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Investigation of the role of microplastics in the transport of potentially toxic element species in the marine environment

By

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‘This thesis is the result of the author’s original research. It has been composed by the author and has not been previously submitted for examination which has led to the award of a degree.’

Dedication

To my husband Osama M. H. Al-Marei.

To the memory of my parents.

Acknowledgements

I would like to express my great thanks and appreciation to Christine M. Davidson, from the Department of Pure and Applied Chemistry, Christine Switzer from the Department of Civil and Environmental Engineering, and John J. Liggat from the Department of Pure and Applied Chemistry for their supervision of this work and to my former supervisor Dr. Helen E. Keenan from the Department of Civil and Environmental Engineering.

I also extend my thanks to all who have helped and supported me all the way through this work: Schlumberger foundation for the award of funding through Faculty of the Future Scheme, Kuwait institute for scientific research for the collaboration and the use of SEM facilities, namely Prof. S. El-Eskandarany, Dr. A. Alhazza'a and Dr. A. Joseph and all who are connected with the entire sampling, sources and references I used for all their efforts that helped me in bringing this work to reality.

Importantly, special thanks go to my husband, Osama M. Al-Marei, my family and friends for their help and support.

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Abbreviations

Acid dissociation constant	pKa
Attenuated total reflectance – Fourier transform infrared	ATR–FTIR
Dichlorodiphenyltrichloroethane	DDT
Energy dispersive x-ray spectroscopy	EDS
High density polyethylene	HDPE
High matrix introduction	HMI
Inductively coupled plasma-mass spectroscopy	ICP-MS
Inductively coupled plasma-optical emission spectrometry	ICP-OES
Limit of detection	LOD
Low density polyethylene	LDPE
Persistent organic pollutants	POPs
Polybrominated diphenyl ethers	PBDEs
Polychlorinated biphenyls	PCB
Polyethylene	PE
Polyethylene terephthalate	PET
Polyhydroxybutyrate	PHB
Poly(hydroxybutyrate-co-hydroxyvalerate)	PHBV, BIO
Polypropylene	PP
Polystyrene	PS
Polyvinyl chloride	PVC
Potentially toxic elements	PTE
Radio frequency	RF
Reference material	RM
Relative standard deviation / standard deviation	RSD / SD
Scanning electron microscope	SEM
Simplified bioaccessibility extraction test	SBET
Total dissolved solids	TDS
X-ray fluorescence spectrometry	XRF

Abstract

There is growing global concern about the impact of microplastics on the marine environment, with evidence emerging that plastic pellets can be a vector for potentially toxic elements (PTE). In this thesis, PTE content was first investigated in petroleum-based (polyethylene, polypropylene and polyethylene terephthalate) and bio-based (poly(hydroxybutyrate-co-hydroxyvalerate)) virgin plastic pellets. Various elements associated with plastics' manufacture were detected. Next, sorption experiments were conducted to assess the capacity of virgin and laboratory-weathered pellets to take up As, Cd, Cr and Pb from controlled media of deionised, fresh and artificial seawater, with analysis by ICP-MS (Agilent 7700x instrument). All types of plastics showed the ability to take up the PTE studied and the total amounts were in the order Pb > As > Cd > Cr when single element solutions were studied and Pb > Cd > Cr > As from a multi-element solution. It was found that weathered pellets took up greater amounts of PTE than virgin ones. The surface of virgin, laboratory-weathered and beached pellets collected from Kuwait and Scotland were then imaged and their chemical composition determined using a scanning electron microscope with energy-dispersive EDS analyser (JEOL JSM-6010LA). Analysis revealed changes in pellet morphology following weathering. Elements detected were associated with aspects of plastic production or taken up from the ambient environment. Beached pellets were identified by ATR–FTIR as predominantly polyethylene and polypropylene. When examples were subjected to sequential cold acid digestion followed by microwave extraction, larger amount of PTE were released by the cold digestion step, indicating the analytes were relatively weakly bound. Samples from Kuwait released higher amounts of PTE than samples from Scotland. *In vitro* bioaccessibility of PTE to simulated fish stomach was estimated using two methods, a modified SBET and a 0.1 M HCl extraction. Lead was found to be the most bioaccessible of the PTE studied.

1 Introduction

1.1 Plastic debris in the marine environment

Plastic is one of the most widely used materials today and makes a strong contribution to almost all areas of manufacturing, mainly due to its flexibility and durability.

The term 'plastic' is derived from the Greek word "*plastikos*" which means 'fit for moulding' and thus the term 'plastics' refers to the materials which show plasticity during their manufacture[3]. Figure 1-1 shows a graph of plastic production from 1950 to 2010. As can be seen, the rise of plastic production was continuous. There was a fall in production at the end of the period covered due to the global financial crisis, but production recovered in subsequent years and it is anticipated that plastic production in 2020 will be 400 million tons[4].

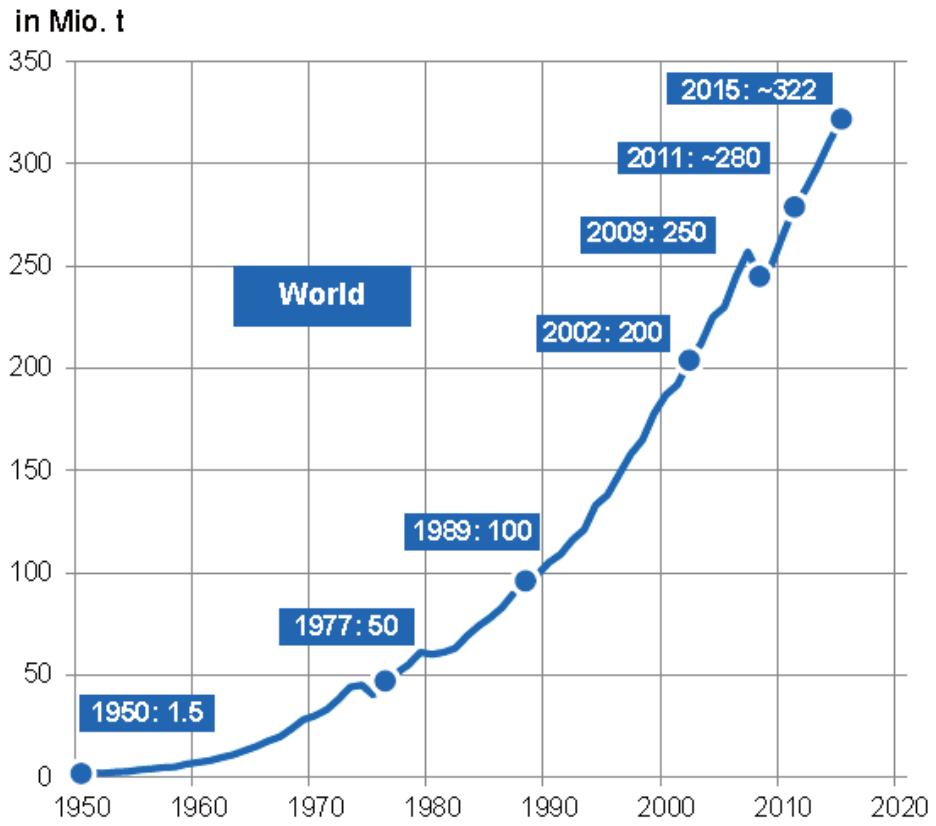


Figure 1-1 Worldwide plastic production in million tons from 1950 - 2015[4].

Plastic debris in the marine environment represents around 10 % of plastic production[5]. It can be considered as being a new challenge presented by an old problem as the dumping of waste into the marine environment is not a new activity, but the knowledge of the fact that this debris is gradually accumulating in high concentrations and awareness of its consequences are relatively recent. Plastic debris, which accounts for about 80-85 % of total marine debris, is found on the seabed, suspended in water or buoyant on the water surface[6-9].

Plastics are persistent in the environment and, because of their indestructible morphology, can seriously affect the ecosystem due to their physical existence and the potential toxins they contain[10]. Furthermore, plastic debris is widely spread throughout the environment due to:

- Plastic's ubiquitous applications, mainly as packaging. (Figure 1-2 shows the different plastic applications in the UK).
- The mismanagement of plastic waste (from on-shore and off-shore sources).
- The lack of legislation to control and process plastic debris.

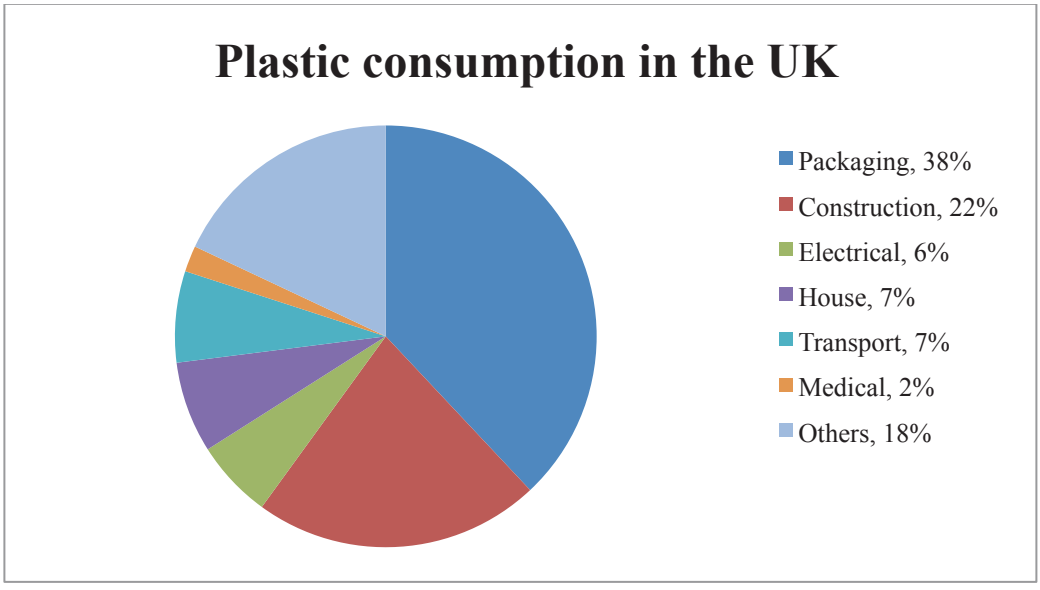


Figure 1-2 Plastic consumption in the UK by different applications (Adapted)[11].

Plastic debris can be categorised according to size as follows[12].

- Macro-debris (size > 20 mm in one dimension at least)
- Meso-debris (5 – 20 mm in one dimension at least)
- Micro-debris (< 5 mm in all dimensions)

The major portion of plastic that is released into the environment due to improper management/treatment accumulates in the ocean[7, 13]. Thus, it is very important to be aware of the effects of plastic debris in the marine environment.

The source of plastic in the marine environment as seen in Figure 1-3a is totally anthropogenic and comes, intentionally or unintentionally, from fishing fleets that dump or lose plastic fishing gear; merchant ships; recreational fishing boats and cruisers; industrial and urban waste that mainly comes from packaging; beach users; waste water effluents; sewage sludge applications and land-based run off through drains.

1.1.1 Microplastic including plastic resin pellets

Of all plastic entering the marine environment, micro-debris is the most dominant. It can be classified as:

1. Primary microplastic: the pre-production plastic resin pellets (nurdles).
2. Secondary microplastic: products of fragmentation of larger plastic objects.

Accumulations of microplastics, mainly pellets, have been reported in different parts of the world since the late 1970s[14-17]. Plastic resin pellets are the industrial raw materials for the production of plastics. They are mainly derived from crude oil and natural gas, but some are derived from biomass sources such as plants and bacteria. As shown in Figure 1-3b, the size of plastic resin pellets is generally a few millimetres. Resin pellets can be released into the environment during their transport to the plastic product factory, as shown in Figure 1-3c, as a consequence of run-off, accidental spillage, or mismanagement from end users. As a growing area, a recent study indicated road marking paint as a source of microplastic in the river Thames[18]. Once microplastic,

including plastic resin pellets, enters the marine environment, they can cause problems within the marine ecosystem, depending on the settling location.

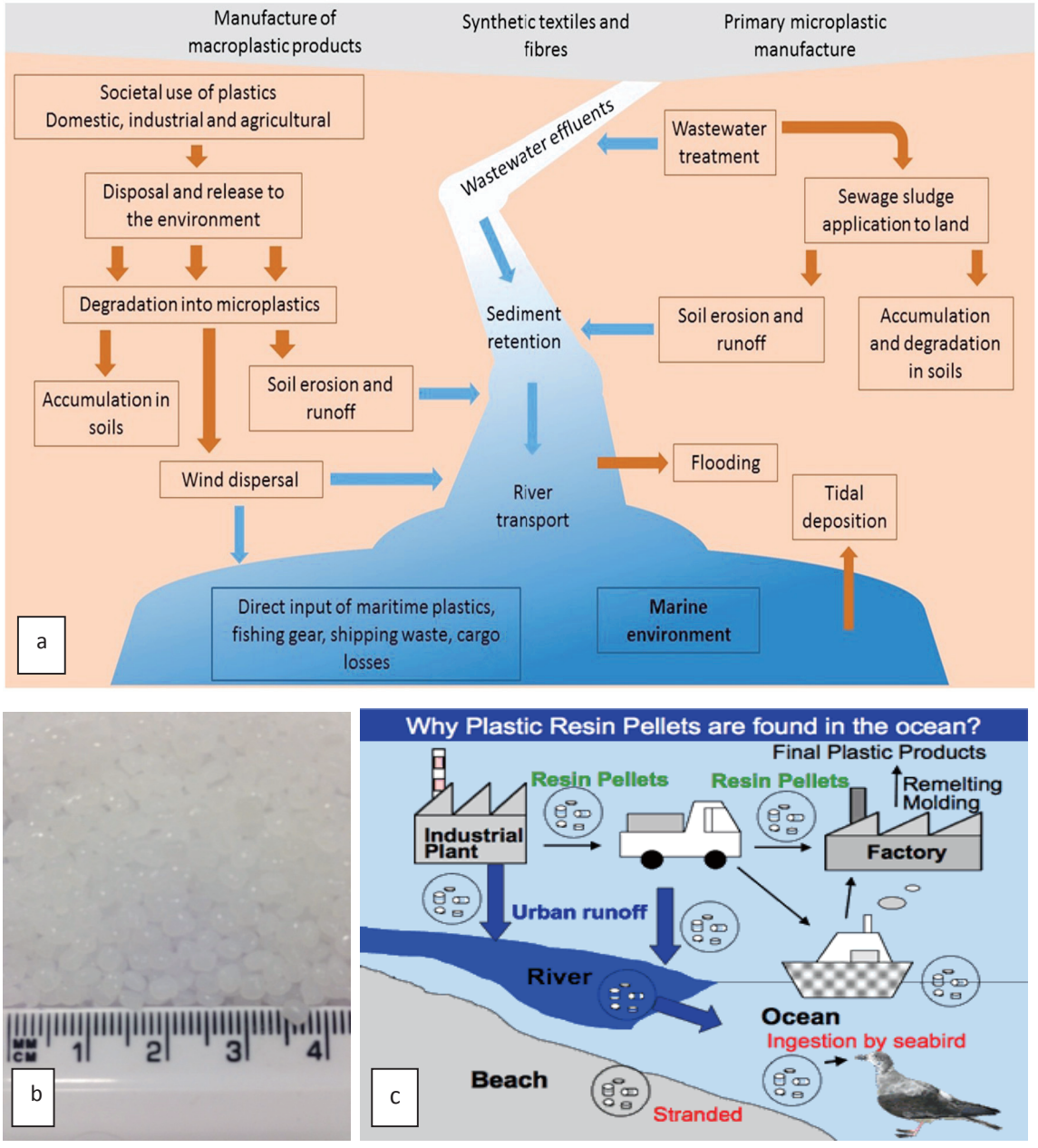


Figure 1-3 a. Microplastic sources and flows to marine environment[19]. b. Plastic resin pellets. c. Source of plastic resin pellets in the marine environment[20].

1.1.2 Presence, distribution and impact of plastic in the marine environment

There are as yet no standardised methods to identify the presence and measure the distribution of plastic debris in the marine environment[21, 22, 23] of collection and counting. Fulmars often provide an effective indicator that there is plastic debris floating in the marine environment[24] and, in the North Atlantic and Pacific Oceans, where the population of fulmars is between 15-30 million, they can be used to draw up regional patterns of plastic debris. Seabird nest also provide an indicator of marine debris including plastic which found in 61 % of *Sula leucogaster* in a study covered two coastal islands in Brazil[25]. Franeker *et al*. found that the industrial and densely populated North Sea area is the primary source of marine debris. Therefore reducing debris at primary sources can directly reduce the accumulation of marine debris[26].

A recent study using data from 24 expeditions (2007 – 2013) and an oceanographic model of floating debris[27] estimated the total number of plastic particles floating in all the oceans to add up to a minimum of 5.25 trillion particles weighing about 269 tons. It also estimated that up to 8 million tons of plastic waste enter the oceans every year[28].

Most marine coastal sediment and sandy beach samples reveal contamination by microplastic fragments and fibre [29-37,] shown in Figures 1-4A, particularly in harbour areas and in the vicinity of industrial sites[9, 30, 32, 38]. Different physical processes such as the debris source and quantities, degradation of macro into microplastic and wind and surface current plays a role in plastic distribution[28, 39]; more than 800 microplastic pellets per square metre was found on a beach in Chile because of transport by the surface current in the South Pacific Subtropical Gyre[40]. Surface current movement and global surface and deep ocean currents, shown in Figures 1-4B, explain the existence of microplastic in remote beaches, Arctic sea ice[41] and in Antartic marine environment[42].

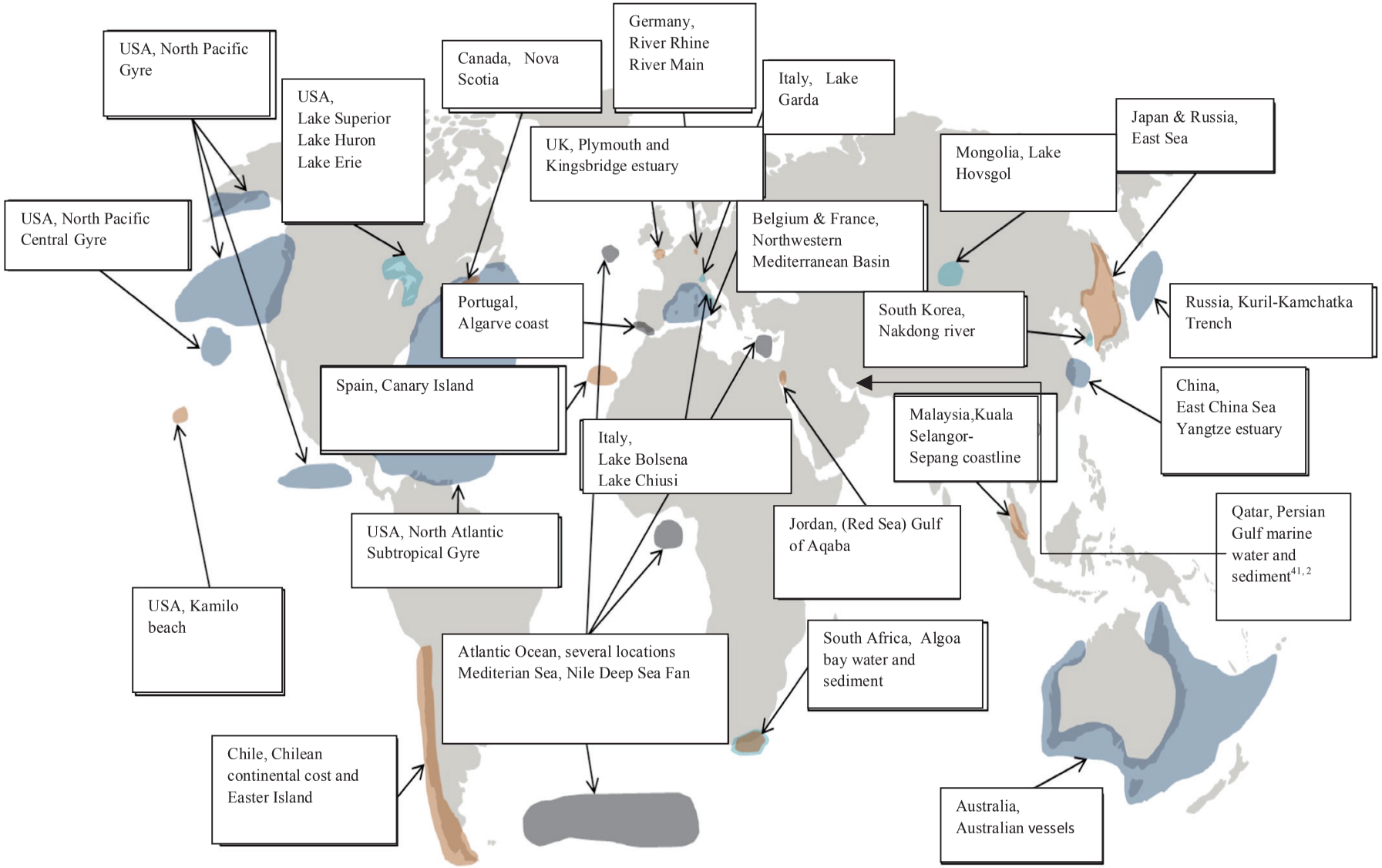


Figure 1-4 The distribution of microplastics in the marine environment (Adapted)[37].

Microplastic was also found in a coastal mangrove ecosystem. Samples collected from seven selected mangrove habitats located around Singapore's coastline indicated the prevalence of microplastics, mainly polyethylene and polypropylene, in all locations[43].

Microplastic is transported to sediment from the water column over time[32], and a depth profile of sediment cores shows a correlation between the amounts of microplastic found and an increase in plastic production[30, 44]. Plastic fragments have also been shown to be ubiquitous in deep sea sediments[45]. In seawater samples, microplastics were extracted[1], and the number of microplastic particles increased as the particle size decreased[32, 38, 46].

The impact that plastic has on the environment and its proliferation potentially classifies it as a potential hazardous waste[47]. Although there is a lack of information on the actual degree of threat posed by plastic pollution to the ocean ecosystem, its physical impact on marine life is widely known[48, 49]. The impact of plastic debris on marine biota and ecosystems has been reviewed and investigated by a number of researchers and organisations[50-55]. Most reports focus on the mechanical impacts that threaten both offshore and onshore organisms. Biological and eco-toxicologic impacts[56, 57] of plastic and its materials have received less attention and is a growing area of research, to date, no bioaccesibility studies on marine fish have yet been reported. The most visible impact of plastic debris on the marine environment and biota is marine specimens choking on pieces of plastic, ingestion, being suffocated and entrapped by floating plastic bags and entangled in plastic ties and nets. The adverse impact of microplastic is mainly due to accumulation and ingestion.

Several plastics or plasticisers were identified as being hazardous to human health[58-60]. The International Agency for Research on Cancer (IARC) considers plastic styrene to be a possible carcinogen and plastic vinyl chloride to be a carcinogen[61] based on cancer bioassays and evidence of carcinogenicity in humans and experimental animals. This is of concern as microplastics in the marine environment can enter the food chain[31] and be ingested by humans at the top of the food chain as shown in Figure 1-5.

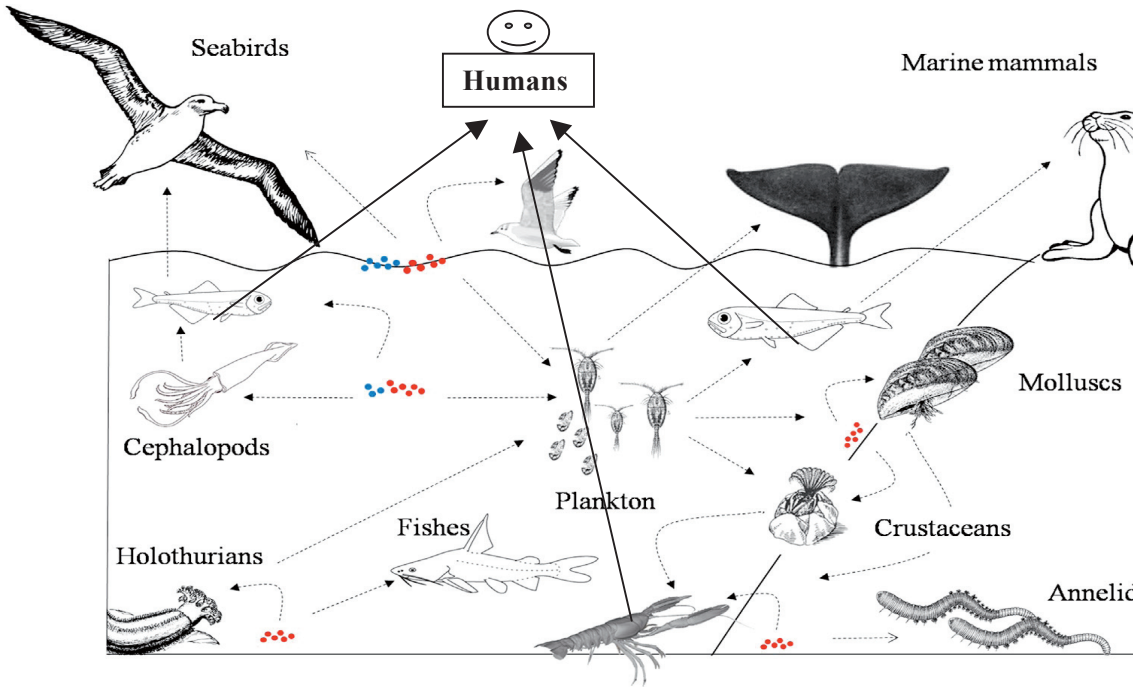


Figure 1-5 Potential routes of microplastics in the marine environment where microplastic, its associated pollutants, and additives may enter the food chain and be ingested by humans at the top of the food chain (Adapted)[14].

1.1.3 Ingestion of plastic by marine biota

One of the major negative effects of plastic debris on the ocean/marine environment is its ingestion by, and entanglement with, marine biota and seabirds that have mistaken plastic debris for food[6, 62].

An analysis of 340 published documents about marine debris[63] found that 292 publications reported ingestion of plastic and entanglement of marine biota with, mostly (92%), plastic debris. Ingestion of plastic was reported for 13,110 marine individuals from 208 species[63].

Experimentally, microplastics were ingested by commercially grown bivalves. *Mytilus edulis* (blue mussel) and *Crassostrea gigas* (pacific oyster) showed the presence of an average of 0.36 particles/g and 0.47 particles/g respectively in their soft tissue[64].

Ingested plastics were reported to be translocated out of the digestive system to for example liver, pancreas or gill in species such as bivalve and fish[65, 66].

A comparison of plastic levels with plankton numbers in the marine environment, especially in the North Pacific central gyre, was conducted to estimate plastic ingestion by marine biota. The gyre was selected because this is where plastics ultimately accumulate. Plastic fragments were found in all samples of plankton, which shows the high possibility of plastic ingestion by marine biota. It was suggested that such measurements should be performed more widely as a standard indicator[67]. Similar results showing the presence of plastic in the planktonic food chain were also found in coastal waters and the Baltic Sea[68-70].

1.1.3.1 Direct and indirect ingestion of plastic by marine-based organisms

A recent study indicated that 26% of marine mammal species, 86 % of sea turtles species, 30% of seabird species, and 0.3 % (50 of 16,754 species) of fish species had ingested plastic[63].

Ingestion of plastic by marine organisms can be mainly divided into two feeding mechanisms; the direct ingestion and the indirect or transferred ingestion. Some marine organisms ingest microplastic directly mistaking by food as they cannot discriminate microplastic from food. This study will concentrate on this type of ingestion.

Indirect ingestion must also be concerned as it is been reported that microplastic entered the primary and low food web such as zooplanktons through ingestion and/or absorption. The migration of such zooplanktons can contribute in introducing microplastic to different depths of the seawater[71].

Essentially, trophic transfer through food chain is the mean of transferring energy and nutrients[72]. However, contaminants also bioaccumulate and transfer through food chain such as methyl mercury and pharmaceuticals in marine organisms[73-75].

trophic transfer of microplastic was investigated in planktonic food web between zooplankton and mysid shrimps, results showed the transfer of microplastic from mesozooplankton trophic level to the higher macrozooplankton level[69]. Similar indirect ingestion via trophic transfer was also studied and found in a higher trophic level from *Mytilus edulis* mussels to *Carcinus maenas* crabs[76], showing the potential transfer of microplastic and its derives between marine organisms and biota.

Recent studies indicate the presence of microplastic or it derives in different marine organisms from different low and high trophic web. According to literature reviewed by Ludovic Hermabessiere *et al*.[77], the most common additives identified in marine organisms and environment were PBDEs, phthalates, nonylphenols, Bisphenol A and antioxidants. Table 1-1 summarises some reported evidence of the direct ingestion of plastic by biota in the marine environment, showing the possibility of ingestion microplastic from low planktonic organisms in the base of the trophic web to the higher organism.

Table 1-1 Summary of some reported evidence of the ingestion of plastic by biota in the marine environment

Marine biota	**Reported evidence**
Planktons	56% of samples contained microplastics. High concentration of phthalates was detected in plankton[78, 79].
Crabs and lobsters	Accumulation of microplastic due to ingestion has occurred in crabs[66, 76, 80]. Microplastic was found in 67 % of 1450 lobster collected from Clyde Sea Area[81].
Fish	Occurrence of plastic in the gastrointestinal tract of marine fish was reported[82-87]. It was estimated that around 1.3 tons of plastic are ingested by fish each year. Around 5500 ingested plastics were examined and bite marks on the plastics indicated that they are ingested because they had been mistaken for food[88]. Microplastic was found in 68 % of 337 semipelagic fish stomach samples from the Mediterranean Sea[89].
Turtles	35% of turtles ingested plastics ranging from 0.01 g to 0.7g[90]. Carnivorous turtles ingested less debris compared to herbivorous turtles. Oceanic turtles were more likely to ingest debris compared to coastal ones[91]. Recent study showed plastic in > 90 % of 55 pelagic Pacific sea turtles [92].
Dolphins	28 % of 106 individuals had ingested plastic fragments[93].
Whales	Phthalates was detected in whales[78, 79]. Marine debris including plastic (~78%) was largely found in 9 of 22 sperm whales along the North Sea coast[94].
Seabirds	Accumulations of plastic in the abdomen of oceanic seabirds were reported[95-97]. In 3 out of 12 birds, plastic derived substances (brominated congeners) were found in abdominal adipose at high levels[98] and also in plastics found in their stomach. plastic was ingested indirectly, and found in predatory birds studied[99].

1.1.3.2 Effect of plastic ingestion on marine-based organisms

The detection of microplastic in aquatic biota, including zooplankton, fish and mammals, increased concerns about its adverse effects on aquatic biota, seabirds and seafood safety.

In birds and marine biota, ingestion of plastic reduces the stomach space, gradually leading to starvation[51]. It can also clog digestive paths and cause injuries and infection which could result in death[5, 6, 98, 100]. Exposure to microplastic reduced the availability of energy through the aerobic pathways of energy production[101]. Figure 1-6 shows some microplastic found in a dead seabird from Limekilns, Scotland.

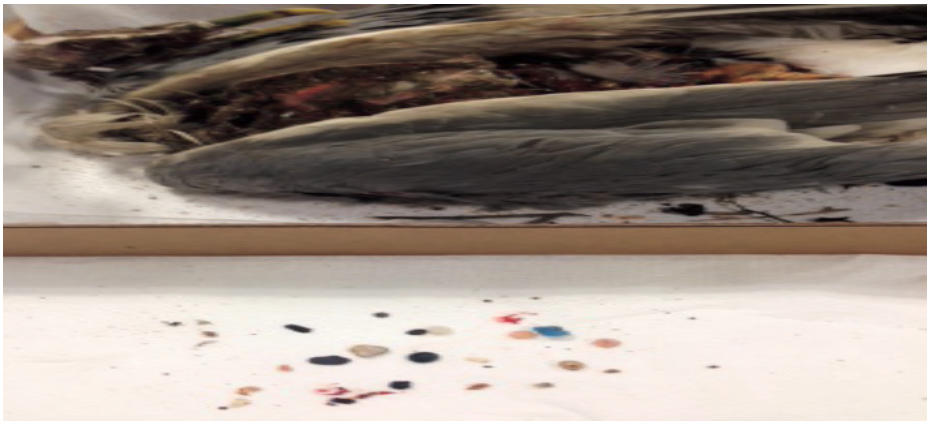


Figure 1-6 Microplastic found in a dead seabird from Limekilns, Scotland

It was also reported that microplastic ingestion hindered acetylcholinesterase (AChE) enzymatic activity[102] in marine biota, thus raising concerns regarding seafood safety as this effect has been linked to Alzheimer's disease in humans[103, 104].

Plastic derived compounds added to plastic or sorbed from ambient environment such as Plybrominated diphenyl ethers PBDEs – flame retardants[105] were transferred to marine organisms' tissues by the ingestion of plastic[98] and affect on endocrine disruption[77].

Bisphenol-A plasticiser was proved to affect the hormonal system of fish and other marine organisms[106], also reducing the growth rate and causing reproductive failure[107].

The PBDEs are type of brominated flame retardants additives that weakly bound (not chemically) to the final products of the polymer[108]. Therefore, it can migrate by different mechanisms to the ambient environment such as volatilisation, abrasion, weathering, direct contact or ingestion. Recent literature pays PBDEs great attention due to its widely use in different applications such as plastic and textiles, which rise the concern about direct (indoor atmosphere and dust) and indirect human exposure (consuming polluted seafood with PBDEs) and health impacts[84, 108].

It was found in bivalves, fish and whale indicating that transfer of PBDEs can occur from ambient seawater, or ingestion of contaminated food or plastic[77, 109-111]. A study conducted by K. Tanaka *et al.* support the above concerns and showed that PBDEs mainly leached and transferred from plastic via fish oil > stomach oil > aqueous solutions[112].

However, further study is needed to identify the specific effect of plastic ingestion, including the effect of plastic additives and contaminants, on marine biota, with bioavailability and bioaccesibility being of ultimate interest. Only bioaccessibility to marine birds was recently studied[113].

1.1.4 Plastic resin pellets as a vector of persistent organic pollutants (POPs)

Plastic resin pellets were investigated as a transport medium and accumulator of toxins in the marine environment[114]. In 2001, pellets were collected from different parts of the Japanese coast and analysed and it was proved that plastic resin pellets had accumulated different toxins.

Plastic resin pellets can act as a vector as well as the source of persistent, bioaccumulative and toxic chemicals in the marine environment[114-119]. Pellets adsorb different toxic material from the environment, such as polychlorinated biphenyls (PCB), and dichlorodiphenyltrichloroethane (DDT). Plastic pellets found in the marine

environment carry two sources of persistent organic pollutants (POPs), one of which derived from additives (additive based), and the other from ambient seawater (sorption based), as shown in Figure 1-7. A study on plastics as the potential transporters of hydrophobic contaminants in the marine environment indicated that plastic has a higher adsorption rate of hydrophobic contaminants when compared with the desorption rate[120].

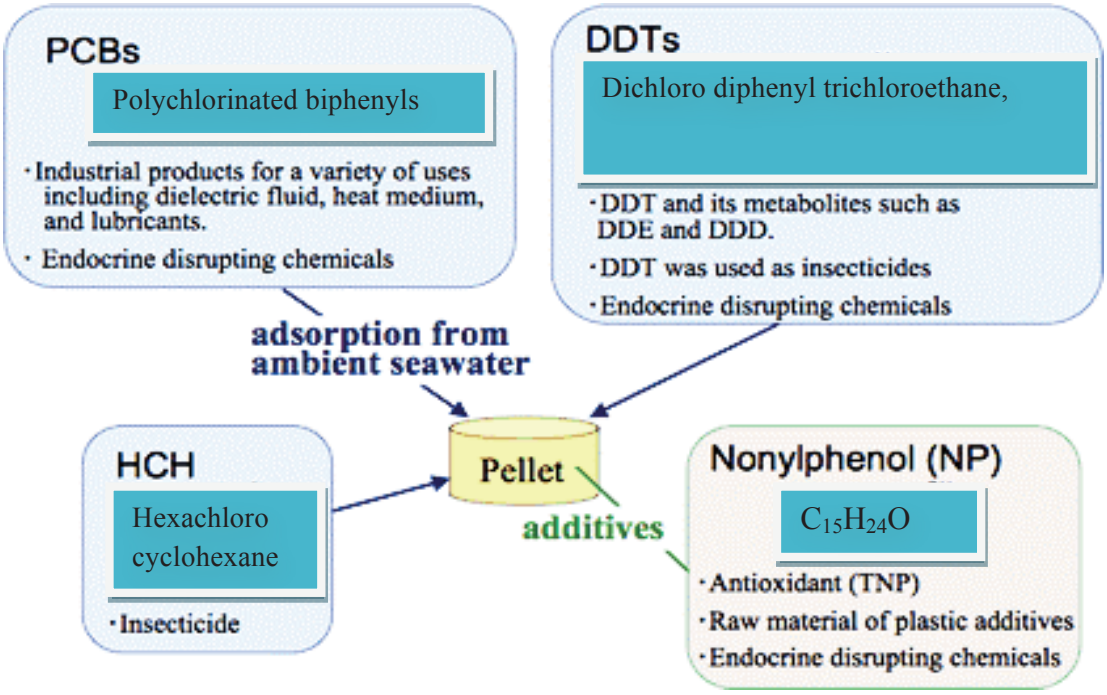


Figure 1-7 Persistent organic pollutants in plastic resin pellets from additives and adsorption sources in the marine environment. The PCBs are: polychlorinated biphenyls, DDTs are: dichlorodiphenyltrichloroethane, HCH is: hexachlorocyclohexane (Adapted)[20].

This area of research has been widely covered in the literature. Since 2005, the International Pellets Watch Programme has called for pellets to be collected from beaches. Beached pellets were used for global monitoring of POPs and to assess POPs pollution in marine environment[121]. As a result, the distributions of pollutants across the world were mapped for example for PCB, as shown in Figure 1-8.

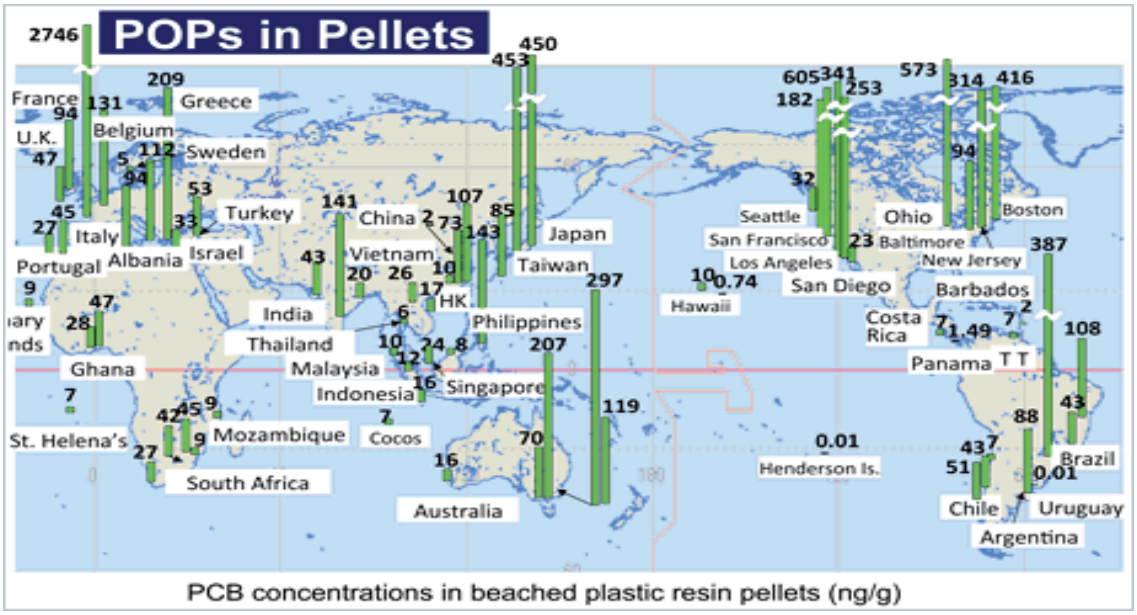


Figure 1-8 Concentration of persistent organic pollutant: polychlorinated biphenyls, in ng g^{-1} in beached pellets by International Pellets Watch[20].

1.1.5 Plastic pellets carrying potentially toxic elements (PTE)

Emerging evidence has indicated that plastic can also be a vector for PTE in the marine environment[117, 122]. A study was performed in the coastal area of South Devon and SW England. Pellets were collected from four sites, ultrasonicated in seawater, sieved, acid digested, and analysed for Al, Cr, Cu, Fe, Mn and Zn by inductively coupled plasma optical emission spectrometry (ICP-OES) and Ag, Cd, Co, Cr, Mo, Sb, Sn and U by inductively coupled plasma mass spectrometry (ICP-MS). One type of plastic pellets (polyethylene) was suspended in seawater for eight weeks. This study showed that plastic pellets can act as an accumulator of metals in the marine environment. The order of metal accumulation in suspended and beach-collected plastic pellets was Fe > Al > Mn > Pb > Cu = Zn > Ag.

Due to its inaccessibility, the Ookushi beach in Japan cannot be cleaned regularly and thus more than 130 m^2 of the beach is covered with litter and debris. The average density of the debris was found to be more than 6 Kg m^{-2}, most of which was plastics.

Cadmium, Cr and Pb were found in the plastic debris collected. The concentration of Pb, Cd and Cr in mg Kg^{-1} was 90 ± 40, 34 ± 16 and 25 ± 10 respectively[123].

The adsorption of trace metals to plastic pellets in the marine environment was also studied[118]. Polyethylene plastic pellets (10 g L^{-1}) were suspended in seawater for 24 hours, then 5 μg L^{-1} of the metals Cd, Co, Cr, Cu, Ni, Pb and Zn were added to the seawater and orbitally shaken at room temperature for 7 days. During this period, subsamples of the water and pellets were collected at different times using a plastic pipette and mesh. Seawater collected during the experiment was acidified with HNO_3 prior to analysis, while 10 % HCl was added to the pellets collected to extract elements been adsorbed during the experiment. Metal loss to the container surface was measured by rinsing the empty plastic container with 10 % HCl. Both virgin and beach-collected pellets were used to assess the adsorption behaviour.

In this study[118], again, plastic pellets were suggested as a transport medium for PTE in the marine environment. Accumulation of metals on the virgin pellets indicated that pellets adsorbed metals rapidly in seawater. Accumulation of metals was higher in the beach pellets than the virgin pellets. It was also reported that the analysis of different plastic pellets collected from South West England showed that the metal concentration in pellets sometimes exceeded that of sediments collected from the same place.

Recently, PTE such as As, Ba, Br, Cd, Cl, Cr, Cu, Hg and Sb were studied and analysed in marine plastic debris using field x-ray fluorescence spectrometry (XRF)[124-126] where the total PTE was detected. Particularly Cd and Pb in PVC plastic debris and other types of plastic debris, and it was attributed to the heat, UV-stabilisers, and coloured inorganic pigments respectively.

Bromine, Cd and Pb was investigated by Massos and Turner[127] in microplastics collected from Woolacombe and Whitsand beaches in South West England. Samples (n = 924) were washed with Millipore Milli-Q water, sieved and brushed and dried at 40 ˚C for 24 h. Limit of detection ranged between 4 –10 μg g^{-1}, 30 – 50 μg g^{-1} and 5 – 20 μg g^{-1} for Br, Cd and Pb respectively. Bromine was detected in ~ 10 % of samples,

according to colours it was mostly found in grey > black > green> blue > orange-brown > white-clear > red microplastic. Cadmium was detected in ~ 7 % of sample, mostly in purple > white-clear > red > grey > black> orange-brown > blue > green. While Pb was found in ~ 7 % , and highly detected in grey > purple > black > blue > red > yellow > green > orange-brown > white-clear. The highest average concentration of Br was found in Whitsand fragments of 1490 μg g^{-1}, whereas the highest averages of Cd and Pb were found in Woolacombe fragments of 968 μg g^{-1} and 1210 μg g^{-1} respectively.

1.2 Polymer types, synthesis and properties

Polymers are molecules built up from small units - monomers - covalently bonded in a special pattern depending on their functionality. Polymers can be natural, elastomer or synthetic. Synthetic polymers (commonly called plastic) can be classified on the basis of their origin of polymerisation as either being petroleum-based or bio-based. According to the British Plastic Federation, 4% of the total global petroleum consumption is used in plastic production.

Polymerisation is the process used in the synthesis of plastic; it is used to convert monomer molecules into a polymer mostly by addition and step-growth condensation[128].

Polymerisation by step-growth condensation is usually used for monomers that have functional groups such as alcohol or carboxylic acid; it normally involves a condensation reaction. The plastic produced is normally different from the starting monomers as a small molecule, such as H_2O, is eliminated. This characteristic of a condensation reaction has an influence on the chemical properties of the plastic produced; such plastic undergoes hydrolysis in the presence of water, especially as the temperature increases[129]. While the addition polymerisation is used for alkene (C_nH_{2n}) monomers, this chain reaction produces plastic similar to the starting monomers' chemical composition.

1.2.1 Polymer types and their uses

Synthetic polymer (Plastic) can be categorised in two main groups according to its physical properties: thermoplastic and thermoset. When heated, shaped and cooled the latter type of plastic becomes very hard and remains hard when heated so cannot be reformed or softened on reheating. This type of plastic is generally used in the construction industry and aeroplanes. Shaped thermoplastic becomes soft on reheating, but after cooling it stays hard which makes it suitable for repeated reshaping and recycling. This raises its demand as a daily use plastic, mainly for use in the packaging industry. From the environmental point of view, biodegradable and recyclable plastics are highly preferred.

There are many plastic types available on the market. Figure 1-9 shows the common polymers derived from crude oil and natural gas. The different types of thermoplastics, their uses and properties will be discussed in the subsequent paragraphs.

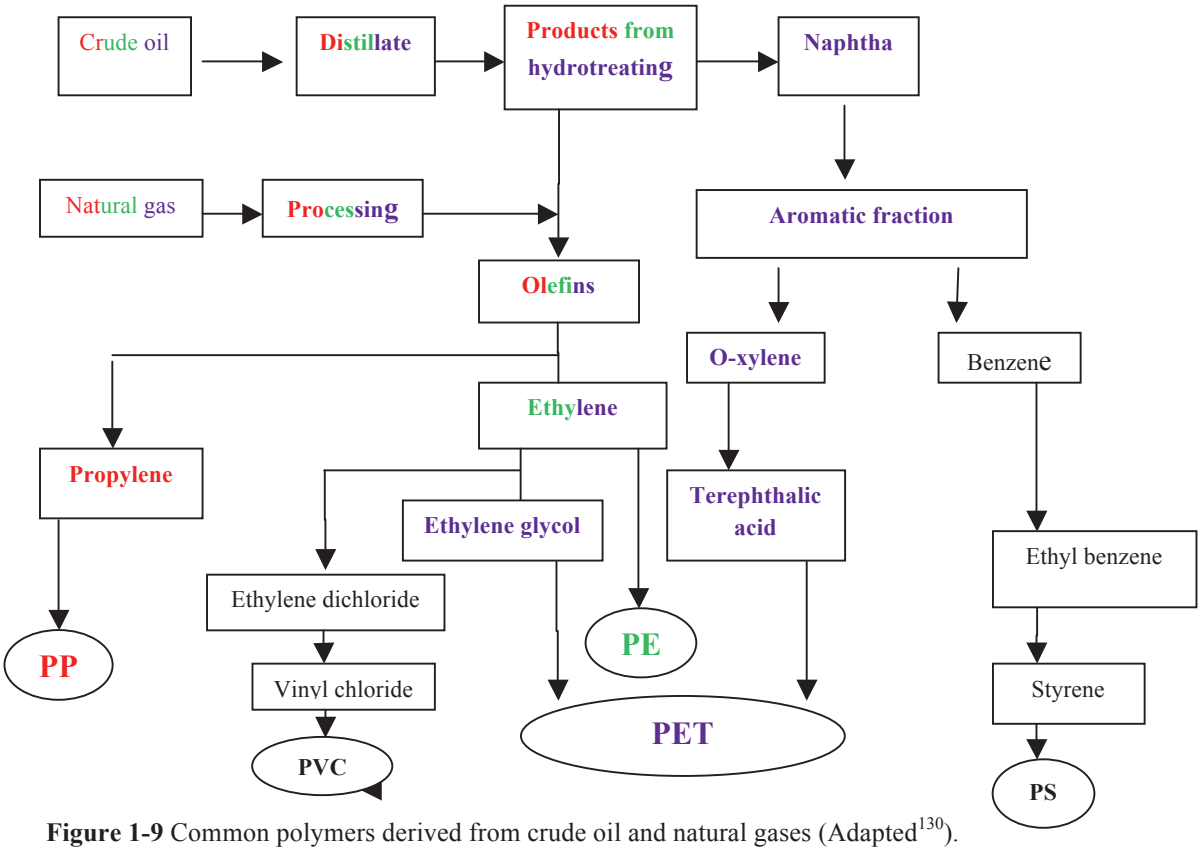


Figure 1-9 Common polymers derived from crude oil and natural gases (Adapted[130]).

1.2.1.1 Polyethylene PE

Additional polymerisation takes place to convert petroleum-based ethylene ($CH_2 = CH_2$) monomers into polyethylene, the most widely used plastic, by stimulating the double bond with an initiator forming the simplest polymer structure, as shown in Figure 1-10.

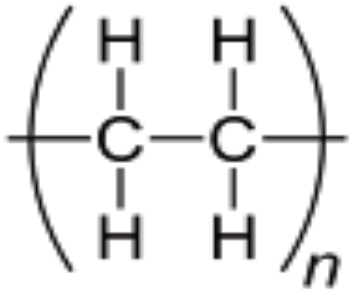


Figure 1-10 Polyethylene chemical structure.

Many grades of PE are available depending on the polymer chain composition and the process of the polymerisation, but all are semicrystalline. Mechanical properties, density and melting temperature decrease as the ramification (chain branching and molecular weight) increase. For example, the melting temperature of low density polyethylene is around 108˚C, while the melting temperature of high density polyethylene is about 135˚C[129]. Figure 1-10 shows the level of chain branching in high and low density PE. Polyethylene is widely used in different applications such as bags, packaging materials, toys, houseware and pipes.

