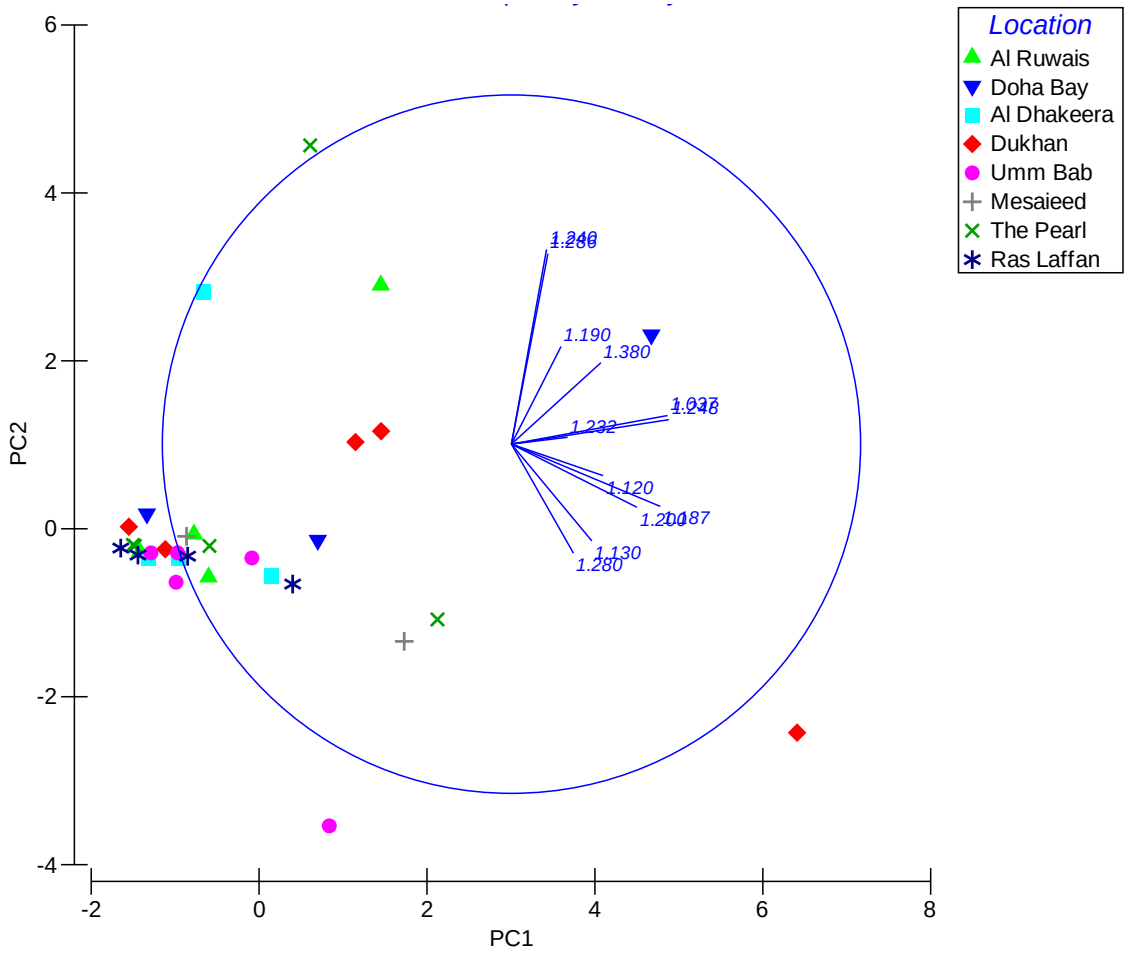


Figure 14: PCA ordination for PAHs, grouped by density, in intertidal macroplastic debris collected in 8 sandy beaches around the coast of Qatar.

4.7 Pollutant contents of plastic pellets deployed in the marine environment

The present study showed a steady decrease in concentration of PCBs in all pellet samples with time and a fluctuation in PAHs concentration during the course of the experiment. Previous field adsorption experiment conducted by Mato et al. (2001) reported a steady increment in pollutants adsorption over a 6 day period.

The difference in PCBs concentration with time was significant ($p \leq 0.05$), however, the difference in concentration among pellets of different polymers was not statistically significant ($p \geq 0.05$) (Table 14). For total PAHs, there was also no significant difference in concentrations with type of polymer ($p \geq 0.05$) or time of exposure ($p \geq 0.05$). The reason for this is multifactorial, but the most probable reason for this decrease and fluctuation could be the fact that the experiment was not performed under a controlled condition. Steady changes in environmental parameters such as pH and temperature may be responsible for the continuous adsorption and desorption of pollutants. Also, factors such as dissolved organic compounds in aqueous phase, sorbate, and sorbent properties are important in determining the rate of (de)sorption (Teuton et al., 2009).

Table 15: ANOVA (Two-factor Without Replication) for change in concentrations of PCBs and PAHs with time of exposure and type of polymer

	Source of Variation	*SS*	*Df*	*MS*	*F*	*P-value*	*F crit*
PCBs	Polymer	960.8074	3	320.2691	2.591076	0.1012	3.490295
	Time	1632.411	4	408.1028	3.301678	0.048236	3.259167
	Error	1483.256	12	123.6047			
	Total	4076.475	19				
PAHs	Polymer	15593062	3	5197687	1.712314	0.217438	3.490295
	Time	34391090	4	8597772	2.832431	0.072482	3.259167
	Error	36425697	12	3035475			
	Total	86409850	19				

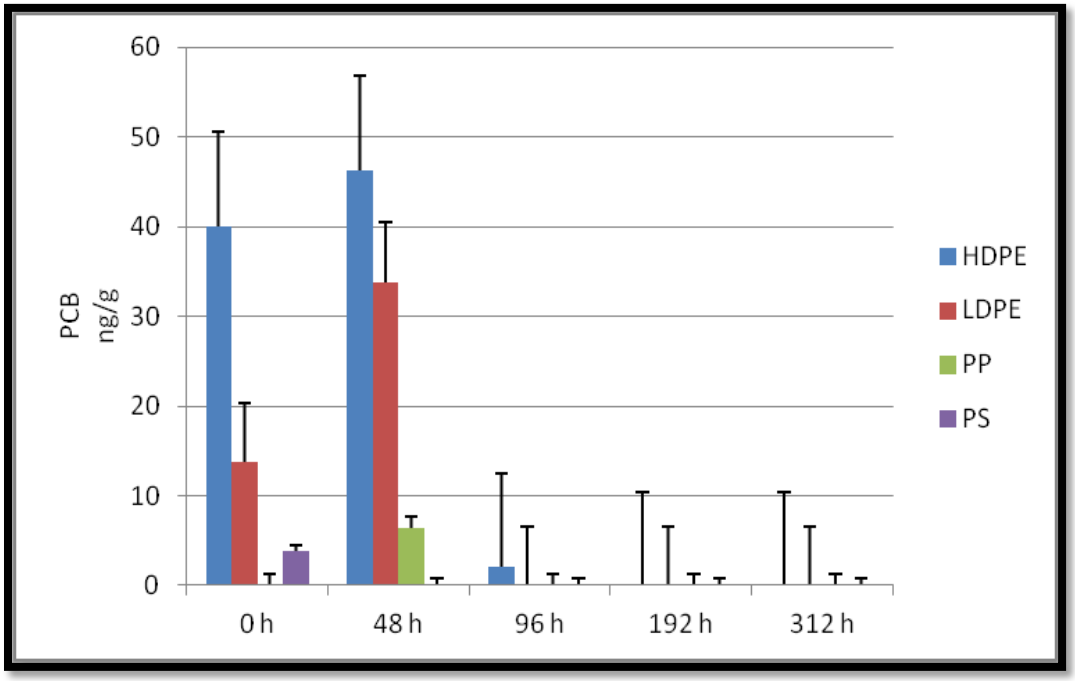


Figure 15: PCBs concentrations in pellets of 4 types of plastic polymer at different times of deployment in surface seawater at Pearl beach, Doha, Qatar

Ambient seawater collected during pellets retrieval also showed a decline in PCBs and PAHs concentration with time, conforming to the sequence of concentration decrease in pellets. The figure below shows the relationship between the declines of PAH levels in plastics and seawater concentration through the period of the experiment.