Generally speaking, PE is chemically stable and a good barrier to fat, water vapour and gases. However, as the density of PE increases, the strength, hardness, stiffness, and barrier properties increase, while the resistance to cracking and transparency decrease[129]. Polyethylene can be affected by the marine environment. Halogens reacts with PE by substitution mechanisms, such as chlorination, where the structural changes take place at around 50˚C or at room temperature with the influence of ultraviolet light[129].

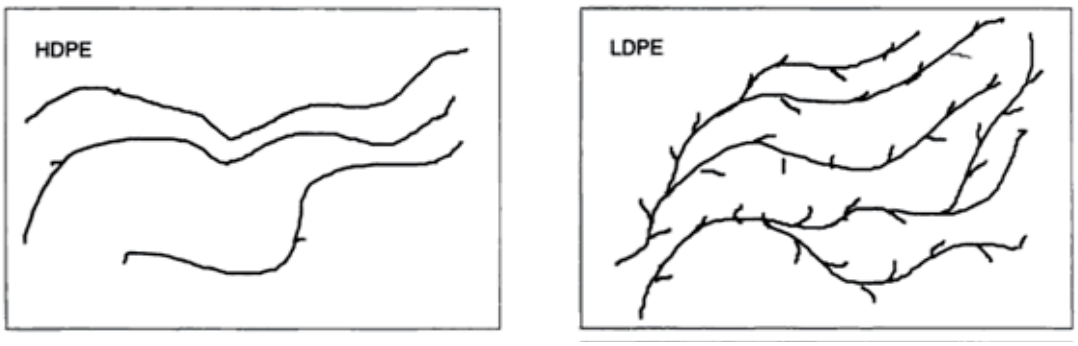


Figure 1-10 The level of chain branching in high and low density polyethylene[131].

1.2.1.2 Polypropylene PP

Additional polymerisation takes place to convert propylene ($CH_2 = CH - CH_3$) into polypropylene, as seen in Figure 1-12, typically using a Ziegler-Natta catalyst (mixture-based catalyst).

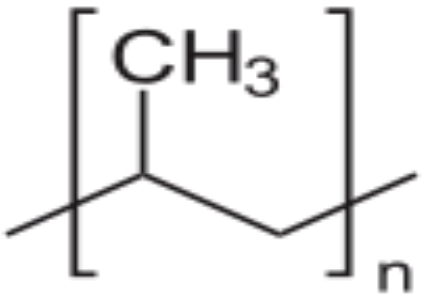


Figure 1-12 Polypropylene chemical structure.

Polypropylene is a good barrier, but its cold temperature resistance is low when compared with that of PE. It has a high melting temperature and high chemical inertness[129, 132]. The tertiary carbon atoms in PP increase its sensitivity towards oxidation. Some of the uses of PP include hot-filled containers and bottles, sterilisable items, water pipes and facial wash products for exfoliation purposes, as seen in Figure 1-13.

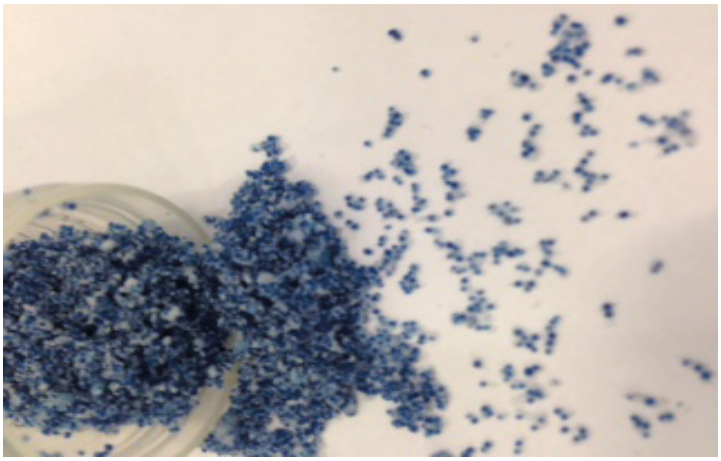


Figure 1-11 Polypropylene microplastic (around 6 g) present in a 150 mL daily wash product.

1.2.1.3 Polyethylene terephthalate PET

Poly(ethylene terephthalate) is a thermoplastic polyester type of plastic produced by the condensation polymerisation reaction of dimethyl terephthalate or ethylene glycol and terephthalic acid, as seen in Figure 1-14. Antimony, titanium, or germanium-based catalysts are usually used, with the commonly used antimony trioxide (Sb_2O_3) catalyst[133]. The syntheses of PET includs the esterifaction of terephthalic acid and the polymerisation of ethylene terephthalate.

- $2(HO\text{-}CH_2CH_2\text{-}OH) + (HOOC\text{-}C_6H_4\text{-}COOH) \rightarrow (HO\text{-}(CH_2)_2\text{-}O\text{-}OC\text{-}C_6H_4\text{-}CO\text{-}O\text{-}(CH_2)_2\text{-}OH) + (2n\text{-}1)\, H_2O$
- $(HO\text{-}(CH_2)_2\text{-}O\text{-}OC\text{-}C_6H_4\text{-}CO\text{-}O\text{-}(CH_2)_2\text{-}OH) \rightarrow (\text{—}O\text{-}(CH_2)_2\text{-}O\text{-}OC\text{-}C_6H_4\text{-}CO\text{—})$

Figure 1-12 Syntheses of PET; esterification of terephthalic acid with ethylene glycol, then polymerisation of ethylene terephthalate.

Poly(ethylene terephthalate) has good barrier properties against gases (low permeability of oxygen and carbon dioxide), fats and water due to its (partial) crystallinity which generally enhances barrier properties. Therefore, nucleating agents and plasticisers are

usually used to increase the PET crystallinity. The melting temperature is about 255˚C, and it is widely used for water and beverage bottles, packaging and in clothing[129]. Figure 1-15 shows the PET pellets and their chemical structure.

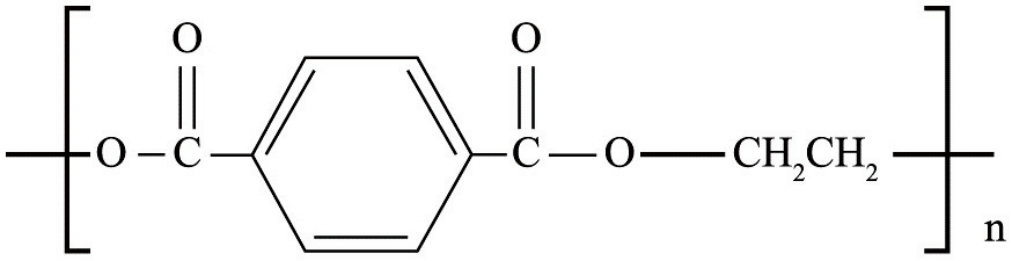


Figure 1-15 Poly(ethylene terephthalate) chemical structure.

1.2.1.4 Bioplastic BIO

Poly(hydroxybutyrate-co-hydroxyvalerate) is a bio-based polyester type of plastic, (Figure 1-16). Microbial biosynthesis of polyhydroxybutyrate (PHB) takes place through condensation of acetyl-Co enzymes A to produce the hydroxybutyryl-CoA monomer used to polymerise PHBV[134-136].

Poly(hydroxybutyrate-co-valerate) has similar properties to PP, with a melting temperature about 168-175˚C plus biodegradability, which is one of the important properties of PHBV.

It has several actual and potential applications in the medical industry and is used also for packaging, paper coating, adhesives and moulded goods.

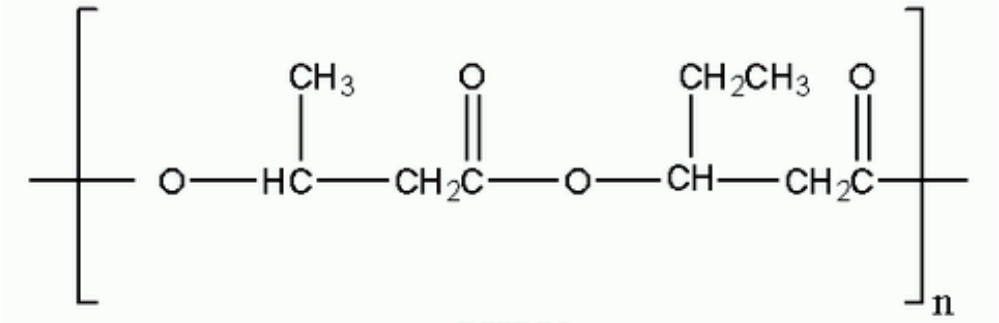


Figure 1-16 Poly(hydroxybutyrate-co-valerate) chemical structure

In this work, the polyolefin plastic HDPE, LDPE, and PP and the polyester PET were selected for study due to their wide use and demand. One type of bio-based plastic BIO was also selected as it is increasingly being used as a potential replacement for petroleum-based plastic to reduce plastic debris and CO_2 emissions as well as to reduce costs.

1.2.2 Degradation and deterioration of plastics

Degradability is defined as the chemical change or indirect physical or mechanical changes occurring in a polymer as a result of environmental factors such as sunlight, heat and chemical reaction[131].

In the marine environment, when taking into account physical processes, degradation takes place in two main forms[137]:

1. Abiotic- degradation by photons (solar radiation), thermal oxidation, and hydrolysis.

2. Biotic- oxobiodegradation by microorganisms.

Biodegradation is defined as the degradation caused by microorganisms such as bacteria and fungi. Biodegradation depends on various factors, such as functional group, molecular weight, chemical structure and the additives added to the polymer, type of organisms and nature of pre-treatment[138]. The physical breakdown is accelerated by a

number of factors, mainly light and heat[139] (photothermal oxidation process)[131]. Physical forces are generally those related to the physical breakdown or cracking down of the polymers[139-141].

On the other hand, microorganisms play a vital role in depolymerisation. During degradation, enzymes from microorganisms break down the polymers into smaller molecules that can be used as energy sources by the organisms. When oxygen is available, aerobic microorganisms are mainly responsible for the degradation process. In contrast, in the anoxic condition, anaerobic microorganisms are mainly responsible. The final products are microbial biomass, CO_2, CH_4 and H_2O. The process is called "mineralisation". A generic biodegradation process for plastic in the marine environment by microorganisms is shown in Figure 1-17.

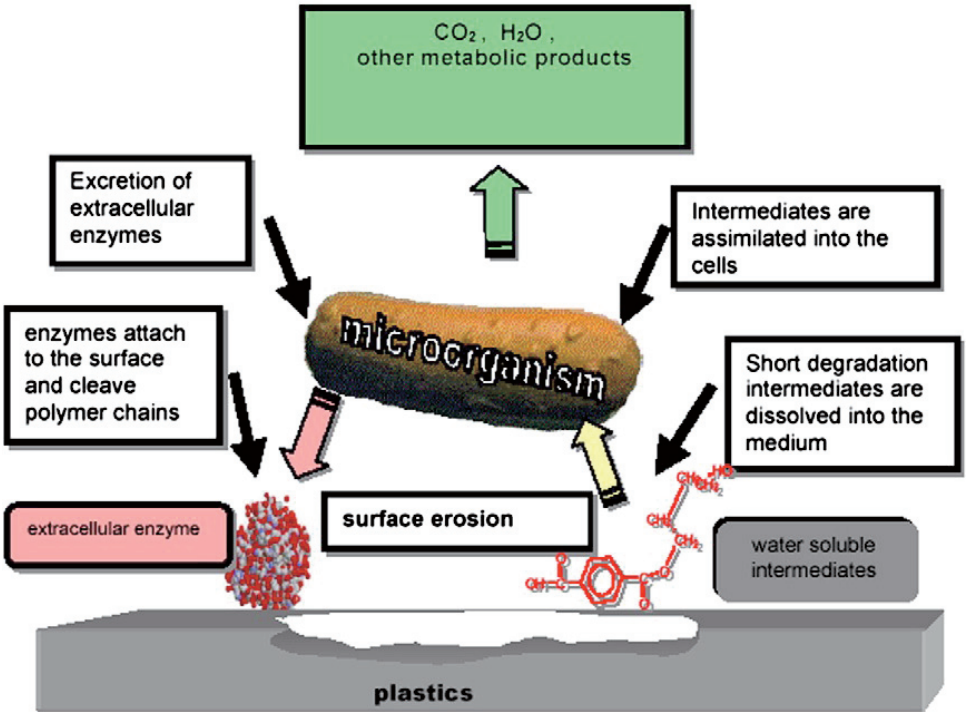


Figure 1-13 General biodegradation process of plastic under aerobic conditions[142].

In general, the higher the molecular weight of the plastics, the lower the degradation rate. Two different case studies have been performed for one type of polyethylene (low density polyethylene - LDPE) in air and in seawater[140]. It was reported that the degradation was less when the LDPE was in seawater than when it was in the air. The lower degradation of LDPE was explained by the fact that temperature build up is lower when plastics float in seawater than when they are in the air. This concept is illustrated in Figure 1-18 that shows that the deterioration of polyethylene floating in seawater is higher than when the material is at a depth where light does not penetrate.

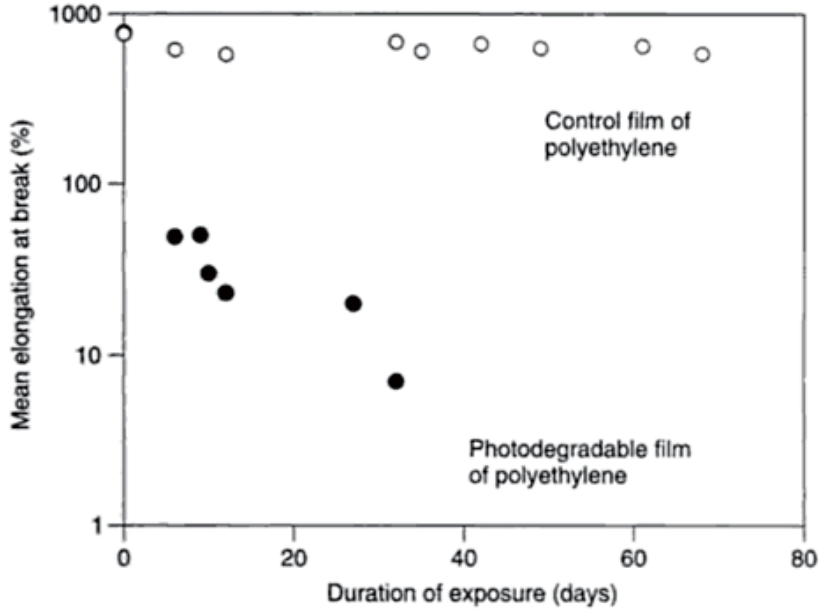


Figure 1-14 Deterioration rate of control polyethylene in deep seawater and enhanced photodegradation of polyethylene floating in seawater[131].

1.2.2.1 Weathering of different types of plastic in marine environment

For plastic selected to be study in this work, abiotic degradation is the most dominant. PE and PP types as seen in sections 1-2-1-1 and 1-2-1-2 have a carbon-carbon backbone

structure while PET and BIO have heteroatom in their backbone as seen in section 1-2-1-3 and 1-2-1-4 respectively.

Generally, microplastics degrade faster than macroplastic due to its higher surface area to volume. However, in marine environment degradation is slow compared to other environments as the degradation conditions are not optimum due to water cooling effect.

Carbon-carbon polymers initially attack by temperature (thermal attack) and UV-radiations, then by auto oxidation as radical reaction takes place (impurities on polymer surface enhances the formation of the radicals). As a consequences, polymer become brittle, cracked and subjected to further degradation and fragmentation[129, 143].

Polymers with heteroatoms in backbone structure have more resistance to temperature and initially attack by water (hydro- attack) where reverse esterification take place causing thermo and photo degradation[143].

1.2.3 Additives and catalyst residue in plastic[129, 130, 144]

Microplastics contain catalyst residues and additives such as plasticisers and fillers. Heterogeneous catalysts (mixture of Ca, Mg, Al, Si, Ti, Cr, V, and Zr metals or metal oxides) and homogeneous catalysts (metals or complexes of metal plus organic molecule) are used in the production process of plastic. Residual catalyst in plastic is possible. Heterogeneous residues are usually not leachable but play an interactive role on the polymer surface.

Additives can be either organic or inorganic chemicals that are used to add commercial value to plastic and to enable its processing. Additives will also remain in the plastic. Examples of some of the additives that are used are given in Table 1-2.

Table 1-2 Examples of some additives used in plastic[129, 145].

Additives	**Function**	**Possible elements**
Antiacids	To reduce or prevent plastic degradation and attack by acids	Al, Ca, Mg, Zn
Antifogging	To improve packaging clarity against condensing on surface.	-
Antimicrobials/ biocide	To prevent microorganisms growth and resist biodegradation of plastic	-
Antioxidant (stabiliser)	To prevent oxygen degradation in thermal processes and autoxidation in use temperature	Ca
Antistatic	To reduce surface electrical charge and dust pickup.	S
Blowing agent	To generate gas for expanding and foaming.	S
Colorant	For colouring purposes.	Cd, Cr, Fe, Ti, Zn
Coupling agent	To provide sufficient adhesion between plastic phases	Ti, Zr
Dehydrating agent, PET	To keep humidity low during melting process	-
Fillers	To reduce the cost, change properties of the final products including modulus and ensure fire and shock resistance.	Al, Ca, K, Mg, Si, Ba
Flame retardant (PBDEs)	To reduce the flammability of the final products	Br, Cl[113]
Heat stabiliser (metal soap)	To reduce or prevent plastic degradation by heat	Ba, Ca, Co, Pb, Sn, Zn
Lubricants	To prevent sticking on the mould or machinery, reduce melt viscosity and reduce friction between particles.	Ca, Si
Nucleating agent	To provide consistent property and morphology.	Na, P, Si
Plasticizers	To enrich plastic with processibility and flexibility.	P
UV stabiliser	To reduce or prevent plastic degradation and oxidation by UV- light	-

1.3 Potentially toxic elements in the marine environment

Potentially toxic elements (PTE) play vital varied roles in the health of living organisms. Some are essential and all are toxic depending on their dose. A general dose-function (response) curve for PTE is given in Figure 1-19. Which shows that every essential PTE is needed in a specific amounts; a lower than the optimum amount can cause deficiency while a higher amount will cause toxicity.

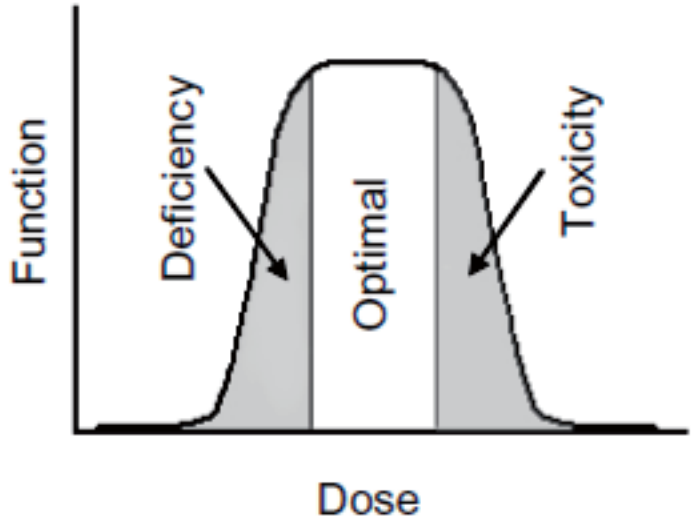


Figure 1-15 Dose-response curve illustrating that lower amounts of essential chemical substances than the optimum can cause deficiency to organisms and health while higher amounts will causes toxicity of chemical substances [146].

Iron and zinc, for example, are necessary for metabolism in certain amounts[146]. It is also known that the environmental effects of PTE greatly depend on their chemical speciation[146].

Contamination by potentially toxic elements in the marine environment has been reported[147] mainly in densely populated and industrialised areas[148] from various sources such as sewage discharge, mining, smelting, waste recycling and from agricultural areas where metals are released from insecticides and fungicides[149, 150].

Distribution and accumulation of PTE in the sediment has been reported[151-155]. In Salina Cruz Bay, Mexico PTE were analysed over twenty years. It was found that the lead and nickel concentrations reached 120 μg g^{-1} and 70 μg g^{-1} of sediment, respectively, probably due to the oil transport activities carried out within the Salina Cruz Bay harbour[156].

The exposure of aquatic animals to metals is classified into two groups: 1) dietary exposure and 2) dissolved exposure. The main route of PTE intake is reported to be dietary exposure. To measure the impact of PTE intake through diet, different studies were conducted for zooplankton and fish[157]. Juvenile rainbow trout were exposed to contaminated sediments of 11 – 129 μg As g^{-1}, 0.2 – 4.9 μg Cd g^{-1}, 24.3 – 73.1 μg Cu g^{-1}, 1.5 – 226 μg Pb g^{-1}, 338 – 1334 μg Zn g^{-1}, with daily feeding rate of 16 % of body weight. It was found that the growth is reduced and claimed to be mainly because of the arsenic. Whereas Zebrafish was fed with the diet- natural contaminated *Nereis diversicolor,* with 15 – 140 μg As g^{-1}, < 2 μg Cd g^{-1}, 16 – 450 μg Cu g^{-1}, < 2 μg Pb g^{-1}, 120 – 320 μg Zn g^{-1}. No impact of growth was found but the PTE contamination caused reduced reproduction.

Similar experiments on whitefish, rainbow trout, seabream and more can be found in the literature. It is reported that PTE can cause problems with growth, reproduction, kidney or liver failure or increased mortality rate. They can also denature proteins and reduce blood pigment functions[150].

Bio-accumulation and assessment of PTE in marine biota and fish is also discussed in the literature [158-162]. In all the studies, it was clear that high levels of metal exposure through diet can be toxic. Increasing concentration of PTE is not only a threat to marine life but also to humans who consume seafood. Some common PTE in marine environment will be discussed below.

1.3.1 Arsenic in the marine environment

Arsenic enters the environment from both natural sources, such as volcanic emissions, hot spring emissions and interaction with rocks and from anthropogenic sources. Mining waste, metal smelting waste, glass manufacturing waste, poultry feed additives, pesticides, herbicides, wood preservatives, cement manufacturing, dust and gases and combustion of fossil fuels are the main man made industrial As contaminants[146, 163].

Speciation can be defined as "the description or the process of identifying and quantifying the different, defined species, forms or phases present in a material" and it is an important factor of the toxicity[164]. Arsenite, arsenate, dimethylarsinate, monomethylarsonate, arsenobetaine and arsenocholine are the most common arsenic species available in environmental and biological samples, the arsenic form of arsenite and arsenate are extremely toxic compared to the other moderate and non toxic forms [164]. In the marine environment arsenic is present as arsenite As^{III} and arsenate As^{V} as illustrated in Figure 1-20. Depending on the pH, the latter is more dominant[165, 166]. Generally, inorganic arsenic is more toxic than organic arsenic[167].

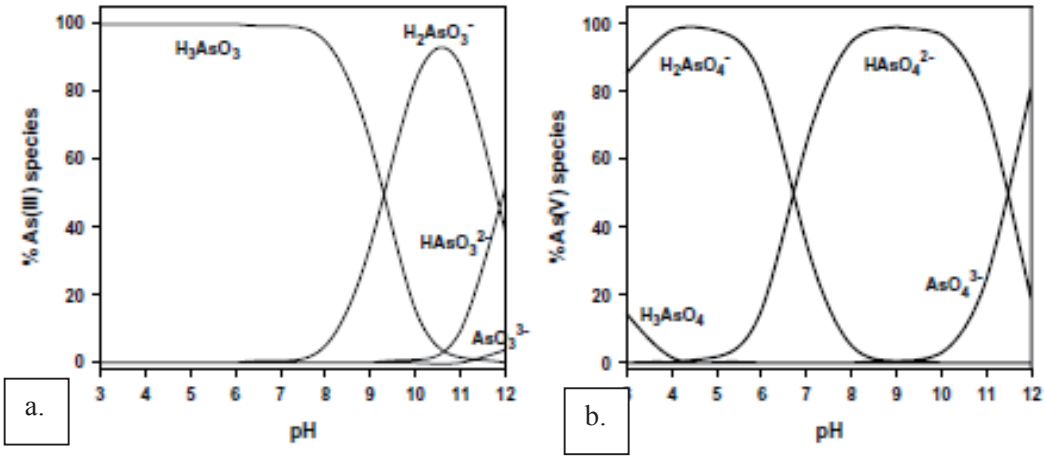


Figure 1-16 Speciation of a. As^{III} and b. As^{V} at different pH in aqueous media[146].

1.3.2 Cadmium in the marine environment

Cadmium may enter the marine environment from sewage and domestic and manufacturing plants waste. In the marine environment, it was found that the availability and toxicity of Cd in marine organisms was inversely dependent on the salinity[168]. As the chloride concentration increased, the level of free Cd ions decreased due to its interaction with chloride. This has been supported by the determination of the uptake of Cd by shrimp, which indicates that the Cd uptake was in inverse relation to the chloride level (salinity). The depth profile of Cd in seawater indicates a correlation between PO_4, a structural element of the biological system, and Cd. The indication is that the concentration and distribution of Cd increases with depth[164, 169, 170]. Figure 1-21 shows the Eh-pH Aqueous Cd species.

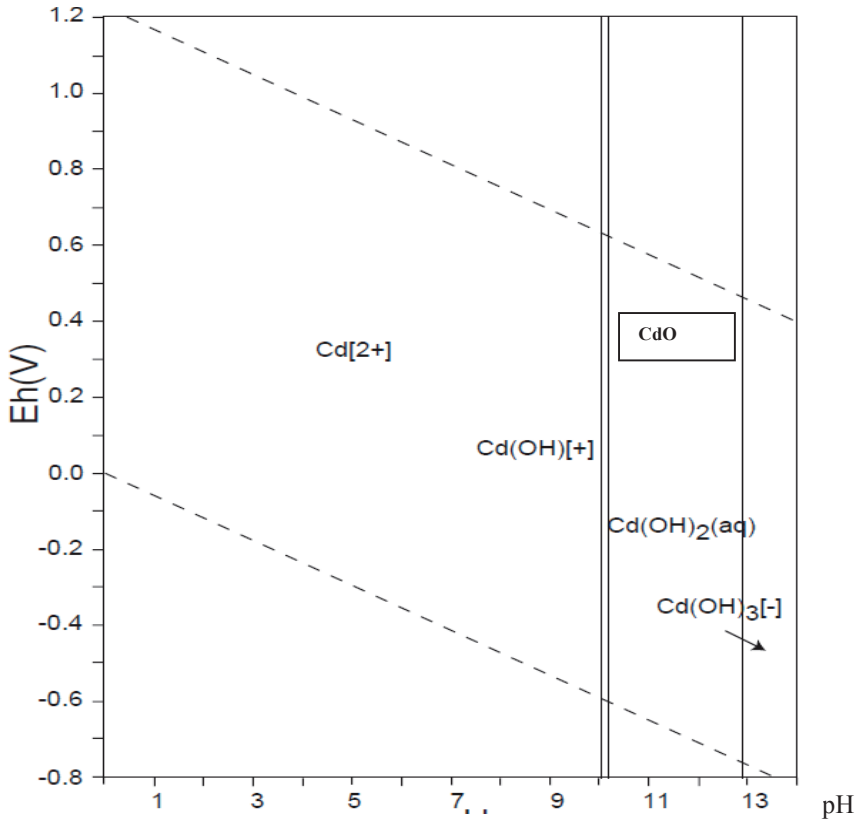


Figure 1-17 Eh-pH cadmium aqueous species(Adapted)[171].

1.3.3 Chromium in the marine environment

Chromium is the seventh most abundant element naturally occurring on earth. Incineration of refused sludge, combustion of oil and coal and industrial processes such as those involved in the production of ferrochrome, steel and alloys, wood, glass and dyes for paints, leather tanning, metal plating and electrical devices are examples of anthropogenic sources of chromium.

In the environment, Cr is present in the range from Cr^{II} to Cr^{VI} of the oxidation states. The most common are Cr^{III} and Cr^{VI}, which are present in seawater. The latter is considered to be carcinogenic, toxic and is present as CrO_4^{2-} in higher concentrations than other species in the marine environment. Aqueous Cr species are pH dependent as shown in Figure 1-22.

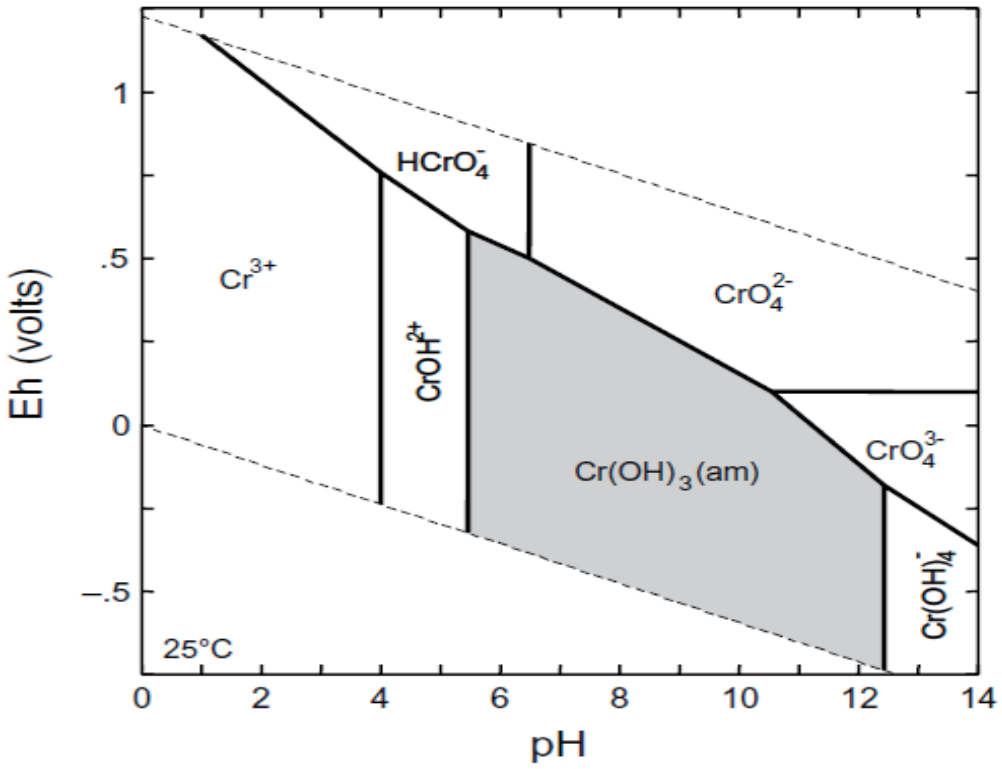


Figure 1-18 Eh-pH chromium aqueous species at 25°C. Cr^{3+} hydrolysis forming $Cr(OH)^{2+}$, $Cr(OH)_3^0$ and $Cr(OH)_4^-$ depending on the pH, while Cr^{6+} occurs as chromate anion CrO_4^{2-}. Below pH 6.5 $HCrO_4^-$ is dominant, and above pH 6.5 CrO_4^{2-} is dominant in solution.

1.3.4 Lead in the marine environment

Lead is a non-essential element that exists naturally in mineral ores, mostly galena PbS. Mining, smelting, combustion of coal and oil, combustion of leaded gasoline, lead-based paints, lead arsenate pesticides, and waste incineration are examples of anthropogenic sources of lead in the environment.

In water, solubility of Pb depends on water pH, water salinity and the organic matter content. Solubility tends to be high in soft, acidic water.

Lead can exist as the Pb^{2+} ionic species at pH < 7.5 in fresh water, but readily complexes with dissolved carbonate at pH > 7.5 and forms lead carbonates, $PbCO_3$ and $Pb_2(OH)_2CO_3$[146, 172] as seen in Figure 1-23. In seawater, lead carbonate complexes are dominant, but lead chloride complexes and surface complexes with iron and manganese oxides can also occur.

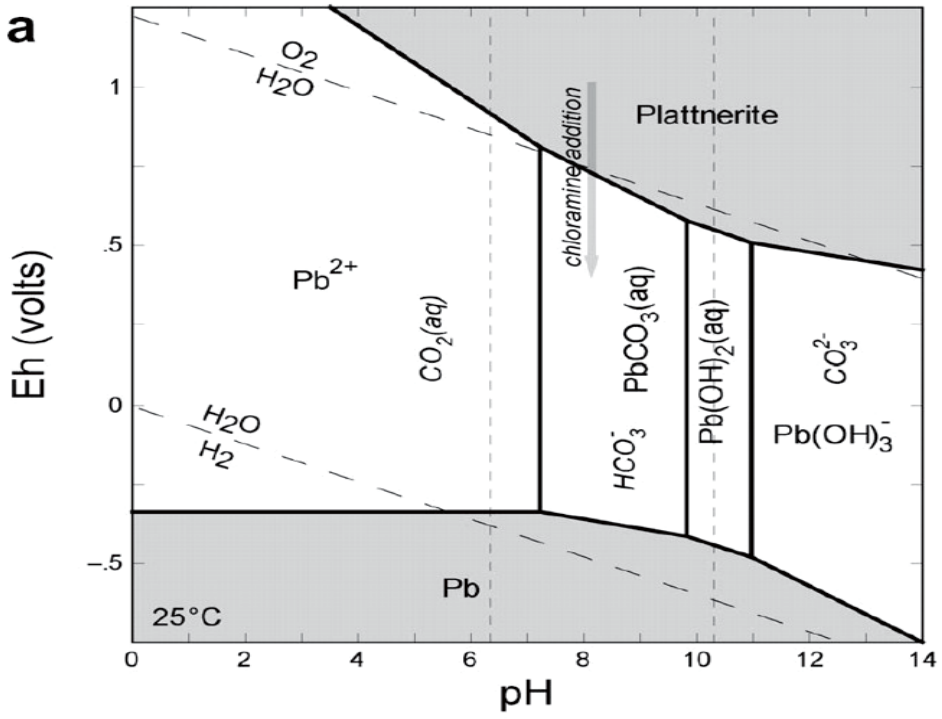


Figure 1-19 Eh-pH lead aqueous species at 25˚C. Pb^{2+} ionic species exist at pH < 7.5 in fresh water. In seawater lead carbonate complexes are dominant.

1.4 Aim of the research

The aim of this work was to investigate the role of microplastic in the transport of selected potentially toxic elements in the marine environment. This was achieved by:

- Determining the key total PTE present in common petroleum-based and bio-based plastic pellets;
- Establishing an individual sorption profile for each key PTE using both types of pellets in different media: deionised water, fresh water and artificial seawater;
- Identifying the critical effects of weathering in the marine environment on pellet surfaces and PTE adsorption behaviour;
- Determining characteristics and potential release of environmentally-relevant PTE from beached pellets collected from field locations; and
- Evaluating the potential bioaccessibility of PTE to marine organisms after direct ingestion of beached plastic pellets.

These aims and objectives were achieved through a programme of desk and laboratory research. Chapter 2 outlines the fundamental of the main applied techniques used in this research. Chapter 3 describes the general experimental procedures used. The results of the laboratory research are presents in Chapters 4-7. Chapter 4 describes the initial investigation of the total PTE in virgin pellets (speciation analysis was not conducted in this study) and the sorption potential of five types of petroleum and bio-based plastic pellets in different media and experimental conditions. Chapter 5 describes the surface of virgin and laboratory-weathered pellets using SEM including surface imaging and elemental analysis of the pellet surfaces, plus the identification of pellets by FTIR. Chapter 6 covers the study of the surface, and the release of PTE from beached pellets collected from Shuwaikh, Kuwait and Limekilns, Scotland. Chapter 7 describes the estimation of simulated *in vitro* bioaccessibility of PTE to marine organisms. Finally, Chapter 8 outlines key conclusions from this work and recommendations for future research.

2 Theory of applied techniques

2.1 Fundamental of inductively coupled plasma mass spectrometry[173-177]

Inductively coupled plasma mass spectrometry (ICP-MS) is an analytical technique for elemental analysis that can give accurate and precise results. It has several advantages over other spectrometry techniques such as being rapid, covering a wide range of elements, and with a high control of interferences.

Analyte is atomised and ionized using an external energy source, the ICP which is made up of the positive ions, electrons, and neutral argon gas in a confined space, produced by inductive coupling of argon gas. The ICP acts as an ion source for the MS which characterised by its temperature range from 7000 – 10000 K. Resulting ions are then separated with respect to mass to charge ratio.

2.1.1 The main components of a typical ICP-MS instrument system

Analysis using ICP-MS consists of several steps and Figure 2-1 illustrates the processes from sample introduction, through mass analysis, to ion detection.

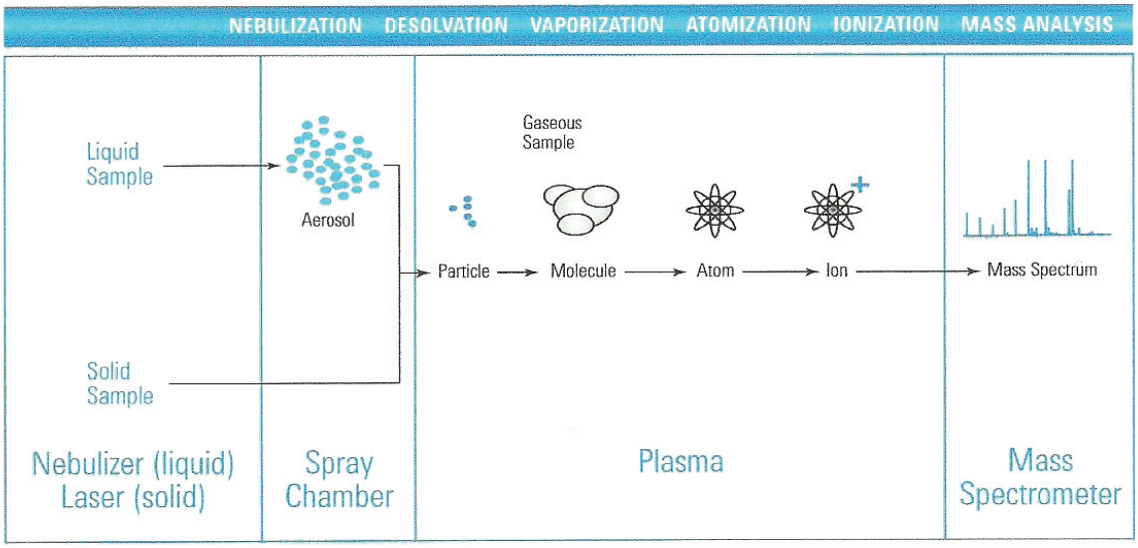


Figure 2-1 Sample pathway in ICP-MS, from sample introduction-nebulisation, desolvation, vaporisation, atomisation, ionisation to the mass analysis process[178].

Sample introduction

The sample is introduced into the ICP in the form of an aerosol. This aerosol is produced by passing the liquid sample through a pneumatic/concentric nebulizer which converts the sample solution into droplets by passing through an orifice into a high velocity gas jet. Sample is then draws up via the sample capillary, by the pressure differential caused from the gas stream passing the orifice, where liquid sample forms a cloud of droplets (aerosol) in the spray chamber.

A peristaltic pump is used to deliver liquid sample at a controlled flow rate, typically 1 ml min^{-1}, and also to drain the spray chamber in order to remove excess sample. The spray chamber, as shown in Figure 2-2, is used to filter out and separate the larger liquid droplets from the gas stream, so only small droplets (1-2 % of the sample) pass into the plasma to maintain it stability. Otherwise, the ICP temperature will decrease and the plasma might be extinguished[173, 177].

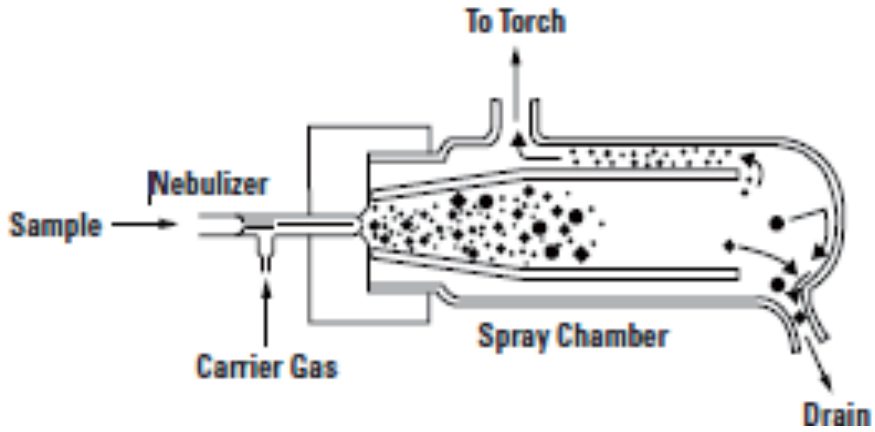


Figure 2-2 Introduction system of ICP-MS: nebulizer and spray chamber[178]

Ion generation and frequency matching RF generator

The ICP ion source is formed within a special torch. This contains three concentric quartz tubes which the argon flows through as shown in Figure 2-3:

- The injector tube that introduces the sample aerosol from the nebulizer at 0.5 – 1.5 L min^{-1} flow rate, forming a hole or channel in the centre of the plasma where the sample passes through.
- The intermediate or auxiliary gas flow that introduces the carrier gas typically at 0.5 – 1.5 L min^{-1} to push the plasma away from the injector tube and prevent deposits at tip otherwise it will melt.
- The outer or coolant gas flow introduces plasma gas at 10 – 15 L min^{-1} and constitutes the plasma. It pushes the plasma away from the torch sides to become thermally isolated and protect the torch from melting; the tangential flow of the gas causes the shape of the plasma. This outer tube is surrounded at the top by a copper coil powered by a RF generator that generates 1.5 – 2.5 KW at 27 – 40 MHz.

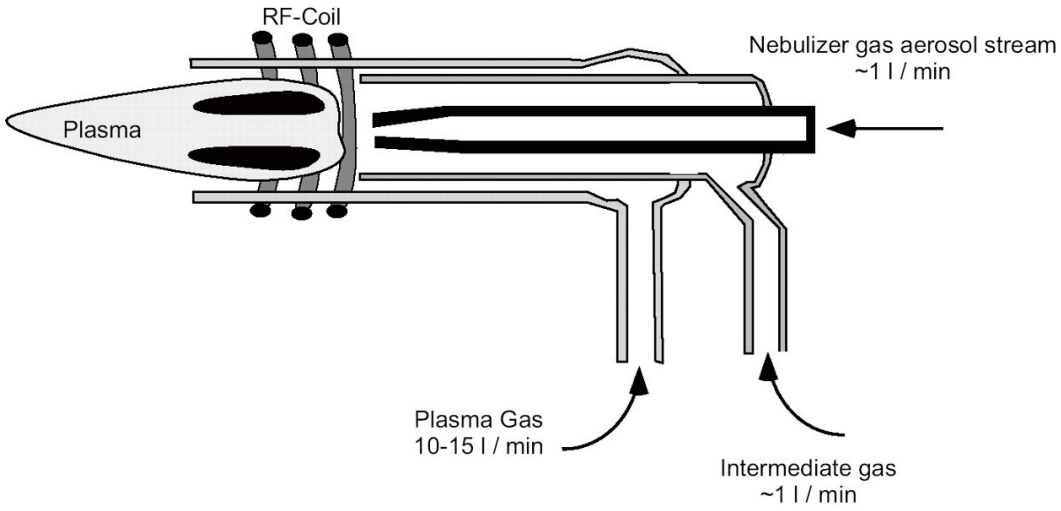


Figure 2-3 ICP-MS Tourch which consist of three concentric quartz tubes [179]

Electrical power from the RF- coil is needed to form and maintain the ICP which is generated in a stream of Ar gas. The spark is initially start from a "Tesla" coil, the spark source of electrons ionize the Ar gas in a self- sustaining process. As the RF is applied in the coil, the intense magnetic field created by the electric current causes collision between free electrons, which were stripped from Ar atoms when the spark was initiated,

and further Ar atoms. This produces Ar^+ ions and further electrons in a chain reaction until a stable, high temperature plasma of about 7000 – 10000 K is formed. The plasma therefore contains Ar atoms, Ar^+ ions and electrons, and it will remain as long as the RF and Ar are supplied. Figure 2-4 summarises the formation of the ICP. As the sample aerosol is passed into the plasma, aerosol droplets are dried, vaporised, atomized and then ionized by the removal of one or more electron from each atom due to the high temperature. The purpose of the high temperature argon plasma is to generate positive ions of the analyte (M^+) by first producing the ground state atoms from dried aerosol and then collision of energetic argon with the ground state atom as in the following:

$$M(H_2O) \rightarrow (M)_n \text{ solid} \rightarrow M \text{ gas} \rightarrow M \text{ ground state atom} \rightarrow M^+$$

Then, the ions formed are extracted from the plasma to the spectrometer interface.

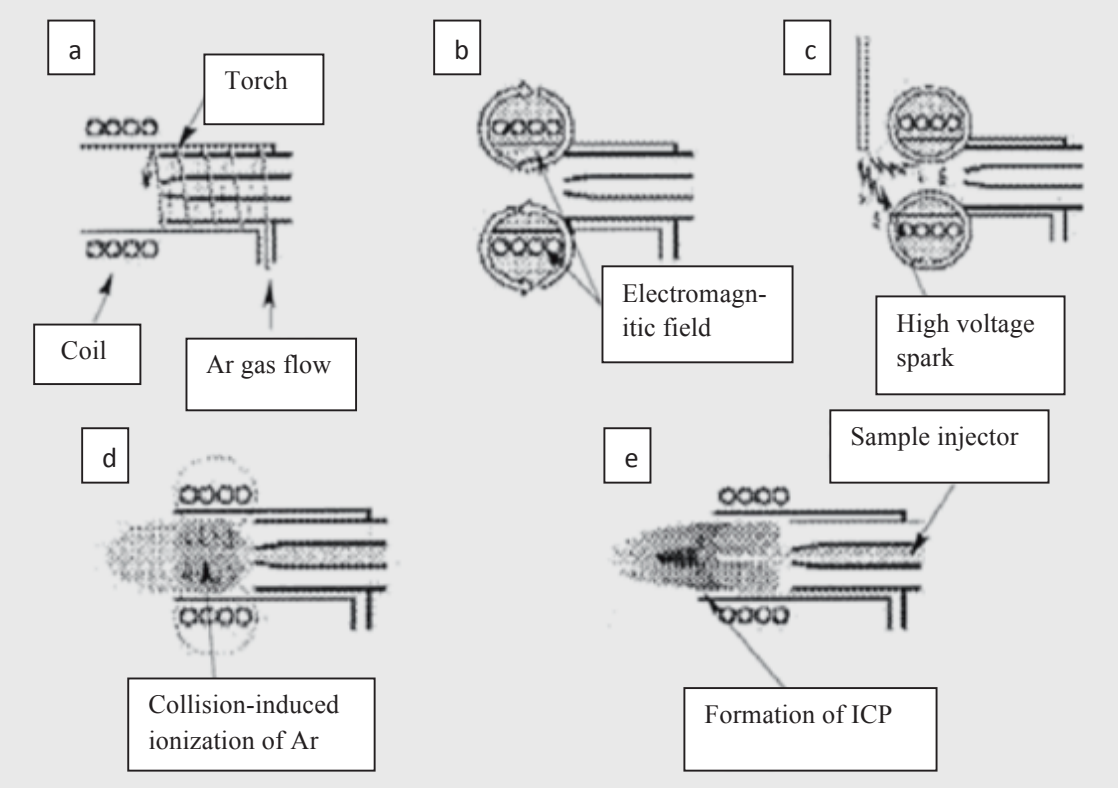


Figure 2-4 Steps of plasma formation- a) Tangential flow of Ar across the outer and middle tube of the torch. b) RF power is applied to the coil, creating an electromagnetic field around it. c) high voltage spark from tesla coil produces electrons. d) Electrons are accelerated by the RF field and collide with Ar producing Ar^+ and more free electrons. e) A self sustaining process is continued and the ICP is formed.

Interface and ion lens focusing

The interface is one of the main features of the ICP-MS which extracts and transfer positively charged ions from the plasma at atmospheric pressure into the vacuum region. It consists of two conical metal cones as seen in Figure 2-5: sampling cone with around 1 mm orifice and skimmer cone with around 0.3 mm orifice. Cones are usually made of nickel due to its robust nature, high thermal conductivity, and its resistance to corrosion. The small orifice of the sampling cone causes a pressure differential and allows ions to pass through to a moderate pressure region of about 2.5 m bar. Then, the skimmer cone which is placed just behind the sampling cone allows a central portion of the ions to pass through to a lower pressure region of about 10^{-4} m bar while maintaining the vacuum beyond where the quadrupole mass analyser and detector are located. The extracted ions are then focused by a series of electrostatic lenses into the mass spectrometer.

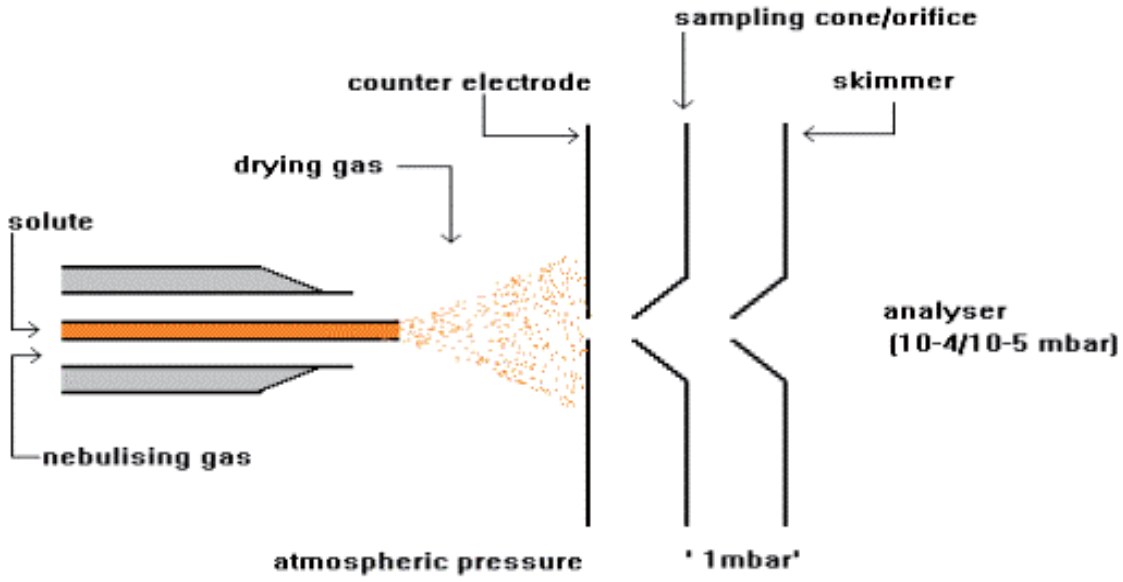


Figure 2-5 Sampling and skimmer cones[178]

Mass spectrometer

The mass analyzer is the stage where the ions are separated by their mass to charge ratio, m/z. The quadrupole is a sequential mass filter, popular due to its ease of use, robustness, mass range, high scanning speed, and relatively low cost. It consists, as shown in Figure 2-6, of two pairs of precisely aligned parallel cylindrical rods, typically stainless steel or molybdenum, of circular or hyperbolic section on the axis of the ion beam, with both RF oscillator and direct DC currents applied to each pair. The result of that is having positive voltages on one pair and negative voltages on the other pair at any point in time, which swaps.

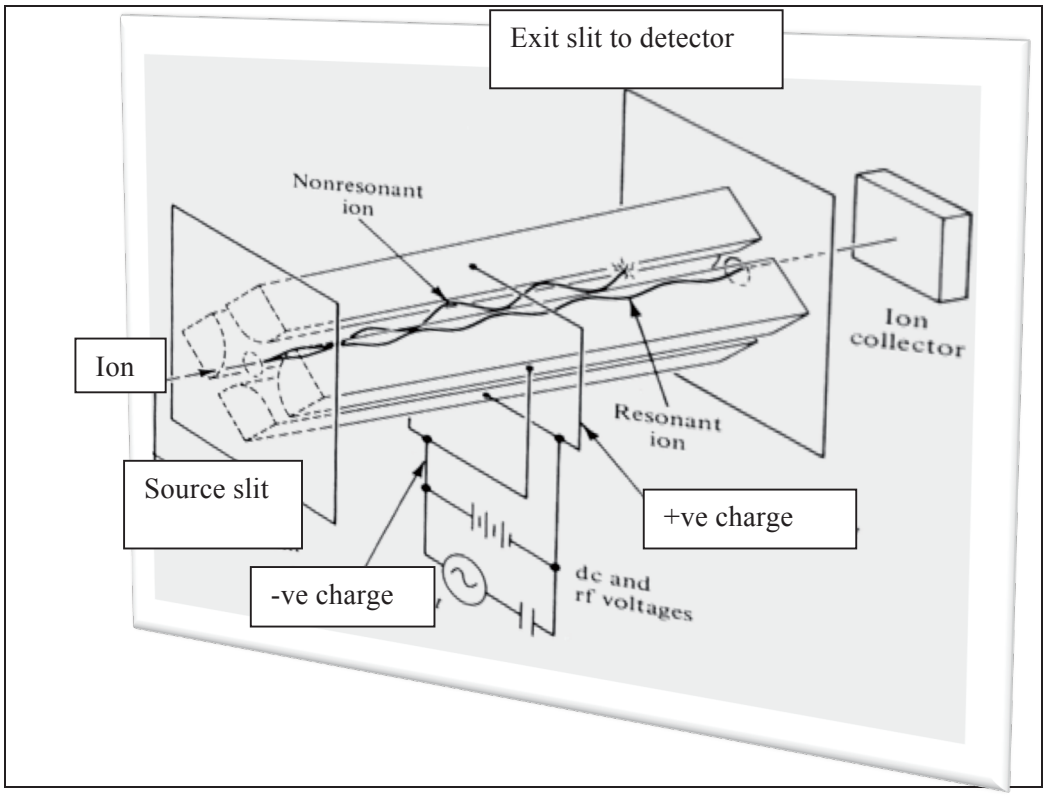


Figure 2-6 Ion path through quadrupole mass analyzer (Adapted)[176]

As the transmitted ion enters the quadrupole, it will undergo transverse motion and will adopt an oscillatory path because DC fields focus positive ions in the positive part and defocus them in the negative part of the cycle repeatedly. The oscillatory path gains

increasing amplitudes until some ions collide with the electrodes and become neutralized. The mass separation takes place by selecting the AC/DC ratio of the rods, which electrostatically steer the preselected m/z ion to the middle of the rods allowing it to pass through to the detector. This is repeated for each m/z ratio, allowing different analytes to be detected.

Detector

The detector in ICP-MS is responsible for the high sensitivity and low random background. The selection of the detector depends on the design of the instrument and the analytical applications. The most widely used ion detector in ICP-MS is the electron multiplier.

The electron multiplier detects ions based on kinetic energy transfer by collision and then generates secondary electrons which are further amplified to generate an electronic current as seen in Figure 2-7. Such amplification is important to obtain a signal as the number of initial ions is generally small. On reaching the last dynode, a large pulse will have build up to be measured as an ion count. The electron multiplier operates under vacuum condition of < 6.67 x 10^{-5} m bar and typically consists of 12-20 discrete dynodes where the first dynode is held at higher negative potential of around -5000 V compared with the rest. The electronic current generated is finally measured and converted into a voltage signal which is transformed to a suitable digital value.

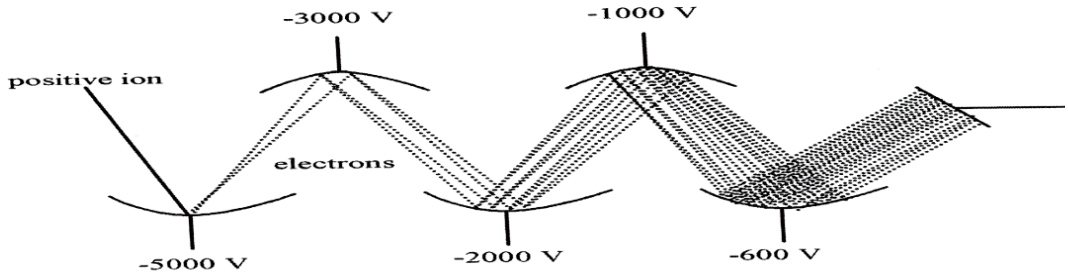


Figure 2-7 Electron multipliers detector[174]

2.1.2 Limitation and interferences of ICP-MS

Spectral interferences and high total dissolved solids (TDS) samples can both cause problems during analysis by the ICP-MS.

In some instruments a special high matrix introduction (HMI) technology is used to extend the TDS range of components to above 0.2 % (2000 mg L^{-1}). This eliminates matrix effects by diluting sample with gas and allows high matrix samples such as seawater to be analysed.

Spectral interferences in quadrupole ICP-MS are:

-Isobaric interferences that occur because of the overlapping of almost identical atomic masses of different elements, such as ^{40}Ca with ^{40}Ar, ^{204}Hg with ^{204}Pb.

- Polyatomic interferences (molecular interferences) that occur because of the mass overlap between the element of interest and polyatomic ions derived from the plasma Ar gas or the reagents used during preparation of the sample, such as:

^{39}K with $^{38}Ar^{1}H^{+}$, $^{51}V^{+}$ with $^{35}Cl^{16}O^{+}$, ^{52}Cr with $^{40}Ar^{12}C^{+}$, $^{36}S^{16}O^{+}$ and $^{35}Cl^{16}O^{1}H^{+}$

$^{56}Fe^{+}$ with $^{40}Ar^{16}O^{+}$,^{75}As with $^{40}Ar^{35}Cl^{+}$, and $^{80}Se^{+}$ with $^{40}Ar^{40}Ar$.

- Doubly charged interferences due to the loss of two electrons (z = 2) instead of one, so the m/z ratio will be half. This is particularly problematic Ba, Ce, La, Sr and ^{173}Th. For example $^{136}Ba^{2+}$ overlaps on $^{68}Zn^{+}$.

A collision/reaction cell (CRC) is used in ICP-MS to remove spectral interference and avoid biased results. It consists of an ion guide located after the ion lenses. The interaction of the collision/reaction gas, such as ammonia, helium, hydrogen or oxygen, with the ion beam removes interferences by:

- Reaction mode: where the gas reacts with interferences to convert it to a different species, such as using hydrogen to eliminate $^{40}Ar^{+}$ interference on $^{40}Ca^{+}$ via the following: $H_2 + {}^{40}Ar^{+} \rightarrow Ar + H_2^{+}$

- Collision mode: where the gas collides with the interferences causing it to lose energy and it is then separated from the higher energy analyte by an energy discriminator.

2.1.3 Data quality objectives[177, 180, 181]

Before processing the data obtained, it is important to ensure the data quality through different data quality objectives such as:

Limit of detection (LOD)

Limit of detection is defined as the lowest concentration of an analyte that can be reliably detected[180]. Instrumental LOD is obtained by the instrument from the relation:

$$\text{LOD} = \frac{3\ (\text{standard deviation of 10 replicates of the lowest concentration of the standards})}{\text{Gradient of the calibration slope}}$$

While the procedural LOD_p is calculated by:

$$\text{LOD}_p = \frac{(\text{LOD x volume of makeup sample x dilution factor})}{\text{Weight of sample}}$$

Relative standard deviation (RSD)

Relative standard deviation is the expression of precision of data. It is obtained by multiplying the SD x 100 and then dividing by the mean (for the repetition values).

$$\text{SD} = \sqrt{\frac{(x_1 - x_m)^2 + (x_2 - x_m)^2 + (x_3 - x_m)^2}{(n-1)}}$$

Where; x_1, x_2 and x_3 are the individual values of each repetition, x_m is the mean value, and n is the number of repetition.

Quality check and practice during the analysis

During the analysis by ICP-MS, a check sample (low concentration standard) was repeatedly run every 10 samples. From each batch of samples, one sample was randomly selected to run separately several times to check for the instrument precision with average SD of ±. Certified reference materials were run twice during the analysis along with the samples.

2.1.4 Agilent 7700x ICP-MS conditions

In current study, Agilent 7700x ICP-MS instrument by Agilent Technologyies, (Wokingham, Berkshire,UK) was used. Plasma conditions are summarised in Table 2-1.

Table 2-1 ICP-MS condition for semi-quantitative and quantitative analysis to determine PTE in virgin plastic resin pellets.

ICP-MS plasma conditions for Agilent 7700x	
RF Power	1550 W
Carrier gas flow	0.85 L min^{-1}
Plasma gas flow	15 L min^{-1}
Auxiliary gas flow	0.9 L min^{-1}
He gas flow	4.5 mL min^{-1}
Nebulizer pump	0.1 rps
Scanning mode	Semi-quantitative for semi-quantitative analysis Multi tune mode for quantitative analysis

Calibration of the instrument for each analysis was achieved by using five matrix matched standard solutions, for each experiment, prepared from the single or multi element Plasma CAL 1000 µg mL^{-1} standards by serial dilution.

2.2 Fundamentals of the analytical scanning electron microscope

The scanning electron microscope (SEM) with energy-dispersive EDS analyser is used for the examination and analysis of the microstructure morphology and chemical composition characterizations of solid samples.

A focused beam of high-energy electrons (from the electron gun as shown in Figure 2-8) is used as a probe to generate a variety of signals at the surface of solid specimens (sample). The signals that derive from electron-sample interactions are used to get information about the microscopic examination and the sample analysis.

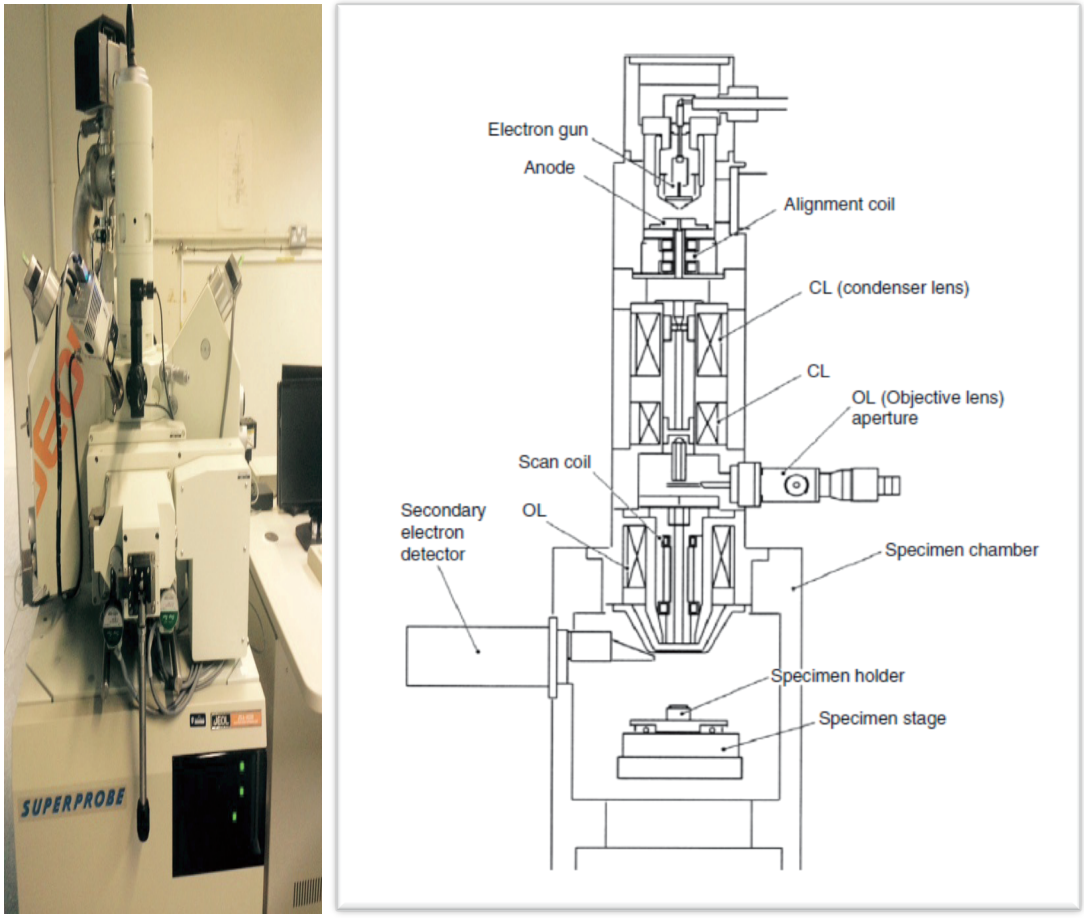


Figure 2-8 Essential components of SEMs include: electron source -gun, electron lenses, sample stage, detectors for all signals of interest and data output device[182].

The electron-sample interaction generates different type of electrons and energy quanta as seen in Figure 2-9 such as auger electrons, backscattered electrons, secondary electrons and X-rays which arise from different depths of the sample surface, providing high resolution microscopic information.

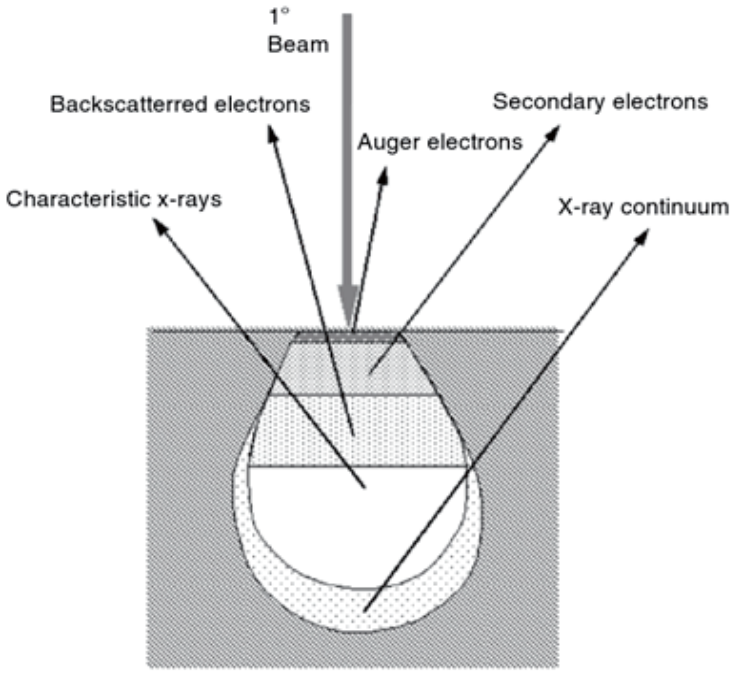


Figure 2-9 Interactions between sample and electron beam in SEM[182].

2.2.1 The main components of SEM[182-185]

Electron gun

The electron gun is located on the top of the SEM column. It is the source of the electron beam which accelerates to between 0.1 and 30 KeV under high vacuum. The gun (tungsten) produces a large diameter electron beam that cannot form a high resolution image as a consequence lenses are used.

Lenses

Lenses (electro-magnetic) are used to focus and define the diameter of the electron beam from about 50 μm down to 1 – 100 nm to produce clear and detailed images. Types of lenses used in SEM are:

- Electron lenses: used to magnify or focus the electron beam size, so a narrow probe is formed on the surface of the specimen.
- Condenser lenses: used to converge the electron beam into a parallel stream after it diverges by passing through the anode plate.
- Objective lenses: used to instruct and channel the electron beam onto a specific point of the specimen surface and to supply further focusing.

Sample chamber

This is located in the lower part of the column where the specimen is placed, and it manipulates the specimen for different angle images.

Detectors

The SEM requires three detectors to cover all signals derived from electron-sample interaction at the surface of specimen. Types of detectors used in SEM are:

- Secondary- electron detector: produces images that reflect morphology and topography (surface imaging including qualitative and quantitative information)
- Back scattered electron detector: determines crystal structures and orientation of mineral decomposition
- X-ray detector: detects photons to produce elemental analysis or scanning.

2.2.2 Limitations of SEM

Samples must be stable, solid and in a size that fits into the specimen holder (< 100 mm), with a maximum vertical dimension of 40 mm. Energy dispersive X-ray spectroscopy which is used as an x-ray detector cannot detect elements with low atomic

number such as H, He and Li, and it has a poor energy resolution and sensitivity to low concentration elements present in the sample[184, 185].

2.2.3 Analytical scanning electron microscope conditions

In current study, analytical scanning electron microscope JSM-6010 LA (SEM-EDS) was used. Table 2-2 shows the conditions used.

Table 2-2 Analytical scanning electron microscope conditions used for the surface imaging and elemental scanning of plastic resin pellets.

Volt	15.00 kV
Magnitude	x30 - x10000
Process time	T4
Live time	100.00 sec
Count rate	~ 1054 CPS

2.3 Fundamental of Infrared (IR) spectroscopy

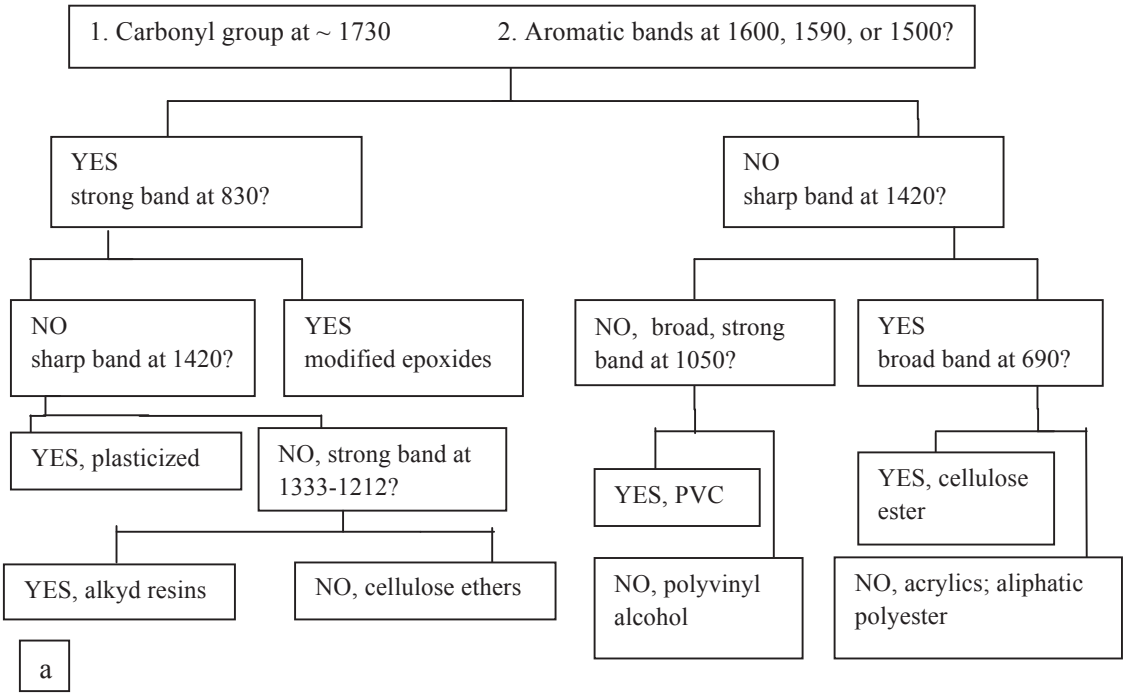
In the infrared (IR) region of the electromagnetic spectrum, absorption takes place due to molecular vibration. Molecular vibration is then separated by energy in the IR in a wavelength ranges from 13000-10 cm^{-1}, divided as:

- near-infrared region at ~ 13000-4000 cm^{-1},
- mid-infrared region at 4000-1300 and 1300-650 cm^{-1}, and
- far-infrared region at 667-10 cm^{-1}.

From such spectra, information about functional groups and groups affected by molecular interactions (hydrogen bonding) can be extracted.

The main application for the IR is structural identification where the band characteristic and group frequencies that appear in the IR spectrum are used to specify the molecular structure.

For materials such as polymers, a decision tree technique is used to identify materials such as drugs and polymers. Figure 2-10 summarises a decision tree of a polymer in the presence of a carbonyl band near 1730 cm^{-1} and the typical spectra region for polymers which was used in this study.



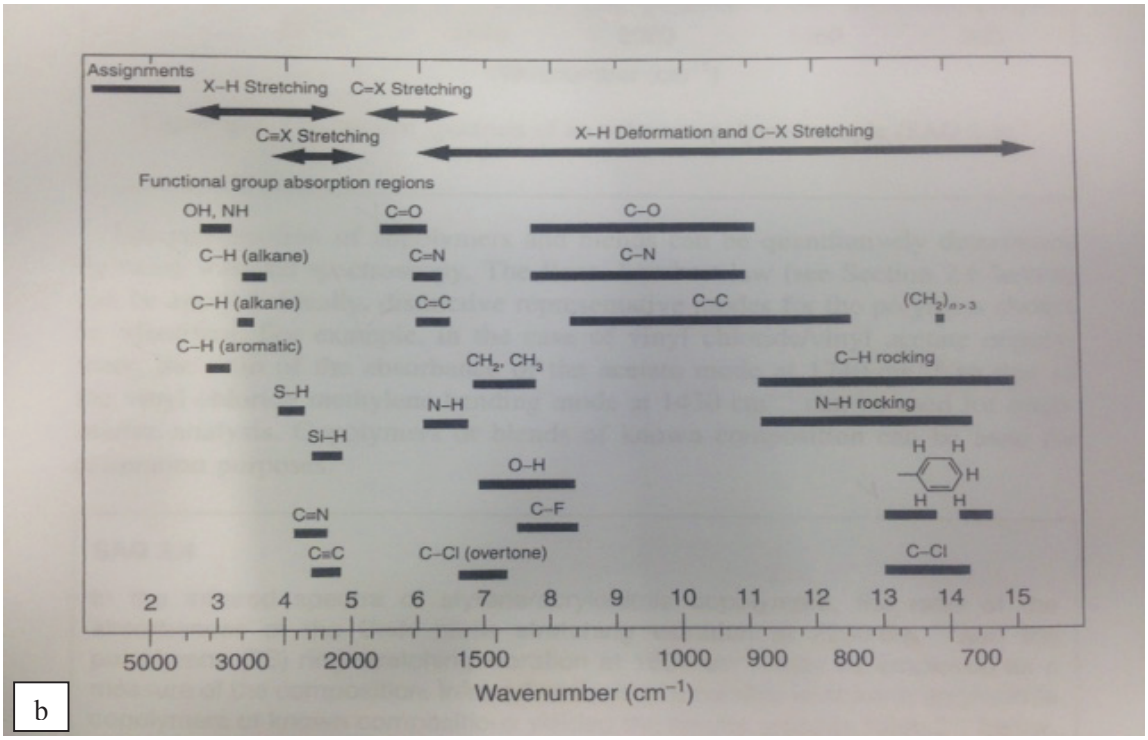


Figure 2-10 a: Decision tree for polymer identification in the presence of carbonyl group. (Adapted)[186], b: Typical spectra region for polymers[183].

2.3.1 The maincomponents of infrared spectroscopy

One class of IR instrument is non-dispersive, where an interference filter with a laser source or an interferometer is used in Fourier transform infrared (FTIR). The main components of the FTIR as seen in Figure 2-11.are

- Infrared source
- Moving and fixed mirrors
- Beam splitter
- Detector

As the infrared radiation of the source hits the mirror above it (collimator), a reflected beam is divided into two halves by the beam splitter to the moving and fixed mirrors, then recombines at the beam splitter. It will then pass through the sample compartment and become focused onto the detector; the resulting signals (an interferogram) store as a memory and undergo mathematical Fourier transformation to the final spectrum presented.

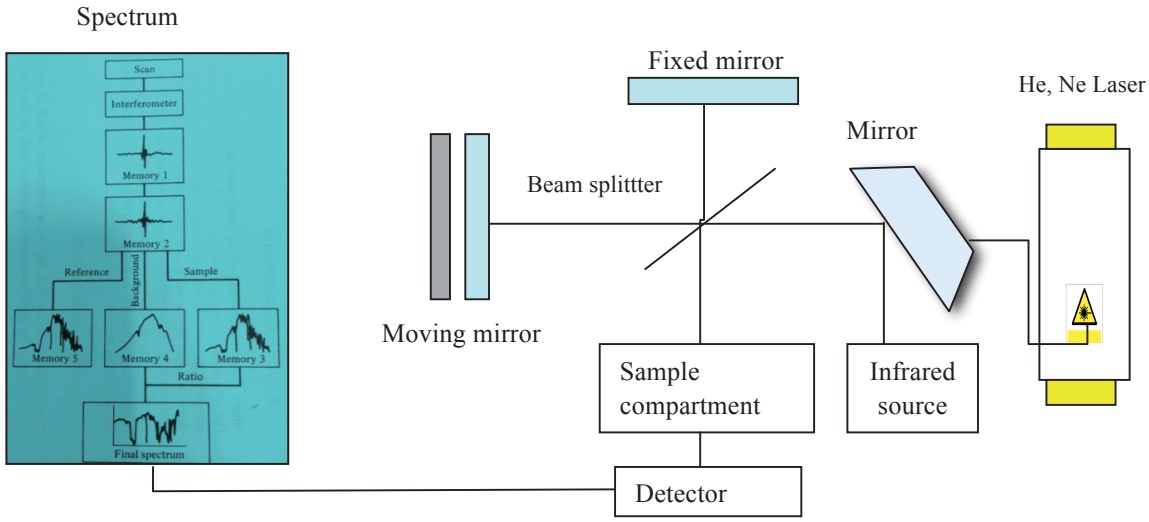


Figure 2-11 Infrared Fourier transform spectrometer block diagram with the instrument functions (Adapted)[176, 187]

In FTIR, as the IR radiation passes through a sample, part will be absorbed and part will be transmitted where both initiated the fingerprint of the sample. So, the final spectrum is a combination between the signals obtained plus a background spectrum.

2.3.2 General advantages of FTIR

The FTIR has several advantages over other classes. It is fast where all measurements of frequencies are made simultaneously; it is self calibrating by the use of helium-neon laser as a wavelength calibration standards; samples need minimum or no preparation prior to analysis; and it is non destructive and easy to use.

2.3.3 The FTIR conditions

In current study, 5500 Series compact FTIR with attenuated total reflectance ATR by Agilent Technologies, (Wokingham, Berkshire,UK) was used to establish and to identify beached pellets. Instrument conditions are shown in Table 2-3.

Table 2-3 FTIR standard conditions used for the plastic pellets identification.

Background valid time limit	10 minutes
Background scans:	128
Samples scans	128
Resolution (cm-1)	8 cm^{-1}
Sampling technology	ATR
Sampling subtype	1-Bounce

3 Experimental methods

3.1 Initial investigation of PTE content in virgin pellets

3.1.1 Apparatus and reagents

Samples were digested with Trace -SELECT nitric acid (HNO_3) for trace analysis which was supplied by Sigma Aldrich (Gillingham, Dorset, UK). A Fisher brand, (Loughborough, UK) 125 mm filter paper was used to filter samples after they had been digested using a MARS Xpress laboratory microwave digestion system CEM, (Buckingham, UK). Along with the samples, polyethylene JSM P 700-1 Plastic Reference Material for Chemical Analysis (RM) supplied by JFE techno-research corporation (Tokyo, Japan) was analysed which was selected because polyethylene represent 50 % of petroleum-based pellets of the current study and covers the PTE of interest. Samples were then analysed by the Agilent 7700x ICP-MS instrument Agilent Technologies, (Wokingham, Berkshire, UK). Internal standard solution for ICP-MS from Agilent technologies, (USA) was used to prepare 3 mg L^{-1} internal standard. Virgin plastic resin pellets were supplied as stated in Table 3-1.

Table 3-1 Virgin plastic resin pellets suppliers

Type of virgin plastic pellets	**Suppliers**
polyethylene (PE)	Producer from the UK*
polypropylene (PP)	Lyondellbasel, Carrington,UK.
polyethylene terephthalate E333 (PET)	DuPont Teijin Films, Wilton-Redcar, UK.
polyhydroxybutyrate (BIO)	Monsanto, Antwerp, Belgium.

* Given by Dr. John Liggat, pure and applied chemistry department, University of Strathclyde, UK.

3.1.2 Procedure

A total of 0.25 g test portion of virgin plastic resin pellets were weighed and placed into microwaveable vessels - this weight was used as recommended by MARS Xpress for plastic microwave digestion, then 10 mL of nitric acid was added and subjected to microwave acid digest as shown in Table 3-2. The solutions were then filtered, made up to the mark in 50 mL volumetric flask, and transferred to 50 mL polypropylene tubes. For analysis by ICP-MS, 10 mL of each sample were sub divided in 10 mL tube, plasma conditions are summarised in Chapter 2, Table 2-1. All samples were diluted X10 and all samples, the RM and blank, were prepared in triplicate. A mixture of (^{7}Li, ^{45}Sc, ^{72}Ge, ^{103}Rh, ^{115}In, ^{159}Tb, ^{175}Lu and ^{209}Bi) internal standard was used during the analysis to correct for a non spectra interferences. This procedure was applied for both; preanalysis semi-quantitative analysis and quantitative analysis.

Table 3-2 The recommended MARS Xpress microwave programs used to digest virgin plastic pellets.

Program	Power		Ramp time (min)	Pressure (psi)	Temp (˚C)	Hold time (min)
PE	400	100%	15	800	200	15
PET	400	100%	15	800	230	15
PP	400	100%	20	800	210	15
BIO	400	100%	15	800	210	15

Standard solutions for the quantitative analysis were prepared to calibrate the instrument (1 – 50 µg L^{-1}). Multi element calibration solutions were prepared by serial dilution of 10 mg L^{-1} of Ag, Al, As, Cr, Cu, Mn, Mo, Ni, Pb, Se, Sn, V, Zn and 1000 mg L^{-1} of Ba, Co, Fe, Mg, Na, Sb and Si using Plasma CAL, SCP Science supplied by Qmx (Essex, UK).

A recent study[188] proposed a method to determine PTE in plastic using laser ablation inductively coupled plasma mass spectrometry but it was only used for plastic reference materials. Therefore, the use of ICP-MS is used as one of the best methods for the analysis of PTE in plastic.

3.1.3 Limitations of the PTE study in plastic pellets

In this study, PTE in different types of plastic pellets were determined by weight. The limitation of this comparison was the neglecting of the density and surface area of each 0.25 g of pellets. The 0.25 g of HDPE, LDPE, PP, PET and BIO plastic pellets were about 19, 6, 9, 4 and 13 pelles respectively.

3.2 Laboratory-weathering of plastic pellets

3.2.1 Apparatus and reagents

Accelerated weathering was carried out using a Atlas SUNTESTXLS+ Weathering benchtop tester Atlas material testing technology Ltd., (Leicester, UK), and then placed in artificial seawater prepared using Lake products LLC sea salt ASTMD 1141-98 13, supplied by Lake products company LLC (Florissant, USA).

3.2.2 Procedure

Virgin plastic pellets were placed in an Atlas SUNTEST XLS+ weathering tester, using (750 W/m^2) irradiance, for three weeks continuously. Samples were exposed to light and heat at a temperature of 32˚C as an extreme temperature for the surface sea water according to the National Oceanic and Atmospheric Administration-NOAA. To ensure the exposure of all pellet surfaces to light, samples were shaken every 3 days. Samples were then placed in artificial seawater (41.953 g of sea salt dissolved in 1 L of deionised water) for the same period of time. Discoloration was observed in different degree on some weathered samples, as seen in Figure 3-1.

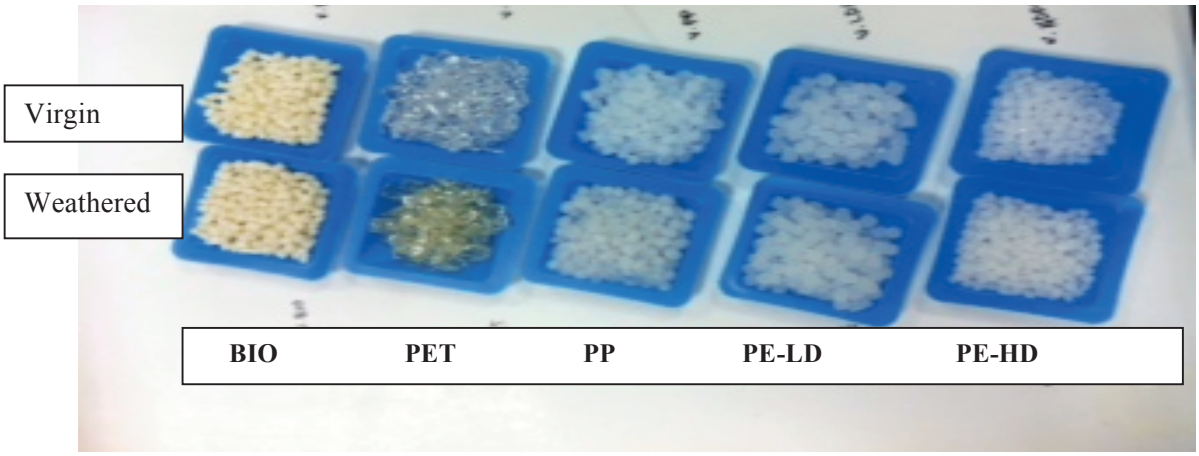


Figure 3-1 Discoloration of virgin plastic resin pellets after three weeks laboratory-weathering.

3.2.3 Limitations of the laboratory-weathering of plastic pellets

In natural weathering of plastic pellets in seawater, pellets exposure to light, heat, seawater and waves movements all together, whereas in laboratory this approach was achieved sequentially.

Laboratory-weathering achieved in this study represent the natural weathering of plastic pellets in seawater, weathering of ingested plastic through trophic transfer was not achieved by this procedure.

3.3 Establishment of the sorption potential of plastic pellets for selected PTE

3.3.1 Apparatus and reagents

A single element standard of arsenic (prepared from As_2O_3) Plasma CAL 1000 µg mL^{-1}; single standard of cadmium (prepared from $Cd(NO_3)_2.4H_2O$) BDH spectrosol 1000 mg L^{-1}, single standard of chromium (prepared from $Cr(NO_3)_3.9H_2O$) Plasma CAL 1000 µg mL^{-1}; single standard of lead (prepared from $Pb(NO_3)_2$) Plasma CAL 1000 µg mL^{-1} was used individually to prepare the selected PTE solution for each experiment by serial dilution. Lake products LLC sea salt ASTMD 1141-98 13 Lake products company LLC, (Florissant, USA), still spring water pH 7.8 which will be called fresh water and deionised water were used for each experiment medium. Trace-SELECT nitric acid for trace analysis Sigma Aldrich, (Gillingham- Dorset, UK) was used to acidify samples to pH< 2 after the sorption experiment and preserved them appropriately for analysis to prevent any loss and stabilise the concentration of analyte. The experiments were carried out in Environmental express 50 mL digestion vials, Fisher 50 mL centrifuge vials were also used to transfer and subdivided the sample for analysis. The experiments took place in a Stuart orbital incubator SI 500 Bibby scientific limited, (Stone, Straffordshire, UK) shaking at 120 rpm and ~25 ˚C. The element uptake was determined by using an Agilent 7700x ICP-MS instrument Agilent Technologies, UK Ltd., (Wokingham- Berkshire, UK). For each experiment, five matrix matched standard solutions were prepared from the single element standards by serial dilution. Table 3-3 shows the fresh water minerals. Table 3-4 shows the sea salt gradient used to prepare the artificial seawater.

Table 3-3 Fresh water-still spring (drinking) water minerals in mg L^{-1}

Water minerals	**Concentration in mg L^{-1}**
Calcium	38
Chloride	12
Magnesium	12
Nitrate	5
Potassium	2.5
Sodium	8
Sulphate	14

Table 3-4 sea salt ASTM D1141-98 gradient used to prepare the artificial seawater

Seasalt ASTM D1141-98	**Proportional percentage of each seasalt components**
NaCl	58.49
$MgCl_2$-$6H_2O$	26.46
Na_2SO_4	9.75
$CaCl_2$	2.765
KCl	1.645
$NaHCO_3$	0.477
KBr	0.238
H_3BO_3	0.071
$SrCl_2$-$6H_2O$	0.095
NaF	0.007

3.3.2 Procedure: single element sorption

A total of 0.5 g of each type of plastic pellet was weighed and placed in a vial containing 50 ml of a 5 µg L^{-1} solution of the selected PTE, this weight was selected to achieve the recommended 1 to 100 weight (g) to volume (mL) as shown in literature[118]. Then it was

subjected to shaking for up to 100 hrs in an orbital incubator at ~ 25 ˚C. Samples were collected at different times (in each time 5 individual vials of the 5 different pellets type samples, blank and control was removed from shaker). Blanks were prepared by placing the plastic pellets in the media to check for any leaching of interested PTE from the pellets to the media of each experiment, whereas the controls were prepared by placing the 50 ml of a 5 µg L^{-1} solution of the selected PTE in the absence of the plastic pellets as a control of any loss of the concentration by the vial walls. Decants were acidified and preserved appropriately for analysis by ICP-MS using the same conditions as in Table 2-1, chapter 2 except for the seawater, where the dilution mode, (HMI) was turned ON. Table 3-5 summarises the procedure of the sorption experiment. Internal standard stock solution for ICP-MS of 100 mg L^{-1} ^{7}Li, ^{45}Sc, ^{72}Ge, ^{103}Rh, ^{115}In, ^{159}Tb, ^{175}Lu and ^{209}Bi from (Agilent technologies, USA) was used to prepare 3 mg L^{-1} internal standard, ^{45}Sc, ^{72}Ge, ^{115}In and ^{209}Bi were mainly selected for the analysis of ^{52}Cr, ^{75}As, ^{111}Cd and ^{208}Pb respectively.

Blanks of each type of pellets placed in the media of each experiment were used during the experiment in order to find out if there was any leaching from the pellets into the solution media, while the controls were used to detect any element uptake by the vials wall in the absence of the plastic pellets.

Table 3-5 Summary of the monoconcentration PTE sorption experiment for different type of plastic pellets

Plastic pellet type	**Weight**	**Medium**	**Control**	**Blank**
virgin pellets	0.5 g	deionised water	5 µg L^{-1}PTE in deionised water	pellets in deionised water
virgin pellets	0.5 g	fresh water	5 µg L^{-1} PTE in fresh water	pellets in fresh water
virgin pellets	0.5 g	seawater	5 µg L^{-1} PTE in seawater	pellets in seawater
weathered pellets	0.5 g	seawater	5 µg L^{-1} PTE in seawater	pellets in seawater

3.3.3 Procedure: multi element sorption

A total of 0.5 g of each type of plastic pellet was weighed and transferred to the vial containing 50 ml of a 5 μg L^{-1} solution of As, Cd, Cr and Pb prepared by serial dilution of the single element stock solutions. Then it was subjected to shaking in an orbital incubator at ~ 25˚C. Samples were collected at a single time (equilibrium time) along with prepared blanks and control. Decants were acidified and preserved appropriately for analysis by ICP-MS as described in Section 3-3-2.

3.3.4 Limitations of sorption study

Adsorption study of selected PTE by plastic pellets was extended to up to 100 hours instead of concentrating it in a shorter time which can better assess the adsorption equilibrium time. However this time was selected to mimic the long period of time that plastic debris including plastic pellets travel in seawater.

Due to the large amount of samples included in this experiment, single rather than triplicate samples were used to investigate the pattern of the sorption during the 100 hours of the experiment.

3.4 Surface study of the plastic pellets using the analytical scanning electron microscope JSM-6010 LA (SEM)

This experiment was conducted to identify the elemental content and the topography of virgin and weathered plastic resin pellets by surface imaging and elemental scanning of individual pellets.

3.4.1 Apparatus

A JFC-1600 Auto fine coater JEOL Ltd, (Tokyo, Japan) was used in the pre-treatment step to coat non-conductive specimens for use in a scanning electron microscope. Plastic resin pellets were placed on Carbon-double sided tape. The analytical scanning electron microscope JSM-6010LA, JEOL was used to scan coated pellets along with polyethylene JSM P 700-1 Plastic Reference Material for Chemical Analysis JFE techno- research corporation, (Tokyo, Japan).

3.4.2 Procedure

A single plastic pellet from each of the virgin and weathered samples was rinsed with deionised water, air dried, and then placed on the C-tape (double sided carbon tape), and then subjected to platinum coating by the auto fine coater as shown in Figure 3-2. Because plastic is not conductive, it is recommended to coat it with a conductive material such as platinum in order to get clear image and to keep the chamber clean as the sample may segment as shown in Figure 3-3. Coated samples were then placed on the specimen holder for surface imaging and elemental scanning by the SEM. Table 2-2 in chapter 2 shows the SEM conditions used for this purpose.

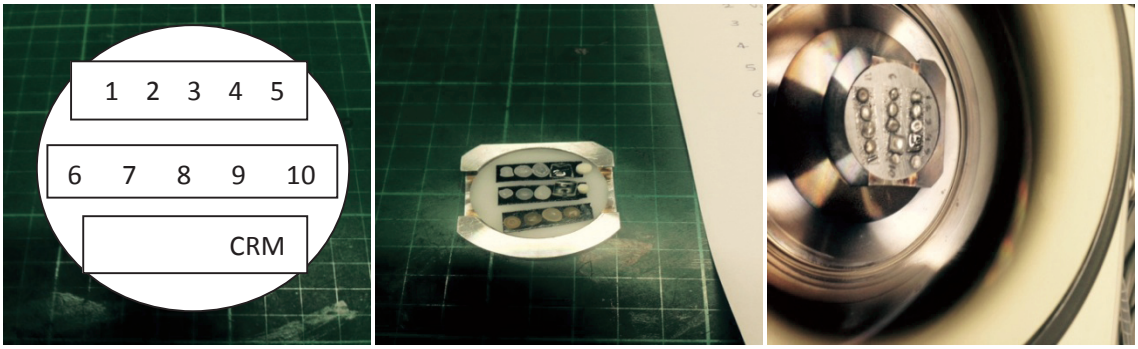


Figure 3-2 Plastic pellets on the C-tape before and after the platinum coating using auto fine coater JEOL. 1: Virgin HDPE, 2: virgin LDPE, 3: virgin PP, 4: virgin PET, 5: virgin BIO, 6: weathered HDPE, 7: weathered LDPE, 8: weathered PP, 9: weathered PET, 10: weathered BIO, and CRM.

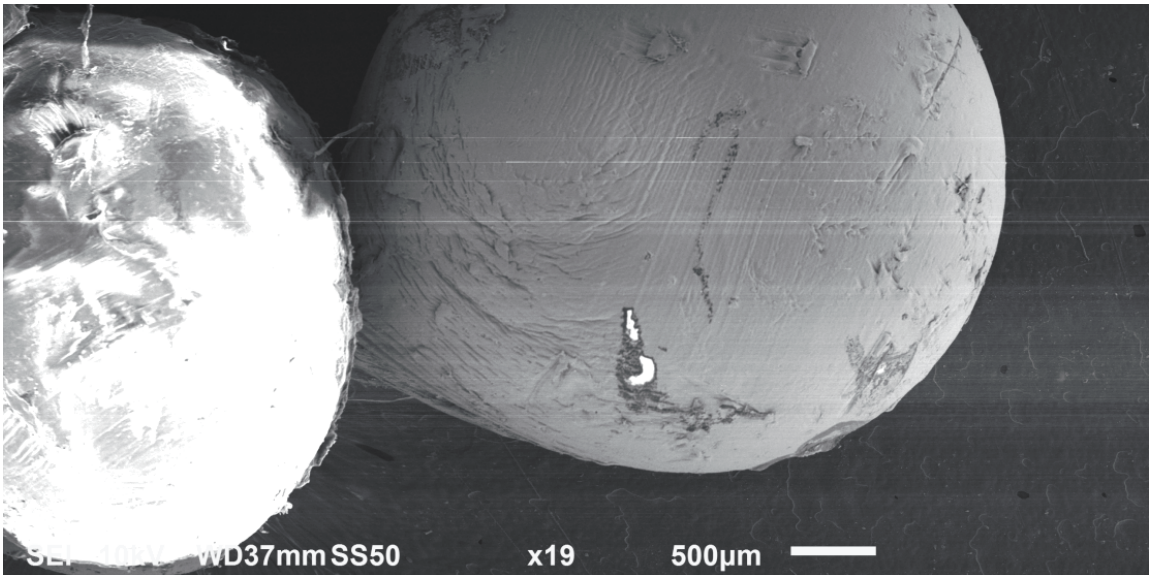


Figure 3-3 The image of uncoated plastic pellet sample using scanning electron microscope. It shows how sample was teared apart (left image).

3.4.3 Limitations of SEM study

The variation of this study was conducted within a single sample of each type of pellets, mainly for the elemental scanning study. Triplicate samples of each type of pellets or more can be more convenient for a robust study and findings. This limitation allows only reporting observations instead of findings.

4 Establishment of the sorption potential of plastic pellets for selected PTE

4.1 Initial investigation of PTE content in virgin pellets

Five types of virgin plastic pellets, high density polyethylene (HDPE), low density polyethylene (LDPE), polyethylene terephthalate (PET), polypropylene (PP), and bio-based polyhydroxybutyrate-co-hydroxyvalerate (BIO) were microwave-acid digested and chemically analysed to determine the total PTE present following the manufacturing process. Total PTE investigation gives no further information about speciation or toxicity can be determined. Semi-quantitative analyses were first conducted by ICP-MS to scan the samples, and thereby provide an overview of the elements present followed by a quantitative analysis via ICP-MS to determine the exact concentration of the selected PTE.

As stated in Section 1-2-3, additives, such as lubricants, heat stabilisers and fillers, and heterogeneous catalysts are used in plastic production. Catalysts contain a mixture of aluminium, calcium, chromium, magnesium, silicon, sulfur, titanium, and zirconium[129], whilst aluminium, antimony, barium, cadmium, calcium, cobalt, iron, lead, magnesium, silicon, sodium, tin, and zinc are expected in different additives[129, 144]. These elements might be present in virgin plastic pellets, and it is important to measure their levels so as to be sure that, when analytes are added in sorption experiments (see Sections 4-2-1 to 4-2-4), they originate predominantly from the spiking solution and not the pellets.

When a semi-quantitative scan of the nitric acid digest of the virgin plastic pellets was carried out, 30 elements were detected (see Appendix 1) the majority of which were, as expected, associated with some aspects of plastics manufacture. Some analytes were selected for quantification. Elements associated with plastics manufacture but detected in low concentrations (e.g. Ca, Zr), elements not associated with plastics manufacture (e.g. U, W), and elements that could not be quantified reliably using ICP-MS (e.g. S) were excluded from quantification. Arsenic was also included, since it is a key element

of environmental concern. As a result, aluminium, antimony, arsenic, barium, cadmium, chromium, cobalt, iron, lead, magnesium, silicon, sodium, tin, and zinc were selected to be analysed quantitatively. The analysis was performed in triplicate, together with a plastic RM.

Table 4-1 shows the recoveries of PTE in the plastic RM with respect to certified values. According to ISO guide-33 (1988) and z-score all values obtained were acceptable compared to the certified values, and average recovery was 101 ± 8 %. Although the RM does not contain all analysed elements, recoveries obtained for the certified elements support the accuracy of the method of analysis used and it also support the reliability of the other elements not included in the RM used.

In all tables presented in this study, the (±) values represent the standard deviation of replicate samples and (n) is the number of sample preparation replicates unless otherwise stated.

Table 4-1 Obtained concentrations of PTE in JSM P 700-1 Plastic Reference Material for Chemical Analysis (n=3)

Elements	**Certified values (µg L^{-1})**	**Obtained values (µg L^{-1})**	***Recovery%**
As	9.1 ± 0.9	10.2 ± 1.1	112*
Cd	5 ± 0.6	4.99 ± 0.08	99.8
Cr	4.9 ± 0.6	4.52 ± 0.27	92.0
Pb	5 ± 0.6	5.05 ± 0.04	101

*The recovery % were calculated based on the main average given certified values which can explain the higher recovery value obtained for As.

Table 4-2 shows the quantified PTE in each type of virgin plastic pellet, presenting means, SD, and RSD values for ease of comparison. Individual concentrations are presented in Appendix 2.

Table 4-2 Quantitative analysis of PTE in high density polyethylene, low density polyethylene, polypropylene, polyethylene terephthalate and polyhydroxybutyrate-co-valerate virgin plastic pellets in µg g^{-1} (n=3).plus the procedure limit of detection.