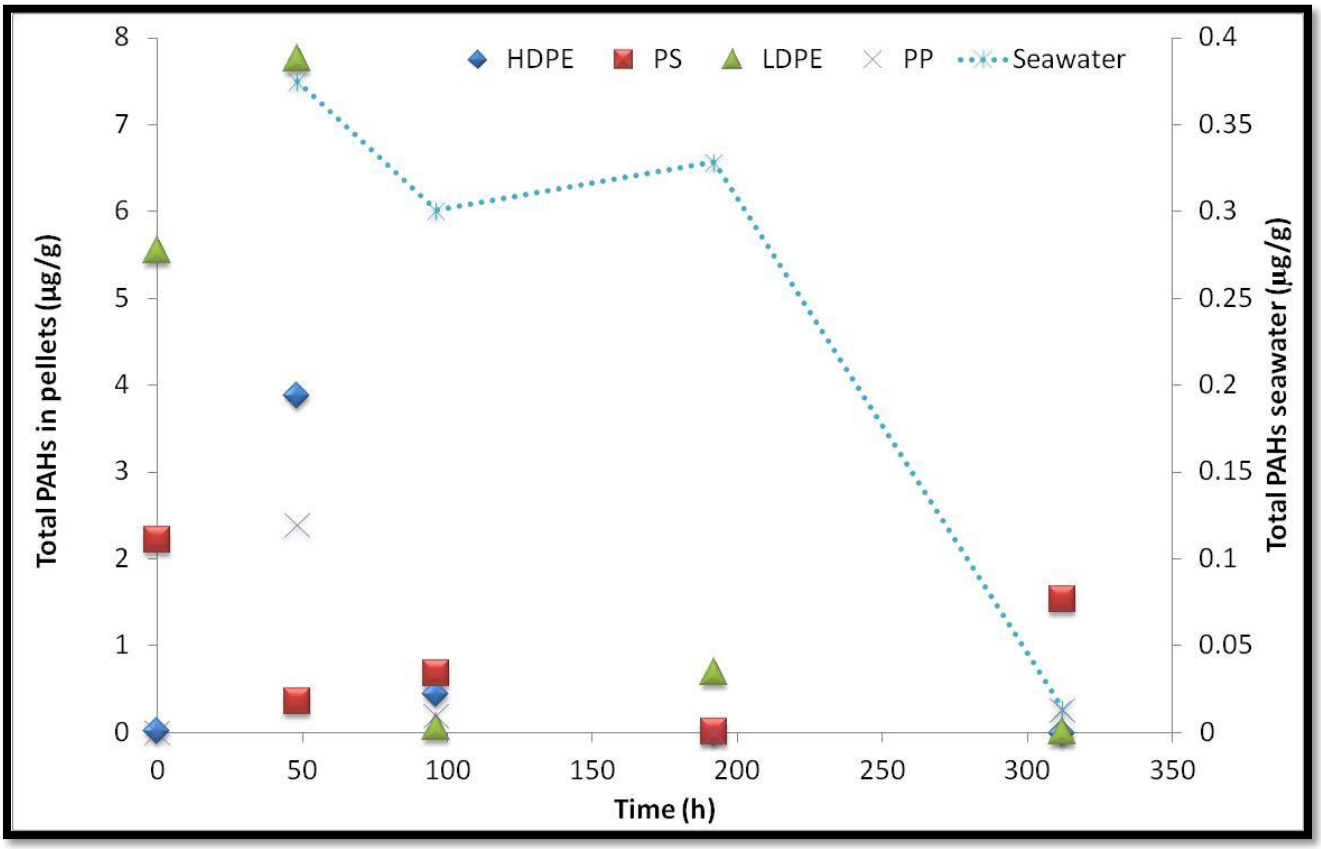


Figure 16: Total PAHs in pellets and seawater

4.7.1 Multivariate analyses of PAHs compounds in plastic pellets

A correlation matrix was used to pick out strongly correlated PAHs compounds (coefficient > 0.9) in plastic pellets. When these collinear compounds were of the same density (Appendix C), they were treated as only one variable and their concentrations summed. The

new correlation matrix with summed concentrations still shows some strongly correlated compounds (Appendix D) but, given that these were of different densities, no further grouping was done.

The Principal Components Analysis (PCA) showed large variations among pellets of different polymers and times of deployment (Figure 24). Initial samples (0 and 48 hours) were clearly the most variable and generally associated with larger concentrations of most PAH compounds, which is consistent with the pattern previously described for total PAHs in pellets and seawater (Figure 23).