Element	HDPE	LDPE	PP	PET	BIO	LOD_p µg g^{-1}
Al						
Mean	23.2	6.18	7.48	4.92	6.57	0.02423
SD	±20.5	±4.04	± 4.94	± 0.494	± 0.5082	
RSD	88.1	65.3	66.1	10.0	7.73	
As						
Mean	0.00441	0.00143		0.0147	0.0058	0.00102
SD	± 0.001	± 0.000602	< LOD	± 0.00124	± 0.000145	
RSD	22.8	42.1		8.46	2.50	
Ba						
Mean	0.687	0.631	0.556	0.697	2.07	
SD	± 0.0329	± 0.02904	± 0.0413	± 0.06029	± 0.0816	0.0062
RSD	4.79	4.59	7.43	8.64	3.94	
Cd						
Mean	0.00356	0.00299	0.00366	0.00418	0.00779	
SD	± 0.000958	± 0.000339	± 0.00151	± 0.00133	± 0.000703	0.00055
RSD	26.9	11.2	41.2	31.8	9.0	
Cr						
Mean	0.115	0.120	0.0931	0.0409	0.192	
SD	± 0.0414	± 0.00761	± 0.0068	± 0.445	± 0.0316	0.0024
RSD	35.6	6.29	7.30	108	16.4	
Co						
Mean	0.0131	0.0136	0.0178	10.8	0.0185	
SD	± 0.00243	± 0.00144	± 0.00668	± 0.249	± 0.00182	0.00037
RSD	18.5	10.5	37.5	2.29	9.82	
Fe						
Mean	13.3	16.4	19.2	12.6	20.4	
SD	± 3.00	± 4.12	± 12.8	± 0.605	± 1.61	0.01122
RSD	22.5	25.0	67.0	4.77	7.88	
Mg						
Mean	287	304	281	284	282	
SD	± 35.8	± 13.4	± 28.6	± 24.1	± 29.6	0.13295
RSD	12.4	4.41	10.1	8.51	10.5	
Na						
Mean	530	560	519	559	489	
SD	± 55.6	± 25.4	± 68.05	± 40.6	± 54.8	0.04737
RSD	10.4	4.54	13.1	7.27	11.2	
Pb						
Mean	0.214	0.206	0.197	0.317	0.213	0.01981
SD	± 0.0812	± 0.05102	± 0.0505	± 0.182	± 0.0117	
RSD	37.7	24.7	25.6	57.3	5.51	
Sb						
Mean	0.00607	0.00501	0.00542	47.3	0.02	
SD	± 0.00268	± 0.00014	± 0.00223	± 0.770	± 0.0107	0.001
RSD	44.1	2.79	41.1	1.62	53.5	

Element	HDPE	LDPE	PP	PET	BIO	LOD_p µg g^{-1}
Si						
Mean	25.9	12.9	10.7	14.2	30.9	
SD	± 22.8	± 3.55	± 0.424	± 1.68	± 1.76	4.495
RSD	88.0	27.3	3.95	11.8	5.71	
Sn						
Mean	0.113	0.0622	0.0228	0.0566	0.0666	
SD	± 0.0562	± 0.00624	± 0.0103	± 0.0216	± 0.0356	0.00069
RSD	49.6	10.0	45.4	38.1	53.5	
Zn						
Mean	35.7	10.3	1.71	5.12	16.84	
SD	± 29.6	± 9.14	± 0.401	± 1.86	± 6.82	0.02361
RSD	82.9	88.3	23.3	36.4	40.5	

4.1.1 Discussion of the results

All results obtained were above the limit of detection except for arsenic in PP which was below the limit of detection (0.000551 µg g^{-1} < 0.00102 µg g^{-1}). Most of the plastic pellet types contained antimony, arsenic, cadmium and silicon at concentrations within a factor of 10 of the respective LOD values (though the LOD for Si was relatively high at 4.49 µg g^{-1}).

The RSD of triplicate samples varied from less than 10 % up to 108 %. The RSDs were generally ≤ 10 % in PET and BIO types of pellets, except for the chromium, tin, and zinc, whereas they were ≥ 10 % in the PE and PP. This can be attributed to the better homogeneity of PTE in PET and BIO compared with PE and PP virgin pellets. Good precision was achieved for barium, magnesium and sodium where all RSDs were ≤ 10 % in all types of pellets. Particularly poor RSDs were obtained for aluminium in HPDE (88 %), chromium in PET (108 %), silicon in HDPE (88 %), and for zinc in HDPE (83 %) and LDPE (88 %). The results for aluminium (21.5, 3.66, 44.5 µg g^{-1}) and zinc (41.9, 3.51, 61.7 µg g^{-1}) were particularly variable among the triplicate samples of HDPE which may be attributed to extreme inhomogeneous distribution of both elements in the sample.

The quantitative results of analysis of the virgin plastic pellets showed that the most abundant elements were sodium and magnesium, with average concentrations of 531 μg g^{-1} and 287 μg g^{-1} respectively, for all pellets studied. The presence of both elements can be explained by the catalyst residue and additives added, plus the cooling and washing process – often involving seawater – that all virgin pellets are subjected to.
The next most abundant elements were, in decreasing concentration, silicon, iron, zinc and aluminium with average concentrations of 18.9 μg g^{-1}, 16.3 μg g^{-1}, 13.9 μg g^{-1}, and 9.67 μg g^{-1} for all pellets studied. All were expected to be present in the virgin pellets from either catalysts, additives, or both as explained in 4-1. The average concentrations of the remainder of the PTE analysed (arsenic, barium, cadmium, chromium, cobalt, lead and tin) were between 0.697 μg g^{-1} and 0.00443 μg g^{-1} except for antimony in PET which was 47.3 μg g^{-1}, cobalt in PET which was 10.8 μg g^{-1} and barium in BIO type of pellets which was 2.07 μg g^{-1}.

Antimony and cobalt were only present at high levels in PET pellets that are commonly used to produce drinking water and beverage bottles. Antimony is used as a stabilizer to protect plastic against heat and UV-light during processing and as a product, and is also used as a catalyst in the late stage polymerization of PET. Due to concern over the risk of antimony leaching into beverages[133, 189, 190], the concentration of antimony in different types of drinking water bottles has been studied, and was found[190] to be between 191-268 mg kg^{-1}. This is substantially higher than the level measured here because additional antimony-containing compounds are added during bottle manufacture. Cobalt is used in PET as a heat stabilizer[129]. Barium can be used in bioplastic to enhance the monomer ability to copolymerize as an inorganic filler and also as a barium chloride catalyst[191-193].

No information about the levels of PTE in virgin plastic pellets has previously been reported to compare the results of the current study with. Potentially toxic elements in plastic products such as toys and food packaging have been reported but often the type of plastic was not specified completely, but instead described by a generic label e.g. as "non PVC"[194-196]. As shown in Table 4-3, average PTE concentrations obtained in

plastic toys were higher than the results obtained in the virgin plastic pellets in the current study[195] which can be due to further additives being added during manufacturing and to pigments used for the final products.

Table 4-3 The concentration μg $g^{-1}$of PTE obtained in plastic toy products and virgin plastic pellets in current study.

Element	Omolaoye et al[194]. Acid digest 12 samples	Korfali et al[195]. 30 samples using EDXRF*	Current Study
Al	-	13.1 ± 21.8	9.67
Ba	-	4.3 ± 1.2	0.928
Cd	0.5 - 373	1.5 ± 4.6	0.00443
Cr	5.0 - 191	25.7 ± 20	0.112
Pb	2.5 -1445	16.6 ± 25.2	0.229
Sn	-	6.24 ± 8.5	0.0642
Zn	266 - 2043	222 ± 673	13.9

*EDXRF: Energy Dispersive X-ray Fluorescence

4.1.2 Conclusion

The PTE were successfully analysed in five types of virgin plastic pellets, the raw materials for manufacture of plastic goods. Detected elements were associated with one or more aspect of plastic production, including the use of metal catalysts and additives, as well as water cooling and washing. Potentially toxic element concentrations ranged from 0.00143 μg g^{-1} for arsenic in LDPE, to 559 μg g^{-1} for sodium in PET. Average concentrations of the elements to be used in the sorption experiments to follow (Chapter 4) were generally low – arsenic 0.00537 μg g^{-1}; cadmium 0.00443 μg g^{-1}; chromium 0.185 μg g^{-1}; and lead 0.229 μg g^{-1} – so leaching of additional analytes from virgin pellets is unlikely to be of concern.

4.2 Establishing the sorption potential of plastic pellets for selected PTE

This experiment was conducted to establish the adsorption potential and assess the capacity of HDPE, LDPE, PET, PP and BIO virgin and laboratory-weathered plastic pellets to uptake the PTE of interest, and to study their behaviour in different media (deionised water at pH 5.8, fresh water at pH 7.8, and artificial seawater at pH 8.5). A series of sorption experiments were performed, with the aim of determining the equilibrium time and the amount of PTE adsorbed under the experiment conditions, and to assess the influence of pellets' weathering on the adsorption of PTE.

The elements arsenic, cadmium, chromium and lead were selected for this study, based on:

- Results obtained in 4-1 where all showed low concentrations present in pellets i.e. leaching of selected elements from virgin pellets is unlikely to be of concern,
- Due to their toxicity and presence in the marine environment from both natural and anthropogenic sources,
- As key elements of environmental concern[197].

Laboratory weathering of petroleum-based HDPE, LDPE, PET, PP, and bio-based BIO virgin plastic pellets was applied to simulate naturally occurring degradation, but in a clean, accelerated, reproducible, and controlled environment, as described in Section 3-2. This artificial weathering process was used in order to avoid any contamination from the ambient environment, and to ensure that the reagents added during the experiments were the only source of the elements under study. Single element sorption experiments were conducted due to the low selectivity of the adsorption process of elements onto sorbent surfaces.

The remainder of this chapter will present the sorption profiles of each studied element in the five types of virgin and laboratory-weathered pellets described in Section 3-3, plus the control for each PTE and media (note that one control was used for PTE in seawater for both virgin and weathered plastic pellets). Blanks were run, but the results are not

included in the plotted figures because blank values were almost nil for all experiments. This indicated that there was no leaching of the elements of interest from the samples under experimental conditions as explained in section 3-3-2.

4.2.1 Arsenic sorption by five types of virgin and weathered plastic resin pellets: HDPE, LDPE, PET, PP and BIO.

4.2.1.1 Arsenic uptake by virgin plastic pellets in deionised water, fresh water and seawater

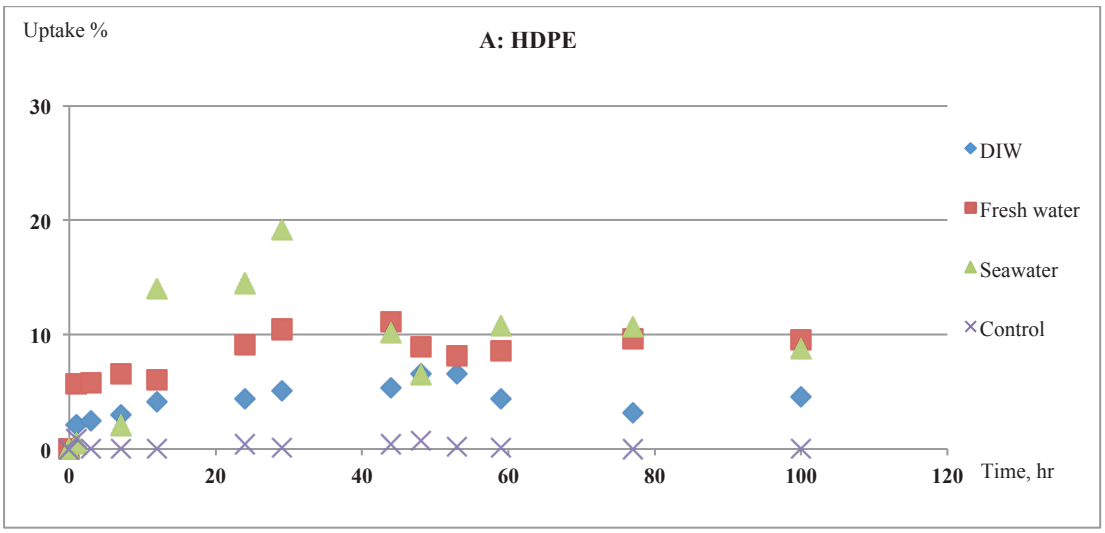
Each type of plastic pellet was shaken for 100 hours in a ~5 µg L^{-1} solution of arsenic (III) prepared in deionised water, fresh water and artificial seawater. The uptake % of arsenic in solutions, after 13 different time periods, is plotted in Figure 4-1.

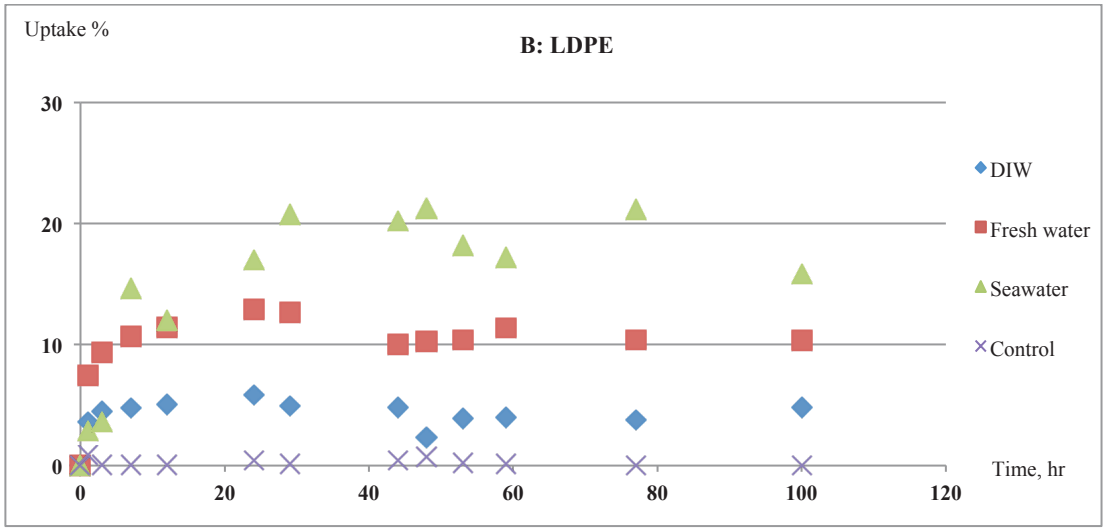
Tables A-1, A-2 and A-3 in Appendix 3 shows the remaining residual arsenic in the deionised water, fresh water and seawater solutions respectively at different times (over 100 hours) measured using ICP-MS, from which the uptake levels of the five types of virgin plastic pellets were determined.

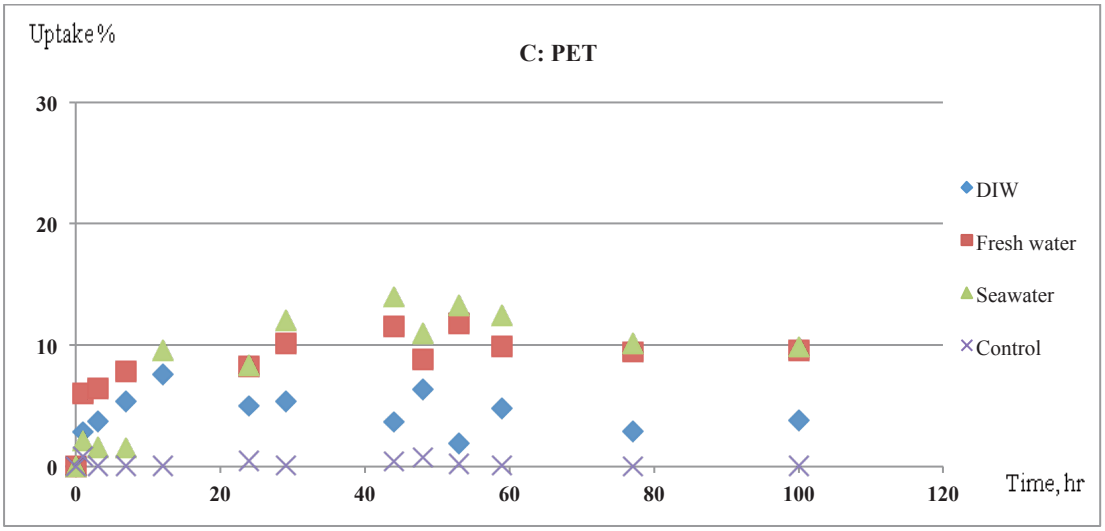
The average precision of the analytical method of 10 replicates is ± 0.0230, RSD is 2.043 %, showing high precision. Table 4-4 shows the analytical method precisions obtained for arsenic analysis in deionised water, fresh water and seawater media.

Table 4-4 Analytical method precisions for arsenic analysis by ICP-MS

Analytical method	As in deionised	As in fresh water	As in seawater
SD	0.0237	0.0236	0.0218
RSD	2.41 %	1.93 %	1.78 %


Uptake %
A: HDPE
30
20
10
0
0
20
40
60
80
100
120
Time, hr
DIW
Fresh water
Seawater
Control


Uptake %
B: LDPE
30
20
10
0
0
20
40
60
80
100
120
Time, hr
DIW
Fresh water
Seawater
Control


Uptake %
C: PET
30
20
10
0
0
20
40
60
80
100
120
Time, hr
DIW
Fresh water
Seawater
Control

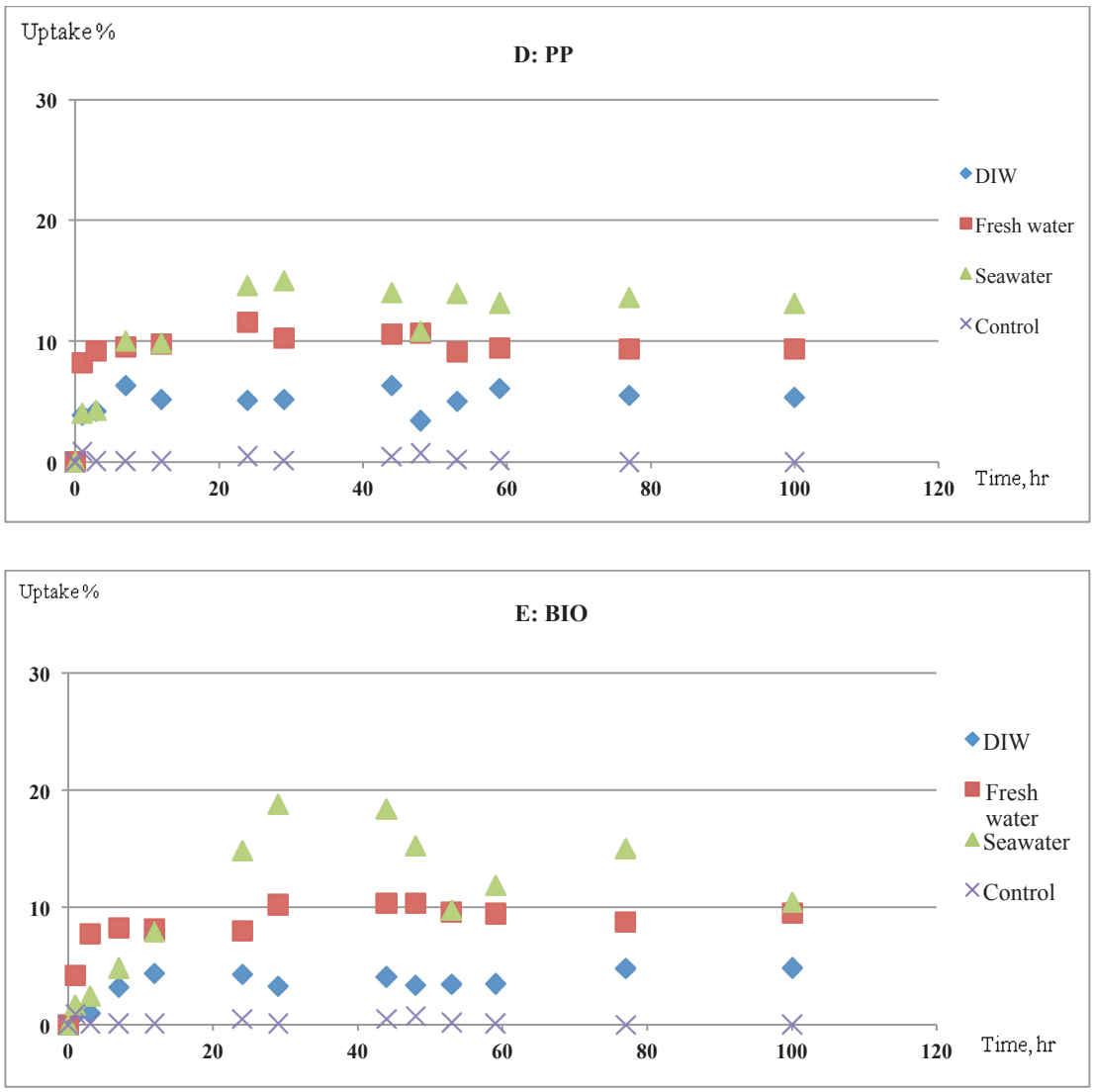


Figure 4-1 Arsenic taken up (loss) from a ~ 5 µg L^{-1} solution of As^{III} in deionised water at pH 5.8, fresh water at pH 7.8 and seawater at pH 8.5 by A: HDPE, B: LDPE, C: PET, D: PP and E: BIO virgin plastic resin pellets over 100 hours of shaking at room temperature. Plus one control profile of As in the absence of pellets. Analytical method SD: ± 0.0237, 0.0236 and 0.0218 in deionised water, fresh water and seawater respectively.

In deionised water media, all values obtained were above the limit of detection, which was 0.00681 µg L^{-1}. A single sample was analysed at each time point, and so no RSD values are shown. This was considered sufficient to establish the sorption profile pattern and to minimise the total number of actual samples to 1040 instead of 3120 samples.

The control values (see Table A-1 in Appendix 3) and Figure 4-1 suggest that the uptake of arsenic by the vial walls during the experiment was not significant, and therefore the loss of arsenic can be attributed to the pellets present in each vial. The average value obtained for the residual arsenic in the control solution was 4.94 ± 0.0159 μg L^{-1}, with an average loss of 0.01 μg L^{-1} for all control results analyses.

The results of the analysis of the residual arsenic in solutions (arsenic loss) indicated that all types of pellets showed relatively poor uptake of arsenic from the deionised water during the experiment. The level of arsenic remained almost the same over time, and was close to the initial spiking concentration of 4.95 μg L^{-1}, therefore equilibrium time cannot be clearly indicated for all types of pellets. However 10-12 hours can be generally considered as equilibrium time for PE, PET and BIO.

The maximum average loss of arsenic concentration was 0.21 μg L^{-1} for PET. This poor uptake of arsenic can be attributed to the nature of As^{III} (see Section 1-3-1), which has a high acid dissociation constant (pKa_1 = 9.2); therefore, the adsorption was expected to be low at a pH much lower than the pKa[198, 199]. On the other hand the enhanced polarity of the pellet surfaces, due to impurities, additives, and catalyst residues, may explain the uptake (limited) that took place in this experiment.

Adsorption of arsenic in aqueous solutions has been studied using different sorbents, such as activated carbons[200], metal oxides[201-203], ion exchange resins[204], and natural biomaterials[205]. However, none was comparable to the medium (deionised water) and sorbent (virgin plastic resin pellets) used in the current experiment, as this is the first time this sorption profile has been established. The results obtained in past studies of arsenic removal at pH values relatively close those in this experiment (5.8) varied depending on the arsenic species and sorbents used.

In the study of Rahaman *et al*.[205] both As^{III} and As^{V} showed maximum adsorption at an acidic pH of 4.0 using a biomaterial sorbent of fish (cod) scales over 130 hours of contact. For As^{V}, where initial concentrations were 540 and 1050 μg L^{-1}, the uptake decreased as the pH increased within the pH 4-12 range. For As^{III}, where the initial

concentrations were 350 and 1150 μg L^{-1}, adsorption was slightly lower, at pH 2, reached a maximum at pH 4, and then decreased as the pH increased. The authors explained this behaviour, stating that, "the adsorptive capacity decreases at pH values more acidic than the pKa value, which was determined to be 2.2". However, the value they quoted was for the As^{V} $pKa_{1,}$ while the pKa_1 of As^{III} was 9.2, pKa_2 12.1, and pKa_3 12.7[206].

In contrast, results obtained by Ghimire *et al.*[207] were in agreement with the current study, where As^{III} adsorption was poor at an acidic pH (whereas As^{V} was efficiently taken up at an acidic pH) using modified orange juice residue as an adsorbent.

In fresh water, values obtained were above the limit of detection, which was 0.00443 μg L^{-1}. The control results (see Table A-2 in Appendix 3) and Figure 4-1 suggest that the uptake of arsenic by the vial walls during the experiment was not significant, and therefore the loss of arsenic can be attributed to the pellets present in each vial. The average value obtained for the remaining arsenic in controls was 4.94 ± 0.0695 μg L^{-1}, with an average loss of 0.05 μg L^{-1} for all control results analyses.

The results of the analysis of the residual arsenic remaining in fresh water solutions showed a lower concentration of arsenic than the initial concentration of 4.99 μg L^{-1}. The maximum average loss of arsenic concentration was 0.49 μg L^{-1} for LDPE. The uptake of arsenic behaviour by all types of pellets was similar.

In the PET profile, one result was above the initial concentration (5.56 μg L^{-1}), which was possibly due to this vial being over-spiked at the start of the experiment. However, an overall profile could still be clearly obtained.

Unlike in deionised water, arsenic was clearly taken up by HDPE, LDPE, PP, PET, and BIO plastic pellets in fresh water. A clear differentiation between deionised and fresh water points was seen in the Figure 4-1. The maximum average uptake in the fresh water medium was 2.3 times more than in deionised water. As the pH of the experimental medium increased from 5.8 to 7.8, the residual arsenic remaining in the solution at

different collection times decreased (i.e. the adsorption increased), which is in agreement with the arsenic pKa explanation given in this Section. The plotted graphs show that the loss of arsenic mostly took place during the first 24 hours of the experiment, which can thus be indicated as the equilibrium time.

In an experiment conducted using iron oxide hydroxide sorbent[208], the arsenic (III) removal reached a maximum (> 95 %) at pH 7 – 8, while it was < 85 % at a lower pH.

The equilibrium times identified in different studies were rather shorter than in the current study, including 160 min[209] and 180 min[208]. This variation can be attributed to the sorbents used and the ambient environment for each experiment. More accurate equilibrium time can be determined by further studying and concentrating on shorter period of time.

In seawater media, all values obtained were above the limit of detection, which was 0.00404 μg L^{-1}. The control results (see Table A-3 in Appendix 3) and Figure 4-1 suggest that the uptake of arsenic by the vial walls during the experiment was not significant, as the case in deionised and fresh water media. The average value obtained for the residual arsenic in the control solution was 5.156 ± 0.0521 μg L^{-1}, with an average loss of 0.044 μg L^{-1} for all control results analyses.

The results of the analysis of the residual arsenic remaining in seawater solutions showed a loss of arsenic than the initial concentration of 5.20 μg L^{-1}, except for two values in the HDPE profile, which were slightly higher. The maximum average loss of arsenic concentration was 0.74 μg L^{-1} for LDPE.

The amount of arsenic taken up by plastic pellets was greater than the amount taken up in deionised and fresh water. The maximum average uptake in seawater was 3.52 times that in deionised water, and 1.51 times more than it was in fresh water; in other words, arsenic-plastic interaction increased as the pH of the media increased, and as the pH of the media became closer to the As^{III} pKa. All plastic pellet types showed almost the same behaviour as was observed in deionised and fresh water.

The plotted graphs show that the equilibrium time was reached within approximately 40 hours, which was more, almost double, the time taken in fresh water. Furthermore, the pattern of sorption in seawater was not as smooth as it was in the fresh water medium except for PP. This can arguably be attributed to the complexity of the seawater matrix.

Comparison between the loss patterns of arsenic in Figure 4-1 showed the overlap in the first few 2-3 times of collection in all types of pellets, mainly between the uptake % in deionised and seawater. Then, a large gap was occurred between them with time. The uptake % of arsenic by PET pellets in seawater was slightly higher or overlaps with fresh water, some overlapping were also occurred by other types of plastic pellets. The LDPE showed a clear differentiation between the loss percent in different media.

4.2.1.2 Arsenic uptake by laboratory-weathered plastic pellets in artificial seawater

Each type of artificially-weathered plastic pellet was shaken for 100 hours in a ~5 μg L^{-1} solution of arsenic (III) prepared in artificial seawater. The uptake % of arsenic in the solution after 13 different time periods, are plotted in Figure 4-2.

Table A-4 in Appendix 3 shows the residual arsenic in solutions at different times, determined by ICP-MS, from which the uptake levels by five types of weathered plastic pellet in artificial seawater were determined.

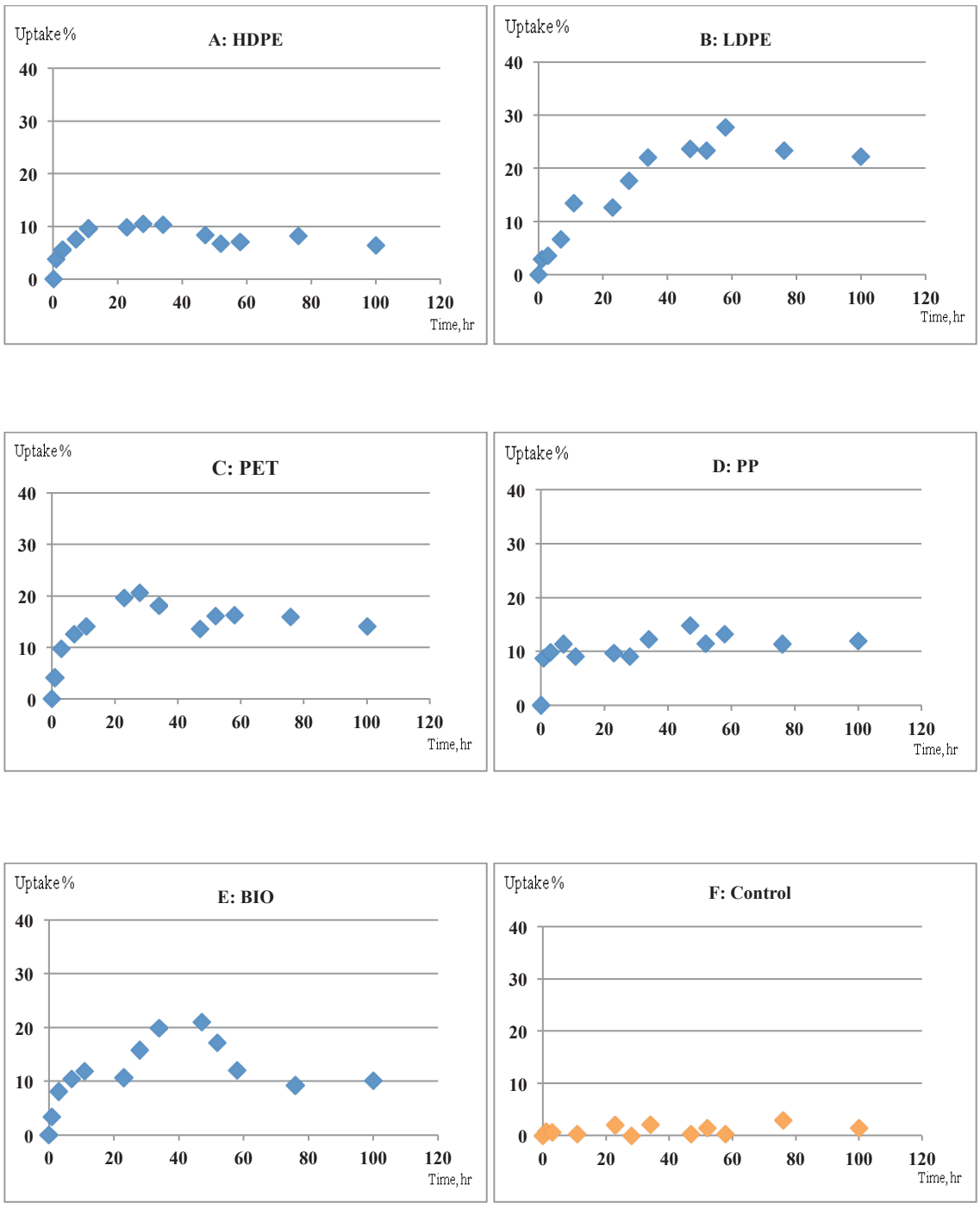


Figure 4-2 Arsenic taken up (loss) from a ~ 5 µg L^{-1} solution of As^{III} by A: HDPE, B: LDPE, C: PET, D: PP and E: BIO laboratory weathered plastic resin pellets in seawater at pH 8.5. F: control profile of As in artificial seawater in the absence of pellets. Analytical method SD: ± 0.0218.

All values obtained were above the limit of detection, which was 0.00404 μg L^{-1}. The control results (see Table A-4 in Appendix 3) and Figure 4-2F suggest that the uptake of arsenic by the vial walls during the experiment was not significant, and therefore the loss of arsenic can be attributed to the pellets present in each vial. The average value obtained for the residual arsenic in the control solution was 5.156 ± 0.0521 μg L^{-1}, with an average loss of 0.044 μg L^{-1} for all control results analyses, as the same seawater control as in 4-2-1-1 was used.

The results of the analysis of the residual arsenic remaining in seawater solutions showed a lower concentration of arsenic than the initial concentration of 5.42 μg L^{-1}. The maximum average loss of arsenic concentration was 0.833 μg L^{-1} for the LDPE.

Weathered pellets in seawater media showed a generally higher uptake of arsenic than the virgin pellets in seawater media, which indicates that the weathering process did affect the surface of the pellets and enhanced the pellet-arsenic interaction in seawater media. The maximum uptake by weathered pellets in seawater was 1.12 times more than by virgin pellets, mostly for LDPE, PET and BIO plastic pellets, which suggests that these types of pellets were probably more affected by the laboratory-weathering process than the rest.

Arsenic removal by adsorption from seawater and artificial seawater equivalent (arsenic-sodium solution) was studied by Mishra *et al*.[210] using a magnetite multi-walled carbon nano tube (filter); the maximum removal efficiency was 67 % for arsenite (and 58% for arsenate) after 15 cycles with an initial concentration of 400 mg L^{-1}. No information about the time consumed for each cycle, or the pH value, was provided.

For ease of comparison between Mishra *et al*. results (maximum removal efficiency 67 %) and the current study results, the equation used was as follows:

% removal efficiency = $(C_0 - C_f)\ 100/\ C_0$

Where C_0 is the initial concentration of As, and C_f is the remaining concentration of As in solution. The maximum removal efficiency values found in the current study were 21.3 % and 27.6 % for virgin and weathered pellets, respectively.

4.2.1.3 Comparison of all arsenic results

A comparison of the arsenic sorption profiles showed that there was no notable uptake of arsenic by any of the plastic pellets in deionised water over 100 hours of shaking. As the TDS and pH increased with the use of fresh and then artificial seawater, the level of uptake increased. The effect of pH can be explained, and it can be attributed to the pKa values, as discussed earlier. It was clear that both the petroleum based and bio based plastic pellets studied showed similar behaviour as was observed in deionised, fresh, and seawater media, which suggests that the As-plastic interaction is non-specific and so independent of the type of plastic used, which is in agreement with the findings of a study conducted on five types of petroleum based pellets[211]

In water, arsenic exists as arsenite (As^{III}) and arsenate (As^{V})[212], as mentioned in Section 1-3-1. In the literature, the interaction between arsenic and plastic pellets surface has not yet been studied. However, arsenic adsorption on other surfaces was usually influenced by the pH, arsenic speciation, and sorbent used.

Using the present sorption data, a calculation was performed (see Appendix 7) to show the total arsenic uptake over 100 hours in each medium in ng g^{-1}, as follows:

- Concentration loss (µg L^{-1}) = initial concentration – concentration determined by ICP-MS

- Mass loss to pellets present in vial (µg) = concentration loss x volume

- Uptake (µg kg^{-1}) = (mass loss µg / wt of pellets in vial g) x 1000 = Uptake (ng g^{-1})

Table 4-5 shows the average uptake of arsenic by each type of pellet in different media.

The results for the general uptake of arsenic by virgin pellets in the studied medium, in descending order, were as follows: uptake in seawater > uptake in fresh water > uptake in deionised water.

Table 4-5 Average uptake of arsenic in different medium by 5 types of pellet in ng g^{-1} during the 100 hrs.

As in	HDPE	LDPE	PP	PET	BIO
Deionised water	23.9	23.8	21.7	23.6	18.5
Fresh water	45.8	57.6	52.3	49.0	46.7
Seawater - virgin	55.2	86.2	63.6	49.3	62.0
Seawater - weathered	46.3	96.3	64.6	85.6	74.2

When comparing the uptake behaviour of virgin pellets and laboratory-weathered pellets, the weathered LDPE, PET, and BIO showed a higher uptake of and greater affinity for arsenic than the virgin pellets in seawater, most notably in the PET type pellets. This suggests that this type of pellets was probably more affected by the weathering process than the others. Discolouration of PET was clear after three weeks of weathering, compared to the other pellet types, as shown in Chapter 3, Figure 3-1. Whilst the arsenic taken up by virgin and weathered PP pellets was close (6.25 and 6.46 respectively), weathered HDPE pellets adsorbed less arsenic than the virgin pellets.

It has been reported that the surface area of PE pellets increased and gained a negative charge, due to the increase in functional groups after weathering in seawater (while PP showed only mechanical changes)[213]. This is in agreement with the LD results obtained in this study, but not with the HD type of PE results obtained in this study. This might be explained by the probability that, in the literature study[213], LDPE pellets type was used (as there was no statement about the specific type of PE pellets studied). As explained in Section 1-2-1-1 and shown in Figure 1-11, the mechanical properties of PE decrease as

the chain branching increases, and so the LDPE is less stable than the HDPE, and therefore the surface of the pellets can be more affected by the weathering process.

The presence of the ester functional groups in both PET and BIO pellets might increase the weathering affects (as observed in Figure 3-1), which could also explain the enhanced affinity for arsenic (see Section 1-2-2-1).

The interaction between arsenic and the surface of plastic pellets can take place due to the enhanced polarity on the surface caused by weathering in seawater, the pH of the experiment medium, and the nature of the arsenic, such as the pKa value of the As^{III} studied.

4.2.2 Cadmium sorption by five types of virgin and weathered plastic resin pellets: HDPE, LDPE, PET, PP and BIO

4.2.2.1 Cadmium uptake by virgin plastic pellets in deionised water, fresh water and seawater

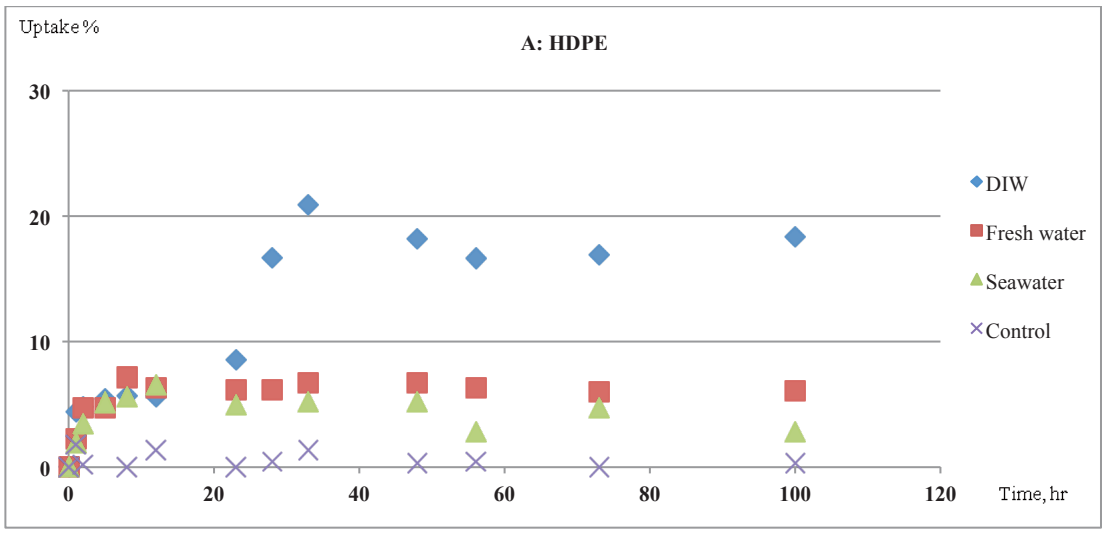
Each type of plastic pellet was shaken for 100 hours in a ~5 μg L^{-1} solution of cadmium prepared in deionised water, fresh water and artificial seawater. The uptake % of cadmium in solutions, after 13 different time periods, is plotted in Figure 4-3.

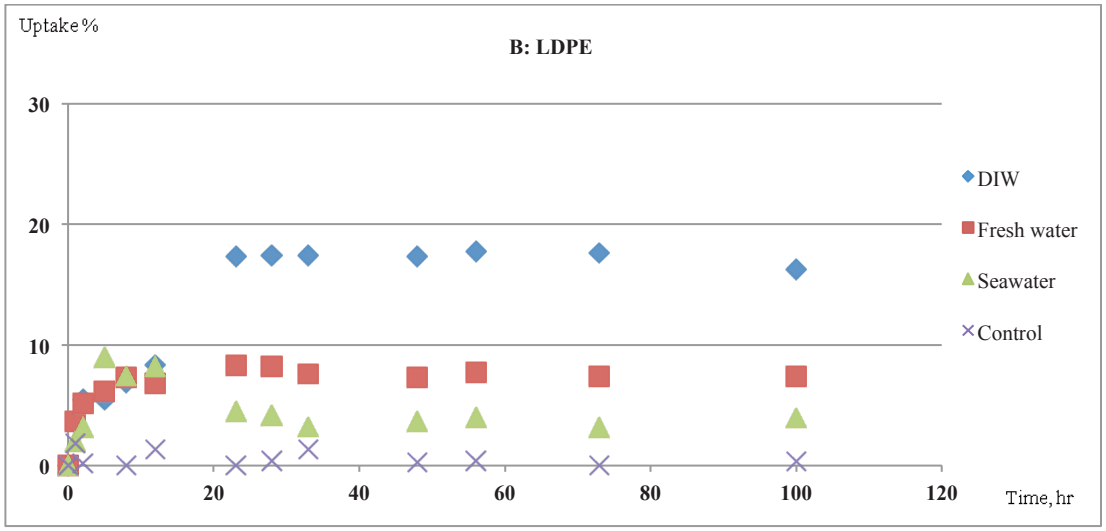
Table A-1, A-2 and A-3 in Appendix 4 shows the residual cadmium remaining in the deionised water, fresh water and seawater solutions respectively at different times (over the 100 hours) determined by ICP-MS, from which the uptake levels by the five types of virgin plastic pellets were determined.

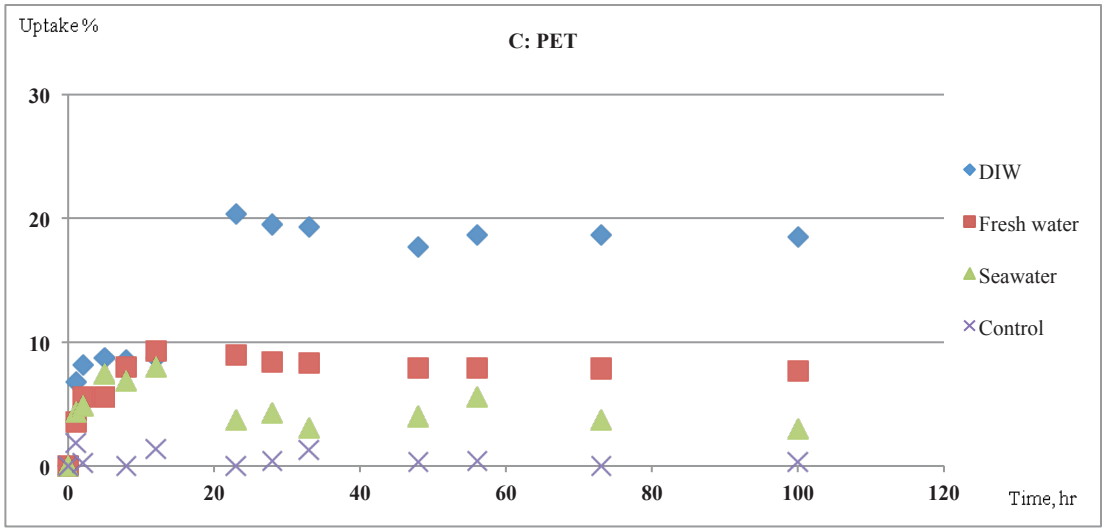
Precision of the analytical method of 10 replicates is ± 0.0115, RSD is 1.17 %, showing good precision. Table 4-6 shows the analytical method precisions obtained for cadmium analysis in deionised water, fresh water and seawater media.

Table 4-6 Analytical method precisions for cadmium analysis by ICP-MS

Analytical method	Cd in deionised	Cd in fresh water	Cd in seawater
SD	0.0102	0.0044	0.02
RSD	1.02	0.442	2.04


Uptake %
A: HDPE
30
20
10
0
0
20
40
60
80
100
120
Time, hr
DIW
Fresh water
Seawater
Control


Uptake %
B: LDPE
30
20
10
0
0
20
40
60
80
100
120
Time, hr
DIW
Fresh water
Seawater
Control


Uptake %
C: PET
30
20
10
0
0
20
40
60
80
100
120
Time, hr
DIW
Fresh water
Seawater
Control

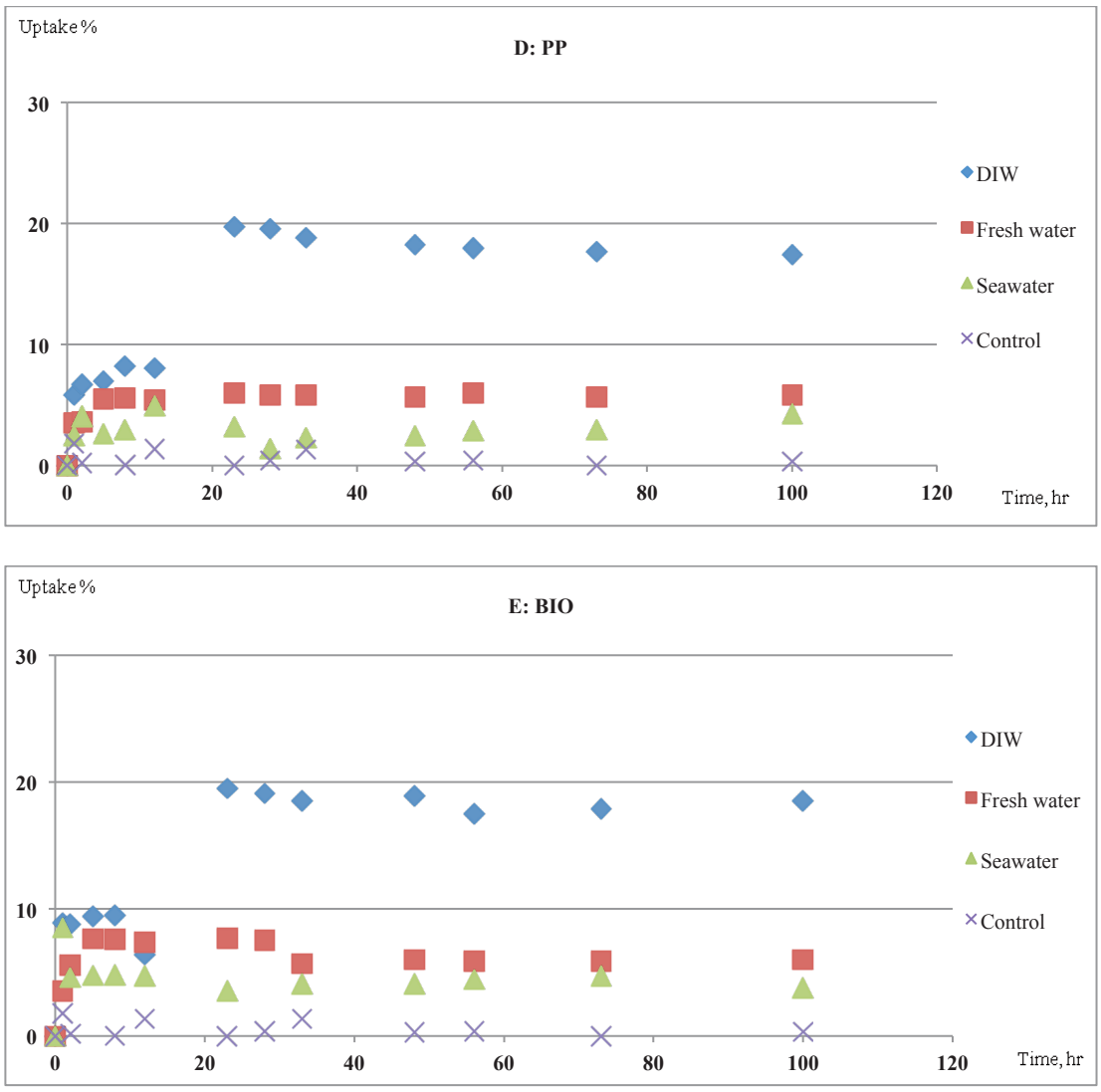


Figure 4-3 Cadmium taken up (loss) from a ~ 5 µg L^{-1} solution of Cd by A: HDPE, B: LDPE, C: PET, D: PP and E: BIO virgin plastic resin pellets in deionised water, fresh water and seawater. Plus one control profile of Cd in the absence of pellets. Analytical method SD: ± 0.0102, 0.0044 and 0.02 in deionised water, fresh water and seawater respectively.

In deionised water media, all values obtained were above the limit of detection, which was 0.000593 μg L^{-1}. The control results (see Table A-1 in Appendix 4) and Figure 4-3 suggest that the uptake of cadmium by the vial walls during the experiment was not significant (negligible compared to the pellet uptake profiles in Figure 4-3), and therefore the loss of cadmium can be attributed to the pellets present in each vial. The average value obtained for the remaining residual cadmium in the control solution was 4.89 ± 0.0458 μg L^{-1}, with an average loss of 0.03 μg L^{-1} for all control results analyses.

The results of the analysis of the residual cadmium remaining in the deionised water solutions showed a lower concentration of cadmium than the initial concentration of 4.92 μg L^{-1}, except one value for LDPE, which was slightly higher. The maximum average loss of cadmium concentration was 0.658 μg L^{-1} for PET.

During the experiment, a clear loss of cadmium to all types of pellet was observed, and the range of cadmium uptake levels by all types of pellet was generally similar. Most of the loss occurred in the first 24 hours of the experiment, which can thus be indicated as the equilibrium time, after which the concentration in each collection remained almost constant over time.

Biphasic adsorption pattern was occurred in 0-12 hours and 22-100 hours, this behaviour was only occurred in this media for all types of pellets used. Between the biphasic adsorption no data was obtained as no samples was collected overnight.

Comparing with arsenic in deionised water, the cadmium loss was clearly higher, and all pellet types studied showed a noticeable uptake of cadmium. The average maximum uptake of cadmium was 3.23 times more than the average maximum uptake of arsenic in deionised water. This can only be explained by the nature of the elements, as all other possible variables were the same.

The bond strength between metal ion and water $[M(H_2O)n]^{z+}$ increases as the charge on the metal increase, and as the radius size decrease. This lead to different structures of hydrated metal ion in water, where M–O bond distance is the main factor to determine

the ionic radii[214]. Cadmium has a lower charge and a higher radius than arsenic (metalloid), which might lead to and explain the greater adsorption of cadmium than arsenic by the pellets in the same medium.

Cadmium removal from aqueous solutions and wastewater has been studied[215-217] using different sorbents. However, the literature on the removal and uptake of cadmium by plastic resin pellets in water is limited, and this phenomenon has only been studied in estuarine and seawater conditions. Interactions between PTE and virgin PE plastic pellets were studied by Holmes *et al*.[218] at a pH range of between 4 and 10.5; the cadmium uptake behaviour was not in agreement with the findings of the current study, where the uptake at low pH was almost nil. This can be attributed to the medium (adjusted pH river water) in which the experiment took place.

In fresh water media, all values obtained were above the limit of detection, which was 0.000231 μg L^{-1}. The control values (see Table A-2 in Appendix 4) and Figure 4-3 suggest that the uptake of cadmium by the vial walls during the experiment was not significant, and therefore the loss of cadmium can be attributed to the pellets present in each vial. The average value obtained for the remaining cadmium in controls was 4.94 ± 0.0393 μg L^{-1}, with an average loss of 0.02 μg L^{-1}, for all control results analyses.

The results of the analysis of the residual cadmium remaining in fresh water solutions showed a lower concentration of cadmium than the initial concentration of 4.96 μg L^{-1}. The maximum average loss of cadmium concentration was 0.36 μg L^{-1} for PET, and the minimum was 0.24 μg L^{-1} for PP.

All types of pellets showed the same profile during the experiment, reaching equilibrium after approximately 24 hours of shaking. The PET, LDPE, and BIO pellets showed a slightly higher uptake than the HDPE and PP.

A comparison of cadmium uptake in fresh water with the uptake in deionised water showed that the uptake in fresh water was clearly lower than the uptake in deionised

water; in other words, the sorption profile of cadmium showed the opposite behaviour compared with the arsenic uptake in deionised water.

This behaviour of cadmium can possibly be explained by the presence of competing elements (competitions availability) in fresh water bearing in mind that adsorption is not a selective process; as seen in Table 3-4, fresh water contains higher levels of Ca, Cl^-, K, Mg, Na, NO_3^-, and SO_4^-, which were not present in deionised water, The cadmium uptake results obtained by Holmes *et al*.[218] (as salinity changed by mixing fresh water with seawater) using virgin pellets (PE) in estuarine conditions were in agreement with the results of the current study, where the uptake of cadmium decreased as the TDS of the medium increased. However, in the same study, the cadmium uptake under different pHs was different to that demonstrated in the present study, where the cadmium uptake increased as the pH increased in Holmes *et al* study. The converse behaviour observed in the current study can be attributed to the media used. In the study by Holmes *et al.* the pH was adjusted in the same media using 0.1 M NaOH or 0.1 M HNO_3, whereas in the current study the pH changed consequentially as the medium of the experiments changed, in other words both pH and TDS were changed.

The presence of competing ions does not influenced arsenic and cadmium similarly. This might be attributed to the greater influence of pH on arsenic as explained in Section 4-2-1-1 over the TDS.

In artificial seawater media, all values obtained were above the limit of detection, which was 0.000595 μg L^{-1}. The control values (see Table A-3 in Appendix 4) and Figure 4-3 suggest that the uptake of cadmium by the vial walls during the experiment was not significant, and therefore the loss of cadmium can be attributed to the pellets present in each vial. The average value obtained for the residual cadmium in the control solution was 4.84 ± 0.0836 μg L^{-1}, with an average loss of 0.07 μg L^{-1}, for all control results analyses.

The results of the analysis of the residual cadmium remaining in the seawater solutions showed a lower concentration of cadmium than the initial concentration of 4.91 μg L^{-1} except for two; one value in the HDPE (5.65 μg L^{-1}) profile and one in the BIO profile, which was slightly higher than the initial value. The maximum average loss of cadmium concentration was 0.22 μg L^{-1} for PET, and the minimum was 0.12 μg L^{-1} for HDPE.

Recalling the quantitative analysis of PTE in the studied pellets, cadmium values were low in all types of pellets, including HDPE, as seen in Table 4-2; the average result was 0.00356 ± 0.000958. However, inhomogeneous distribution of some PTE in HDPE was suggested in Section 4-1-1. Therefore, this single value (5.65 μg L^{-1}) can be attributed either to over-spiking of cadmium, or to an individual pellet in this experiment vial.

The results of the analysis also indicated a lower uptake compared with the uptake that took place in fresh and deionised water. This can be explained by the presence of competing elements as the TDS of the medium (deionised water < fresh water < seawater) increases, and to the possible cadmium compounds formed in water, such as $Cd_3(PO_4)_2$, depending on the sea salt gradient used (as seen in Table 3-4).

The sorption pattern showed a slight increase in cadmium level after approximately 30 hours, after which it remained constant. The blank results obtained during the experiment were nil, eliminating the possible release of cadmium from the pellets as the cause; such a pattern could be explained as a desorption of some adsorbed cadmium.

The results obtained by Holmes *et al*.[218] for cadmium uptake (as salinity changed by mixing fresh water with seawater) using virgin pellets (PE) were in agreement with those of the current study, where the uptake of cadmium decreased as the TDS of the medium increased.

Comparison between the loss patterns of cadmium in Figure 4-3 showed an overlap in loss percent in all media by all types of pellets, mainly PE and PET, in the first 12 hours of the experiment. Then, a clear gap was occurred between deionised water and other

media due to the high adsorption (loss) of cadmium in this medium by all types of pellets.

4.2.2.2 Cadmium uptake by laboratory-weathered plastic pellets in artificial seawater

Each type of laboratory-weathered plastic pellet was shaken for 100 hours in a ~5 μg L^{-1} solution of cadmium prepared in artificial seawater. The uptake % of cadmium in the solution, after 13 different time periods, is plotted in Figure 4-4.

Table A-4 in Appendix 4 shows the residual cadmium remaining in the solution at different times (over the 100 hours) determined by ICP-MS, from which the uptake levels by the five types of laboratory-weathered plastic pellets in seawater were determined.

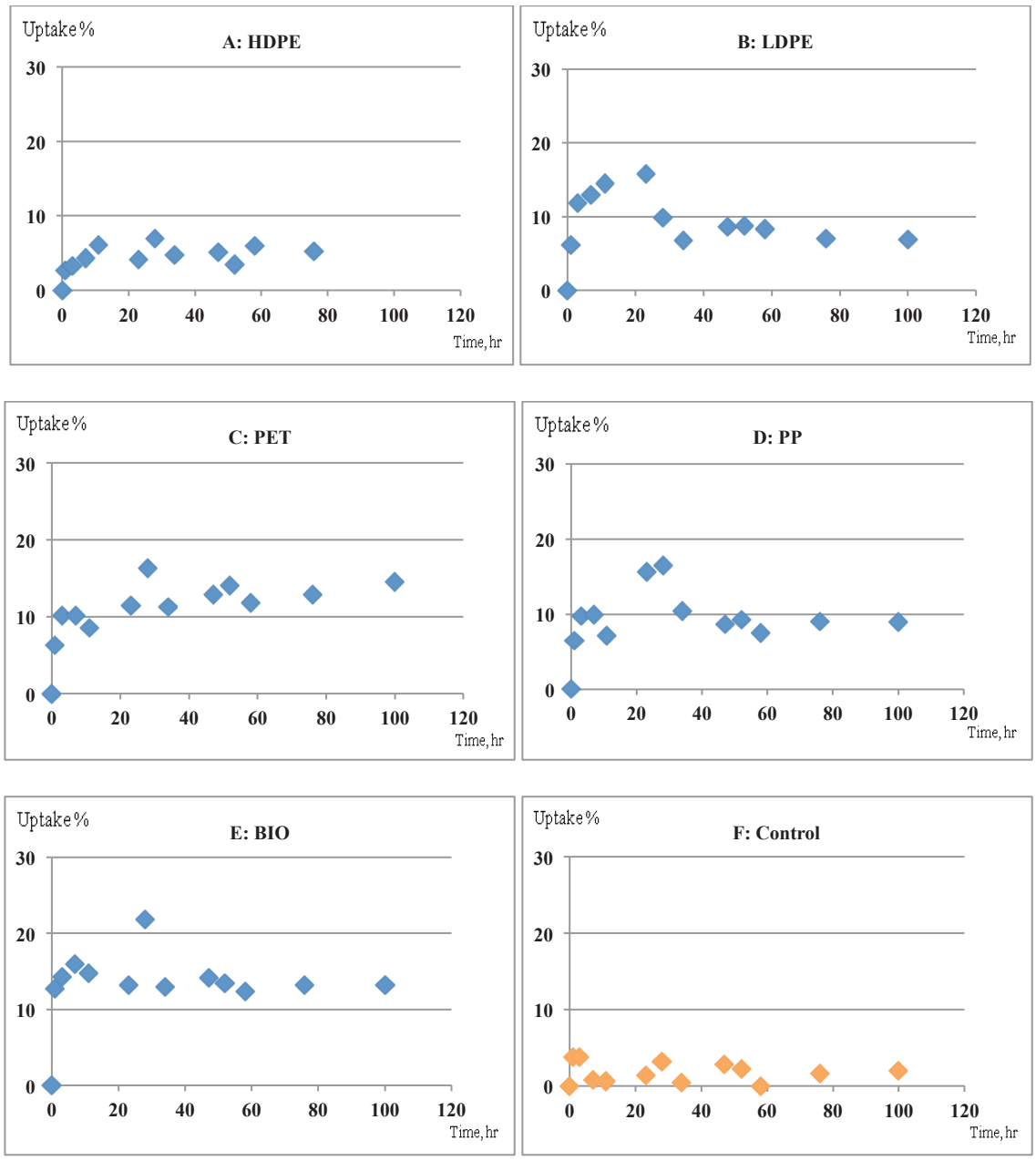


Figure 4-4 Cadmium taken up (loss) from a ~ 5 µg L^{-1} solution of Cd by A: HDPE, B: LDPE, C: PET, D: PP and E: BIO laboratory-weathered plastic resin pellets in artificial seawater. Plus control profile of Cd in artificial seawater in the absence of pellets. Analytical method SD: ± 0.02.

All values obtained were above the limit of detection, which was 0.000595 μg L^{-1}. The control values (see Table A-4 in Appendix 4) and Figure 4-4F suggest that the uptake of cadmium by the vial walls during the experiment was not significant, and therefore the loss of cadmium can be attributed to the pellets present in each vial. The average value obtained for the residual cadmium in the control solution was 4.84 ± 0.0836 μg L^{-1}, with an average loss of 0.07 μg L^{-1} for all control results analyses.

The results of the analysis of the residual cadmium remaining in the seawater solutions showed a lower concentration of cadmium than the initial concentration of 4.81 μg L^{-1}, except for one value in the HDPE profile that was higher. The maximum average loss of cadmium concentration was 0.64 μg L^{-1} for BIO, and the minimum was 0.16 μg L^{-1} for HDPE.

Weathered pellets in seawater showed a generally higher uptake of cadmium than the virgin pellets, which indicates that the weathering process affected the surface of the pellets and enhanced the pellet-cadmium interaction in seawater. The maximum uptake by weathered pellets in seawater was almost 3 times more than by virgin pellets, mostly by the BIO, suggesting that all types of pellets were highly affected by the weathering process, except for HDPE.

The beached pellets (weathered naturally in the marine environment) results obtained by Holmes *et al*.[118, 218] , as well as those for virgin pellets (PE) were in agreement with those of the current study, and showed a generally higher uptake of PTE than by the virgin pellets studied.

4.2.2.3 Comparison of all cadmium results

The cadmium sorption profiles showed that the uptake of cadmium was greatest in all plastic pellets in deionised water. As the TDS of the sorption medium increased, with the use of fresh water and artificial seawater, the level of Cd uptake by virgin plastic pellets decreased. It subsequently increased when the laboratory-weathered pellets were used in seawater. It was clear that both the petroleum based and bio based plastic pellets studied showed similar behaviour as was observed in deionised, fresh, and seawater medium, which suggests that the Cd-plastic interaction is non-specific and so independent of the type of plastic, a finding that is in agreement with a study conducted on five types of petroleum based pellets[211]. The cadmium-pellets interaction showed the opposite behaviour compared with arsenic uptake, which was explained earlier in Section 4-2-2-1.

Using the present sorption data, the cadmium uptake in ng g^{-1} was calculated at each time point (see Appendix 7). Table 4-7 shows the average uptake of each type of pellet in different medium.

The results for the general uptake of cadmium by virgin pellets in the studied medium, in descending order, were as follows: uptake in deionised water > uptake in fresh water > uptake in seawater.

Table 4-7 Average uptake of cadmium in different medium by 5 types of pellets in ng g^{-1} during the 100 hrs.

Cd in	HDPE	LDPE	PP	PET	BIO
Deionised water	65.6	73.9	75.7	76.9	78.9
Fresh water	32.1	35.5	26.7	40.0	35.1
Seawater - virgin	23.2	25.0	15.8	26.2	25.1
Seawater - weathered	24.8	46.2	51.6	60.8	74.5

Comparing the behaviour between virgin pellets and laboratory-weathered pellets in seawater, there was greater uptake of cadmium in all types of weathered pellets compared to virgin pellets. Weathered BIO, PET, and PP had a higher uptake of and more affinity for cadmium than the other types, most notably the BIO pellets. This suggests that this type of pellet was more affected by the weathering process, most likely in a way that enhanced the Cd-pellets interaction, than the other pellet types. Discoloration of PET was clear after three weeks of weathering compared to the other types, as shown in Chapter 3, Figure 3-1.

As explained in Section 4-2-1-3, the surface of PE pellets and PP shows different changes due to weathering in seawater[213]. This is in agreement with the PP and LD results obtained in this study, but not for the HD type of PE, as the differences in uptake were limited (1.6 ng g^{-1}). This might be explained by the probability that, in the above study[213], LDPE pellets type was used, as there was no state about the specific type of PE pellets been studied. As explained in Section 1-2-1-1 and shown in Figure 1-11, the mechanical properties of PE decrease as the chain branching increases, and so the LD is less stable than the HD, and is therefore likely to be more affected by the weathering process.

As mentioned in Section 4-2-1-3 and Section 1-2-2-1, the presence of the ester functional groups in both PET and BIO pellets might increase the weathering effects (as observed in Figure 3-1), which also could explain the affinity for cadmium.

Weathered PP showed a much higher affinity for cadmium (35.8 ng g^{-1}) in seawater compared with arsenic, which was only 1 ng g^{-1}. This might be attributed to the PP surface changes as a result of weathering, such as porosity size and the element radius size.

The interaction between cadmium and the surface of plastic pellets can be explained by the enhanced polarity on the surface caused by weathering in seawater, as well as other surface changes, such as porosity size and changes due to weathering, the TDS of the experiment medium, and the nature of the cadmium, such as the ionic radius.

4.2.3 Chromium sorption by five types of virgin and weathered plastic resin pellets: HDPE, LDPE, PET, PP and BIO

4.2.3.1 Chromium uptake by virgin plastic pellets in deionised water, fresh water and seawater

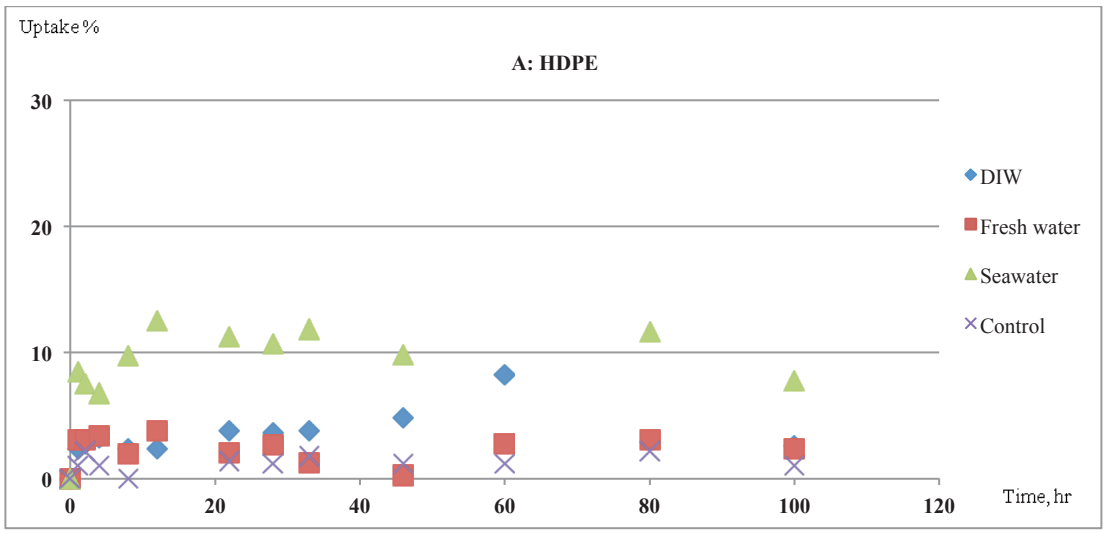
Each type of plastic pellet was shaken for 100 hours in a ~5 μg L^{-1} solution of chromium prepared in deionised water, fresh water and artificial seawater. The uptake % of chromium in the solutions, after 13 different time periods, is plotted in Figure 4-5.

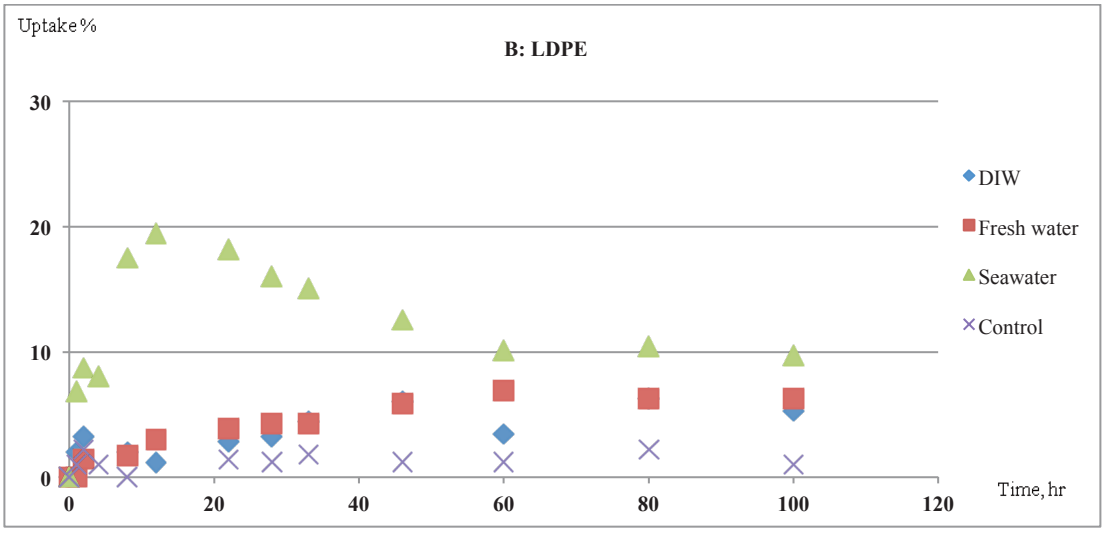
Table A-1, A-2 and A-3 in Appendix 5 shows the remaining residual chromium in the deionised water, fresh water and artificial seawater solutions respectively at different times over the 100 hours, determined by ICP-MS, from which the uptake levels of the five types of virgin plastic pellets in deionised water were determined.

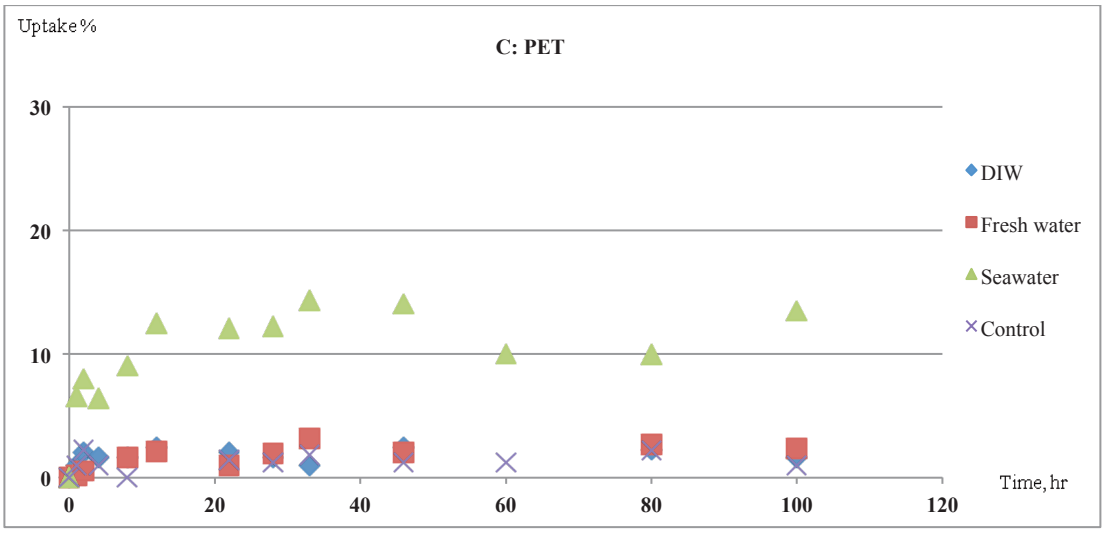
The average precision of the analytical method of 10 replicates is ± 0.0352, RSD is 3.69 %, showing high precision. Table 4-8 shows the analytical method precisions obtained for chromium analysis in deionised water, fresh water and seawater media.

Table 4-8 Analytical method precisions for chromium analysis by ICP-MS

Analytical method	Cr in deionised	Cr in fresh water	Cr in seawater
SD	0.055	0.0149	0.0358
RSD	5.67 %	1.47 %	3.95 %


Uptake %
A: HDPE
30
20
10
0
0
20
40
60
80
100
120
Time, hr
DIW
Fresh water
Seawater
Control


Uptake %
B: LDPE
30
20
10
0
0
20
40
60
80
100
120
Time, hr
DIW
Fresh water
Seawater
Control


Uptake %
C: PET
30
20
10
0
0
20
40
60
80
100
120
Time, hr
DIW
Fresh water
Seawater
Control

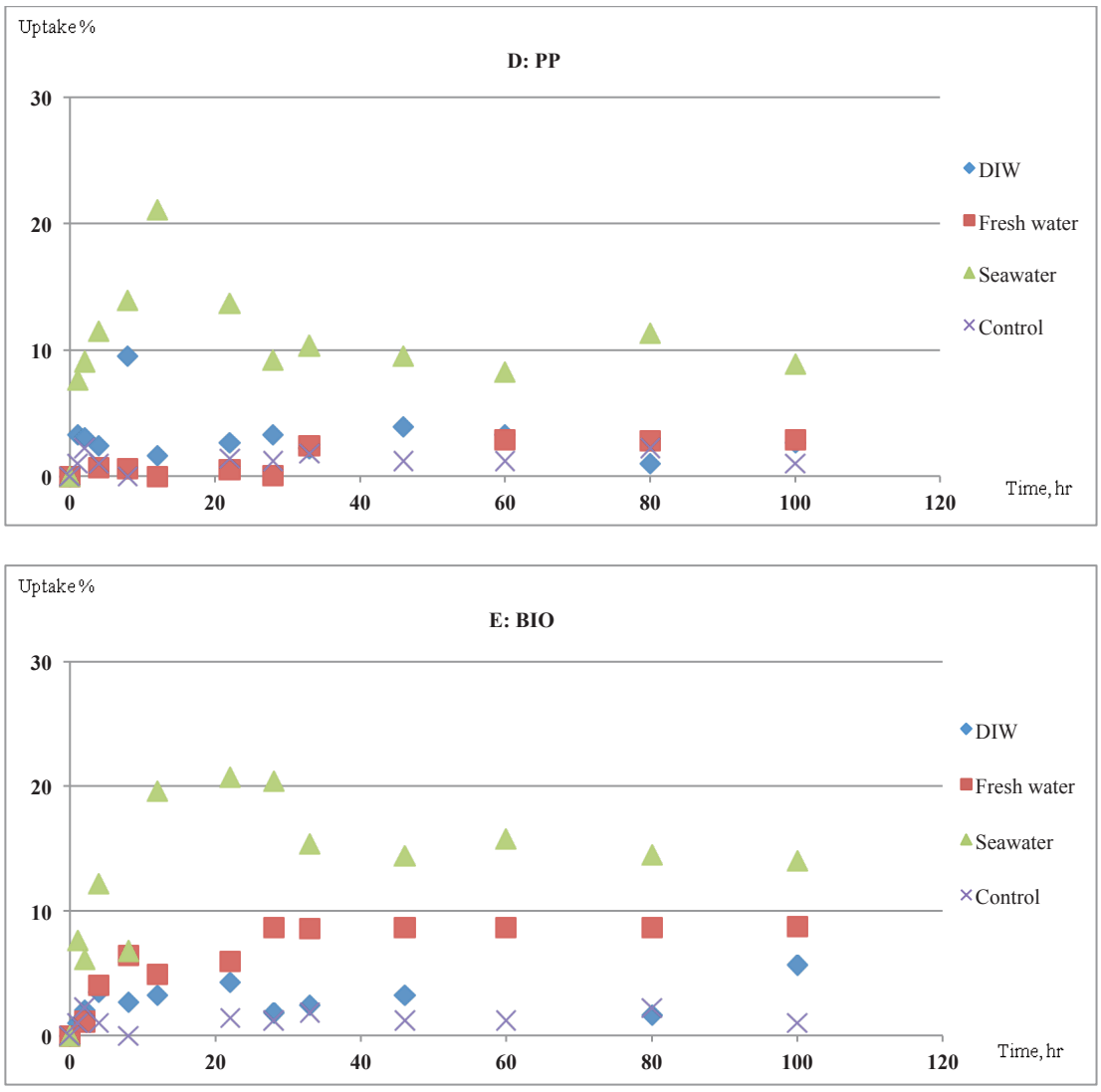


Figure 4-5 Chromium taken up (loss) from a ~ 5 µg L^{-1} solution of Cr by A: HDPE, B: LDPE, C: PET, D: PP and E: BIO virgin plastic resin pellets in deionised water, fresh water and artificial seawater. Plus one control profile of chromium in the absence of pellets. Analytical method SD: ± 0.055, 0.0149 and 0.0358 in deionised water, fresh water and seawater respectively.

In deionised water media, Chromium values obtained were above the limit of detection, which was 0.00388 μg L^{-1}. The control values (see Table A-1 in Appendix 5) and Figure 4-5 suggest that the uptake of chromium by the vial walls during the experiment was not significant, and therefore the loss of chromium can be attributed to the pellets present in each vial. The average value obtained for the residual chromium remaining in the control solution was 4.90 ± 0.0338 μg L^{-1}, with an average loss of 0.035 μg L^{-1} for all control results analyses.

The results of the analysis of the residual chromium remaining in deionised water solutions indicated that all types of pellets showed relatively poor uptake of chromium during the experiment, and was close to the initial spiking concentration of 4.94 μg L^{-1}. The maximum average loss of chromium concentration was 0.17 μg L^{-1} for BIO, and the minimum was 0.10 μg L^{-1} for PP.

According to the uptake pattern, equilibrium for all types of pellets was achieved after ~ 40 hours of shaking except for HDPE where the equilibrium was not clear but considered to be reached after ~ 20 hours. This can be attributed to the low uptake % of chromium by HDPE in this medium.

One point of each type of pellets profile except for BIO was slightly above the initial spike concentration, according to the blank values, leaching of chromium from pellets was eliminated as explained in Section 4-2. However, inhomogeneous distribution of PTE in pellets was generally observed and suggested as explained in Section 4-1-1. The vial being over-spiked at the start of the experiment can also be a possible reason.

This behaviour of poor uptake by virgin pellets in deionised water was seen in the arsenic profile, unlike for cadmium where the maximum average uptake of cadmium was 3.87 times more than it was in chromium. Both arsenic and chromium have higher charge and smaller atomic radius (~115 and ~140 pm respectively) than the cadmium ~155 pm[219], therefore the metal ion-water have stronger bond. This might explain the greater adsorption of cadmium than arsenic and chromium in deionised water as explained in Section 4-2-2-1.

The literature on the removal and uptake of chromium by plastic resin pellets in water is limited and this phenomenon has only been studied in estuarine and seawater conditions. Interactions between PTE and virgin PE plastic pellets were studied by Holmes *et al.*[218] at a pH range of between 4 and 10.5; the chromium uptake behaviour was not in agreement with the findings of the current study, where the uptake at low pH was high compared with higher pH points. This can be attributed to the medium (adjusted pH river water) in which the experiment took place.

In fresh water media, all values obtained were above the limit of detection, which was 0.00138 μg L^{-1}. The control values (see Table A-2 in Appendix 5) and Figure 4-5 suggest that the uptake of chromium by the vial walls during the experiment was not significant. Mainly one point was above the initial concentration by 0.313 μg L^{-1}, but it did not affect on the purpose of the control. The average value obtained for the remaining chromium in controls was 5.31 ± 0.12 μg L^{-1}, with an average loss of 0.019 μg L^{-1}, for all control results analyses.

The results of the analysis of the residual chromium remaining in fresh water solutions generally showed a close concentration of chromium to the initial concentration of 5.33 μg L^{-1}, and the relative uptake levels of chromium by all types of pellets were similar except for BIO. The maximum average loss of chromium concentration was 0.30 μg L^{-1} for BIO, and the minimum was 0.02 μg L^{-1} for PP.

Generally, the current profiles showed more points which were slightly above the initial spiked concentration especially in PP and a single high point in the LDPE profile (5.96 μg L^{-1}) which was possibly due to this vial being over-spiked at the start of the experiment. However, an overall trend could still be clearly obtained.

As in deionised water, chromium uptake was relatively poor. However, slightly more chromium was taken up in fresh water by LDPE, PP, and BIO compared to the uptake in deionised water. The maximum average uptake of chromium in fresh water was 1.7 times more than it was in deionised water for BIO. Both HDPE and PET had unexpected converse behaviour to the rest.

Equilibrium times were similar to those reached in deionised water. Overlapping between the uptakes (loss) levels of chromium in deionised and fresh water media was occurred during the 100 hours in all plastic pellets profiles except for BIO due to the general poor uptake of chromium in both media.

The chromium uptake results obtained by Holmes *et al*.[218] as salinity changed by mixing fresh water with seawater using virgin pellets (PE) were in agreement with the results of the current study, except for HDPE and PET, where the uptake of chromium increased as the TDS of the media increased. However, in the same study, the chromium uptake at different pHs was different to that demonstrated in the present study, except for HDPE and PET, where the chromium uptake increased as the pH increased in the current study. The converse behaviour observed in the current study can be attributed to the medium used. In the study by Holmes *et al*. the pH was adjusted in the same medium using 0.1 M NaOH or 0.1 M HNO_3, whereas in the current study the pH changed consequentially as the medium of the experiments changed, in other words both pH and TDS were changed.

In artificial seawater media, all values obtained were above the limit of detection, which was 0.00602 μg L^{-1}. The control values (see Table A-3 in Appendix 5) and Figure 4-5 suggest that the uptake of chromium by the vial walls during the experiment was not significant, and therefore the loss of chromium can be attributed to the pellets present in each vial. Mainly one point was above the initial concentration by 0.22 μg L^{-1}, but it did not affect on the purpose of the control. The average value obtained for the residual chromium in the control solution was 5.19 ± 0.11 μg L^{-1}, with an average loss of 0.02 μg L^{-1}, for all control results analyses.

The results of the analysis of the residual chromium remaining in seawater solutions showed a lower concentration of chromium than the initial concentration of 5.21 μg L^{-1} except for one value in the HDPE profile (8.24 μg L^{-1}) which was possibly due to this vial being over-spiked at the start of the experiment. All studied pellets showed a clear

loss of chromium during the experiment. The maximum average loss of chromium concentration was 0.673 µg L^{-1} for BIO, and the minimum was 0.201 µg L^{-1} for HDPE.

Unlike in deionised water and fresh water, chromium uptake in seawater by all studied pellets was greater. The maximum average uptake in the seawater was 3.95 times more than in deionised water, and 2.24 times more than in fresh water. Generally, as the pH and TDS of the experimental medium increased, the residual chromium remaining in the solution at different collection times decreased.

The uptake of chromium behaviour has no clear correlation with regard to the TDS. However, aqueous Cr species are pH dependent (see Section 1-3-3, Figure 1-22). For example, at a pH above 6.5 Cr is dominant as CrO_4^{2-}, whereas at a pH below 6.5 $HCrO_4^-$ is dominant which might influence the chromium adsorption on pellet surfaces.

The plotted graph shows that the equilibrium time was reached in about 40 hours of the experiment. The pattern of the sorption in seawater was generally not smooth, adsorption followed by some desorption was occurred in the first 40 hours, then it was almost constant until the end of the experiment. This can be attributed to the complexity of the seawater matrix.

The chromium uptake results obtained by Holmes *et al*.[218] as salinity changed by mixing fresh water with seawater, using virgin pellets (PE) were in agreement with the results of the current study, where the uptake of chromium increased as the TDS of the medium increased.

This behaviour can clearly be observed, as shown the profiles in all medium obtained, but cannot be readily explained. In Holmes *et al*.[218] speciation explanation on this regard was stated. In literature, chromium removal from water was studied[220, 221], the pH effect was reported to influence chromium uptake. Chromium removal studied by Rengaraj et al.[220] was in agreement with results obtained in current study whereas other studies were not

4.2.3.2 Chromium uptake by laboratory-weathered plastic pellets in artificial seawater

Each type of laboratory weathered plastic pellet was shaken for 100 hours in a ~5 μg L^{-1} solution of chromium prepared in artificial seawater. The uptake % of chromium in the solution, after 13 different time periods, is plotted in Figure 4-6.

Table A-4 in Appendix 5 shows the residual chromium remaining in the solutions at different times, determined by ICP-MS, from which the uptake levels by the five types of laboratory-weathered plastic pellets in artificial seawater were determined.

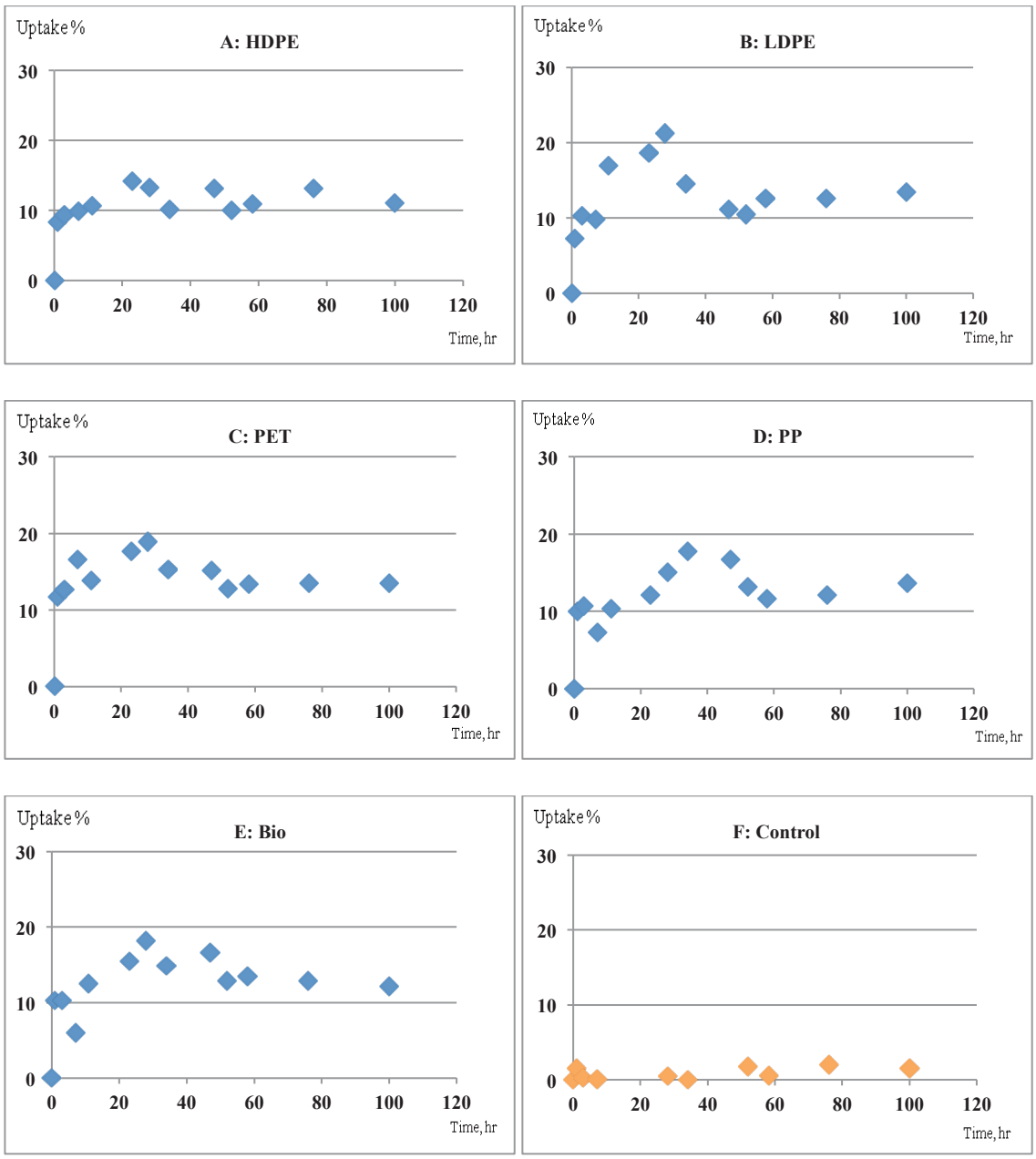


Figure 4-6 Chromium taken up (loss) from a ~ 5 µg L^{-1} solution of Cr by A: HDPE, B: LDPE, C: PP, D: PET and E: BIO laboratory-weathered plastic resin pellets in artificial sea water. F: control profile of chromium in artificial seawater in the absence of pellets. Analytical method SD: ± 0.0358.

All values obtained were above the limit of detection, which was 0.00425 μg L^{-1}. The control values (see Table A-4 in Appendix 5) and Figure 4-6F suggest that the uptake of chromium by the vial walls during the experiment was not significant, and therefore the loss of chromium can be attributed to the pellets present in each vial. Mainly one point was above the initial concentration by 0.22 μg L^{-1}, but it did not affect on the purpose of the control. The average value obtained for the residual chromium in the control solution was 5.19 ± 0.11 μg L^{-1}, with an average loss of 0.02 μg L^{-1}, for all control results analyses.

The results of the analysis of the residual chromium remaining in seawater solutions using laboratory weathered pellets showed a lower concentration of chromium than the initial concentration of 5.048 μg L^{-1}. The maximum average loss of chromium concentration was 0.681 μg L^{-1} for PET, and the minimum was 0.522 μg L^{-1} for HDPE.

The "odd point" (time = 28 hr) in the LDPE profile can arguably be attributed to an error in this vial at the start of the experiment, during preparation of samples prior to the ICP-MS analysis. An overall profile can still be clearly obtained.

Weathered pellets in seawater media showed relatively higher uptake of chromium than the virgin pellets, which generally indicates that the weathering process did affect the surface of the pellets and enhanced the pellets-chromium interaction to a certain extent. Notable is the PET which suggested that this type of pellets was probably more affected by the weathering process than the rest and that was clear from the colour changing of PET after three weeks weathering comparing with the rest as shown in Chapter 3, Figure 3-1. The maximum uptake by weathered pellets in seawater was slightly more than by virgin pellets, whereas the minimum uptake by weathered pellets was 2.59 times more than by virgin for HDPE.

4.2.3.3 Comparison of all chromium results

The chromium sorption profile showed a limited uptake of chromium by plastic pellets in deionised water. As the pH and TDS of the medium increased with the use of fresh water and artificial seawater, the level of chromium uptake by virgin plastic pellets increased gradually (except for HDPE and PET in fresh water). It was clear that both the petroleum based and bio based plastic pellets studied showed similar behaviour going from deionised to fresh to seawater media, which suggests that the Cr-plastic interaction is non-specific and so independent of the type of plastic, a finding that is in agreement with a study conducted on five types of petroleum based pellets[211].The chromium-pellets interaction showed similar behaviour compared to arsenic, and opposite trends in uptake compared to cadmium as explained earlier.

Using the present sorption data, a calculation of chromium uptake in ng g^{-1} was calculated at each time point (see Appendix 7). Table 4-9 shows the average uptake of each type of pellet in different medium.

Table 4-9 Average uptake of chromium in different medium by 5 types of pellet in ng g^{-1} during the 100 hrs.

Cr in	**HDPE**	**LDPE**	**PP**	**PET**	**BIO**
Deionised water	20.5	20.2	9.40	15.8	18.1
Fresh water	14.8	23.5	11.2	10.12	39.8
Seawater- virgin	55.6	71.5	63.9	60.1	71.4
Seawater- weathered	61.6	71.8	68.5	78.2	78.5

The results for the general uptake of chromium by virgin pellets in the studied medium, in descending order, were as follows: uptake in seawater > uptake in fresh water > uptake in deionised water.

Comparing the behaviour of uptake between virgin pellets and laboratory-weathered pellets in seawater, all studied pellets (except for LDPE where uptake levels were close; 71.5 ng g^{-1} and 71.8 ng g^{-1} using virgin and weathered pellets respectively) had higher uptake of chromium in weathered pellets compared to virgin pellets, especially by PET type of pellets.

It has been reported that the surface area of PE pellets increases and gains a negative charge due to the increase of functional groups after weathering in seawater, while PP only shows mechanical changes[213]. As mentioned in Section 4-2-1-3, the presence of the ester functional groups in both PET and BIO pellets might increase the weathering effects, which therefore could explain the affinity for chromium.

The interaction between chromium and the surface of plastic pellets can be explained by the enhanced polarity on the surface caused by weathering in seawater, as well as the medium where the experiment took place (changing pH and TDS), and the nature of the chromium.

4.2.4 Sorption experiment profile of lead using five types of both virgin and weathered plastic resin pellets: HDPE, LDPE, PET, PP and BIO

4.2.4.1 Lead uptake by virgin plastic pellets in deionised water, fresh water and artificial seawater

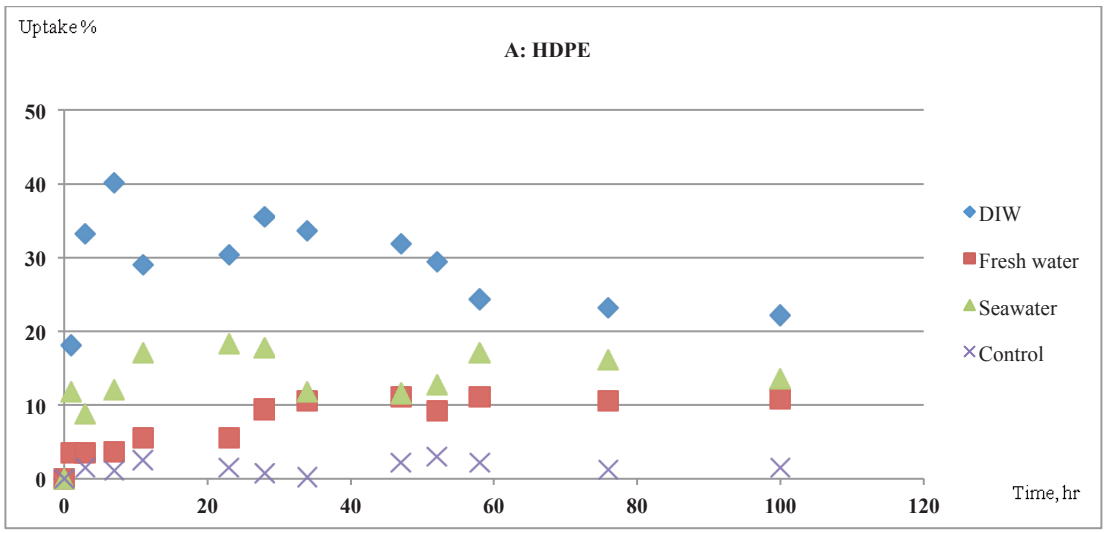
Each type of plastic pellet was shaken for 100 hours in a ~5 µg L^{-1} solution of lead prepared in deionised water, fresh water and artificial seawater. The uptake % of lead in the solutions, after 13 different time periods, is plotted in Figure 4-7.

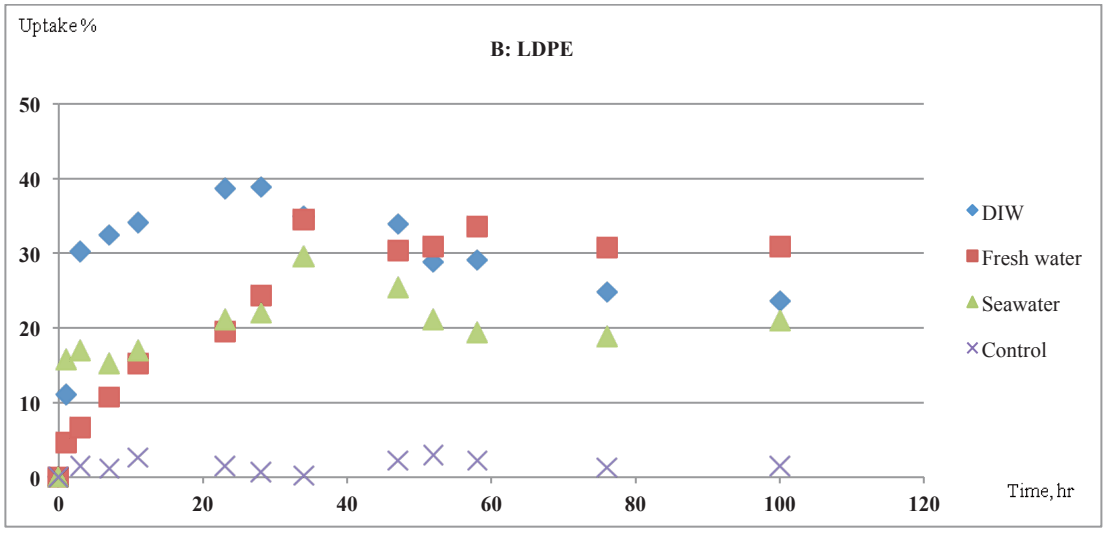
Tables A-1, A-2 and A-3 in Appendix 6 show the residual lead remaining in the deionised water, fresh water and artificial seawater solutions respectively at different times over the 100 hours, determined by ICP-MS, from which the uptake levels by the five types of virgin plastic pellets were determined.

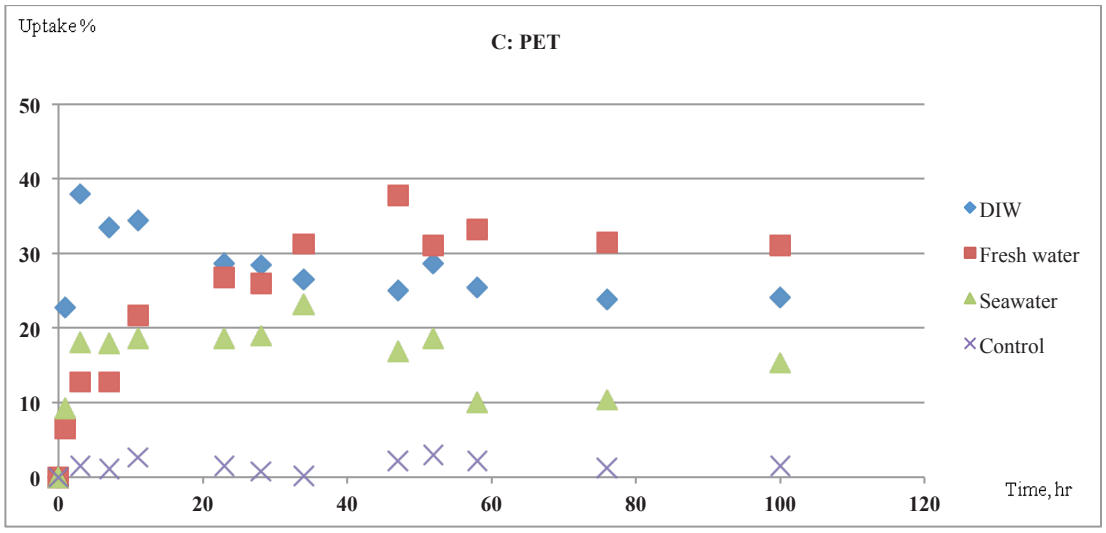
Precision of the analytical method of 10 replicates is ± 0.0471, RSD is 5.1 %, showing high precision. Table 4-10 shows the analytical method precisions obtained for lead analysis in deionised water, fresh water and seawater media.