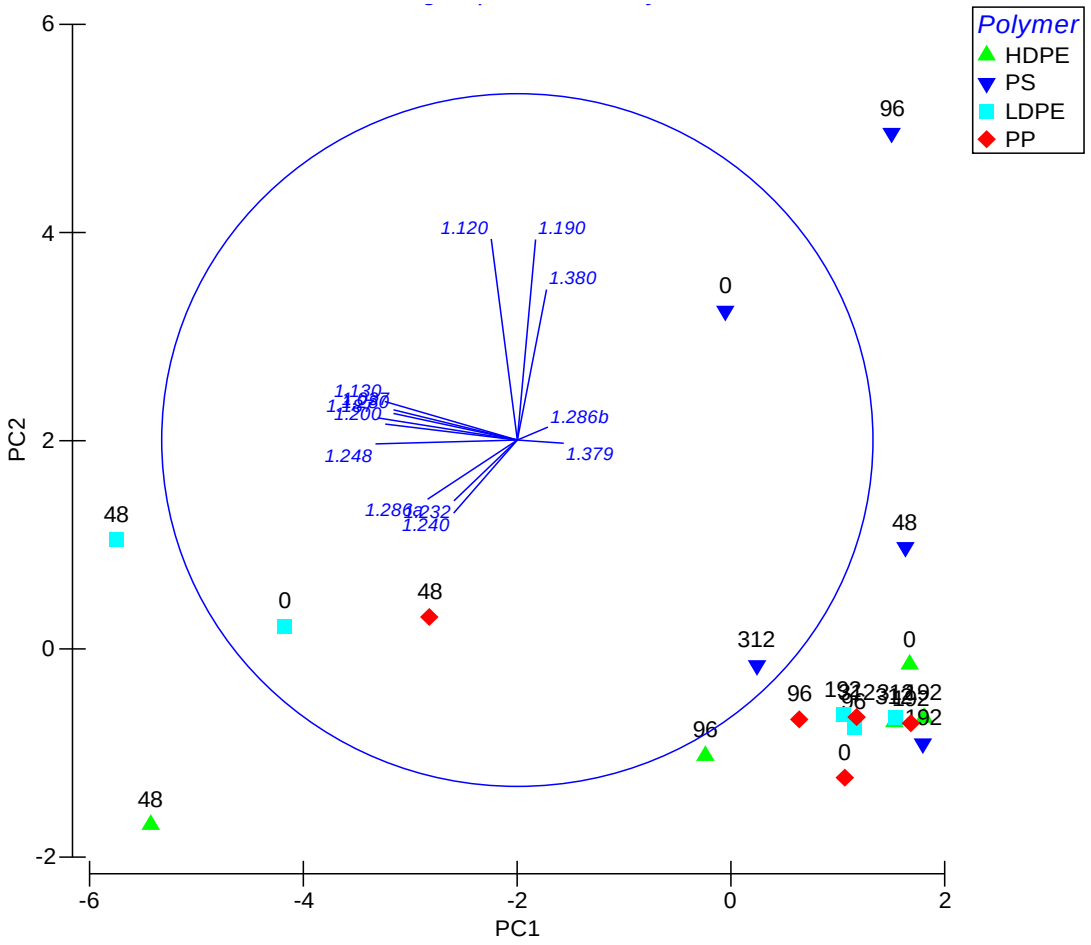


Figure 17: PCA ordination for PAHs, grouped by density, in 4 types of plastic polymer (high density polyethylene, low density polyethylene, polypropylene, and polystyrene) at different times of deployment (hour) in surface seawater at Pearl beach, Doha, Qatar

Long-term experiments spanning several weeks to months in a less perturbed environment is recommended in future studies for better understanding of (de)sorption of contaminants by resin pellets. As pellets age and erode on seawater, sorption of pollutants is accelerated due to an increase in surface area and the adsorption capacity of the pellets is increased (Mato et al., 2001).

Resin pellets are manufactured to have different surface structures and this determines their affinities to OPs. Endo et al. (2005) reported that PE pellets have more affinity to adsorb

PCBs than PP pellets. However, this was not corroborated by the findings of this study. This could be as a result of the short residence time in which the pellets were exposed to the seawater. Perez et al. (2010) reported that the long duration of polymers at sea causes a reduction in the molecular weights. Frias et al. (2010) further explained that the reduction in molecular weight affects the properties of polymers in such a way that aged pellets have increased ability to adsorb OPs.

Plastic pellets are composed of organic polymers that possess crystalline and amorphous regions. Molecules in the crystalline regions are well arranged in a crystal lattice whereas, molecules in amorphous regions are irregularly arranged in a loose or flexible manner, somewhat identical to liquids. This amorphous region is the site for sorption of hydrophobic pollutants and has rubbery or glassy internal structure (Teuten et al., 2009). Glassy Polymers such as PS are more condensed, rigid and have closed internal nanoscale pores that can act as sorption site via two mechanisms (1) Linear dissolution (partitioning/adsorption) and (2) non-linear hole filling (Xing & Pignatello 1997). In the latter mechanism, organic pollutants bind to regions of the pellets with the highest affinity for the pollutants (Chiou & Kile 1998). Saturation of this region occurs and sorption then becomes limited to regions with least affinity for organic pollutants.

For adsorption to take place in rubbery polymers such as HDPE, energy from UV light is required to break down chemical bonds in the main polymer chain (Singh and Sharma 2008) and create new functional groups such as esters and ketones, which are responsible for sorption (Tribedi and Sil, 2013). Esters and other functional groups synthesized change plastic surfaces from being hydrophobic to becoming hydrophilic (Kalliopi and Hrissi, 2015),

thereby enabling adsorption of a wider range of pollutants (both hydrophilic and hydrophobic). Other factors responsible for the creation of functional groups include biodegradation and thermal oxidation (Kalliopi and Hrissi, 2012).

As highlighted earlier, the residence time is also important in determining (de)sorption of organic pollutants. Comparing two categories of PE pellets (virgin and eroded), Kalliopi and Hrissi, (2012) reported that eroded PE has a rough surface topography which is filled with cavities as compared to virgin pellets. This, thus, causes a corresponding increase in the formation of functional groups on the eroded pellet as erosion continues. The longer a PE pellet stays in the ocean, the more the functional groups that will be synthesized on the surface and the more hydrophilic the surface becomes (Kalliopi and Hrissi, 2012).

There is a relationship between plastic degradation and pollutant adsorption. Microorganisms can accelerate and impede degradation of plastics in the marine environment (Carson et al., 2013). In the latter case, biofilms attached to plastic surface shield plastics from sunlight, hence, prevents photodegradation. As discussed above, energy from sunlight is required to break chemical bonds in the main polymer chain of HDPE, LDPE, PP, etc before adsorption of pollutants occurs. Hence, delayed photodegradation initiated by microorganisms impedes adsorption of OPs on plastics. Similarly, microorganisms reduce pollutant adsorption through another mechanism. Fouling makes plastic lose their buoyancy and hence causes plastic to be suspended in the water column and ultimately get to the benthic region (Andrady, 2011). Concentration of pollutants in these regions is much lower than concentration at the sea surface. Hence, pollutants adsorbed on the surfaces of plastics are expected to be very low.

Conclusion

This study provides the first insight on the spatiotemporal variability of microplastics in Qatar and the Gulf region. The results showed that microplastics are pervasive both in beach sediments and Open Ocean in Qatar. Spatial variability did not exist in sediments of Qatar coastal zone. Conversely spatial variability existed in seawater samples but no temporal variability was recorded. Isolated microplastics both in sediments and seawater samples had a heterogeneous distribution of size range, color, plastic shape, and polymer type, although a particular size range tend to be dominant

in all samples. The temporal variability of microplastics in sediments of the Qatari coastal zone requires further investigation for understanding.

Similarly, macroplastics obtained from shoreline were heterogeneously distributed based on the size range, color, plastic shape, and polymer type across stations. Chemical analysis revealed the occurrence of OPs with endocrine effects on all obtained macroplastics, and concentration of pollutants was consistent in all sites.

Results from field adsorption experiment revealed that resin pellets steadily desorbed pollutants from their surfaces with time. This is not consistent with the results obtained in other experiments elsewhere. However, a prolonged field experiment is necessary to fully understand the mechanism of adsorption and desorption of contaminants on/from virgin pellets.

Further studies on a larger scale are imperative to monitor the plastic pollution of shorelines and open ocean and also to monitor the uptake and impacts of OPs adsorbed on microplastics on the neuston and benthos ecosystems, and also the biomagnifications of these pollutants up the marine food web.

References

- Allsopp M, Walters A, Santillo D, Johnston P (2006). Plastic debris in the world's oceans. Greenpeace
- Andrady, A.L., Song, Y., 1991. Fouling of floating plastic debris under biscayne bay exposure conditions. Marine pollution bulletin 22 (12), 117–122.
- Andrady, A.L., 2003. Plastics and the environment. In: Anthony L. Andrady (Ed.), Publisher: John Wiley and Sons, ISBN 0-471-09520-6.
- Anthony L. Andrady (2011). Microplastics in the marine environment. Marine pollution bulletin 62, 1596-1605

- Backhurst, M.K., Cole, R.G., 2000. Subtidal benthic marine litter at Kawau Island, north-eastern New Zealand. J. Environ. Manage. 6, 227–237
- Barnes, D.K.A., Galgani, F., Thompson, R.C., Barlaz, M., 2009. Accumulation and fragmentation of plastic debris in global environments. Philosophical Transactions of the Royal Society B: Biological Sciences 364, 1985–1998.
- Blight, L.K., Burger, A.E., 1997. Occurrence of plastic particles in seabirds from the eastern North Pacific. Marine Pollution Bulletin 34, 323–325.
- Browne, Mark A., Dissanayake, Awantha., Galloway, Tamara S., Lowe, David M., Thompson, Richard C., 2008. Ingested microscopic plastic translocates to the circulatory system of the mussel, Mytilus edulis (L). Environ. Sci. Technol. 42 (13), 5026–5031.
- Browne, M.A., Galloway, T.S., Thompson, R.C., 2010. Spatial patterns of plastic debris along estuarine shorelines. Environmental Science & Technology 44, 3404– 3409.
- Carpenter, E.J., Anderson, S.J., Harvey, G.R., Miklas, H.P., Peck, B.B., (1972). Polystyrene spherules in coastal water. Science 178, 749–750.
- Claessens, M., Van Cauwenberghe, L., Vandegehuchte, M. B. & Janssen, C. R (2013). *New techniques for the detection of microplastics in sediments and field collected organisms*. Marine pollution bulletin 70, 227– 233.
- Coe, J., Rogers, D., (1996). Marine Debris Sources, Impacts, and Solutions. Springer Verlag, New York.