Table 4-10 Analytical method precisions for lead analysis by ICP-MS

Analytical method	Pb in deionised	Pb in fresh water	Pb in seawater
SD	0.0333	0.031	0.0771
RSD	3.45 %	2.89 %	8.96%


Uptake %
A: HDPE
50
40
30
20
10
0
0
20
40
60
80
100
120
Time, hr
DIW
Fresh water
Seawater
Control


Uptake %
B: LDPE
50
40
30
20
10
0
0
20
40
60
80
100
120
Time, hr
DIW
Fresh water
Seawater
Control


Uptake %
C: PET
50
40
30
20
10
0
0
20
40
60
80
100
120
Time, hr
DIW
Fresh water
Seawater
Control

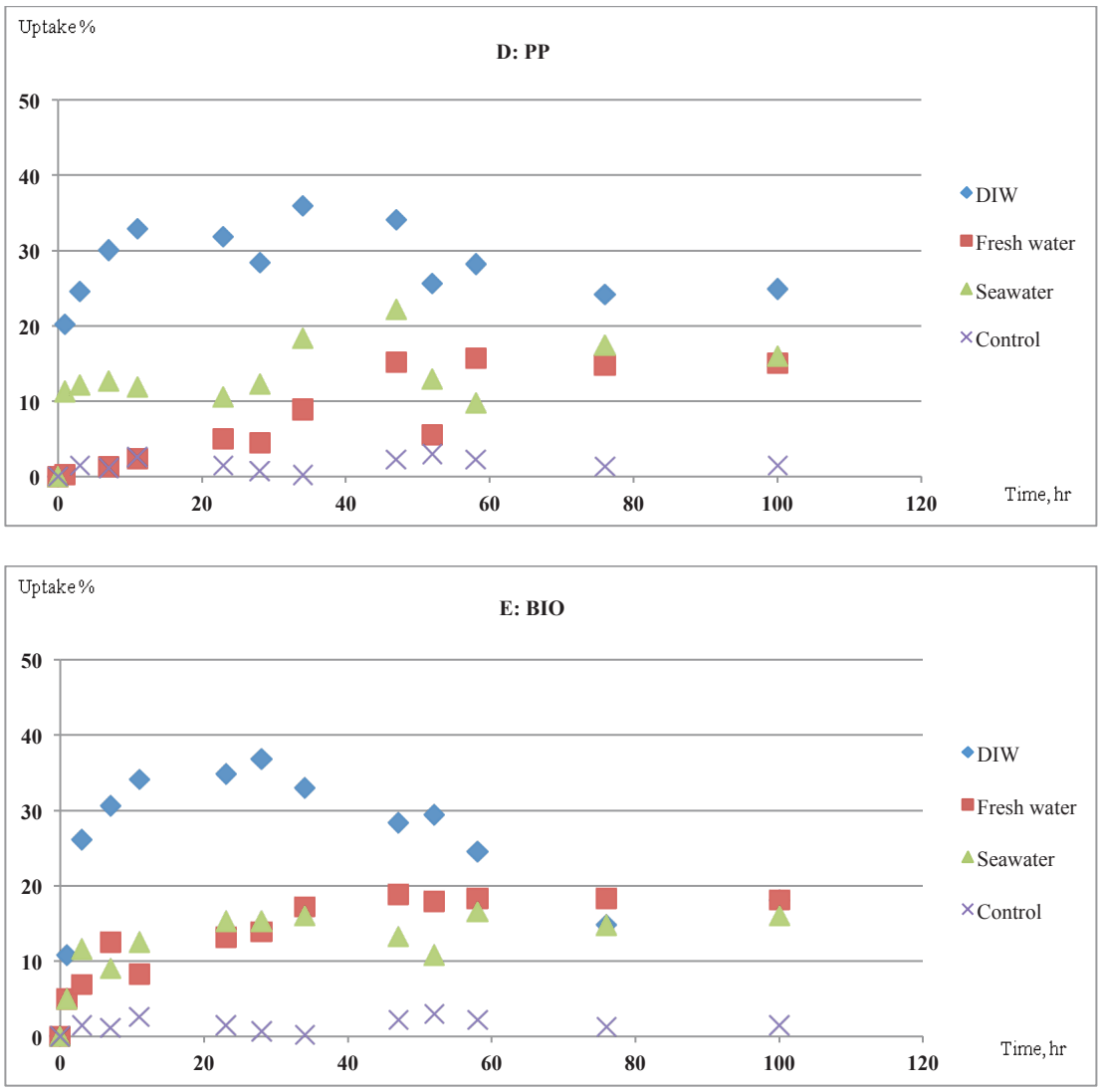


Figure 4-7 Lead taken up (loss) from a ~ 5 µg L^{-1} solution of Pb by A: HDPE, B: LDPE, C: PET, D: PP and E: BIO virgin plastic resin pellets in deionised water, fresh water and artificial seawater. Plus one control profile of lead in the absence of pellets. Analytical method SD: ± 0.0333, 0.031 and 0.0771 in deionised water, fresh water and seawater respectively.

In deionised water media, all values obtained were above the limit of detection, which was 0.00882 μg L^{-1}. The control results (see Table A-1 in Appendix 6) and Figure 4-7 suggest that the uptake of lead by the vial walls during the experiment was not significant (negligible compared to pellets uptake profiles Figure 4-7), and therefore the loss of lead can be attributed to the pellets present in each vial. The average value obtained for the residual cadmium in the control solution was 4.79 ± 0.1 μg L^{-1}, with an average loss of 0.06 μg L^{-1} for all control results analyses.

The results of the analysis of the residual lead remaining in the deionised water solutions showed a lower concentration of lead than the initial concentration of 4.85 μg L^{-1}. The maximum average loss of lead concentration was 1.34 μg L^{-1} for LDPE, and the minimum was 1.21 μg L^{-1} for BIO. Showing general close uptake by all plastic pellets studied.

During the experiment, a clear loss of lead by all studied pellets was observed. Most of the loss occurred in the first 20 – 30 hours of the experiment which can be indicated as the equilibrium time. Then the pattern was slightly "wavy" over time until ~ 60 hrs, blank results, which were nil, eliminate the possible release of lead from the pellets. However, it might be explained as a desorption of some adsorbed lead or due to inhomogeneous distribution of lead in individual pellets.

Comparing the results for lead to the previous results obtained in deionised water, lead showed a greater uptake (loss) by pellets than other studied PTE. The maximum average uptake of lead was 6.3 times more than the arsenic maximum average uptake, 2 times more than the cadmium maximum average uptake, and 7.9 times more than the chromium maximum average uptake in the same medium. This can only be attributed to the nature of the elements and its availability as all other possible variables were the same (as explained earlier in Section 4-2-2-1). Lead has a lower or similar charge, and a higher radius than all studied PTE, which might lead to and explain the greater adsorption (availability) of lead than the arsenic, cadmium and chromium by the pellets in the same medium, specifically deionised water.

The literature on the uptake of lead by plastic resin pellets in water is limited and this phenomenon has only been studied in estuarine and seawater conditions. Interactions between PTE and virgin PE plastic pellets were studied by Holmes *et al*.[218] at a pH range of between 4 and 10.5; the lead uptake behaviour was not in agreement with the findings of the current study, where the uptake at low pH and close to current study was low (~2.5 % of Pb was adsorbed), whereas in current study the range of lead adsorbed was between 24.9 – 27.7 %). This can be attributed to the medium (adjusted pH river water) in which the experiment took place i.e. higher TDS than the TDS in current study for the deionised water. Whereas in current study, the pH achieved by changing the media from deionised to fresh to seawater i.e. both pH and TDS are change.

In fresh water media, all values obtained were above the limit of detection, which was 0.00157 µg L^{-1}. The control values (see Table A-2 in Appendix 6) and Figure 4-7 suggest that the uptake of lead by the vial walls during the experiment was not significant, and therefore the loss of lead can be attributed to the pellets present in each vial. The average value obtained for the remaining lead in controls was 5.36 ± 0.102 µg L^{-1}, with an average loss of 0.04 µg L^{-1}, for all control results analyses.

The results of the analysis of the residual lead remaining in fresh water solutions showed a lower concentration of lead than the initial concentration of 5.4 µg L^{-1}. The maximum average loss of lead concentration was 1.26 µg L^{-1} for PET, and the minimum was 0.37 µg L^{-1} for PP. Unlike in deionised water, a big gap was occurred between the losses of lead by plastic pellets studied.

During the experiment, a clear uptake of lead in all types of pellets was observed, especially by LDPE, PET and BIO. All types of pellets showed the same profile pattern during the experiment by reaching the equilibrium after around 30 – 40 hours of shaking. Generally, the sorption profile of lead showed the opposite behaviour compared with arsenic and chromium and similar behaviour to cadmium uptake in fresh water.

A comparison of lead uptake in fresh water with the uptake in deionised water showed that the uptake in fresh water was lower than it was in deionised water. This behaviour

of lead can possibly be explained by the presence of competing elements in fresh water which were not present in deionised water, bearing in mind that adsorption is not a selective process.

The lead uptake results obtained by Holmes *et al*.[218] as salinity changed by mixing fresh water with seawater using virgin pellets (PE) were generally in agreement with the results of the current study, where the uptake of lead decreased as the TDS of the medium increased. However, in the same study, the lead uptake at different pHs was different to that demonstrated in the study, where the lead uptake increased as the pH increased in Holmes *et al*. study. The converse behaviour observed in the current study can be attributed to the medium used as explained earlier where the pH was adjusted in the same medium (river water) using 0.1 M NaOH or 0.1 M HNO_3, whereas in the current study the pH changed consequentially as the medium of the experiments changed i.e. both pH and TDS were changed. This suggests that the TDS influence was greater than the pH influence on Pb-pellets interaction.

In artificial seawater media, all values obtained were above the limit of detection, which was 0.00429 μg L^{-1}. The control values (see Table A-3 in Appendix 6) and Figure 4-7 suggest that the uptake of lead by the vial walls during the experiment was not significant, and therefore the loss of lead can be attributed to the pellets present in each vial. The average value obtained for the residual lead in the control solution was 5.00 ± 0.07 μg L^{-1}, with an average loss of 0.03 μg L^{-1}, for all control results analyses.

The results of the analysis of the residual lead remaining in seawater solutions showed a lower concentration of lead than the initial concentration of 5.03 μg L^{-1}. The maximum average loss of lead concentration was 0.94 μg L^{-1} for LDPE, and the minimum was 0.60 μg L^{-1} for BIO, showing relatively close uptake by all plastic pellets studied.

The results of the analysis also indicated a lower uptake of lead by PET, LDPE and BIO compared with the uptake that took place in fresh and deionised water. This can be explained by the presence of competing elements, as the TDS of the medium (deionised water < fresh water < seawater) increases, depending on the sea salt gradient used as

seen in Table 3-4. Unexpectedly, the uptake of lead by HDPE and PP was higher than it was in fresh water but less than in deionised water i.e. the general pattern remained similar for all studied pellets.

The results obtained by Holmes *et al*.[218] for lead uptake (as salinity changed by mixing fresh water with seawater) using virgin pellets (PE) remained generally in agreement with those of the current study, where the uptake of lead decreased as the TDS of the medium increased. However, in the same study and as mentioned in 4-2-4-1, the lead uptake at different pHs was different to that demonstrated in the present study, where the lead uptake increased as the pH increased in Holmes *et al*. study. The converse behaviour observed in the current study can be attributed to the media used. In the study by Holmes *et al*. the pH was adjusted in the same medium (river water) using 0.1 M NaOH or 0.1 M HNO_3, whereas in the current study the pH changed consequentially as the medium of the experiments changed i.e. both pH and TDS were changed.

4.2.4.2 Lead uptake by laboratory-weathered plastic pellets in artificial seawater

Each type of laboratory weathered plastic pellet was shaken for 100 hours in a ~5 μg L^{-1} solution of lead prepared in artificial seawater. The uptake % of lead in the solution, after 13 different time periods, is plotted in Figure 4-8.

Table A-4 in Appendix 6 shows the residual lead remaining in the solution at different times (over the 100 hours), determined by ICP-MS, from which the uptake levels by five types of weathered plastic pellets in artificial seawater were determined.

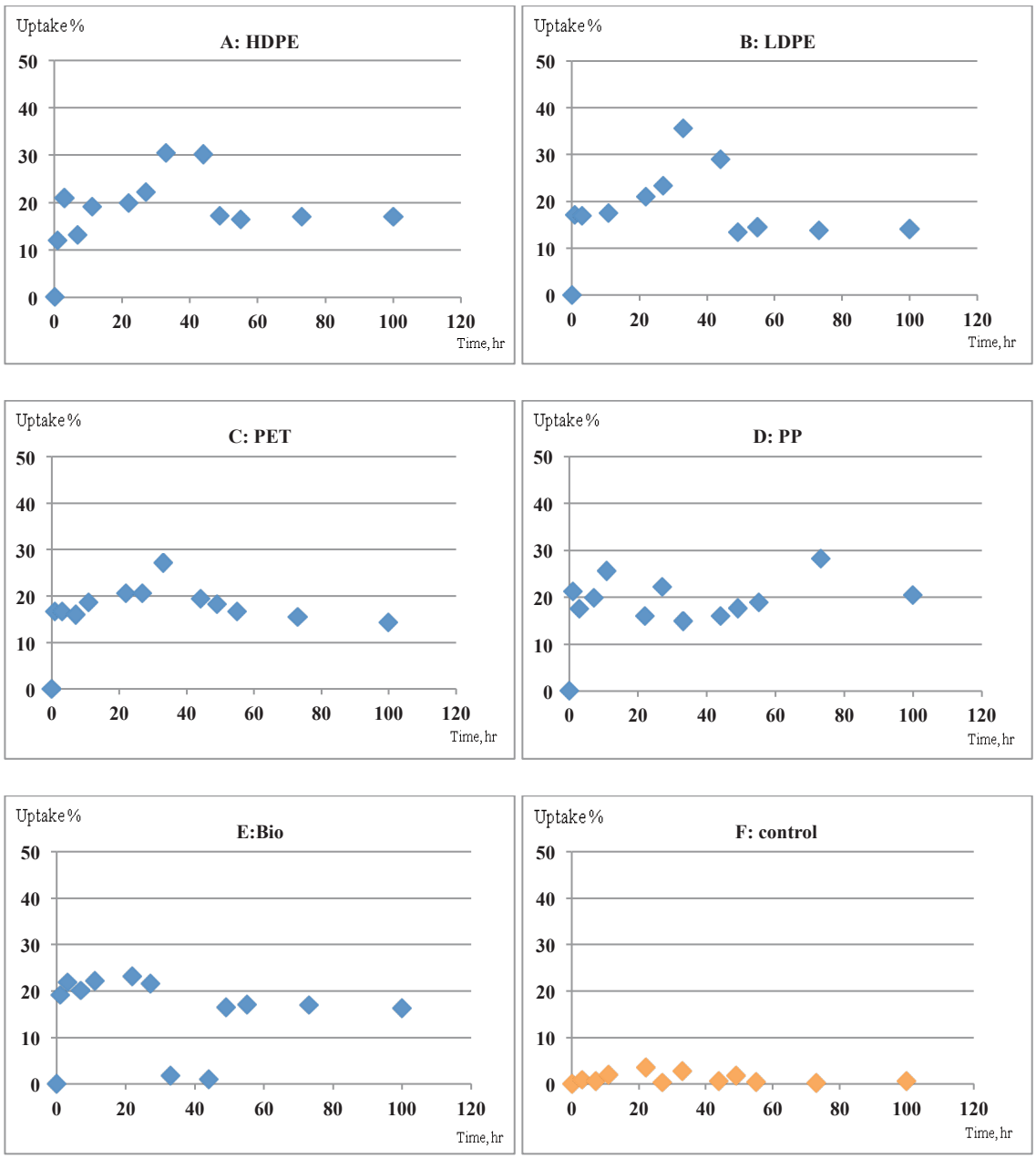


Figure 4-8 Lead taken up (loss) from a ~ 5 µg L^{-1} solution of Pb by A: HDPE, B: LDPE, C: PP, D: PET and E: BIO laboratory-weathered plastic resin pellets in artificial sea water. F: control profile of lead in artificial seawater in the absence of pellets. Analytical method SD: ± 0.0771.

All values obtained were above the limit of detection, which was 0.00429 μg L^{-1}. The control values (see Table A-4 in Appendix 6) and Figure 4-8F suggest that the uptake of lead by the vial walls during the experiment was not significant, and therefore the loss of lead can be attributed to the pellets present in each vial. The average value obtained for the residual lead in the control solution was 5.00 ± 0.07 μg L^{-1}, with an average loss of 0.03 μg L^{-1}, for all control results analyses.

The results of the analysis of the residual lead remaining in seawater solutions showed a lower concentration of lead than the initial concentration of 5.03 μg L^{-1} except for one value in the LDPE profile. The maximum average loss of lead concentration was 0.90 μg L^{-1} for HDPE and PP, and the minimum was 0.69 μg L^{-1} for LDPE (due to the high value obtained in LDPE profile).

In LDPE profile, one result was above the initial concentration (6.93 μg L^{-1}), in BIO profile two results were very close to the initial concentration and showed no uptake which was possibly due to these vials being over-spiked at the start of the experiment. An overall profile can still be clearly obtained.

Weathered pellets in seawater showed a generally higher uptake of lead than the virgin pellets, which indicates that the weathering process did affect the surface of the pellets and enhanced the pellet-lead interaction in seawater. The maximum uptake by weathered pellets in seawater was close to the maximum uptake by virgin pellets (which was also observed in chromium laboratory-weathered profile), this might be attributed to the studied element nature such as the radius size and the weathered surface changes such as the surface porosity or due to the affect of individual odd values obtained in the profile.

The beached pellets (weathered naturally in the marine environment) results obtained by Holmes *et al*.[118, 218] as well as those for virgin pellets (PE) were in agreement with those of the current study, and showed a generally higher uptake of PTE than by the virgin pellets studied.

4.2.4.3 Comparison of all lead results

The lead sorption profiles showed that the uptake of lead was greatest in all plastic pellets in deionised water. As the TDS of the sorption medium increased with the use of fresh water and artificial seawater, the level of uptake of Pb uptake by virgin plastic pellets decreased. It subsequently increased when the laboratory-weathered pellets were used in seawater. It was clear that both the petroleum based and bio based plastic pellets studied showed generally similar behaviour as was observed in deionised, fresh and seawater medium which suggests that the Pb-plastic interaction is non-specific and so independent of the type of plastic, a finding that is in agreement with a study conducted on five types of petroleum based pellets[211]. The Pb-pellets interaction showed the converse behaviour compared with arsenic uptake which was explained earlier.

Using the present sorption data, the lead uptake in ng g^{-1} was calculated at each time point (see Appendix 7). Table 4-11 shows the average uptake of each type of pellet in different medium.

The results for the general uptake of lead by virgin pellets in the studied medium, in descending order, were as follows: uptake in deionised water > uptake in fresh water > uptake in seawater.

Table 4-11 Average uptake of lead in different medium by 5 types of pellets in ng g^{-1}

Pb in	HDPE	LDPE	PP	PET	BIO
Deionised water	157	164	156	150	148
Fresh water	47.9	138	49.0	148	86.2
Seawater- virgin	77.9	110	75.5	88.0	71.2
Seawater- weathered	111	108	106	99.4	90.9

Comparing the behaviour between virgin pellets and laboratory-weathered pellets in seawater, there was generally higher uptake of lead in weathered pellets compared to virgin pellets in seawater, with the exception of LDPE which sorbed slightly less lead than the virgin ones.

Weathered HDPE and PP had a higher uptake of and more affinity for lead than the other types. This suggests that this type of pellets were probably more affected by the weathering process, most likely in a way that enhanced the Pb-pellets interaction than the other pellets types. This affinity was also observed by weathered PP for cadmium in seawater.

It has been reported that the surface area of PE pellets increases and gains a negative charge due to the increase of functional groups after weathering in seawater, while PP only shows mechanical changes[213]. This is in agreement, for the first time in this study, with the HD results obtained in this study, and also with the PP.

As mentioned in Section 4-2-1-3, the presence of the ester functional groups in both PET and BIO pellets might increase the weathering effects (as observed in Figure 3-1) which may explain their affinity for lead.

The interaction between lead and the surface of plastic pellets can be explained by the enhanced polarity on the surface caused by weathering in seawater, as well as other surface changes such as porosity size and changes due to weathering, the TDS of the experiment medium, and the nature of the lead such as the radius diameter.

4.3 Multi element sorption experiment profile for selected PTE

This experiment aimed to study the sorption potential of arsenic, cadmium, chromium and lead using a multi-element solution, rather than a set of individual element solutions, at the concentration of 5 µg L^{-1} per element in artificial seawater. The effect of this on the sorption behaviour and capacity of laboratory-weathered HDPE, LDPE, PET, PP and BIO plastic pellets at equilibrium time was investigated.

4.3.1 The uptake of arsenic, cadmium, chromium and lead by laboratory-weathered plastic pellets in multi-element artificial seawater

Each type of laboratory-weathered plastic pellet was shaken in a ~ (5 µg L^{-1}) multi-element solution consisting of arsenic, cadmium, chromium and lead prepared in artificial seawater. The residual PTE concentrations in the solution determined by ICP-MS at equilibrium were used to determine the percentage of uptake adsorption capacity[222] by all types of pellet at equilibrium, as shown in Table 4-12.

Table A-1 in Appendix 8 shows the residual PTE concentrations in the solutions. It was then used to determine the uptake by five types of weathered plastic pellets in artificial seawater, followed by the calculation of the percentage mass uptake.

Table 4-12 Arsenic, Cd, Cr and Pb mass percent taken up (adsorption capacity) by different plastic pellets at 5 µg L^{-1} spiked multi concentration in artificial seawater, (n= 3).

PTE (5 µg L^{-1}) in seawater	**% Mass* uptake, HDPE**	**% Mass uptake, LDPE**	**% Mass uptake, PET**	**% Mass uptake, PP**	**% Mass uptake, BIO**
As	2.64	2.93	3.55	1.93	4.90
Cd	17.7	16.7	20.1	5.8	19.6
Cr	7.65	5.42	7.97	6.22	6.85
Pb	19.3	19.1	19.7	21.2	21.3

* % mass uptake = (average concentration loss in solution after the experiment (µg L^{-1}) X 100) / initial concentration (µg L^{-1}) before the experiment

All values obtained were above the limit of detection, which was 0.00522 μg L^{-1} for arsenic, 0.00261 for cadmium, 0.00853 for chromium and 0.00665 for lead. A good degree of precision was achieved where the RSD of triplicate samples were < 10 % for all types of pellet studied. The RSD values for the obtained arsenic concentrations were 1.05, 2.34, 0.50, 1.74 and 0.18 for HDPE, LDPE, PET, PP and BIO respectively. The RSD values for cadmium were 0.865, 1.163, 1.596, 1.960 and 0.592 for HDPE, LDPE, PET, PP and BIO respectively. The RSD values for chromium concentrations were 0.403, 2.51, 1.43, 1.05, and 1.57 for HDPE, LDPE, PET, PP and BIO respectively. The RSD values for the lead concentrations were 0.489, 4.16, 0.338, 2.89, and 1.78 for HDPE, LDPE, PET, PP and BIO respectively.

The control values (see Table A-1 in Appendix 8) suggest that the uptake of the analytes by the vial walls during the experiment was not significant, and the loss of PTE can therefore be attributed to the pellets present in each vial.

The results of the analysis of the residual arsenic, cadmium, chromium and lead remaining in the seawater solutions showed a lower concentration compared with the initial concentrations of 5.17 μg L^{-1}, 5.65 μg L^{-1}, 6.27 μg L^{-1} and 5.46 μg L^{-1} respectively. This indicated that there was a loss of PTE studied the experiment for all types of pellet.

The adsorption capacity (the percentage of mass taken up) of pellets showed that all types of pellets studied showed a higher affinity for cadmium and lead than for arsenic and chromium, except for PP, which only showed this affinity for lead. All types of pellets had the lowest affinity to arsenic. This may be attributed to the nature of the individual elements and their availability to be adsorbed by the surface of the pellets. It was clear that elements with a small ionic radius size were unlikely to be able to compete with those with a large radius size (~115, ~140, ~155 and ~180 pm for arsenic, cadmium, chromium and lead respectively[219]). This finding supports the possibility of electrostatic attraction and the effect of the size of the hydration sphere on the attraction of PTE–pellets.

Recalling the results obtained in Sections 4-2-1-2, 4-2-2-2, 4-2-3-2 and 4-2-4-2 concerning the uptake of arsenic, cadmium, chromium and lead respectively by laboratory-weathered pellets in seawater using a single element solution, and for ease of comparison, the % removal efficiency equation (see Section 4-2-1-4) was applied for the concentration of 5 µg L^{-1} for all pellets studied. Table 4-13 shows the removal efficiency of PTE studied in an individual (5 µg L^{-1}) and multi-element (5 µg L^{-1} of each of As, Cd, Cr and Pb) seawater medium.

Table 4-13 The removal efficiency of As, Cd, Cr and Pb at equilibrium in 5 µg L^{-1} individual and after the equilibrium in multi element (5 µg L^{-1} As, Cd, Cr and Pb, n= 3) seawater medium.

As in seawater	**%Removal efficiency* by HDPE**	**%Removal efficiency by LDPE**	**%Removal efficiency by PET**	**%Removal efficiency by PP**	**%Removal efficiency by BIO**
Individual element	8.4	21.5	16.7	11.6	14.4
Multi element	2.64	2.93	3.55	1.93	4.9
Cd in seawater	**%Removal efficiency by HDPE**	**%Removal efficiency by LDPE**	**%Removal efficiency by PET**	**%Removal efficiency by PP**	**%Removal efficiency by BIO**
Individual element	3.32	8.9	13.1	8.9	14.3
Multi element	17.8	16.8	20.1	14.8	19.6
Cr in seawater	**%Removal efficiency by HDPE**	**%Removal efficiency by LDPE**	**%Removal efficiency by PET**	**%Removal efficiency by PP**	**%Removal efficiency by BIO**
Individual element	12.0	23.2	15	14	14.5
Multi element	7.78	5.55	8.10	6.35	7.00
Pb in seawater	**%Removal efficiency by HDPE**	**%Removal efficiency by LDPE**	**%Removal efficiency by PET**	**%Removal efficiency by PP**	**%Removal efficiency by BIO**
Individual element	21.1	20.2	19.0	19.9	15.1
Multi element	19.4	19.0	19.5	21.2	21.2

* % Removal efficiency = % removal efficiency = $(C_0 - C_f)$ 100/ C_0 where; C_0 is the initial concentration, and C_f is the remaining concentration in soln.

Arsenic and chromium showed greater removal by all laboratory-weathered pellets studied from a single element solution in seawater, compared with in a multi-element seawater medium, whereas cadmium showed greater removal from the multi-element medium than the single element medium. The removal of lead was not affected by the seawater medium, and it remained almost similar, with the exception of BIO, which showed higher removal efficiency in the multi-element seawater. This result is in agreement with the statement earlier in this section that arsenic and chromium are unlikely to compete with cadmium and lead.

Therefore, the lower uptake of both arsenic and chromium can be attributed to the presence of competing elements (cadmium and lead) in the multi-element solution. In principle, the results obtained indicate that the uptake of cadmium and lead is more likely to be applicable to the real-life marine environment than would be the case for arsenic and chromium.

4.4 Overall comparison and findings

Potentially toxic elements were successfully analysed in petroleum-based and bio-based virgin plastic pellets. For all types of pellet, the detected elements, notably sodium, magnesium, followed by silicon, iron, zinc and aluminium, were expected and associated with the production of plastic. Certain elements, namely antimony and copper, were detected in PET at much greater concentrations than in the other types of pellet studied. High RSDs suggest that the distribution of PTE in plastic pellets was not uniform.

The sorption potential of plastic pellets was successfully established for arsenic, cadmium, chromium and lead. The total arsenic uptake by virgin pellets over 100 hours showed that uptake was higher in seawater than in fresh water, with the lowest uptake found in the deionised water medium, which was clearly influenced by the pH.

In contrast, the highest uptake of cadmium and lead by pellets was in deionised water, followed by fresh water. The lowest was in seawater, except for HDPE and PP in lead profile. The medium level of TDS has a clear effect on this behaviour.

The uptake behaviour of chromium fluctuating slightly and was generally similar to the uptake behaviour of arsenic; its highest uptake was in seawater. The lowest uptake was in deionised water for LDPE, PP and BIO, whereas for HDPE and PET the lowest uptake was in fresh water.

The equilibrium time was generally between 24 – 40 hours, and was not always easy to indicate especially when the uptake was low and in case of fluctuant sorption profile.

Petroleum-based and bio-based pellets showed similar uptake behaviour. Low density PE generally showed higher affinity to PTE than the HDPE. The LDPE, PET and BIO types of pellets generally showed more affinity to PTE during the sorption experiments than HDPE and PP. This suggests that the "environmentally friendly" bio-based plastic may cause the same problem as the petroleum-based pellets when it reaches the marine environment, i.e. it can act as a vector for transport of PTE.

The results suggest that the bigger the atomic radius of the metal PTE, the higher the uptake by plastic pellets; total lead uptake was 2183 ng g^{-1}, total cadmium uptake was 877 ng g^{-1} and total chromium uptake was 864 ng g^{-1} over the whole profile. Total arsenic uptake was 1046 ng g^{-1}

It was found that compared to virgin plastic pellets, laboratory-weathered surface pellets generally showed greater affinity for PTE adsorption in seawater, which is in agreement with the literature[213].

When using a multi-element seawater medium, the adsorption capacity of cadmium and lead was greater than for arsenic and chromium. This suggests that arsenic and chromium were unlikely to compete with cadmium and lead for uptake onto the surface of pellets, at least under the experimental conditions studied. The total adsorption

capacity supports the previous suggestion regarding the correlation between the size of the atomic radius and uptake by pellets (Pb total adsorption capacity > Cd > Cr > As).

5 Surface study of virgin and laboratory-weathered plastic pellets using an analytical scanning electron microscope and the identification of plastic pellets using ATR-FTIR

5.1 Surface study of the plastic pellets using an analytical scanning electron microscope JSM-6010 LA

The study of the surface of pellets includes the acquisition of plastic pellet surface images and elemental scanning using an analytical scanning electron microscope (SEM). This study examined both virgin and laboratory-weathered HDPE, LDPE, PET, PP and BIO plastic pellets to identify the elemental contents on pellets' surfaces and the surface morphology of individual pellets. It is important to study the surfaces of pellets because this is where the adsorption of PTE takes place, and any differences noted might help to explain the results obtained in Chapter 4.

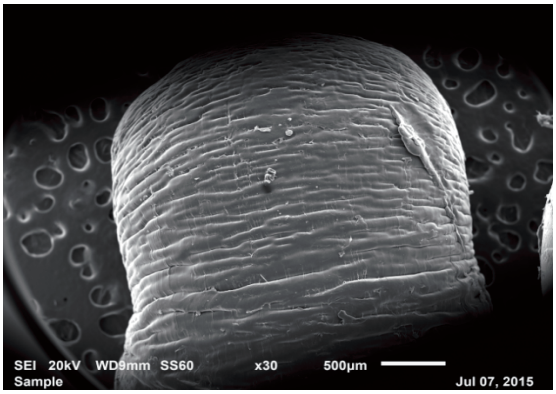
However, it is important here to restate the limitation of this study (see Section3-4-3) of using more than one point of study of a single sample rather than replicates samples of each type of pellets. Studying the same pellets before and after laboratory-weathering will be also recommended to avoid the limitation of the surface study. This limitation allows only reporting observations instead of findings.

5.1.1 Imaging of virgin and laboratory-weathered plastic pellet surfaces using an analytical scanning electron microscope

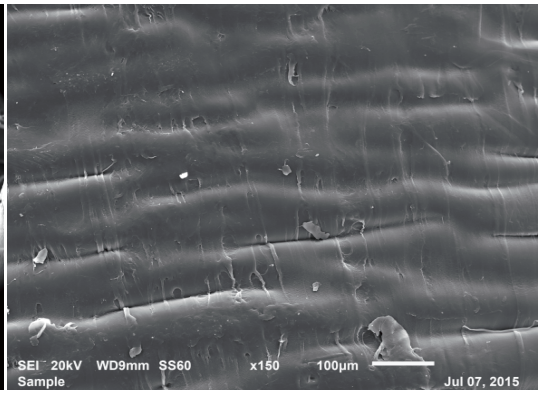
Five types of virgin and laboratory-weathered plastic pellets were imaged in order to visualise the surface of virgin pellets and to spot any topographical changes on the surface of weathered pellets that cannot be observed by the naked eye. At least one corresponding magnification was always applied, to virgin and laboratory-weathered pellets of the same plastic to aid comparison.

5.1.1.1 Surface imaging of virgin and laboratory-weathered HDPE

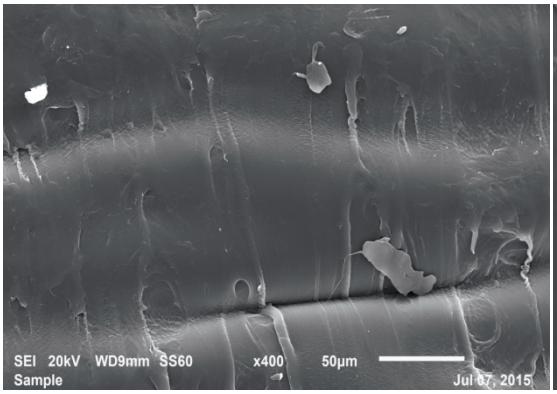
Figure 5-1 shows the surface topography of an individual virgin and an individual laboratory-weathered HDPE pellet in magnifications ranging from x30 to x2000.



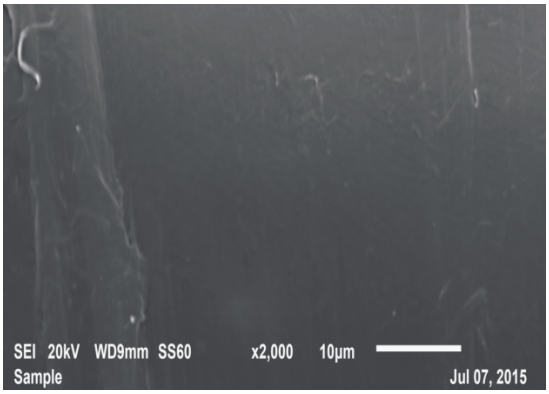
A



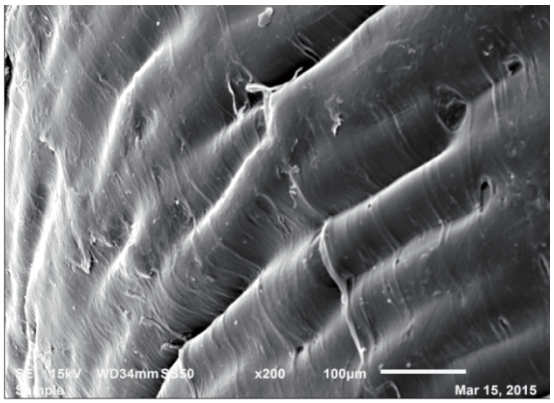
B



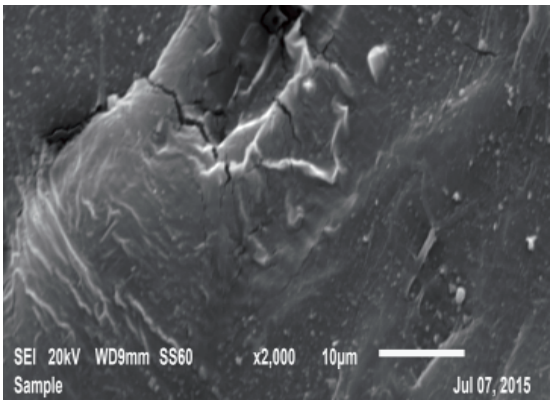
C



D



E



F

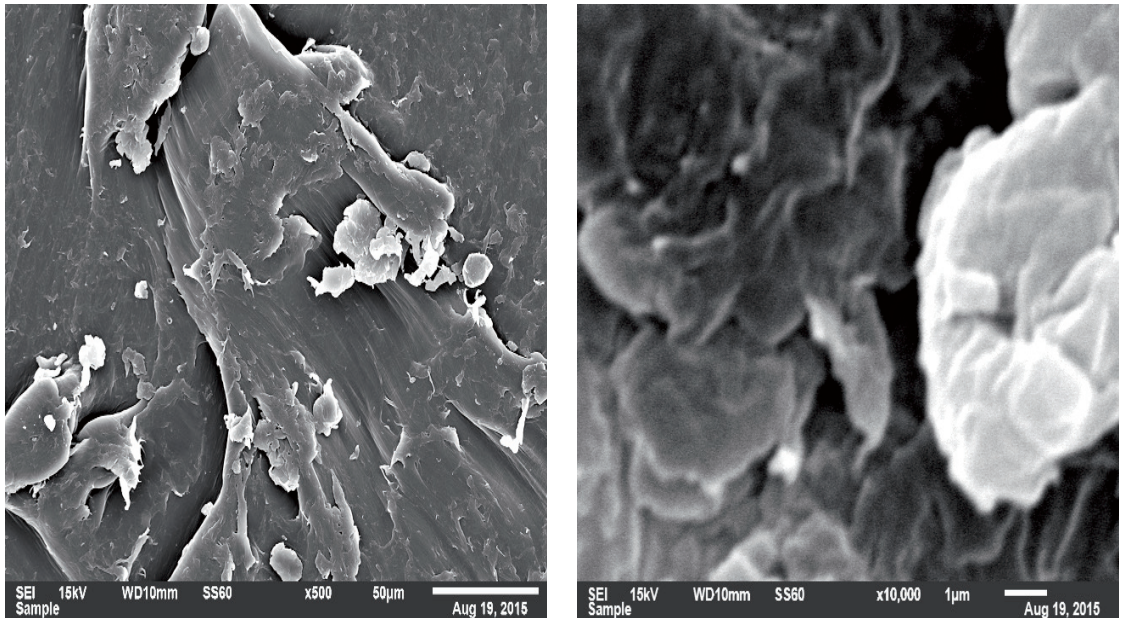
Figure 5-1 Imaging of a virgin HDPE pellet surface using scanning electron microscope at different magnifications. A: x30 (scale bar = 500 µm), B: x150 (scale bar = 100 µm), C: 400 (scale bar = 50 µm), D: 2000 (scale bar = 10 µm), and a laboratory-weathered HDPE pellet E: x200 (scale bar = 100 µm), F: x2000 (scale bar = 10 µm).

Surface morphology of platinum coated pellet was successfully visualised using SEM. The surface of the virgin pellet was clearly undulating (see Figure 5-1 A and B). A black narrow line that reflected a deep fold in this particular area was clear in Figure 5-1 C. In contrast to the results obtained by Kalliopi and Hrissi[213], in this study, the surface images of virgin HDPE indicated that the surface was not smooth. This surface roughness may increase the surface area, leading to better adsorption, and might contribute to the adsorptive ability of virgin pellets described in Section 4-2.

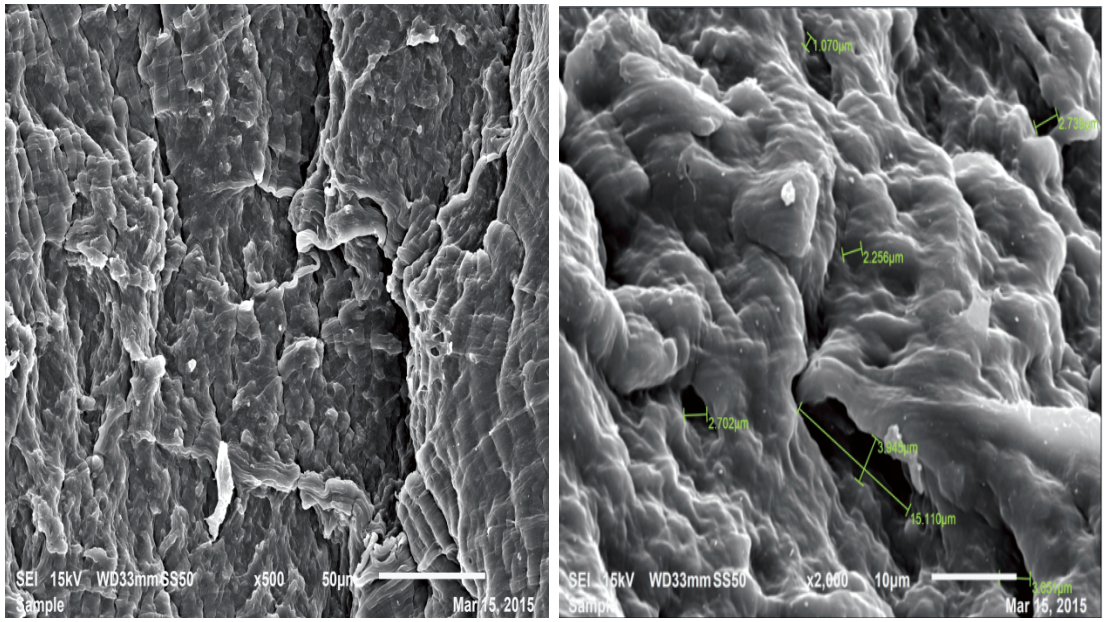
A comparison between virgin and weathered plastic pellets showed some minor changes, with deeper folds on the wavy surface of the weathered HDPE in Figure 5-1 E than in the virgin one. Cracks also appeared on the surface of the weathered pellets (Figure 5-1 F), and there were some changes compared with the -relatively smooth surfaces observed in the- image of the corresponding virgin pellet Figure 5-1 D. Although no discolouration of HDPE was observed after the laboratory-weathering period (see Section 3-2-2), the SEM images revealed some changes on the pellet surface. Recalling results obtained in chapter 4, Section 4-2, weathered HDPE pellets showed generally a slight higher uptake compared with virgin HDPE. However, any assumption cannot be claim as sample size was not high enough.

5.1.1.2 Surface imaging of virgin and laboratory-weathered LDPE

Figure 5-2 shows the surface topography of an individual virgin and an individual laboratory-weathered LDPE pellet, at various magnifications.



A B



C D

Figure 5-2 Imaging of virgin LDPE pellet surface using scanning electron microscope at different magnifications. A: x500 (scale bar = 50 µm), B: x10000 (scale bar = 1 µm) and laboratory-weathered LDPE pellet C: x500 (scale bar = 50 µm), D: x2000 (scale bar = 10 µm).

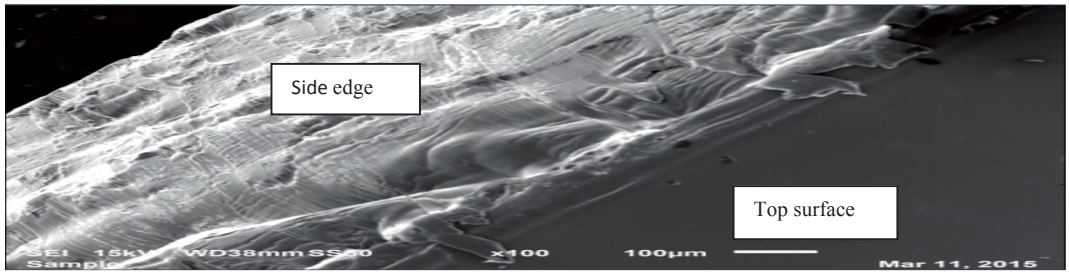
The surface image of virgin LDPE (see Figure 5-2 A) indicated that the pellet surface was not smooth, which is not in agreement with the description of Kalliopi and Hrissi[213] where two virgin pellets of PE (HDPE and LDPE) were visualised by SEM enlarged 1000 and 5000 times. Instead, clear roughness and layers were observed. White regions on the surface were clearly imaged, mainly at the edges of the layer-like parts, which were not abundant on the virgin HDPE. White areas in SEM images usually indicate a high concentration of metal elements in a particular position[223]. This supports two points discussed earlier in Section 4-2: first, that the presence of elements on the surface of virgin pellets can be attributed to the residual elemental catalyst and additives used in the production of pellets; it is randomly distributed, as shown in image A and B. Secondly, this observation may also explain the affinity of LDPE for PTE compared with HDPE, as described in Section 4-2-1-5. The x10000 magnification image B was applied to visualise the topography of the white part to ensure that it was part of (rather than a deposit on) the pellet surface.

The effect of weathering on the surface of LDPE is clearly shown in Figure 5-2 C, compared with the virgin image A at the corresponding magnification (x500). Roughness and cavities were dominant on the surface, as also shown in image D.

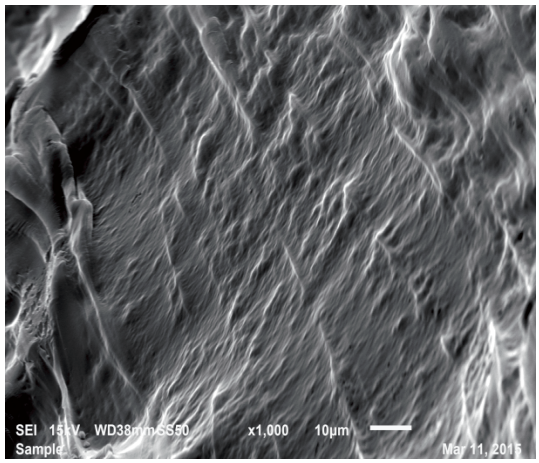
Unarguably, the LDPE surface changed more in response to laboratory-weathering compared with the HDPE. This can be attributed to physical properties of PE, as discussed in 1-2-1-1. This observation is in agreement with the results obtained in section 4-2, where weathered LDPE uptake generally more PTE than the weathered HDPE.

5.1.1.3 Surface imaging of virgin and laboratory-weathered PET

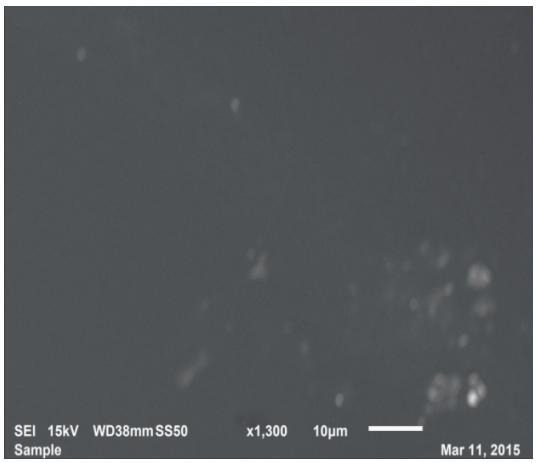
Figure 5-3 shows the surface topography of a single virgin and a single laboratory-weathered PET pellet at different magnifications.



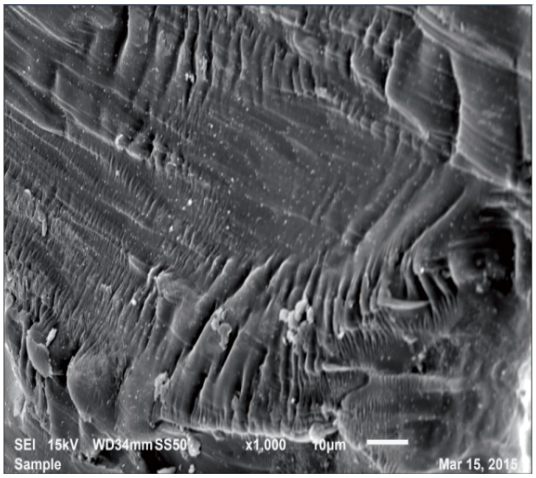
A



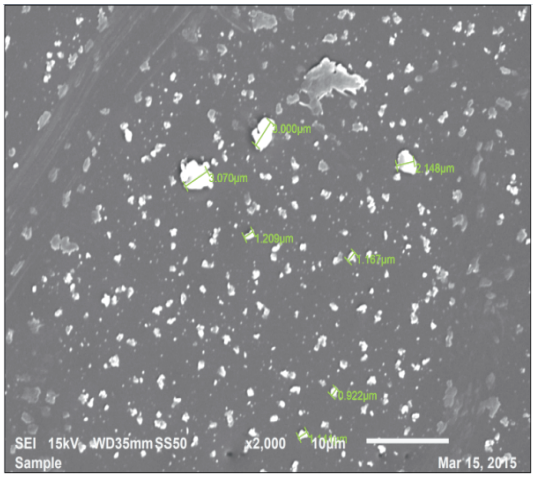
B



C



D



E

Figure 5-3 Imaging of virgin PET pellet surface imaging using scanning electron microscope at different magnifications. A: x100 (scale bar = 100 µm) side and top surface, B: x1000 (scale bar = 10 µm) side, C: x1300 (scale bar = 10 µm) top and laboratory-weathered PET pellet D: x1000 (scale bar = 10 µm) side, E: x2000 (scale bar = 10 µm) top.

Surface images of virgin PET indicated that this type of pellet has a planar shape (in contrast to the other types of pellet, which are more spherical) and a distinct edge, with a very smooth morphology on the top surface and rough morphology on the side surface, as shown in image A, Figure 5-3. Roughness with some white parts was clear on the side edge of the PET, as seen in the top left of Figure 5-3 B, whereas the plain image of Figure 5-3 C indicates the top surface was smooth with few white dots. As mentioned in Section 5-1-1-2, white dots in virgin pellets can be attributed to the elemental residual catalyst and the additives used.

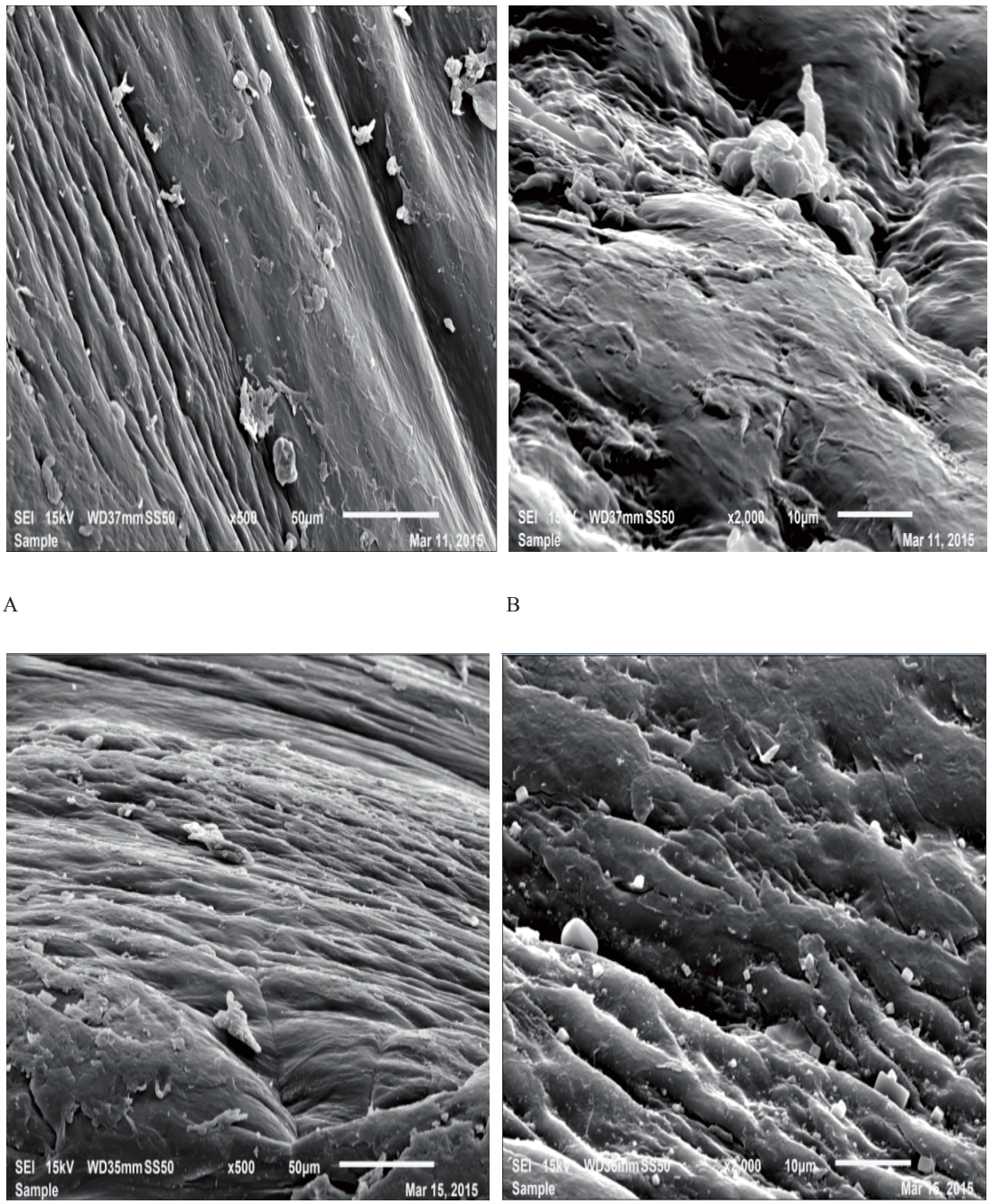
The weathering process has a significant effect on both sides of the surface, as shown in images D and E compared with virgin images B and C. The side edge showed further roughness, grooves and cavities with tiny white dots, while the top surface was dominated with white and grey dots, which may be attributed to the surface becoming eroded, by heat, UV light or surface hydrolysis, and scratched. Abundant white dots in weathered pellets can be attributed to elemental adsorption from the artificial seawater or may be a - deposition of sea salt - in which the laboratory-weathering took place.

The changes observed in SEM images, along with the discolouration seen in Section 3-2-2, support the affinity of weathered PET compared to virgin PET for PTE studied during the experiments reported in Section 2-4.

In literature, similar images have been reported[224] (Figure 10 in the publication) for microplastic collected from fish gut where PE, PET, PP and PVC particles were added to the fish diet. These white (bright) regions and the presence of titanium were attributed to the white pigments used in plastic.

5.1.1.4 Surface imaging of virgin and laboratory-weathered PP

Figure 5-4 shows the surface topography of a single virgin and a single laboratory-weathered PP pellet at various magnifications.



A B

C D

Figure 5-4 Surface imaging of a virgin PP pellet using scanning electron microscope at different magnifications. A: x500-scale 50 µm, B: x2000-scale 10 µm and laboratory-weathered PP pellet C: x500-scale 50 µm, D: x2000-scale 10 µm.

In contrast to the result obtained by Kalliopi and Hrissi[213] for two virgin PP, the surface images of virgin PP in this study indicated that the surface was not as smooth as described in the above-mentioned study. This might be attributed to individual pellet, producer or magnifications. As seen in Figure 5-4 A, some parts of the surface were rougher than others. Some white dots and flakes also appeared, possibly due to the uneven distribution of impurities on the pellet. A more close-up image (B) of x2000 magnification showed that the roughness looked like an aged tree root with some cavities.

Weathering was not clearly visualized in image C compared with the corresponding virgin image A, especially when concentrating on the left-hand side of the image A where the roughness appeared. The roughness and cavities were relatively similar on both images. However, white dots were dominant in the weathering pellet, as seen in the image D, which can be attributed to the elemental adsorption during the weathering process or as mentioned in Section 5-1-1-4 to the "deposition of sea salt". As mentioned earlier, all assumptions and supposition cannot be claim due to the sample size limitation.

According to the results obtained in this study (Section 4-2), the uptake of PTE by weathered PP is different. Almost the same values of arsenic and chromium were taken up by weathered and virgin PP, whereas weathered PP showed higher uptake of cadmium and lead than the virgin PP. The SEM images revealed that the surface of this type of pellet did not undergo notable weathering over the three-week period, which may explain its low affinity for some PTE. More time or different conditions (higher temperature) may be required to reach the point at which further erosion could be visualised.

5.1.1.5 Surface imaging of virgin and laboratory-weathered BIO

Figure 5-5 shows the surface topography of a single virgin and a single laboratory-weathered BIO pellet at various magnifications.

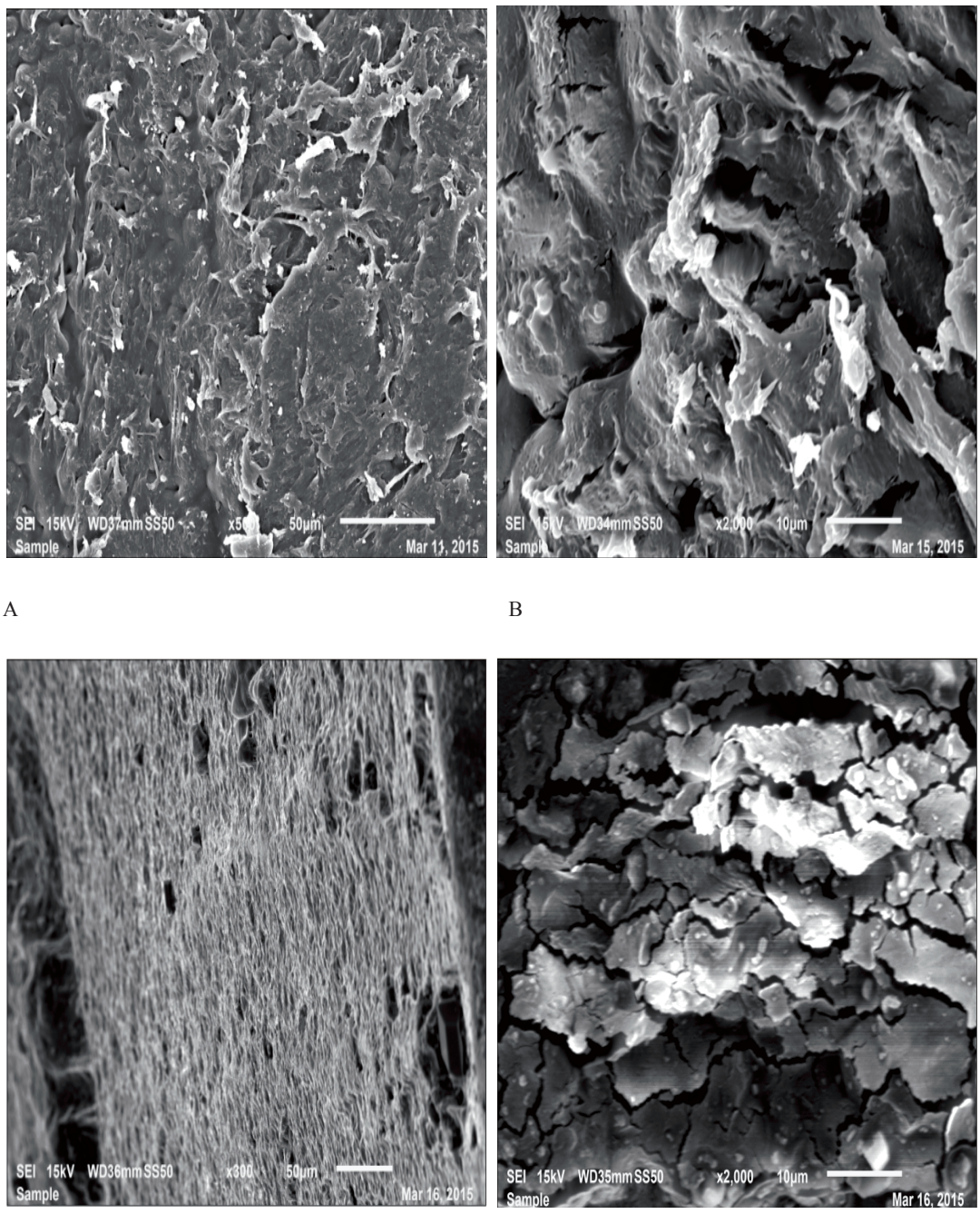


Figure 5-5 Surface imaging of a virgin BIO pellet imaging using scanning electron microscope at different magnifications. A: x500 (scale bar = 50 µm), B: x2000 (scale bar = 10 µm) and laboratory-weathered BIO pellet C: x300 (scale bar = 50 µm), D: x2000 (scale bar = 10 µm).

The images of the virgin BIO pellet indicated that the surface was not smooth, as shown in Figure 5-5 A, with white areas and dots distributed throughout. White dots in virgin pellets may be attributed to the impurities, residual catalyst or additives used in the production of plastic pellets. A higher magnification (x2000 image B) of the virgin pellet clearly visualised some deep cavities and cracks, which appeared black in the images. The presence of cracks and cavities may increase the surface area and promote adsorption on the pellet surface, which was generally observed in the sorption study (Section 4-2).

The BIO surface was significantly eroded due to the weathering process. A lower magnification of x300 was used to cover a larger area of the surface to show both large deep cavities on the right and left-hand side of image C and the middle spongy topography. Weathering may make the surface more porous and enhance the adsorption of PTE. A higher magnification showed that cracks were dominant, and that the surface was rougher than the corresponding virgin image B. This was in agreement with the microplastic surface cracks imaged by SEM (x1000) for samples collected from the Pacific Ocean[224]. The entire surface was rough, with several cavities (black areas), as shown in image D at a higher magnification of x2000; cracks are also shown in image D.

5.1.2 Overall SEM imaging observations

It is important to mention that conclusions cannot be made out of a single pellet study of each type of pellets. Therefore all the outcomes were built on observations. In future work, increasing number of samples, using the same individual pellet before and after weathering and studying pellets are highly recommended to overcome the limitation of the current study.

All types of virgin pellet studied showed roughness on the surface when examined by SEM, except for PET, which has two different morphologies: a rough side edge and a smooth top surface. This was not in agreement with the visual description of PE and PP obtained by Kalliopi and Hrissi[213]. This can be attributed to individual examined pellet, product differentiation, or the techniques used. These differences may explain the general affinity of virgin pellets for PTE in the current study.

Surface imaging of virgin and laboratory-weathered pellets showed that after three weeks of weathering different degrees of changes were visualised in each type of plastic pellets. The HDPE and PP showed minor surface changes, compared with LDPE, whilst the PET and BIO types had clear changes to their surface morphology. Although this observation based on a single pellet study, it supports the earlier finding of a higher uptake of PTE by LDPE, PET and BIO pellets after weathering.

Surface imaging of laboratory-weathered pellets did not show a significant topographical change in all types of pellets, the previous results of sorption experiments in Section 4-2 showed that, for all types of weathered pellets, the uptake of PTE was generally higher in seawater compared with virgin pellets.

Generally, white dots and areas, which represent concentrated metals, appeared on the surface of all virgin pellets, notably in LDPE and BIO, which may be attributed to impurities and residual catalyst and additives used during the pellet production process. On the surface of weathered pellets, a white colour can be attributed to the metal

adsorption during the weathering process in artificial seawater or might be deposits of dry sea salt (All pellets were rinsed with deionised water prior to analysis).

In the current study, weathering took place due to heat, photo-degradation, and hydrolysis in the absence of any biotic degradation in artificial seawater. The different degree of surface erosion for each type of pellets can be attributed to the backbone structure of each type. Bio-based pellets and pellets with functional groups, such as esters, were highly eroded, compared to the pellets with only a hydrocarbon backbone, which makes some pellets more susceptible to weathering than others.

5.1.3 Elemental analysis of the surface of virgin and laboratory-weathered plastic pellets using an analytical scanning electron microscope

All pellets studied showed an indication of metal elements on their surface, as seen in Section 5-1. Two separate points on individual HDPE, LDPE, PP, PET and BIO plastic pellets were subjected to surface elemental analysis to determine major elements present. It must be emphasised that this is not a quantitative analysis, only a qualitative estimate to identify residual elements from pellets manufacture and those adsorbed on the pellet's surfaces from the artificial seawater used during laboratory-weathering.

5.1.3.1 Elemental scanning of virgin and laboratory-weathered HDPE, LDPE, PET, PP and BIO pellets

Table 5-1 shows the elemental mass percent results obtained by SEM-EDS for two points on each pellet.

Table 5-1 Mass % of major elements at two points on the surface of platinum coated virgin and laboratory-weathered HDPE, LDPE, PET, PP and BIO pellets using SEM

Pellets	Elements detected at Point A	Mass %	Elements detected at Point B	Mass %
Virgin HDPE	Carbon	70.1	Carbon	67.0
	Platinum*	10.6	Oxygen	30.1
	Oxygen	9.75	Zirconium	2.88
	Zirconium	7.38		
	Molybdenum	2.20		
Weathered HDPE	Carbon	72.0	Carbon	60.0
	Platinum*	18.4	Platinum*	16.3
	Sodium	7.70	Chlorine	12.6
	Chlorine	1.24	Sodium	7.0
	Magnesium	0.6	Oxygen	3.50
			Magnesium	0.40
			Sulfur	0.24
Virgin LDPE	Carbon	62.3	Carbon	59.4
	Platinum*	20.6	Platinum*	23.2
	Zirconium	14.4	Zirconium	13.7
	Molybdenum	2.16	Molybdenum	3.7
	Sulfur	0.53		
Weathered LDPE	Carbon	56.2	carbon	40.8
	Platinum*	22.5	platinum*	18.1
	Zirconium	13.5	oxygen	14.2
	Oxygen	3.6	zirconium	13.5
	Molybdenum	3.4	sulfur	7.60
	Chlorine	0.75	sodium	5.60
Virgin PET	Platinum*	50.0	Carbon	47.0
	Zirconium	25.0	Platinum*	32.0
	Carbon	21.4	Zirconium	14.0
	Oxygen	3.90	Oxygen	6.7
Weathered PET	Carbon	41.5	Oxygen	23.3
	Platinum*	24.4	Platinum*	17.4
	Oxygen	14.0	Molybdenum	16.6
	Zirconium	11.8	Zirconium	12.5
	Chlorine	4.90	Calcium	11.3
	Sodium	3.40	Carbon	11.0
			Sulfur	7.9

Pellets	Elements detected at Point A	Mass %	Elements detected at Point B	Mass %
Virgin PP	Carbon	64.3	Oxygen	43.7
	Oxygen	12.4	Platinum*	17.7
	Platinum*	12.2	Aluminium	15.7
	Zirconium	7.4	Zirconium	10.4
	Aluminium	1.9	Carbon	8.7
	Molybdenum	1.84	Molybdenum	2.3
			Magnesium	0.8
			Sulfur	0.7
Weathered PP	Carbon	44.4	Carbon	53.5
	Platinum*	23.3	Platinum*	22.2
	Chlorine	13.0	Zirconium	16.3
	Zirconium	10.8	Molybdenum	4.20
	Sodium	8.3	Chlorine	1.80
			Magnesium	1.20
			Sulfur	0.80
Virgin BIO	Carbon	52.0	Carbon	41.3
	Oxygen	25.0	Platinum*	24.0
	Platinum*	13.5	Oxygen	22.6
	Zirconium	9.9	Zirconium	13.0
Weathered BIO	Carbon	56.2	Carbon	55.0
	Platinum*	22.5	Platinum*	15.4
	Oxygen	13.5	Oxygen	15.3
	Zirconium	3.6	Zirconium	10.3
	Molybdenum	3.4	Molybdenum	2.30
	Chlorine	0.75	Chlorine	1.10
			Sodium	0.53

* Platinum present due to pre-analysis platinum coating of plastic pellets, it was not eliminated from data to show that elements detected in each point always count for a 100 % mass.

Elemental scanning of virgin plastic pellets revealed that the distribution of elements on each pellet surface was not uniform between separate points scanned. The most common elements were carbon, oxygen, platinum, and zirconium, while the less common were aluminium, magnesium, molybdenum and sulfur.

Carbon was expected to be a main element in the pellets' backbone. Oxygen was expected in the PET and BIO types, as it is present in the structure of their ester functional group. The presence of oxygen in the other pellets studied may be attributed to the use of a metal oxide catalyst during the production process[145]. Platinum was present in all virgin and weathered samples as a result of the coating process used in the preparation of all samples for the SEM. The detection of zirconium was unexpected and further investigated (Appendix 9).

The presence of molybdenum and sulfur can be attributed to the catalysts or additives used during the production process, such as stabilisers. Aluminium and magnesium were only detected in virgin PP. This may be attributed to the use of inorganic fillers, which contain hydrated aluminium and magnesium[129] (see Table1-2).

Virgin pellets were quantitatively analysed using ICP-MS (see Appendix 9). The results indicated the concentrations of zirconium were 2.24 ± 2.18, 0.0324 ± 0.016, 7.1 ± 6.31, 0.251 ± 0.4, and 1.02 ± 1.37 μg g^{-1} in HDPE, LDPE, PET, PP and BIO, respectively. Concentrations varied markedly between triplicate samples of each type of pellet, suggesting that its presence is non-uniform. The analyte may be present due to impurities, or residues from the metal-catalyst mixture, including zirconium, that used in the production process [129].

In laboratory-weathered pellets, the most common elements were carbon, oxygen, chlorine and sodium, as well as sulfur, which were present in all petroleum-based pellets. Calcium, magnesium and molybdenum were less common. The presence of calcium, chlorine, magnesium, sodium and sulfur may be attributed to adsorption or deposition from the ambient environment of artificial seawater during the weathering process.

The elements mass % detected was not a valid comparison as it was generally different in each point of an individual pellet. For example, oxygen mass % in virgin HDPE was 9.75 % in point A, whereas it was 30.1 % in point B as seen in Table 5-1. Elements detected in each point always count for a 100 mass percent.

Comparing with results obtained in Section 4-1 for virgin pellets quantitative analysis by ICP-MS, aluminium and magnesium were detected by ICP-MS in all pellets studied. Whereas by SEM aluminium and magnesium were only detected in PP. Elements such as molybdenum and zirconium were not quantitatively analysed due to their low concentrations in the semi-quantitative analysis.

Both virgin and laboratory-weathered pellets showed random distribution of PTE on the pellet surfaces which was in agreement with the visual images obtained earlier in Section 5-1-1where the individual pellet surface was not uniform.

5.1.4 Overall SEM elemental analysis observations

The most common detected elements in virgin pellets were carbon, oxygen and zirconium, whereas aluminium, magnesium, molybdenum and sulfur were less common.

In laboratory-weathered pellets, the most common elements were the same as those in virgin pellets (carbon, oxygen and zirconium) plus chlorine, sodium and sulfur, whereas, less common detected elements were calcium, magnesium and molybdenum. The presence of chlorine, sodium, sulfur, magnesium and calcium in laboratory-weathered pellets suggests that plastic pellets were affected by the ambient environment (artificial seawater).

Elemental scanning of plastic pellets revealed that the distribution of elements on each pellet surface was not uniform, as shown in Table 5-1 and 5-2, where different elements and/or different mass % were scanned at each point on an individual pellet. This leads to the conclusion that each individual pellet is different, and the elemental scanning by SEM only represent the point of the analysis on the surface.

5.2 The identification of pellets using ATR-FTIR

5.2.1 Identification and establishment of internal references spectra for plastic pellets

Plastic can be identified using FTIR. Virgin plastic pellets of PE, PP, PET and BIO that used in current study were used to establish internal reference spectra of the average of 20 individual pellets. Figures 5-6 to 5-9 show the internal references spectrum of PE, PET, PP, and BIO pellets respectively. This will be use along with the spectral library to identify collected beached pellets.

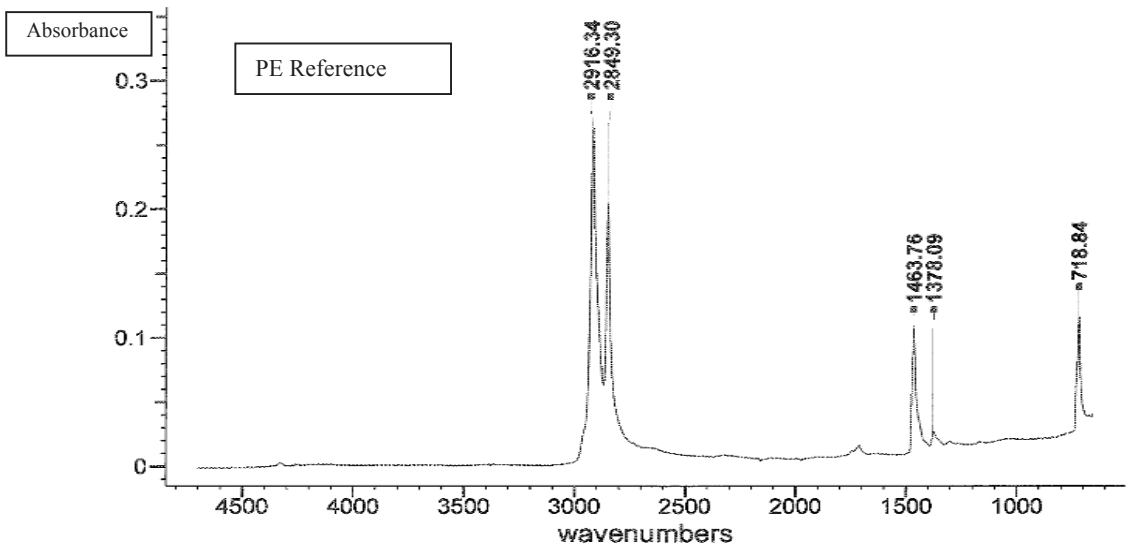


Figure 5-6 The FTIR- reference spectra of PE plastic pellet (n=20).

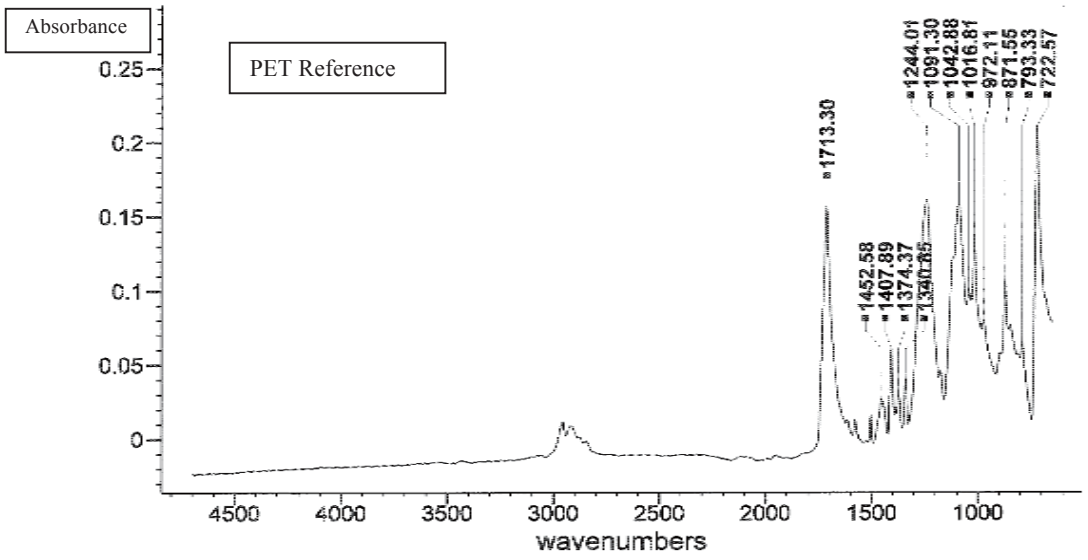


Figure 5-7 The FTIR- reference spectra of PET plastic pellet (n=20).

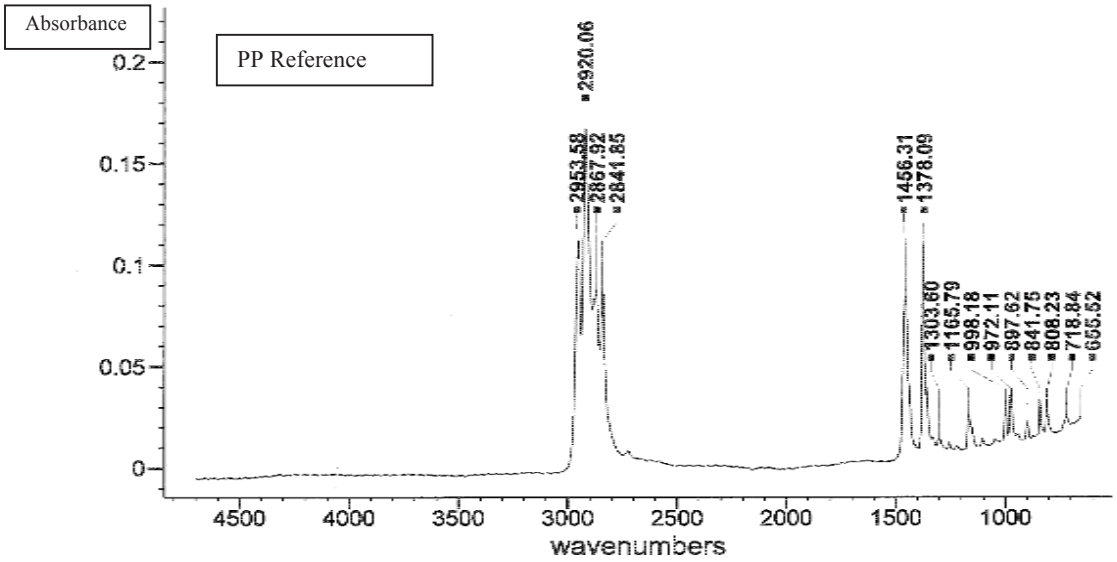


Figure 5-8 The FTIR- reference spectra of PP plastic pellet (n=20).

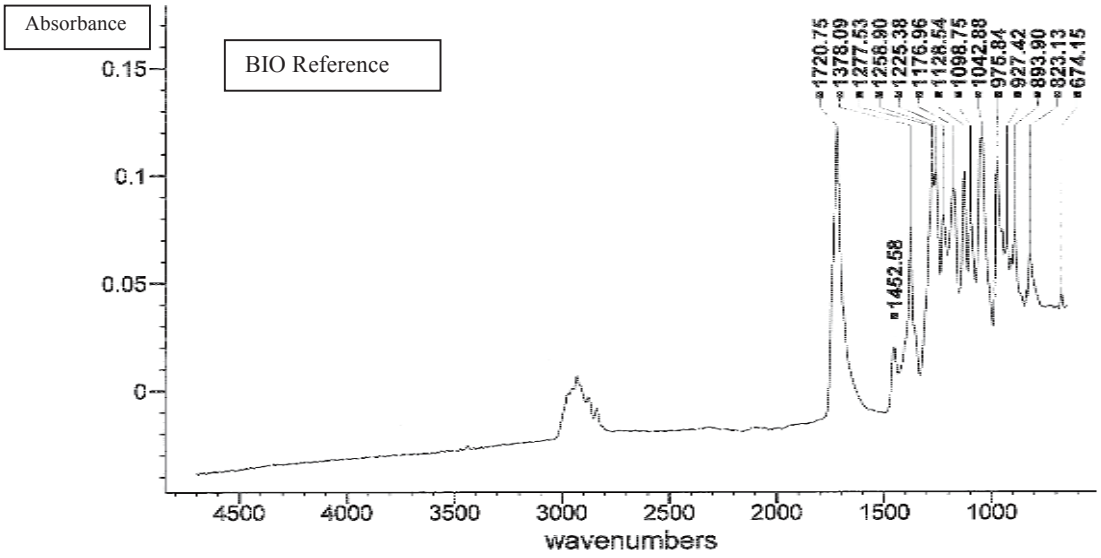


Figure 5-9 The FTIR- reference spectra of BIO plastic pellet (n=20)

5.2.2 Identification of naturally-weathered pellets

Samples were air dried, sieved, rinsed with deionised water and then classified using FTIR. One hundred plastic pellets were randomly selected, and individually subjected to 5500-Agilent Technologies ATR-FTIR, Stockport, (Cheshire, UK) to identify the type of pellets collected. The obtained spectra were then compared to the typical infrared peaks of the polymers[183] (see Figure 2-10 b), spectral library and the internal spectra library and the internal reference spectra of each type of pellet obtained in this study (see Section 5-2-1). Figures 5-10 to 5-13 show examples of PE and PP IR-spectra of beached pellets collected from Kuwait in 2014 and Scotland in 2014, 2015 and 2016. Details about beached sample collection will be described in Chapter 6.

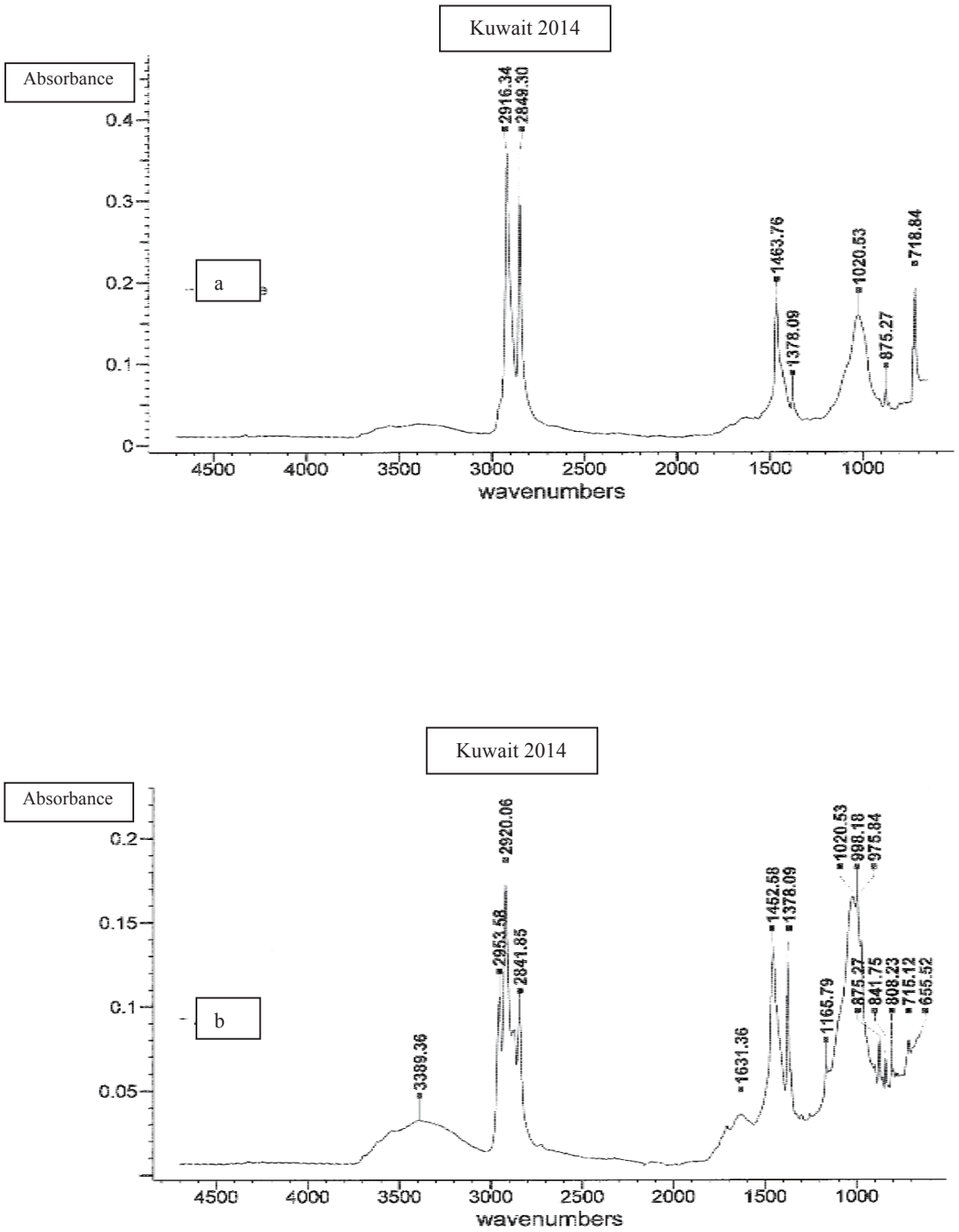


Figure 5-10 The beached pellets FTIR spectra of a: Kuwait PE and b: Kuwait PP collected from Shuwaikh beach in 2014.

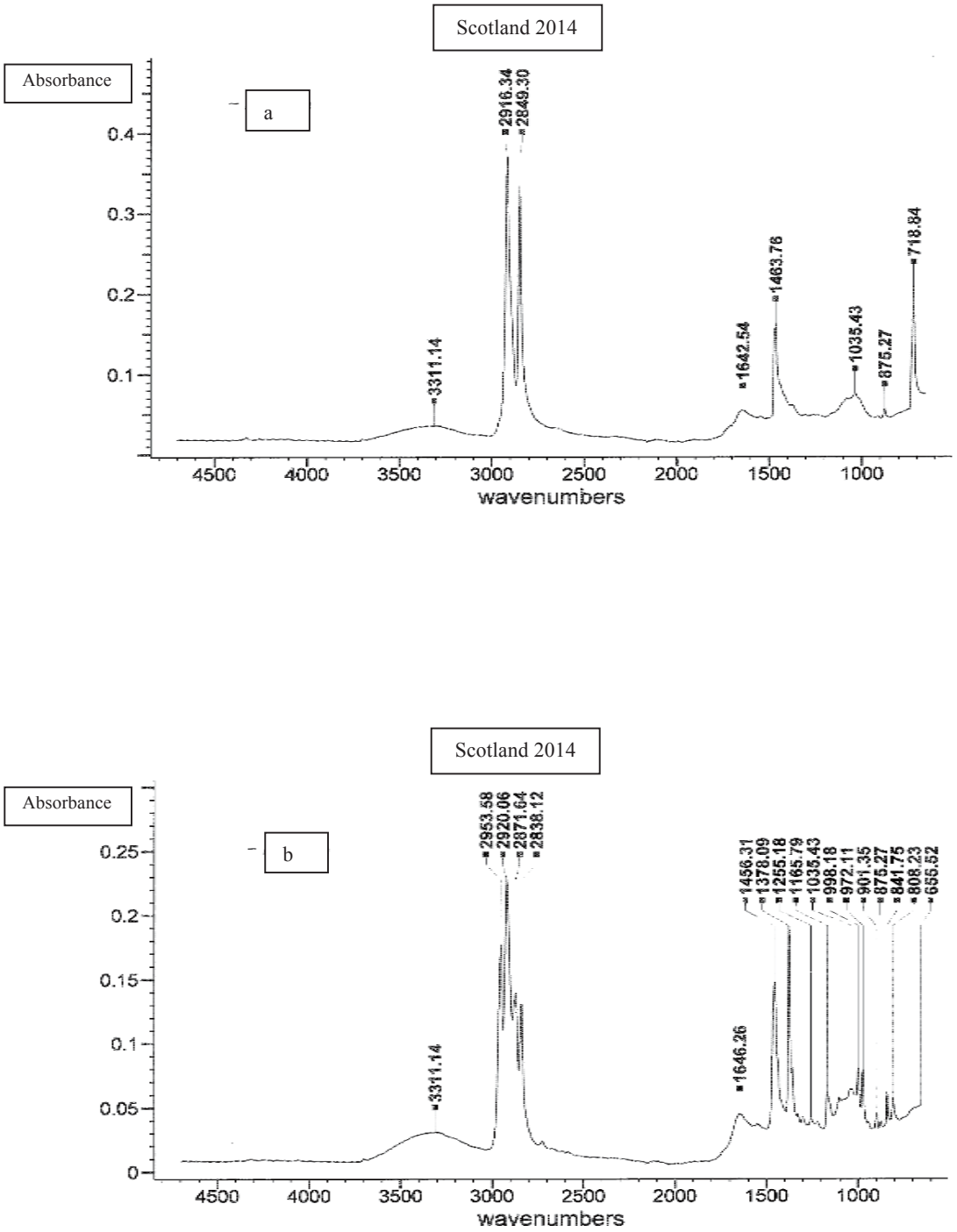


Figure 5-11 The beached pellets FTIR spectra of a: Scotland PE and b: Scotland PP collected from Limekilns in 2014.

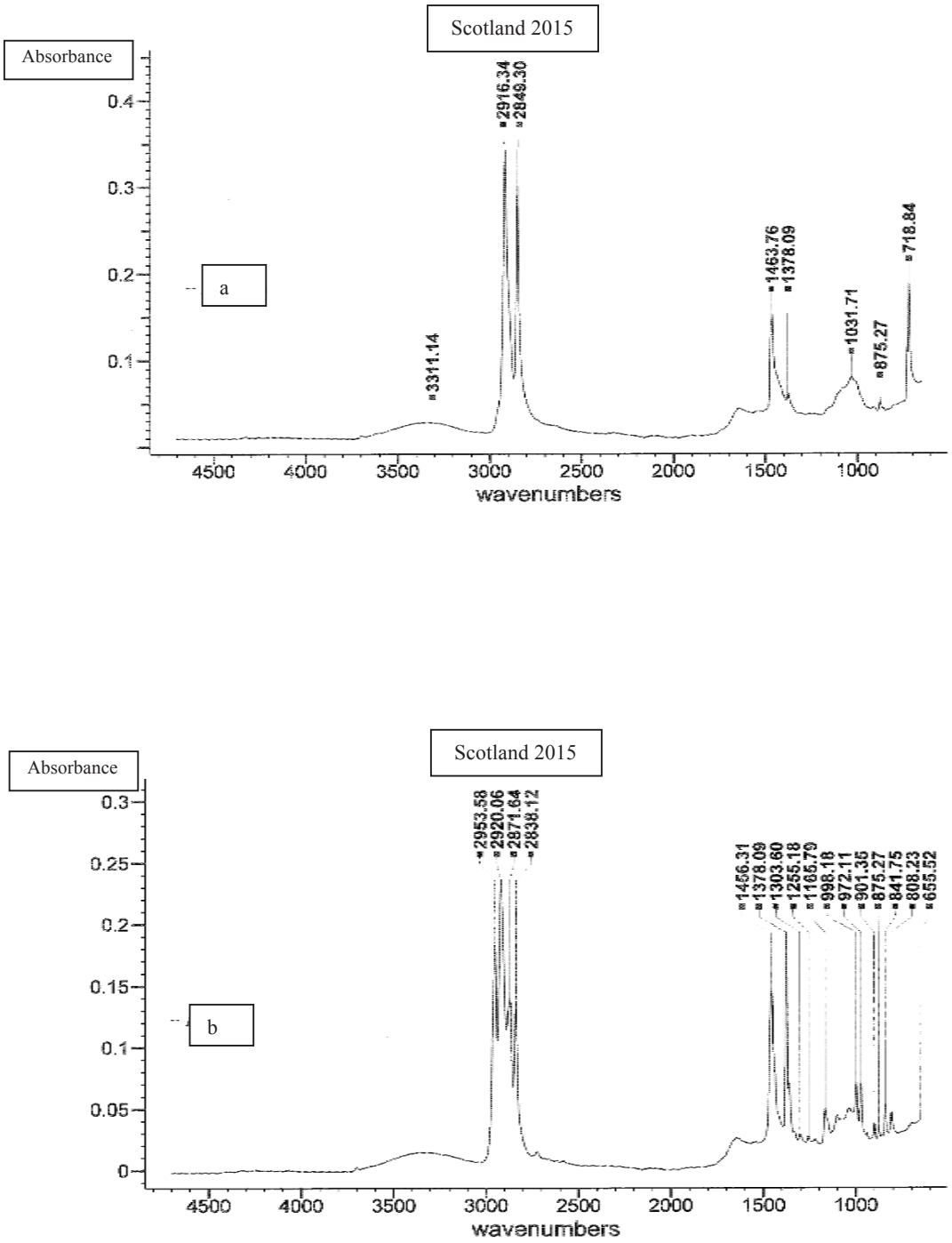


Figure 5-12 The beached pellets FTIR spectra of a: Scotland PE and b: Scotland PP collected from Limekilns in 2015.

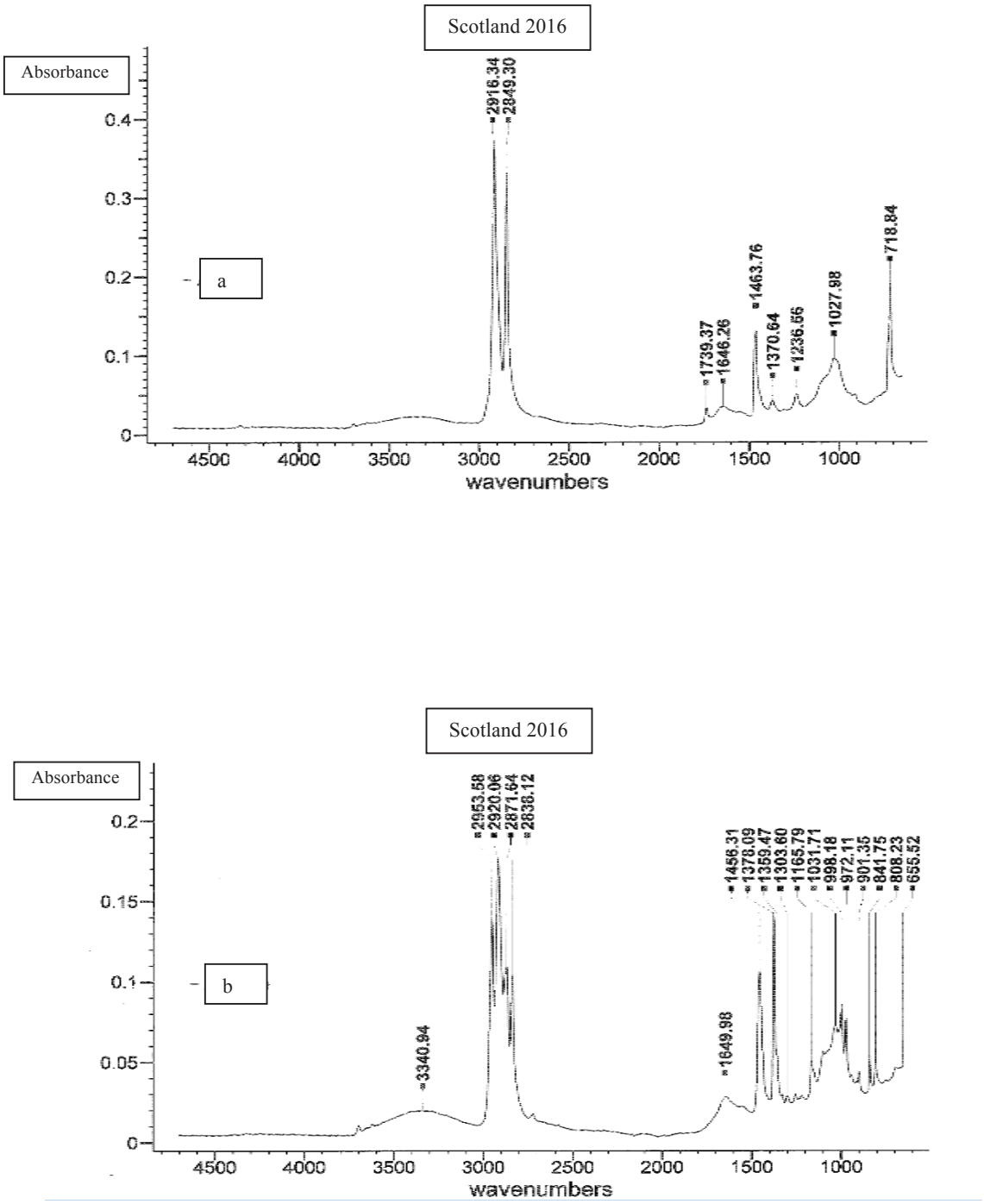


Figure 5-13 The beached pellets FTIR spectra of a: Scotland PE and b: Scotland PP collected from Limekilns in 2016.

Infrared spectra are divided into three main regions: far-IR, mid-IR and near-IR at wavenumbers (< 400 cm^{-1}), (400 – 4000 cm^{-1}) and (4000 – 13000 cm^{-1}) respectively[225]. Spectra obtained for beached pellets collected from Kuwait and Scotland were in the mid-IR region, mainly at the X-C region at 4000 – 2500 cm^{-1} and fingerprint region at 1500 – 600 cm^{-1}. The spectra were compared to the reference spectra of virgin pellets and double checked with respect to the typical infrared peaks expected for each polymer (see Figure 5-6 to 5-9).

Due to its simple back bone of repeated $–C_2H_4–$, PE (Figure 5-10 to 5-13 a) had a simple spectrum In the X-C region, a sharp dual peak, representing two regions of alkane C-H at (2840 – 3000 cm^{-1}), appeared in all beached PE at 2916 cm^{-1} and 2849 cm^{-1} which was in agreement with the PE reference (Figure 5-6). The fingerprint region of all spectra had the same peaks as seen in the PE reference at 718.84 – 1463.76 cm^{-1} for C-H, C-C and CH_2, plus an extra peak at (1020.53 – 1035 cm^{-1}) for C-C in all PE spectra.

Spectra for pellets identified as PP (Figure 5-10 to 5-13 b) had the expected multiple peaks for C-H at (2840 – 3000 cm^{-1}) in the X-C region. That was in agreement with the PP reference. The fingerprint region of all PP spectra obtained showed peaks at 1456.31 – 655.62 cm^{-1} for C-H, C-C and CH_2 and CH_3. This was in agreement with the fingerprint peaks in PP reference.

Interestingly, one broad peak for N-H at 3311.14 cm^{-1} was detected in all PE spectra, to varying degrees and in all PP spectra at 3389.36 – 3311.14 cm^{-1}. In addition, small pre-fingerprint region peaks at 1642.54 cm^{-1} and 1646.26 appeared in Scotland 2014 and 2016 PE samples respectively for N-H. A pre-fingerprint peak at 1631.36 – 1649.98 cm^{-1} for N-H which was also detected in all PP spectra except for Scotland 2015 sample. Both the broad peak for N-H and the small pre-fingerprint region peak for N-H found in all beached pellets can be attributed to primary amines that naturally occur in the marine environment as a result of metabolic process in organisms and dissolved organic matter[226]. This finding can be correlated to the built-up layers and supports other observations that the pellets were affected by the exposure to ambient environment.

6 Investigation of beached plastic pellets collected from Kuwait and Scotland

This study was conducted to visualise the surface, identify the type of plastic, and to desorb and determine the levels of PTE in plastic of pellets collected from beaches in Kuwait and Scotland – where they eventually settled – by implementing cold and microwave-assisted acid digestion sequentially. Only one location in each country was selected, as the main purpose of this stage in the research was to investigate the beached pellets themselves, and to establish the desorption procedure for them, rather than to compare the numbers of pellets collected or the PTE content of multiple different locations in each country.

6.1 Sampling locations and analytical methods

Plastic resin pellets were collected from Shuwaikh Beach, Kuwait (29˚21’37”N 47˚57’12”E) and from the foreshore at Limekilns, Scotland, UK (56˚2'2"N 3˚29'11"W) during the period from 2014 – 2016. Shuwaikh samples were personally collected, whereas Limekilns pellets were collected with a class from Civil and Environmental Engineering Department – University of Strathclyde.

The Shuwaikh Beach area, as shown in Figure 6-1, is located on Kuwait Bay which experiences many pressures due to natural causes such as the extreme weather conditions; human and industrial activities; plus the consequences of the Iraqi-invasion in 1990 and the Gulf War in 2003. The site is located close to Shuwaik Port and the Al-Zour refinery project. Harbour, densely populated areas and industrial sites are generally contaminated with microplastic, and considered as a primary source of marine debris including plastic[26] as mentioned in Section 1-1-2. According to the Kuwait National Petroleum Company-KNPC[227], the Al-Zour project will be a world-scale refinery, with olefins manufacturing capability, such as ethylene crackers, ethylene glycol units, polyethylene pellets (PE), and polypropylene pellets (PP), and aromatic polyethylene terephthalate pellets (PET) and purified terephthalic acid units, which will begin

production officially end of 2017. This location was selected due to ease of access. Furthermore, any leakage from this plant will reach Kuwait Bay via the surface current, as seen in Figure 6-2; therefore, it is vital to monitor this area prior to the commencement of production and regularly after. The rest of the refineries in Kuwait are located in the south, where entering or sampling is highly restricted.

The sampling method used in Kuwait was simple and did not include any collection of sediment due to legislation restricting soil sampling. Plastic pellets were collected from approximately 5 cm depth at low tide, from the tideline as seen in Figure 6-3, using hands and tongs, and kept in a clean, screw cap bottle. Sampling was performed in January 2014.

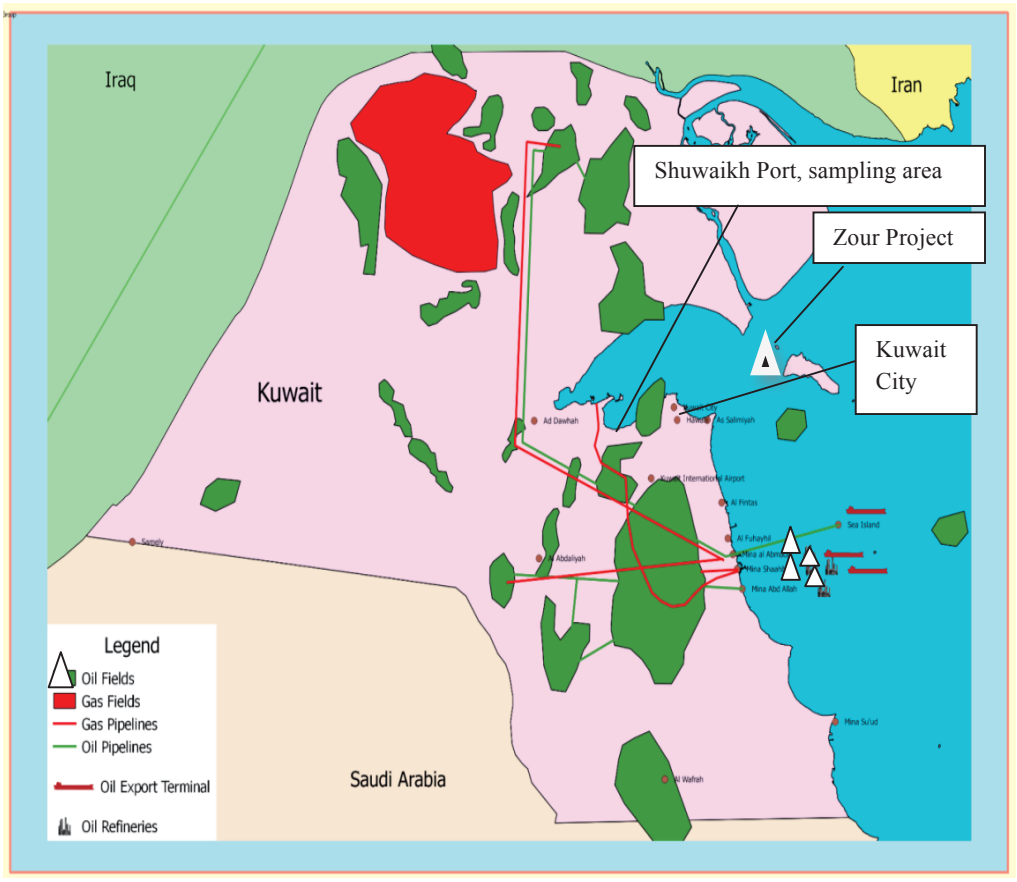


Figure 6-1 Kuwait map showing the sampling area near Shuwaikh Port and oil refineries, and the plastic pellets production project (adapted[228]).