- Cole M., Lindeque P, Halsband C, Galloway T, 2011. Microplastics as contaminants in the marine environment: A review. Marine Pollution Bulletin 62: 2588–2597
- Derraik, J.G.B., 2002. The pollution of the marine environment by plastic debris: a review. Marine Pollution Bulletin 44, 842–852.
- DOC—Department of Conservation, 1990. Marine Debris. Wellington, New Zealand.
- Doyle, M.J., Watson, W., Bowlin, N.M., Sheavly, S.B., 2011. Plastic particles in coastal pelagic ecosystems of the Northeast Pacific ocean. Marine Environmental Research 71, 41–52.
- EPA, 2007. Method 3550C. United States Environmental Protection Agency
- Cadogan, D. F. & Howick, C. J. in Ullmann's Encyclopedia of Industrial Chemistry 599–618 (2000). doi:10.1002/14356007.a20_439.
- EPA, 2008. Municipal solid waste generation, recycling and disposal in the United States: 2007 facts and figures. United States Environmental Protection Agency, Office of Solid Waste (5306P), EPA530-R-08-010, pp. 1–167. www.epa.gov.
- Fendall, L.S., Sewell, M.A., 2009. Contributing to marine pollution by washing your face: Microplastics in facial cleansers. Marine Pollution Bulletin 58, 1225–1228.
- Fergusson, W.C., 1974. Summary. In: Staudinger, J.J.P. (Ed.), Plastics and the Environment. Hutchinson and Co, London, p. 2.

- Garrity, S.D., Levings, S.C., 1993. Marine debris along the Caribbean coast of Panama. Marine Pollution Bulletin 26, 317–324
- Gregory, M. R., and P. G. Ryan. 1997. Pelagic plastics and other seaborne persistent synthetic debris: a review of Southern Hemisphere perspectives. In Marine Debris—Sources, Impacts and Solutions, Coe, J. M., D. B. Rogers, eds. New York: Springer-Verlag, pp. 49–66.
- Gregory, M.R., 2009. Environmental implications of plastic debris in marine settings: entanglement, ingestion, smothering, hangers-on, hitch-hiking and alien invasions. Philosophical Transactions of the Royal Society B: Biological Sciences 364, 2013–2025.
- Ivar do Sul, J.A., Spengler, A., Costa, M.F., 2009. Here, there and everywhere, small plastic fragments and pellets on beaches of Fernando de Noronha (Equatorial Western Atlantic). Marine Pollution Bulletin 58, 1236–1238.
- Dekiff JH, Remy D, Klasmeier J, Fries E, 2014. Occurrence and spatial distribution of microplastics in sediments from Norderney. Environ Pollut.;186:248-56. doi: 10.1016/j.envpol.2013.11.019.
- Heudorf, U., Mersch-Sundermann, V. & Angerer, J., 2007. Phthalates: toxicology and exposure. Int. J. Hyg. Environ. Health 210, 623–34.
- Kalliopi N. Fotopoulou and Hrissi K. Karapanagioti (2015). Surface properties of beached plastics. Environmental Science and Pollution Research.
- Kanehiro, H., Tokai, T., Matuda, K., 1995. Marine litter composition and distribution on the seabed of Tokyo Bay. Fisheries Engineering 31, 195–199.

- Kukulka T, Proskurowski G, More´t-Ferguson S, Meyer DW, Law KL (2012). The effect of wind mixing on the vertical distribution of buoyant plastic debris. Geophys Res Lett 39: 6 pp. doi:201210.1029/2012GL051116.
- Laist, D.W., 1997. Impacts of marine debris: entanglement of marine life in marine debris including a comprehensive list of species with entanglement and ingestion records. In: Coe, J.M., Rogers, D.B. (Eds.), Marine Debris: Sources, Impacts and Solutions. Springer-Verlag, New York.
- Lattin, G.L., Moore, C.J., Zellers, A.F., Moore, S.L., Weisberg, S.B., 2004. A comparison of neustonic plastic and zooplankton at different depths near the southern California shore. Marine Pollution Bulletin 49, 291–294.
- Leys, S.P., Eerkes-Medrano, D.I., 2006. Feeding in a Calcareous Sponge: Particle Uptake by Pseudopodia. Biol. Bull. 211, 157–171.
- Lindeque, P. K. & Smerdon, G. R (2003). *Temporal Transcription of Two Antennapedia Class Homeobox Genes in the Marine Copepod Calanus helgolandicus*. Mar Biotechnol 5, 604–615.
- Lithner, D., Larsson, Å., Dave, G., 2011. Environmental and health hazard ranking and assessment of plastic polymers based on chemical composition. Science of the Total Environment 409, 3309–3324.
- Lobelle, D., Cunliffe, M., 2011. Early microbial biofilm formation on marine plastic debris. Marine Pollution Bulletin 62, 197–200.
- Lozano, R.L., Mouat, J., 2009. Marine Litter in the North-East Atlantic Region: Assessment and Priorities for Response. KIMO International.

- Mascarenhas, R., Santos, R., Zeppelini, D., 2004. Plastic debris ingestion by sea turtle in Paraiba, Brazil. Marine pollution bulletin 49 (4), 354–355.
- Maximenko N, Hafner J, Niiler P (2012). *Pathways of marine debris derived from trajectories of Lagrangian drifters*. Marine pollution bulletin 65: 51–62. doi:10.1016/ j.marpolbul.2011.04.016.
- MCS, 2010. Marine Conservation Society – Beachwatch 2009. Methods and Full Results.
- Miriam C. Goldstein, Andrew J. Titmus, Michael Ford, 2013. *Scales of Spatial Heterogeneity of Plastic Marine Debris in the Northeast Pacific Ocean*. PLoS ONE 8(11): e80020. doi:10.1371/journal.pone.0080020
- Mohamed Nor Nur Hazimah, Obbard Philip Jeffrey, 2014. Microplastics in Singapore's coastal mangrove ecosystems. Marine Pollution Bulletin 79:278–283.
- Moore, C.J., 2008. Synthetic polymers in the marine environment: a rapidly increasing, long-term threat. Environ. Res. 108 (2), 131–139.
- Morét-Ferguson, S., Law, K.L., Proskurowski, G., Murphy, E.K., Peacock, E.E., Reddy, C.M., 2010. The size, mass, and composition of plastic debris in the western North Atlantic Ocean. Marine Pollution Bulletin 60, 1873–1878.
- Moser, M.L., Lee, D.S., 1992. A fourteen-year survey of plastic ingestion by western North Atlantic seabirds. Colonial Waterbirds 15, 83–94.
- Muthukumar, T., Aravinthan, A., Lakshmi, K., Venkatesan, R., Vedaprakash, L., Doble, M., 2011. *Fouling and stability of polymers and composites in marine environment*. Int. Biodeter. Biodegrad. 65 (2), 276–284.

- Nakashima, S., Sturgeon, R. E., Willie, S. N. & Berman, S. S (1988). *Acid digestion of marine samples for trace element analysis using microwave heating.* Analyst 113,159 163, doi:10.1039/an9881300159.
- Noren, F., 2007. Small plastic particles in Coastal Swedish waters. KIMO Sweden.
- O'Brine, T., Thompson, R.C., 2010. Degradation of plastic carrier bags in the marine environment. Marine Pollution Bulletin 60, 2279–2283.
- Ogata Yuko, Hideshige Takada, Kaoruko Mizukawa, Hisashi Hirai et al., 2009. International Pellet Watch: Global monitoring of persistent organic pollutants (POPs) in coastal waters. 1. Initial phase data on PCBs, DDTs, and HCHs. Marine Pollution Bulletin 58:1437–1446.
- Patel, M.M., Goyal, B.R., Bhadada, S.V., Bhatt, J.S., Amin, A.F., 2009. Getting into the brain: approaches to enhance brain drug delivery. CNS Drugs 23, 35–58.
- PlasticsEurope, EuPC, EuPR, & EPRO., 2012. Plastics-the Facts 2012. An analysis of European plastics production, demand and waste data for 2011.
- Railkin, A.I., 2003. Marine Biofouling: Colonization Processeses and Defenses, CRC Press.
- Robards, M.D., Piatt, J.F., Wohl, K.D., 1995. Increasingfrequency of plastic particles ingested by seabirds in the subarctic North Pacific. Marine Pollution Bulletin 30, 151–157.

- Roy, P.K., Hakkarainen, M., Varma, I.K., Albertsson, A.-C., 2011. Degradable polyethylene: fantasy or reality. Environmental Science & Technology 45, 4217–4227.
- Ryan, P.G., Connell, A.D., Gardner, B.D., 1988. Plastic ingestion and PCBs in seabirds: is there a relationship? Marine pollution bulletin 19, 174–176.
- Ryan, P.G., Moore, C.J., van Franeker, J.A., Moloney, C.L., 2009. Monitoring the abundance of plastic debris in the marine environment. Philosophical Transactions of the Royal Society B: Biological Sciences 364, 1999–2012.
- Ryan, P.G., Moloney, C.L., 1990. Plastic and other artefacts on South African beaches: temporal trends in abundance and composition. South African Journal of Science 86, 450–452
- Singh B, Sharma N (2008) Mechanistic implications of plastic degradation. Polym Degrad Stabil 93:561–584.
- Sivan, A., 2011. New perspectives in plastic biodegradation. Current Opinion in Biotechnology 22, 422–426.
- Smith R (2005). Biodegradable polymers for industrial applications. Woodhead Publishing limited, Cambridge England, p 357.
- Talsness, C.E., Andrade, A.J.M., Kuriyama, S.N., Taylor, J.A., vom Saal, F.S., 2009. Components of plastic: experimental studies in animals and relevance for human health. Philosophical Transactions of the Royal Society B: Biological Sciences 364, 2079–2096.

- Teuten, E.L., Rowland, S.J., Galloway, T.S., Thompson, R.C., 2007. Potential for plastics to transport hydrophobicm contaminants. Environ. Sci. Technol. 41 (22), 7759–7764.
- Teuten, E.L., Saquing, J.M., Knappe, D.R.U., Barlaz, M.A., Jonsson, S., Bjorn, A., Rowland, S.J., Thompson, R.C., Galloway, T.S., Yamashita, R., Ochi, D., Watanuki, Y., Moore, C., Pham, H.V., Tana, T.S., Prudente, M., Boonyatumanond, R., Zakaria, M.P., Akkhavong, K., Ogata, Y., Hirai, H., Iwasa, S., Mizukawa, K., Hagino, Y., Imamura, A., Saha, M., Takada, H., (2009). Transport and release of chemicals from plastics to the environment and to wildlife. Philosophical Transactions of the Royal Society B: Biological Sciences 364, 2027e2045.
- Thompson, R.C., Olsen, Y., Mitchell, R.P., Davis, A., Rowland, S.J., John, A.W.G., McGonigle, D., Russell, A.E., 2004. Lost at sea: where is all the plastic? Science, 838.
- Thompson, R.C., 2006. Plastic debris in the marine environment: consequences and solutions. In: Krause, J.C., Nordheim, H., Bräger, S. (Eds.), Marine Nature Conservation in Europe. Federal Agency for Nature Conservation, Stralsund, Germany, pp. 107–115.
- Thompson, R., Moore, C., Andrady, A., Gregory, M., Takada, H., Weisberg, S., 2005. New directions in plastic debris. Science 310, 1117.

- Timmers, M.A., Kistner, C.A., and Donohue, M.J., 2005. Marine Debris of the Northwestern Hawaiian Islands: Ghost Net Identification. Hawaii Sea Grant Publication.
- Tourinho, P.S., Ivar do Sul, J.A., Fillmann, G., 2010. Is marine debris ingestion still a problem for the coastal marine biota of southern Brazil? Marine Pollution Bulletin 60, 396–401.
- Tribedi P, Sil KA (2013) Low-density polyethylene degradation by Pseudomonas sp. AKS2 biofilm. Environ Sci Pollut R 20:4146–4153
- van Franeker, J.A., 2010. Fulmar litter EcoQO Monitoring in the Netherlands 1979– 2008 in Relation to EU Directive 2000/59/EC on Port Reception Facilities. IMARES, Wageningen UR.
- van Franeker, J.A., Blaize, C., Danielsen, J., Fairclough, K., Gollan, J., Guse, N., Hansen, P.-L., Heubeck, M., Jensen, J.-K., Le Guillou, G., Olsen, B., Olsen, K.-O., Pedersen, J., Stienen, E.W.M., Turner, D.M., 2011. Monitoring plastic ingestion by the northern fulmar Fulmarus glacialis in the North Sea. Environmental Pollution 159, 2609–2615.
- mademoiselleVoparil, I.M., Mayer, 2000. Dissolution of sedimentarypolycyclic aromatic hydrocarbons into the lugworm's (Arenicola marina) digestive fluids. Environ. Sci. Technol. 34, 1221–1228.
- Wolfe, D.A., 1987. Persistent plastics and debris in the ocean: an international problem of ocean disposal. Marine Pollution Bulletin 18, 303–305.

- Zarfl, C., Matthies, M., 2010. Are marine plastic particles transport vectors for organic pollutants to the Arctic? Marine Pollution Bulletin 60 (10), 1810–1814.

Appendix A

Correlations among PAHs compounds in samples of macroplastics.

		NA	ANY	ANA	FL	PH	ANTH	FLAN	PY	B[a]ANTH	CH	B[b]FLAN	B[k]FLAN	BP	I[123-cd]PY	D[a,h]AN	B[ghi]PERY
	Dens	**1.037**	**1.187**	**1.200**	**1.120**	**1.130**	**1.280**	**1.248**	**1.248**	**1.190**	**1.190**	**1.286**	**1.286**	**1.240**	**1.379**	**1.232**	**1.380**
NA	**1.037**																
ANY	**1.187**	0.48															
ANA	**1.200**	0.43	0.81														
FL	**1.120**	0.26	0.47	0.04													
PH	**1.130**	0.26	0.17	0.12	0.08												
ANTH	**1.280**	0.18	0.16	0.11	0.08	**0.98**											
FLAN	**1.248**	0.30	0.23	-0.05	0.29	0.06	-0.05										
PY	**1.248**	0.40	0.54	0.40	0.17	0.10	0.02	**0.84**									
B[a]ANTH	**1.190**	0.05	0.16	-0.05	0.12	-0.02	-0.03	0.79	0.79								
CH	**1.190**	0.06	0.16	-0.05	0.12	-0.02	-0.03	0.81	0.81	**1.00**							
B[b]FLAN	**1.286**	0.06	0.16	-0.07	0.12	-0.03	-0.04	0.78	0.77	0.93	**0.94**						
B[k]FLAN	**1.286**	0.12	0.03	-0.09	-0.01	-0.05	-0.04	0.33	0.31	0.41	0.41	0.67					
BP	**1.240**	0.12	0.11	-0.07	0.06	-0.03	-0.03	0.64	0.64	0.81	0.81	**0.93**	0.87				
I[123-cd]PY	**1.380**	0.04	0.16	-0.05	0.12	-0.02	-0.03	0.82	0.82	**0.98**	**0.98**	**0.95**	0.40	0.78			
D[a,h]AN	**1.232**	0.06	0.22	0.03	0.08	-0.02	-0.02	0.74	0.80	0.93	0.94	**0.91**	0.40	0.76	**0.96**		
B[ghi]PERY	**1.380**	0.00	0.16	-0.05	0.12	-0.03	-0.03	0.78	0.80	0.98	0.98	**0.94**	0.39	0.78	**1.00**	**0.95**	

Appendix B

Correlations among PAHs congeners in samples of macroplastics, grouped per density

	1.037	**1.187**	**1.2**	**1.12**	**1.13**	**1.28**	**1.248**	**1.19**	**1.286**	**1.24**	**1.38**	**1.232**
1.037												
1.187	0.48											
1.2	0.42	0.82										
1.12	0.36	0.53	0.08									
1.13	0.25	0.17	0.11	0.14								
1.28	0.17	0.16	0.10	0.13	0.98							
1.248	0.65	0.55	0.48	0.30	0.19	0.02						
1.19	0.26	0.02	-0.02	0.05	0.03	-0.02	0.22					
1.286	0.16	-0.00	-0.07	0.03	-0.03	-0.05	0.10	0.15				
1.24	0.18	-0.02	-0.05	-0.02	-0.03	-0.03	0.05	0.32	0.97			
1.38	0.45	-0.00	-0.02	0.06	0.08	-0.10	0.67	0.24	0.15	0.08		
1.232	0.20	0.23	0.26	-0.07	0.04	0.02	0.12	-0.05	0.07	0.05	0.17	

Appendix C

Correlation matrix for PAH compounds in pellets.

		NA	ANY	ANA	FL	PH	ANTH	FLAN	PY	B[a]ANTH	CH	B[b]FLAN	B[k]FLAN	BP	I[123-cd]PY	D[a,h]AN	B[ghi]PERY
	Density (g/cm3)	**1.037**	**1.187**	**1.200**	**1.120**	**1.130**	**1.280**	**1.248**	**1.248**	**1.190**	**1.190**	**1.286**	**1.286**	**1.240**	**1.379**	**1.232**	**1.380**
NA	**1.037**																
ANY	**1.187**	0.86															
ANA	**1.200**	0.74	**0.92**														
FL	**1.120**	0.26	0.27	0.21													
PH	**1.130**	0.82	0.91	0.83	0.29												
ANTH	**1.280**	0.75	0.83	0.74	0.22	0.93											
FLAN	**1.248**	0.82	0.93	0.88	0.17	0.84	0.76										
PY	**1.248**	0.88	**0.97**	0.89	0.16	0.89	0.81	**0.97**									
B[a]ANTH	**1.190**	-0.06	-0.07	-0.09	0.86	-0.04	-0.10	-0.13	-0.15								
CH	**1.190**	-0.04	-0.05	-0.07	0.85	0.04	-0.02	-0.09	-0.12	**0.98**							
B[b]FLAN	**1.286a**	0.36	0.58	0.53	-0.09	0.39	0.36	0.66	0.61	-0.18	-0.14						
B[k]FLAN	**1.286b**	-0.15	-0.18	-0.16	-0.06	-0.18	-0.22	-0.17	-0.17	0.30	0.29	0.09					
BP	**1.240**	0.13	0.33	0.35	-0.13	0.17	0.13	0.54	0.38	-0.17	-0.11	0.82	-0.05				
I[123-cd]PY	**1.379**	-0.17	-0.25	-0.36	0.06	-0.28	-0.24	-0.27	-0.27	-0.01	-0.05	-0.01	0.13	-0.22			
D[a,h]AN	**1.232**	0.34	0.30	0.29	-0.09	0.27	0.21	0.51	0.44	-0.20	-0.18	0.30	-0.15	0.36	-0.19		
B[ghi]PERY	**1.380**	-0.15	-0.16	-0.13	0.50	-0.17	-0.21	-0.18	-0.19	0.65	0.62	-0.10	-0.08	-0.05	-0.07	-0.16	

Appendix D

Correlations matrix for PAH compounds in pellets, grouped per density.

Density	1.037	1.187	1.2	1.12	1.13	1.28	1.248	1.19	1.286a	1.286b	1.24	1.379	1.232	1.38
1.037														
1.187	0.86													
1.2	0.74	0.92												
1.12	0.26	0.27	0.21											
1.13	0.82	0.91	0.83	0.29										
1.28	0.75	0.83	0.74	0.22	0.93									
1.248	0.85	0.96	0.89	0.17	0.87	0.79								
1.19	-0.05	-0.06	-0.08	0.86	-0.00	-0.06	-0.13							
1.286a	0.36	0.58	0.53	-0.09	0.39	0.36	0.64	-0.16						
1.286b	-0.15	-0.18	-0.16	-0.06	-0.18	-0.22	-0.17	0.30	0.09					
1.24	0.13	0.33	0.35	-0.13	0.17	0.13	0.47	-0.15	0.82	-0.05				
1.379	-0.17	-0.25	-0.36	0.06	-0.28	-0.24	-0.27	-0.03	-0.01	0.13	-0.22			
1.232	0.34	0.30	0.29	-0.09	0.27	0.21	0.48	-0.19	0.30	-0.15	0.36	-0.19		
1.38	-0.15	-0.16	-0.13	0.50	-0.17	-0.21	-0.18	0.64	-0.10	-0.08	-0.05	-0.07	-0.16	

Appendix E

Incidence of microplastics in intertidal sandy beaches

Sample Location	Sampling date	Subsample	Number of plastic particles				Mean	SD	Size range (mm)	Color
			TOTAL	Fibre	Film	Fragment				
Ras laffan	25/12/2014	1	5	4	1	0	1.67	2.08	0.5 – 5	Blue, colorless, Black
		2	7	2	4	1	2.33	1.53	≤ 0.5 – 10	Red, blue, discolored, black, grey
		3	9	4	5	0	3.00	2.65	0.5 – 10	Blue, discolored, green, colorless, black
Al Dhakeera	25/12/2014	1	7	3	3	1	2.33	1.15	≤ 0.5 – 5	Black, green, red
		2	6	2	4	0	2.00	2.00	≤ 0.5 – 5	Blue, black, red
		3	6	0	6	0	2.00	3.46	≤ 0.5 – 5	Blue, green, black
The Pearl	25/12/2014	1	19	12	4	3	6.33	4.93	≤ 0.5 – 5	Blue, purple, green, red, colorless, grey, black
		2	7	3	4	0	2.33	2.08	≤ 0.5 – 5	Discolored, blue, black
		3	5	1	4	0	1.67	2.08	≤ 0.5 – 5	Blue, grey, purple, black
Doha Bay	25/12/2014	1	16	7	8	1	5.33	3.79	≤ 0.5 – 5	Blue, green, red, black
		2	12	4	2	6	4.00	2.00	≤ 0.5 – 5	Green, blue, red, colorless
		3	3	1	2	0	1.00	1.00	0.5 – 5	Blue, grey
Mesaieed	5/3/2015	1	4	1	3	0	1.33	1.53	1 – 5	Blue, grey
		2	6	3	1	2	2.00	1.00	≤ 0.5 – 5	Blue, black
		3	4	1	3	0	1.33	1.53	0.5 – 5	Green, blue
Umm Bab	4/3/2015	1	4	1	3	0	1.33	1.53	0.5 – 5	Blue
		2	4	2	1	1	1.33	0.58	0.5 – 5	Red, blue
		3	5	1	3	1	1.67	1.15	≤ 0.5 – 5	Blue, black
Dukhan	4/3/2015	1	10	6	3	1	3.33	2.52	≤ 0.5 – 5	Blue, red, black
		2	4	2	2	0	1.33	1.15	0.5 – 5	Red, grey, black
		3	7	5	1	1	2.33	2.31	≤ 0.5 – 5	Red, blue, black
Sample	**Sampling**	**Replicate**	**Number of plastic particles**				**Mean**	**SD**	**Size range**	**Color**

Location	date		TOTAL	Fibre	Film	Fragment			(mm)	
Al Ruwais	2/3/2015	1	4	1	1	2	1.33	0.58	0.5 – 5	Green, blue, black, grey
		2	4	3	1	0	1.33	1.53	1 – 5	Blue, red
		3	4	3	0	1	1.33	1.53	0.5 – 5	Red, green, black

Appendix F

Table 16: Concentrations by PCBs and PAHs in 4 pellet samples at different times

PAH (ng/g)	HD1	HD2	HD3	HD4	HD5	PS1	PS2	PS3	PS4	PS5
NA	0.90	1842.19	ND	ND	ND	848.19	ND	ND	7.46	ND
ANY	0.92	33.11	9.24	ND	ND	11.58	0.46	1.82	ND	ND
ANA	1.76	226.59	116.89	ND	ND	79.05	27.57	34.83	ND	ND
FL	1.02	25.59	ND	ND	ND	265.77	41.27	218.37	ND	ND
PH	0.87	754.19	135.70	ND	ND	415.65	81.46	102.59	ND	683.34
ANTH	0.95	792.62	133.86	ND	ND	417.16	76.05	97.45	ND	828.11
FLAN	1.06	98.49	28.56	ND	0.78	18.69	ND	ND	ND	ND
PY	1.10	71.52	7.39	ND	2.48	8.59	ND	ND	1.44	ND
B[a]ANTH	0.46	ND	ND	ND	ND	87.33	70.93	120.21	ND	ND
CH	0.67	8.94	4.36	ND	ND	68.00	54.72	89.94	ND	19.56
B[b]FLAN	0.52	3.61	1.06	ND	ND	0.03	0.45	0.15	1.33	ND
B[k]FLAN	0.57	0.20	0.35	ND	ND	ND	4.65	ND	1.75	ND
BP	0.81	11.24	6.57	ND	ND	ND	ND	ND	ND	ND
I[123-cd]PY	1.18	ND	ND	1.29	ND	1.48	ND	ND	2.80	ND
D[a,h]AN	0.94	13.85	ND	ND	0.78	ND	ND	ND	0.05	0.52
B[ghi]PERY	4.55	0.06	0.96	0.21	ND	0.33	ND	12.29	0.04	ND
	HD1	**HD2**	**HD3**	**HD4**	**HD5**	**PS1**	**PS2**	**PS3**	**PS4**	**PS5**
Total PAHs	**18.28**	**3882.19**	**444.94**	**1.50**	**4.04**	**2221.85**	**357.57**	**677.63**	**14.87**	**1531.52**
Total PCB	40.10	46.33	2.06	ND	ND	3.78	ND	ND	ND	ND

Table 17: Concentrations by PCBs and PAHs in 4 pellet samples at different times

PAH (ng/g)	LD1	LD2	LD3	LD4	LD5	PP1	PP2	PP3	PP4	PB5
NA	3137.74	4669.08	ND	ND	ND	ND	169.36	ND	ND	ND
ANY	26.52	46.76	1.71	ND	ND	ND	30.71	ND	ND	0.75
ANA	274.93	289.46	50.22	ND	0.40	ND	289.85	155.26	ND	26.71
FL	57.33	84.57	ND	ND	ND	ND	53.48	ND	ND	1.75
PH	921.08	1209.07	ND	ND	10.47	ND	825.62	3.91	ND	62.77
ANTH	966.96	1297.19	ND	688.41	ND	ND	926.13	34.70	ND	164.94
FLAN	79.72	74.65	ND	ND	0.86	ND	45.99	ND	ND	1.46
PY	62.19	78.18	ND	ND	3.07	ND	44.20	ND	ND	3.88
B[a]ANTH	2.05	6.94	1.00	ND	1.03	ND	4.33	2.96	ND	0.98
CH	3.56	6.52	4.62	ND	ND	ND	4.93	2.67	ND	ND
B[b]FLAN	0.09	1.37	0.47	0.46	ND	0.09	0.97	0.95	ND	ND
B[k]FLAN	ND	ND	ND	ND	ND	ND	ND	0.30	ND	ND
BP	ND	ND	0.08	ND	ND	ND	ND	2.61	ND	0.78
I[123-cd]PY	ND	0.11	ND	0.99	ND	0.36	0.02	ND	0.78	ND
D[a,h]AN	13.64	ND	1.94	ND	ND	16.16	ND	ND	0.87	0.20
B[ghi]PERY	ND	ND	0.02	0.13	ND	ND	0.06	1.60	ND	ND
Total	5545.82	7763.89	60.05	690.00	15.83	16.61	2395.64	204.95	1.65	264.19
Total PCB	13.70	33.81	ND	ND	ND	ND	6.35	ND	ND	ND

Appendix G

Table 18: PAHs concentration in ambient seawater samples

PAHs (ng/g)	S1 (48 h)	S2 (96 h)	S3 (192 h)	S4 (312 h)
NA	63.77	61.82	230.93	ND
ANY	ND	ND	4.85	0.20
ANA	137.94	94.69	50.47	0.51
FL	16.06	15.81	15.52	0.25
PH	95.00	62.41	180.15	7.72
ANTH	60.83	43.94	24.26	1.75
FLAN	10.88	6.99	13.69	1.94
PY	14.59	8.19	13.76	ND
B[a]ANTH	27.54	21.83	11.91	ND
CH	ND	ND	3.63	ND
B[b]FLAN	ND	ND	1.89	0.03
B[k]FLAN	ND	ND	0.57	ND
BP	ND	ND	9.31	1.26
I[123-cd]PY	7.06	0.96	2.18	ND
D[a,h]AN	0.00	14.41	ND	0.49
B[ghi]PERY	5.10	31.68	1.39	0.11
Total	**438.77**	**362.71**	**564.49**	**14.26**

Appendix H

Table 19: PCBs concentration in ambient seawater samples

Congeners	S1 (48 h)	S2 (96 h)	S3 (192 h)	S4 (312 h)
1	46.29	nd	13.17	5.74
2	4.1	1.08	nd	0.36
3	3.7	nd	nd	0.67
4	165.15	73.32	43.86	30.14
5	nd	nd	nd	nd
6	0.16	nd	nd	nd
7	2.65	0.92	0.63	nd
8	5.55	4.72	nd	nd
9	3.65	nd	nd	1.9
10	7.11	nd	nd	nd
11	nd	nd	nd	nd
12	2.48	nd	nd	nd
13	4.22	nd	nd	nd
14	nd	nd	nd	nd
15	5.37	nd	nd	nd
16	nd	nd	nd	nd
17	nd	nd	nd	nd
18	nd	nd	nd	4.55
19	nd	nd	nd	3.11
Total PCBs (ng/g)	**222.43**	**32.53**	**19.78**	**16.52**

Appendix I

Table 20: Contamination by PCBs and PAHs in 34 macroplastic samples from intertidal sandy beaches

	SL1	SL2	UB1	UB2	UB3	UB4	UB5	RL1	RL2	RL3	RL4	RL5	DK1	DK2	DK3	DK4	DK5
PAHs (ng/g)																	
NA	ND	ND	ND	2196.70	ND	2996.03	1513.86	ND	15424.42	ND	71.91	ND	ND	15964.65	20735.28	14289.08	4536.57
ANY	ND	670.89	23.25	9.92	ND	54.80	7.47	39.39	118.88	ND	9.43	ND	ND	129.29	1213.27	123.38	27.79
ANA	ND	377.26	ND	ND	689.65	ND	ND	ND	247.87	ND	62.98	2221.61	ND	570.04	7861.89	610.32	ND
FL	ND	1167.21	156.72	123.50	213.91	305.99	29.74	778.12	331.40	ND	53.60	ND	ND	155.13	251.13	206.19	63.64
PH	ND	2507.34	1182.68	308.95	1706.70	1994.02	19505.43	ND	2255.15	ND	379.66	ND	ND	2523.66	4533.30	2657.78	518.00
ANTH	ND	**2826.57**	1244.26	321.47	1899.21	2097.47	20852.99	ND	2408.42	ND	402.91	ND	ND	2686.86	4752.24	2802.01	590.77
FLAN	ND	361.21	107.40	3.21	ND	156.24	ND	ND	82.43	ND	22.32	ND	ND	2.98	24.88	179.14	ND
PY	ND	6.46	152.75	27.44	ND	308.36	ND	ND	91.41	ND	46.58	ND	ND	6.89	1515.50	193.74	16.43
B[a]ANTH	ND	97.57	257.07	ND	97.09	62.69	ND	0.50	ND	9.40	6.64	ND	5.71	3.40	18.54	420.57	ND
CH	ND	75.61	195.29	ND	8.43	23.22	ND	ND	1.72	4.45	4.27	ND	2.74	72.86	14.55	317.63	ND
B[b]FLAN	0.21	85.11	12.00	2.66	5.39	ND	ND	0.57	ND	0.47	0.16	1.31	40.77	170.68	6.79	132.69	0.52
B[k]FLAN	2.53	7.08	3.15	1.19	1.60	ND	0.40	1.18	0.41	0.85	0.11	0.87	52.52	128.40	ND	107.13	0.91
BP	3.73	0.16	1.30	4.74	1.04	4.85	2.48	1.38	2.58	1.94	3.51	5.38	0.30	101.54	11.78	110.82	7.48
I[123-cd]PY	1.38	ND	ND	ND	0.71	8.50	ND	ND	0.08	ND	ND	5.89	1.21	15.03	0.27	7.75	1.36
D[a,h]AN	**18.79**	1.39	ND	ND	ND	ND	1.37	ND	ND	ND	ND	1.23	0.48	12.96	7.72	0.83	ND
B[ghi]PERY	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Total PAH	26.63	8183.84	3335.86	2999.78	4623.73	8012.17	41913.74	821.15	20964.77	17.10	1064.08	2236.28	103.73	22544.38	40947.13	22159.03	5763.47
Total PCBs (ng/g)	596.26	24.88	30.54	ND	14.00	59.22	ND	567.46	ND	19.85	ND	ND	13.04	ND	ND	39.50	23.29

Table 21: Contamination by PCBs and PAHs in 34 macroplastic samples from intertidal sandy beaches

	DB1	DB2	DB3	DB4	AD2	AD3	AD4	AD5	PB1	PB2	PB3	PB4	PB5	AR1	AR2	AR3	AR4
PAHs (ng/g)																	
NA	ND	5432.09	10676.79	20052.71	1876.63	4319.45	ND	10346.20	6081.96	4684.72	ND	22271.05	ND	3722.65	ND	2608.40	11538.05
ANY	ND	324.77	116.42	162.68	28.09	32.99	19.72	104.37	105.10	44.94	ND	238.62	ND	49.70	97.45	101.98	113.14
ANA	ND	121.38	184.48	569.19	ND	ND	993.79	495.97	241.53	487.10	63.39	532.09	86.45	268.72	61.84	263.54	488.44
FL	ND	361.92	288.34	279.58	31.62	91.39	ND	275.72	207.67	122.93	ND	652.34	2.11	363.04	ND	62.99	185.37
PH	ND	1301.31	2548.03	4041.29	497.09	1098.05	ND	2079.23	1522.46	1376.71	ND	4534.71	ND	1255.02	ND	1025.64	2040.34
ANTH	ND	1354.70	2702.91	ND	533.27	1165.17	ND	2221.30	1900.45	1445.47	ND	4873.35	ND	1352.93	ND	1078.83	2149.19
FLAN	15.22	1616.61	91.69	1183.08	8.07	40.47	ND	130.12	103.02	82.62	105.36	277.23	147.01	37.19	ND	43.09	158.26
PY	ND	2666.23	100.86	1254.98	22.64	51.61	ND	145.24	124.99	116.95	ND	278.44	ND	39.87	ND	49.21	142.69
B[a]ANTH	108.24	12328.06	40.19	473.43	ND	13.06	ND	49.83	0.12	15.01	25.38	70.32	37.40	8.68	6.38	460.60	2497.44
CH	81.95	10582.73	38.54	687.38	ND	8.46	ND	36.84	6.66	8.85	15.88	52.42	30.43	3.95	3.12	368.95	1913.04
B[b]FLAN	36.55	2086.13	14.01	198.17	335.69	1.38	0.07	6.58	600.25	27.87	1.18	1.89	1.51	1.46	0.33	22.62	127.39
B[k]FLAN	7.55	269.19	3.32	49.96	257.33	ND	0.38	0.76	463.76	25.48	0.38	1.29	0.64	0.10	0.94	19.73	115.32
BP	4.36	677.52	4.80	61.46	263.16	7.42	1.15	13.14	404.95	31.26	0.38	8.62	1.35	2.24	2.82	6.88	199.72
I[123-cd]PY	7.98	497.68	18.38	37.79	1.28	0.53	1.24	ND	0.39	ND	1.00	ND	ND	0.87	1.21	0.41	4.88
D[a,h]AN	ND	75.69	0.88	2.94	2.17	0.54	0.26	ND	0.50	0.40	ND	ND	ND	0.01	ND	ND	1.00
B[ghi]PERY	ND	964.56	ND	4.91	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.55
Total PAH	261.84	40660.58	16829.64	29059.52	3857.02	6830.51	1016.61	15905.30	11763.79	8470.31	212.94	33792.38	306.89	7106.43	174.10	6112.86	21674.80
Total PCBs (ng/g)	23.30	25.07	13.59	36.11	14.30	ND	ND	12.89	2.30	ND	12.34	ND	3.53	10.44	1004.68	27.57	16.24