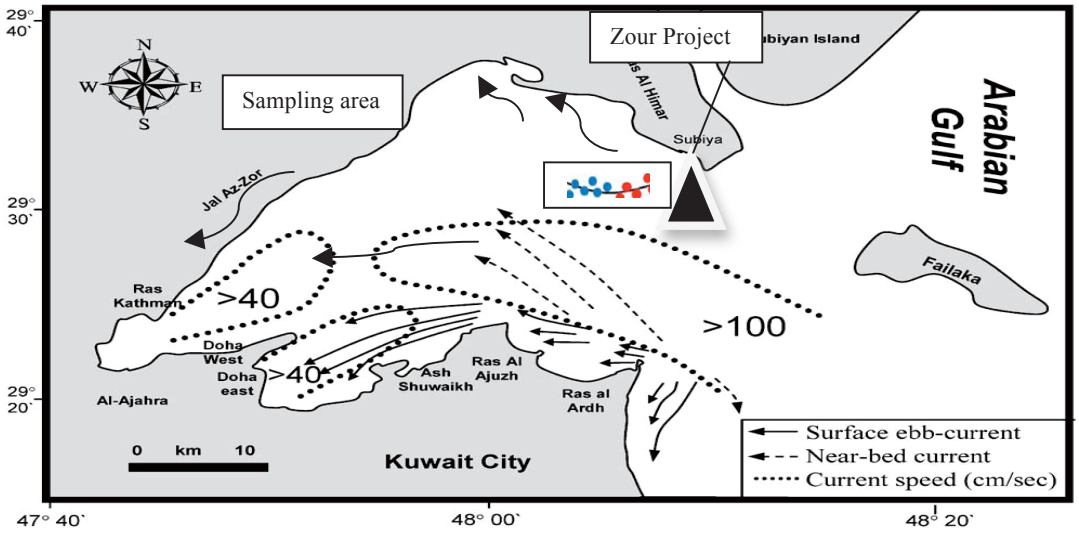


Figure 6-2 Surface and deep current in Kuwait Bay (adapted)[229].

Figure 6-3 Tideline sampling position in Shuwaikh beach, Kuwait.

Limekilns, as seen in Figure 6-4, is located in the Firth of Forth region, which is home to various industries such as fishing, shipping, oil refinery, plastic pellet production and

power generation. Being an industrial and populated area makes Limekilns a primary source of pellets, as mentioned in 1-2-1.

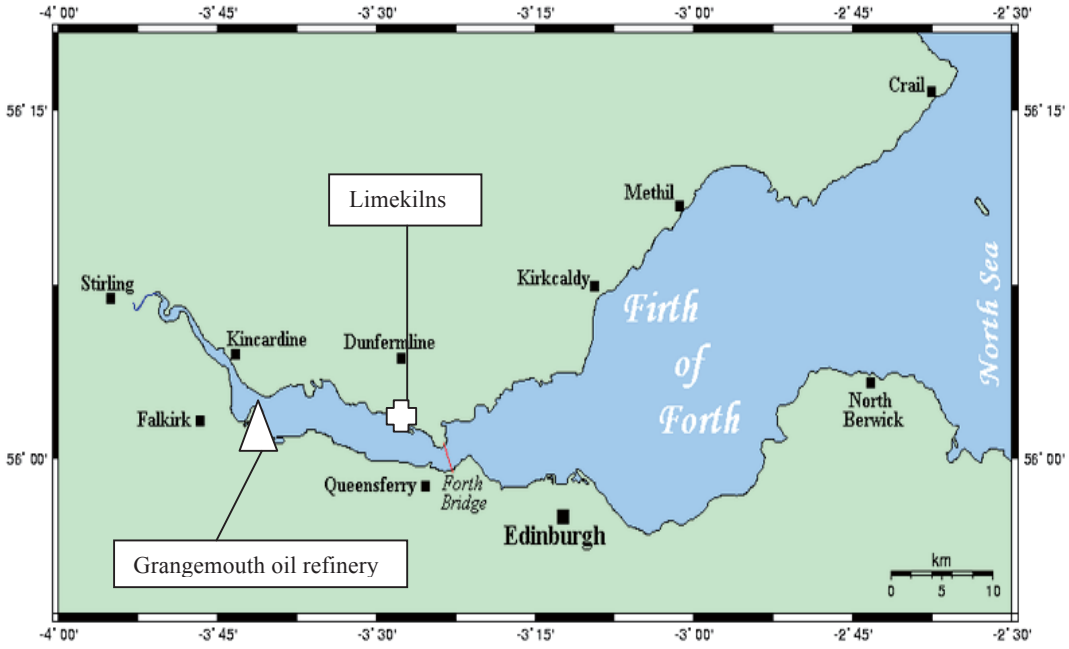


Figure 6-4 The sampling area at Limekilns, Firth of Forth, Scotland (Adapted[230]).

According to INspec Ethylene Oxide Specialities-INEOS[231], Grangemouth refinery is considered a world-scale petrochemical plant, manufacturing synthetic products such as ethylene, propylene, and polyethylene (PE) and polypropylene (PP) polymers.

Samples were collected from the vegetation line (see Figure 6-5 a) at low tide, using a quadrat technique[232, 233] in January 2014, 2015 and 2016. Using 60 cm x 60 cm quadrat frame, eight sampling locations on a beach of length approximately 100 m were identified. Then sediment up to approximately 5 cm depth was collected in a 10 L, labelled bucket to avoid omitting target pellets due to blown or drifting sand[234] or sediment. The samples were then air dried in the laboratory for a week, and sieved to minimised the size of the sample by removing larger materials prior to the collection of the plastic pellets using hands and tongs. Figure 6-5 shows the Limekilns quadrat

sampling method and picking out plastic pellets. Although sampling procedure in Kuwait was different from Limekilns quadrat technique, the main target was to collect microplastic in 5 cm depth to keep the comparison between both locations possible.

The vegetation line for Limekilns and the high tideline for Shuwaikh were selected for sampling because, prior to the current study (2011, as a practice with Dr. Robert Bray, Civil and Environmental Engineering Department – University of Strathclyde), samples were collected from three locations, starting with vegetation line and moving towards the strand line in Limekilns. However, plastic resin pellets were only accumulated at the vegetation line and sampling was easier comparing to the other two locations, whereas almost nothing was recovered from the strand line locations, which was reported in relevant literature as the top boundary of the beach[235]. This observation suggested that the vegetation line acts as a trap for plastic pellets. On the other hand, plastic pellets were also trapped between wall rocks in Limekilns at the high tide where the water reach this wall as seen in Figure 6-6. The advantages of sampling from vegetation line over any other natural trapped areas:

- The vegetation line or the equivelant high tide line are common to all beaches. In contrast, natural traps are exclusive to certain beaches; therefore such locations can not be standarised for sampling.
- Aging of plastic pellets collected from the vegetation line can be estimated as they are accumulated in sediment layer, i.e. pellets collected from the surface layer are more likely to be the most recent.

Figure 6-5 Sampling and picking out plastic resin pellets in Limekilns, Scotland, using a quadrat technique. a: quadrat frame at vegetation line, b: digging ~5 cm depth sediment, c: examples of pellets being collected, d: obtaining the sample in bucket filled with sediment, e: sediment after air drying in the lab, f: picking out pellets manually after sieving, g: different pellets collected.

Figure 6-6 a: limekilns wall where merine debris trapped, b: plastic pellets mixed with other vegetation and wooden materials become trapped between rocks, c: trapped materials including transparent and colured plastic resin pellets.

6.1.1 Surface study of beached plastic pellets using an analytical SEM

Beached pellets collected from Kuwait and Scotland were imaged and subjected to elemental analysis in the same way as described in Sections 5-1-2 and 5-1-3.

6.1.2 Identification method of type of pellet by FTIR

As described in chapter 5, Section 5-2-2.

6.1.3 Sequential desorption method

Examples of each type of plastic pellet as determined by FTIR were subjected to a two-step extraction procedure: cold leaching for 48 hours in 20 % *aqua regia* using Trace-SELECT nitric and hydrochloric acid for trace analysis Sigma Aldrich, (Gillingham, Dorset, UK); followed by microwave-assisted digestion in nitric acid using a MARS Xpress laboratory microwave digestion system CEM, (Buckingham, UK), as mentioned in 3-1-2, Table 3-2.

6.1.3.1 Cold acid digestion

After identification of the collected pellets was complete, 0.25 g, as recommended by MARS Xpress programs (see Section 3-1-2), of each type was weighed, then added to 2 mL of 20 % *aqua regia* and shaken at 150 rpm for 48 hours at room temperature, along with three blanks and polyethylene JSM P 700-1 Plastic Reference Material for Chemical Analysis (RM) supplied by the JFE techno-research corporation (Tokyo, Japan). Samples were then filtered and decants were made up to 50 mL and kept in a fridge prior to analysis by ICP-MS.

6.1.3.2 Microwave acid digestion

Plastic pellets from the above step and the RM were subjected to microwave acid digestion with HNO_3 acid, along with three new blanks, depending on the pellets type as described in 3-1-2, Table 3-2.

6.2 Pellet identification and surface study of beached plastic pellets using scanning electron microscope (SEM)

6.2.1 Pellet identification by FTIR analysis

As an example, in one sampling quadrat frame in Limekilns (60 cm x 60 cm), 1729 pellets were manually counted as follows: 1587 transparent pellets, 57 black pellets, 41 yellow pellets, 40 blue pellets, and 4 grey-greenish pellets. One hundred transparent pellets randomly selected from each year of collection were classified using FTIR analysis. In this study, only transparent samples were used as the pigments in coloured pellets may affect on the PTE content[127] as mentioned in Section 1-1-5.

The pellets collected and identified from Limekilns were 68 % polyethylene and 32 % polypropylene, this was in agreement with results obtained in literature where PE was more abundant microplastic collected from Northern Adriatic Sea[236], which might be attributed to the availability or the density of the pellets. Samples from Kuwait were 48 % polyethylene and 48 % polypropylene, and the rest were unclassified as polymers (see Section 5-2-2 Examples for PE and PP IR-spectra of beached pellets collected from Kuwait and Scotland).

6.2.2 Imaging of beached plastic pellet surfaces using an analytical scanning electron microscope

Figure 6-7 shows naturally-weathered PE beached pellets collected from Kuwait and Scotland between 2014 and 2016, in x500 to x1000 magnifications. Different magnifications were used in order to obtain a clear and representative image for each pellet.

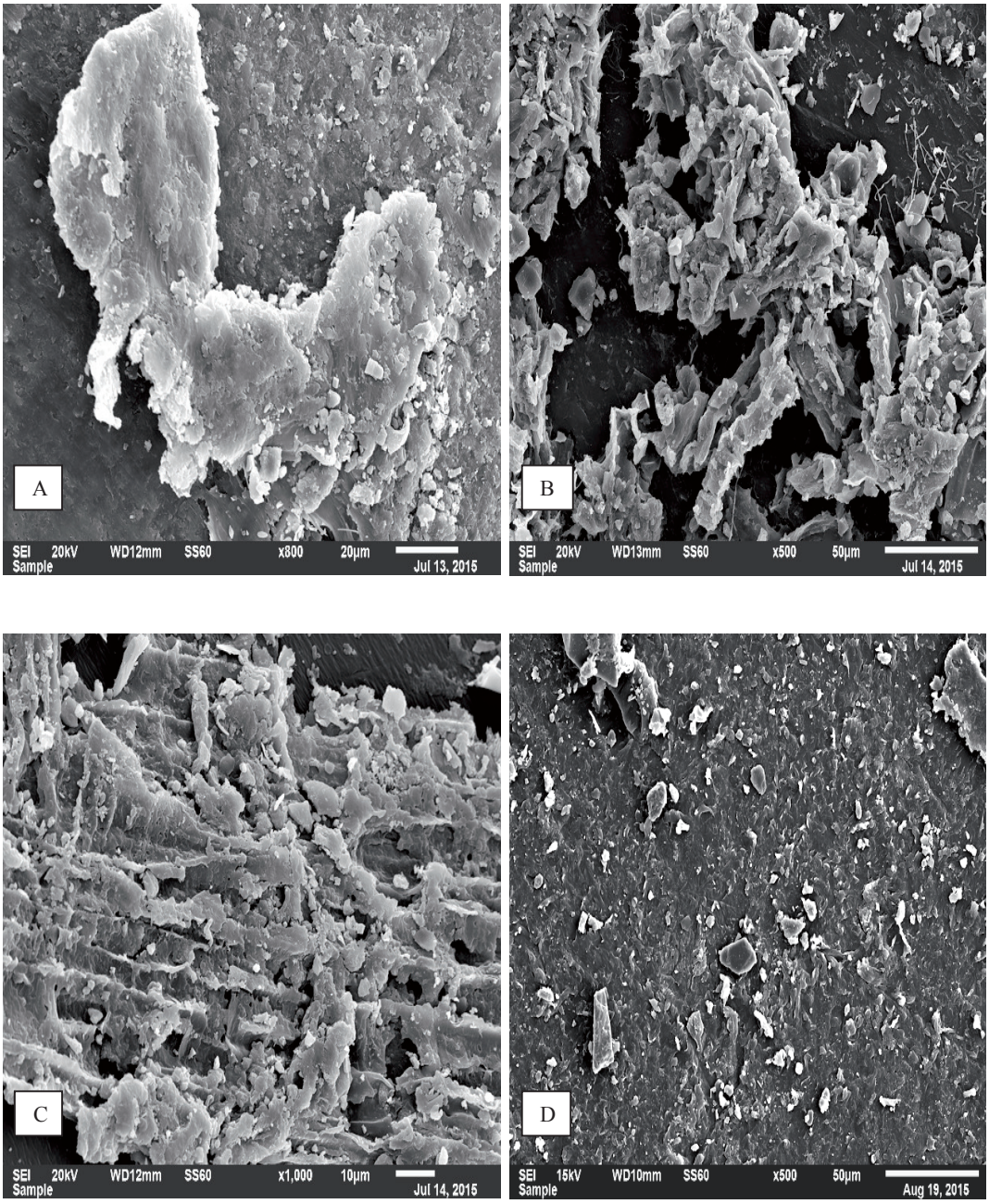


Figure 6-7 Beached pellets (PE) surface imaging. A: x800, scale bar 20 µm Kuwait, 2014; B: x500, scale bar 50 µm Scotland, 2014; C: x1000, scale bar 10 µm Scotland, 2015; and D: x500, scale bar 50 µm Scotland, 2016.

The surface images of the pellets collected from beaches in Kuwait and Scotland showed that all surfaces were rough, with white areas that represent more concentrated metal elements in a particular position[223] of the surface. Layer build-up was observed in all studied pellets except for the Scotland (2016), which can be attributed to accumulation of material from the ambient environment, such as organic matter (biofilms). Limitation of layers build-up on Scotland (2016) might be because this pellet was exposed to weathering for a shorter time than the rest of the beached pellets.

This assumption of bioaccumulation layers on plastic pellets surface is supported by literature. In the marine environment, bioaccumulation (biofouling) is likely to occur on weathered plastic pellet surfaces[224]. Indeed, Ye and Andrady[237] reported that, in their study, floating plastic formed a biofilm and gelatinous film when exposed to sea water. Furthermore, it has been reported that the buildup level was seasonal on polyolefins and plastic debris[238, 239]. Maximum contamination has been observed on plastic between July and September by Muthukumar *et al*.[239] and in August by Sudhakar *et al*.[238], and has generally been shown to decrease by November and then reappear in January, samples for this study were collected in this time. Also, It has been reported that plastic is a favourite substrate for spat and oyster larvae[240]. Therefore, observed layers build-up could be attributed to gradual accumulation over the time since the pellets were released into the environment.

6.2.3 Elemental analysis of beached plastic pellet surfaces using a scanning electron microscope

Table 6-1 presents the elemental mass percentage results obtained by the SEM at two points of each studied beached pellets collected from Kuwait and Scotland, and a plastic reference material- JSM P 700-1.

Table 6-1 Elemental scanning by SEM in two scanned points of beached pellets collected from Kuwait and Scotland.

Pellets	Point A detected elements	Mass %	Point B detected elements	Mass %
Beached-Kuwait 2014	Carbon	41.56	Carbon	40.55
	Platinum*	21.7	Platinum*	20.62
	Oxygen	16.77	Oxygen	17.05
	Zirconium	10.74	Zirconium	8.11
	Silicon	4.20	Chlorine	6.0
	Calcium	3.35	Calcium	4.14
	Magnesium	1.66	Silicon	3.52
Beached-Scotland 2014	Carbon	50.57	Carbon	48.4
	Oxygen	18.72	Oxygen	18.74
	Platinum*	9.87	Silicon	1.06
	Sodium	8.66	Sulfur	0.60
	Zirconium	7.18	Chlorine	1.16
	Molybdenum	1.80	Calcium	3.75
	Calcium	1.36	Zirconium	11.71
	Silicon	0.72	Molybdenum	2.57
	Sulfur	0.53	Platinum*	12.01
	Chlorine	0.59		
Beached-Scotland 2015	Carbon	48.4	Carbon	60.4
	Oxygen	24.4	Oxygen	18.4
	Chlorine	1.6	Chlorine	6.08
	Calcium	1.36	Zirconium	13.64
	Zirconium	6.67	Platinum*	1.4
	Platinum*	16.4		
	Silicon	1.16		
Beached-Scotland 2016	Carbon	71.8	Carbon	60.31
	Zirconium	10.53	Zirconium	8.94
	Platinum*	17.6	Platinum*	16.1
			oxygen	12.8
			Silicon	1.24
			Sulfur	0.61
Plastic-RM	Carbon	80.13	Carbon	60.3
	Zirconium	6.41	Zirconium	13.17
	Platinum*	13.45	Platinum*	23.07
			Sulfur Molybdenum	0.61
				2.81

* Platinum present due to pre-analysis platinum coating of plastic pellets, it was not eliminated from data to show that elements detected in each point always count for a 100 % mass.

The elemental scanning results generally showed that calcium, carbon, chlorine, oxygen, platinum, silicon and zirconium were common in the (individually analysed) beached pellets collected from Kuwait and Scotland. Less common elements were magnesium, molybdenum, sodium and sulfur.

Carbon and oxygen were expected as both were the most common elements found in virgin and laboratory-weathered pellets as cited in Section 5-1-4, and can be attributed to the pellet structural back bone and the use of metal oxide catalyst as discussed in Section 5-1-3-1. Zirconium's presence was investigated earlier in 5-1-3-1 and it can be attributed to the use of metal catalyst mixture including zirconium. Platinum was detected as a result of using platinum coating prior to SEM analysis. However, the presence of significant levels of calcium and silicon were generally exclusive to beached pellets. The presence of silicon can be attributed to the contact between the pellets and the beach sand where the pellets eventually settled, whereas the calcium deposits can be linked to the marine organisms settled on the plastic surface, where calcium is a component of their skeleton and shells[241]. However, further study is needed to proof and claim this assumption.

In the current study, calcium was only detected in laboratory-weathered PET elemental scanning by SEM, as seen in Table 5-1. This could be attributed to the ambient artificial seawater, because $CaCl_2$ makes up 2.76 % of the sea salt used for laboratory-weathering (see Table 3-5), or more likely to the use of fillers and lubricants that contain calcium for this type of pellet (see Table 1-2).

Calcium was detected in all beached pellets except for those collected in Scotland, 2016. These pellets also showed notably less surface deposits compared with the other beached pellets, as demonstrated in Figure 6-7. This suggests a correlation between the build-up of layers on pellet surface and calcium, perhaps because these pellets were exposed to weathering in the marine environment for a shorter period of time compared to other pellets.

Generally, comparing mass % of elements obtained for beached and laboratory-weathered pellets showed that the mass percent of elements attributed to the ambient marine environment (seawater), were generally higher in laboratory-weathered pellets over the beached pellets. Chlorine, magnesium, sodium and sulfur levels in laboratory-weathered pellets were (0.75 – 13 %), (0.4 – 1.2 %), (0.53 – 8 %) and (0.24 – 7.6 %) respectively, whereas in beached pellets they were (0.59 – 6.08 %), 1.66 %, 0.66 % and (0.53 – 0.61 %) respectively. This might be attributed to the complexity of seawater, where various components and motions might lead to some desorption of adsorbed PTE, over the artificial seawater or possibly to the preferential deposits of some artificial seasalt components used to prepare the artificial seawater. All pellets were rinsed with deionised water prior to analysis as described in Section 3-4-2. Concerning this, it is worth mentioning that the mass percent obtained by SEM represents only a single point on the pellet surface, and so may not be representative of the whole.

Certified elements of; arsenic, cadmium, chromium and lead in plastic reference material were not detected by SEM due to their low concentrations (see Table 3-1).

6.3 Investigation of PTE content in beached pellets using two step digestions

6.3.1 The release of PTE from beached plastic pellets using a two-stage extraction procedure

To assess how strongly the PTE were associated with the plastic, samples of PE and PP pellets were subjected to a two-step extraction procedure: cold leaching for 48 hours in 20 % *aqua regia* (which was previously been reported in literature[117, 118]), followed by microwave-assisted digestion in nitric acid (which is the recommended method for analysis of plastic as described in Section 3-1-2), along with three blanks and a plastic RM. Table 6-2 presents the recoveries of PTE in the plastic RM with respect to certified values.

Table 6-2 Obtained concentrations (μg L^{-1}) of PTE in JSM P 700-1 Plastic Reference Material for Chemical Analysis (n=3)

Elements	Certified values	Obtained values Step 1	Step 1 recovery %	Obtained values Step 2	Step 2 recovery %	*Total recovery %
As	9.1 ± 0.9	2.44 ± 0.23	26.8	7.90 ± 0.27	87.0	114
Cd	5 ± 0.6	0.359 ± 0.025	7.18	4.72 ± 0.043	94.4	101
Cr	4.9 ± 0.6	0.840 ± 0.15	17.0	3.88 ± 0.09	79.0	96
Pb	5 ± 0.6	0.745 ± 0.04	14.9	4.52 ± 0.16	90.0	105

*The recovery % were calculated based on the main average given certified values which can explain the higher recovery value obtained for As, Cd and Pb.

The values obtained showed that greater release of PTE occurred in the microwave acid digestion step rather than the cold leaching. This result was expected as the PTEs in the RM were incorporated during manufacturing rather than sorbed on their surfaces. According to z-score and ISO guide-33 (1988), the total values obtained (sum of step 1 and 2) were acceptable in terms of the certified values.

Table 6-3 presents the quantities of arsenic, cadmium, chromium and lead recovered from beached pellets in the first step of cold leaching.

Table 6-3 Concentration of PTE (μg g^{-1}) in beached pellets collected from Kuwait and Scotland using 20 % *aqua regia* cold digestion (step 1).

location	Kuwait		Scotland		Scotland		Scotland	
Type	**PE**	**PP**	**PE**	**PP**	**PE**	**PP**	**PE**	**PP**
Year	**2014**	**2014**	**2014**	**2014**	**2015**	**2015**	**2016**	**2016**
As	12.5	5.59	6.59	1.89	3.26	2.25	4.35	1.23
Cd	0.371	0.0676	0.242	0.071	0.316	0.133	0.474	0.156
Cr	19.1	5.15	14.9	3.02	12.1	1.01	14.5	9.93
Pb	28.4	19.3	25.7	7.73	17.8	7.84	47.8	17.9

Pellets from the first step of leaching were subjected to the second step of microwave acid digestion. Table 6-4 shows the arsenic, cadmium, chromium and lead recovered from beached pellets in the second step.

Table 6-4 Concentration of PTE (μg g^{-1}) in beached pellets collected from Kuwait and Scotland using microwave acid digestion (step 2).

location	Kuwait		Scotland		Scotland		Scotland	
Type	**PE**	**PP**	**PE**	**PP**	**PE**	**PP**	**PE**	**PP**
Year	**2014**	**2014**	**2014**	**2014**	**2015**	**2015**	**2016**	**2016**
As	5.65	2.12	2.78	0.011	2.19	0.27	< LOD	< LOD
Cd	0.040	0.048	0.0198	0.027	0.112	0.115	0.175	0.157
Cr	77.2	24.1	9.96	8.61	10.9	4.16	2.72	0.497
Pb	7.02	9.96	10.06	10.1	10.9	5.33	5.86	7.65

Figures 6-8 to 6-11 illustrate the concentrations of PTE obtained in each digestion steps, for ease of comparison.

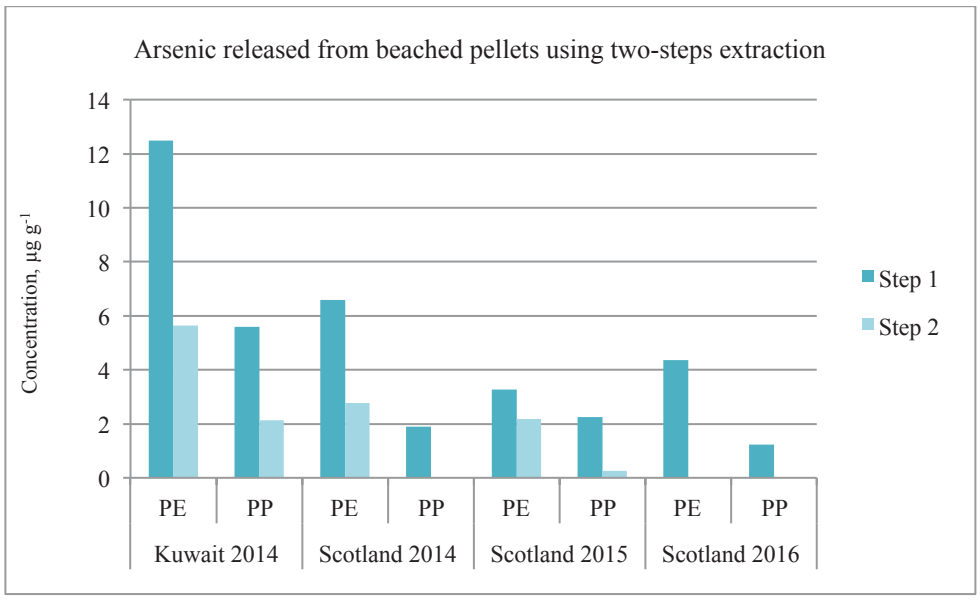


Figure 6-8 Concentration of As (µg g^{-1}) obtained after two steps digestion; cold leaching and microwave acid digestion for beached polyethylene PE and polypropylene PP plastic pellets collected from Kuwait and Scotland.

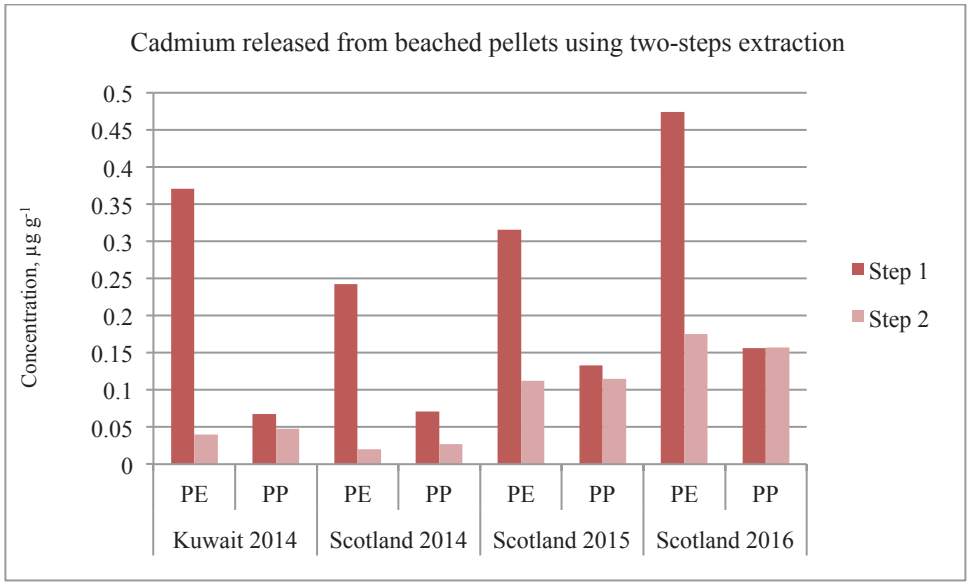


Figure 6-9 Concentration of Cd (µg g^{-1}) obtained after two steps digestion; cold leaching and microwave acid digestion for beached polyethylene PE and polypropylene PP plastic pellets collected from Kuwait and Scotland.

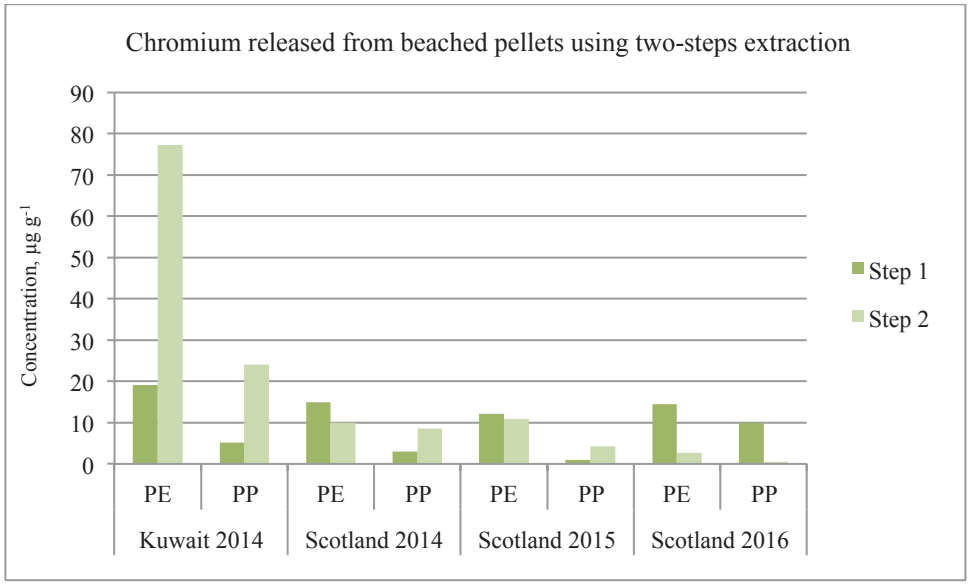


Figure 6-10 Concentration of Cr (µg g^{-1}) obtained after two steps digestion; cold leaching and microwave acid digestion for beached polyethylene PE and polypropylene PP plastic pellets collected from Kuwait and Scotland.

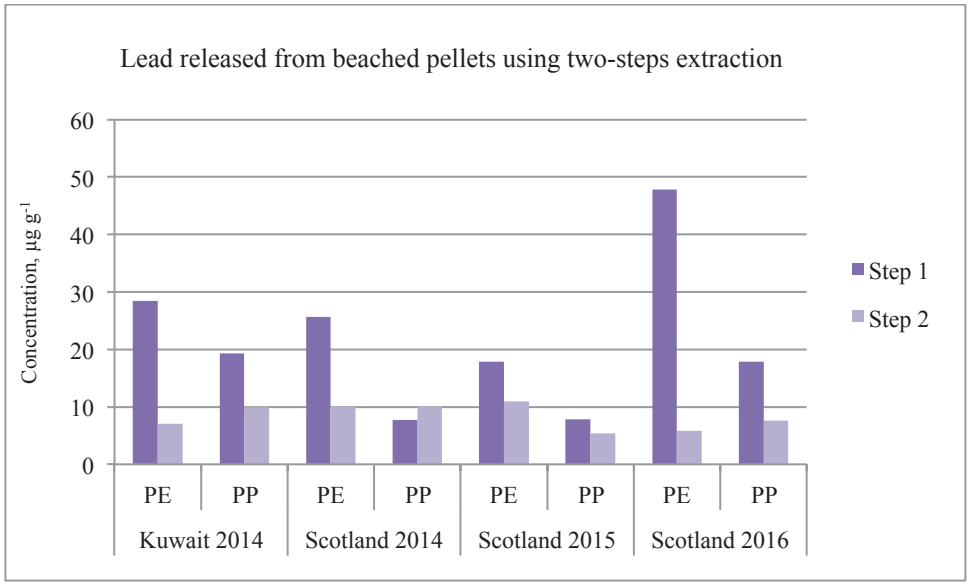


Figure 6-11 Concentration of Pb (µg g^{-1}) obtained after two steps digestion; cold leaching and microwave acid digestion for beached polyethylene PE and polypropylene PP plastic pellets collected from Kuwait and Scotland.

The obtained values of arsenic, cadmium, chromium and lead in the first and second desorption steps were all above the procedure limits of detection, which was 0.00121 μg g^{-1} for arsenic, 0.00124 μg g^{-1} for cadmium, 0.00798 μg g^{-1} for chromium, and 0.00226 μg g^{-1} for lead, except for the arsenic levels in the microwave-assisted digestions of the PE and PP samples collected in Scotland in 2016.

The quantitative results of the analysis of the beached plastic pellets after cold leaching showed that analyte concentrations were higher in the polyethylene than in the polypropylene pellets at both locations. This can be attributed to the properties of each type (see Section 1-2-1) and the degree of weathering. In each PE and PP sample the concentration of lead was the highest, whereas the cadmium had the lowest concentrations.

The concentrations of arsenic and chromium were higher in the Kuwait than in all UK samples, notably the arsenic concentration in both PE and PP samples. Cadmium and lead concentrations were also higher in the Kuwait samples compared to the UK samples, except for the Scotland 2016 sample, which had a higher concentration of cadmium in the PE and PP samples and a higher concentration of lead in the PE samples. The results suggest that the ambient environments of the pellets collected from Kuwait were richer in PTE than the UK location. The bay in Kuwait suffers from continuous stress and PTE are increasing as reported in literature: seawater collected from the bay in 1995-1996 had an average concentration of 1.16 and 2.02 μg L^{-1} for chromium and lead, respectively[242], and the concentration of lead increased to 7.01 μg L^{-1} in 2001[243]. It was also reported by Pouring *et al*.(2005)[244] that the lead concentration in Kuwait marine sediment was the highest (209 μg g^{-1}) compared to other Gulf region locations.

Among the samples from Scotland, those collected in 2015 showed lower concentrations of arsenic, chromium, and lead than the samples collected the year before. Lead was notably higher in the 2016 samples compared to earlier years. As the seasonal effect is excluded since all samples were collected at the same time of year, this variation can be

attributed to the lack of replicates or to the ambient environment of the location where the pellets were collected, which suggest that plastic pellets give an indication of the level of PTE contamination in marine environments. Analysing water and sediment along with pellets from each location is recommended for further study.

A comparison between the results obtained from the two steps of analysis generally revealed that larger amounts of PTE were released in the first step of the extraction than in the second step. Table A-1 in Appendix 9 shows the percentage of PTE recovered from the total concentration obtained in Table 6-3 and 6-4 by the cold leaching and microwave digestion steps. This suggests that the PTE were relatively weakly sorbed from the marine environment on the surface of pellets. An exception to this general finding was that the concentration of chromium after the microwave digestion was notably higher than after the cold leaching in Kuwait samples, and in the Scotland 2014 and 2015 PP samples. This could suggest that the chromium was more tightly incorporated and that cold leaching conditions were not sufficient to leach this element. A longer leaching time may be required.

Table 6-6 shows literature data on the concentration of PTE obtained in beached plastic collected in the UK using cold digestion leaching, together with the results obtained in the current study using the first stage of sequential digestion (cold leaching). In one study, beached plastic pellets were collected, ultrasonicated, and then digested with 20 % *aqua regia* and shaken overnight, from four beaches in South Devon, South West England[117]. In the other, four locations in South West England[118] were sampled and pellets were digested with 20 % *aqua regia* and shaken for 48 hours. One location (Saltram) was common to both studies. Reported values obtained for PTE were varied even at Saltram indicating that plastic pellets from the same site differ widely in PTE concentrations. Generally, PTE concentrations obtained in the current study were significantly higher than what was obtained in above mentioned studies. This might be attributed to the ambient environment where the pellets were collected, or leaching of some adsorbed PTE due to the pre digestion ultrasonicated step used in the literature studies.

Table 6-6 The concentration of PTE obtained in beached plastic collected in the UK and PTE obtained in current study after cold-leaching step.

Element	Ashton *et al.*[117] (2010) South Devon, South West England		Holmes *et al.*[118] (2012) South West England		Current Study Limekilns-Scotland (2014 – 2016)		Shuwaikh-Kuwait (2014)	
	Four locations	Saltram	Four locations	Saltram	PE	PP	PE	PP
As (μg g^{-1})	–		–		3.26 –6.59	1.23–2.25	12.5	5.59
Cd (ng g^{-1})	1.7 ± 0.8 – 10.0	5.0	1.09 ± 1.39 – 76 ± 134	1.65± 1.19	242–474	71–156	371	67.6
Cr (ng g^{-1})	19 ± 5 – 151	151	44 ± 39.5 – 751 ± 142	237 ± 159	12100–14900	1010–9930	19100	5150
Pb (μg g^{-1})	0.15 ± 0.04 – 1.08	1.08	0.149±0.181–1.64 ± 2.4	0.02 ±1.24	17.8–47.8	7.73–17.9	28.4	19.3

6.4 Overall comparison and findings

Surface study of naturally-weathered pellets visualised the pellets and showed that the surface morphology of all pellets studied was rough. An accumulation of built-up layers was observed on the surface of beached pellets except for one sample (Scotland-2016). As such materials were not observed in laboratory-weathered pellets studied in Section 5-1-1, this observation may be attributed to the accumulation of biofilms on the pellets' surfaces. It has been reported in literature that biofilms and gelatinous films were formed on floated plastic pellet surfaces in marine environment[237].

Elemental analysis of PTE on beached pellets indicated that the common elements were calcium, carbon, chlorine, oxygen, platinum, silicon, and zirconium; less common elements detected were molybdenum, sodium and sulfur. All detected elements were attributed either to the pellets structural back bone; residual and impurities remaining from metal-oxide and metal mixture catalysts or additives used during the production process of pellets; or from the ambient marine environment. Most of the detected elements were also found in laboratory-weathered pellets except for calcium and silicon which were dominant in beached pellets except for one sample (calcium was not

detected in Scotland-2016 sample). Silicon can be mainly attributed to the contact with beach sand where pellets eventually settled, whereas calcium can be attributed to the seawater and marine organism deposits on plastic surface. A correlation between the build-up of material on surfaces and the presence of calcium was observed from SEM results as seen in Scotland-2016 sample compared to the other. The SEM mass percent of elements attributed to seawater: chlorine, magnesium, sodium and sulfur, were lower in beached pellets compared to laboratory-weathered pellets. This finding can be attributed to the complexity of seawater compared to the artificial seawater or, as assumption, due to some remaining seasalt on laboratory-weathered pellets surfaces after been rinsed with deionised water.

Identification of pellets by FTIR showed that most pellets collected from Kuwait and Scotland were PE and PP. Kuwait pellets were 48 % PE and 48 % PP, whereas Scotland pellets were 68 % PE and 32 % PP.

Arsenic, cadmium, chromium and lead were successfully released and extracted from PE and PP beached pellets by two stage extraction: cold digestion and microwave assisted digestion. Greater release of PTE occurred in the first stage of cold leaching except for chromium. This suggests that sorption of PTE in naturally-weathered pellets is weak, and therefore pellets are not only capable of taking up PTE (as also shown in chapter 4) but can easily release them, thus acting as a source of PTE to the marine environment and organisms. The concentrations obtained for PTE were higher in PE than in PP pellet at both locations. This can be attributed to the properties of pellets and their weathering degree. In both type of pellets, lead level was the highest whereas the lowest was the cadmium (which was in agreement with lead results obtained in chapter 4).

Comparison between Kuwait and Scotland samples showed that arsenic concentration was significantly higher in Kuwait sample. Cadmium, chromium and lead were also higher in Kuwait sample except for cadmium and lead in Scotland-2016 sample. This can be attributed to the ambient environment as Kuwait Bay suffers from continues stress as discussed in Section 6-1. Samples collected from Limekilns-Scotland (2014-2016) showed that in 2014, the concentrations of arsenic, chromium and lead were

higher than 2015 samples. In 2016, lead was notably higher than it was in 2014 and 2015.

This variation of PTE concentrations may be attributable to variability in the ambient environment and plastic pellets may give an indication of some PTE in the surrounding environment.

7 Estimation of bioaccessibility of PTE to marine organisms after ingestion of beached plastic pellets

As discussed earlier in Section 1-1-3 marine biota including fish ingest microplastics including plastic pellets mistaking them for food. Adverse physical effects of plastic ingestion, such as injuries to the digestive system and inhibition of energy due to reduction of food, have been reported. However, bioaccessibility of PTE to fish due to ingestion has not been studied yet.

In chapter 6, it was shown that PTE bound to beached pellets are weakly bound and easily desorbed. Therefore, in this chapter bioaccessibility of arsenic, cadmium, chromium and lead from beached PE and PP plastic pellets to fish will be studied, aiming to contribute in fulfilling this knowledge gap and to assess the hazard of ingestion of petroleum based plastic resin pellets to simulated solution of fish stomach and possibly to the food chain.

7.1 Bioaccessibility and availability of PTE

Bioaccessibility and bioavailability are used to determine the potential interaction and noxious effect of a certain contaminant or PTE on a certain organism[146, 245]. Bioaccessibility of PTE can be defined as the *in vitro* fraction of PTE that is released in the gastro- intestinal environment and thus is ready for absorption and metabolism[246], whereas bioavailability is defined as the *in vivo* fraction of the ingested PTE that reaches the systemic circulation[247, 248]. Bioavailability can only be determined *in vivo*, whereas bioaccessibility is estimated *in vitro*. The oral *in vitro* methodology is commonly used as it does not involve any ethical issues, and is rapid, reproducible and low in cost[249]. Several *in vitro* methods were developed (mainly to assess human bioaccessibility). A common one is the simplified bioaccessibility extraction test (SBET) that was first validated for lead uptake[250] and modified from physiologically based extraction test which simulate both stomach and intestinal tract[251]. However other elements such as arsenic and cadmium were since assessed successfully, and the method is commonly

used due to its simplicity comparing with methods such as the physiologically based extraction test and unified bioaccessibility method[252].

Consideration of each PTE studied, total PTE content, the pH of the extraction used, presence of further organic or inorganic such as organic matters are an important means of oral bioaccessibility determination[253-255] which involve extraction of PTE using simulated gastric fluids.

Conventional SBET method conditions, glycine 0.4 M at pH 1.5 and 37˚C for 1hour, was modified in this study to mimic fish stomach by increasing both temperature and time of extraction process, whereas glycine and pH were remain as in conventional method. Glycine is a simple amino acid used as extraction solution in SBET because of its role in metabolic functions, extracting and transport nutrients including metals and metalloids[255, 256].

7.1.1 Fish digestive system

The digestive system of fish generally includes the mouth, esophagus, stomach, gizzard, gall bladder, spleen, pyloric caeca, intestine and rectum and anus. Figure 7-1 shows the digestive system of the fish. Simulating the conditions of the fish digestive process, fluids, temperature, time and pH is important in developing a fit-for-purpose bioaccessibility test for simulated fish stomach.

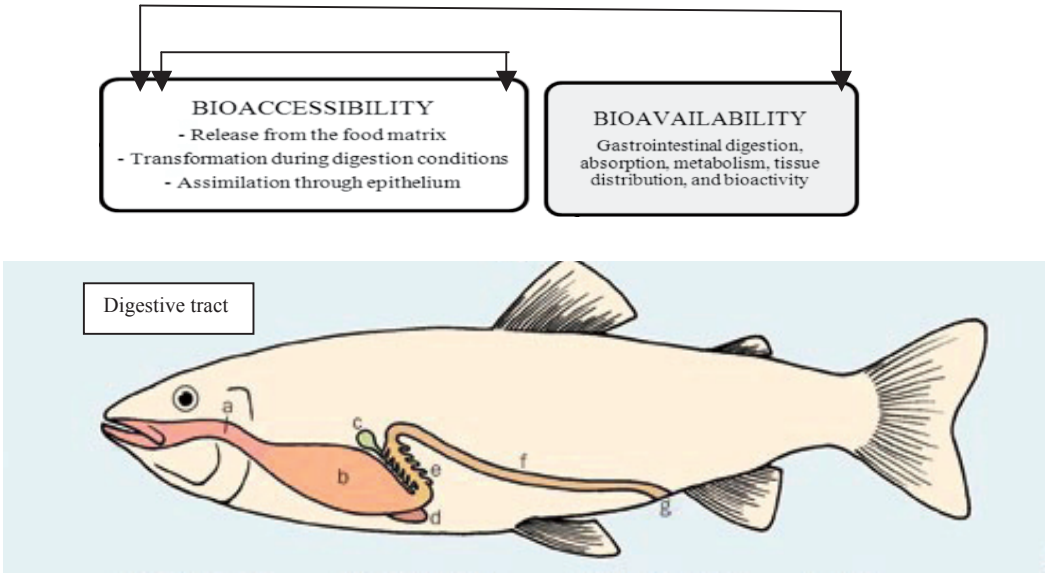


Figure 7-1 Fish digestive system including the mouth, a: esophagus, b: stomach, c: gall bladder, d: spleen, e: pyloric caeca, f: intestine and g: anus (Adapted)[257].

Ingestion behaviour and pH in the fish stomach was studied[258] at different times of the day along with the stomach variable fullness. It was found that, in a daily cycle, fish ingested ~11.5 % of their wet body weight, and the stomach was nearly full for around 12-13 hours. The highest pH of the stomach was ~3.5 between midnight and early morning when the stomach was almost empty. As the fish stomach gradually reached the highest fullness during the day, the pH of the stomach dropped to 1.5 or 1.4 due to the secretion of gastric acids and enzymes.

Various conditions were studied by Pena-Icart *et al.*[259] to determine bioavailability of PTE to marine fish from coastal sediments using different acids (acetic acid and hydrochloric acid), enzymes (pepsin and trypsin), temperatures (10, 20 and 40 ˚C) and pHs (1, 2, 3, 4, and 5) during 1, 12 and 24 hours. Extraction with HCl at pH 1, at 40 ˚C for 12 hours was proposed and recommended for optimum extraction. This method was therefore adapted for use in the current study, with parallel application of the well-established SBET procedure for comparison. The SBET bioaccessibility is established for humans, and corresponds mainly to the stomach; the typical procedure is to use 0.4

M glycine extractant, at pH 1.5 for one hour at 37 ˚C. Time and temperature were modified in the current study to mimic fish stomach.

7.2 Determination of the bioaccessibility of PTE to simulated fish stomach from plastic pellets using modified SBET and HCl extraction methods

7.2.1 Apparatus and reagents

Samples were placed in wide-mouth bottles with extraction fluid of either trace metal grade HCl, which was supplied by Sigma Aldrich (Gillingham, Dorset, UK), or 0.4 M analytical reagent grade glycine solution supplied by Fisher scientific (Loughborough, UK). The pH of extractions was adjusted by HCl and measured by SevenGo^{TM} pH meter supplied by Mettler-Toledo Ltd. (Leicester, UK). Wide-mouth bottles were shaken in a Stuart orbital incubator SI 500 Bibby scientific limited, (Stone, Straffordshire, UK). A 0.45 μm Luer-lok cellulose disk filter in a 20 mL disposal syringe was used to filter and transfer samples after extraction to clean tubes. Extracts were preserved until analysis by a Agilent 7700x ICP-MS instrument supplied by Agilent Technologies, (Wokingham, Berkshire, UK).

7.2.2 Procedure

A total of 0.5 g of transparent beached PE and PP plastic pellets collected from Limekilns, Scotland, in 2017 were weighed and placed in wide-mouth bottles. A 50 mL aliquot of (freshly made) extraction solution (glycine or HCl) was added. Samples were placed and shaken in the incubator (30 rpm) at 40 ˚C for 16 hours (as 12 hours was not convenient with the laboratory access). Samples were then filtered by a syringe attached with a cellulose disk filter as seen in Figure 7-2. Triplicate blanks for each procedure were also applied.

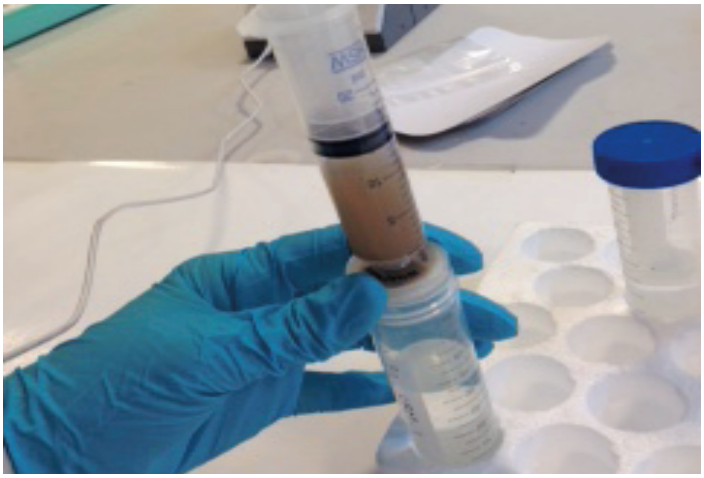


Figure 7-2 Sample filtration by syringe attached to a 0.45 μm cellulose disk filter.

SBET extraction solution (1L): Glycine 0.4 M was prepared by dissolving 30.03 g of glycine in ~ 900 mL deionised water and heated in a water bath until the extraction solution reached 40 ˚C. The pH was adjusted to 1.5 ± 0.05 using HCl and the solution was made up to the final volume of 1L.

HCl extraction solution (1L): Hydrochloric acid 0.1 M was prepared by diluting 8.458 mL of HCl in 900 mL deionised water, and heated in a water bath until the extraction solution reached 40 ˚C. The pH was adjusted to 1 ± 0.05 using HCl. The solution was then made up to the final volume of 1L.

Mass balance check: this was conducted as quality control and as no CRM is available to check the accuracy of the bioaccessibility tests used in the current study. It includes:

- A: Cold *aqua regia* extraction

  A total of 0.5 g of beached PP and PE pellets, collected from the same place, at the same time as those used in the bioaccessibility test, were weighed, and cold digested using 20 % *aqua regia* for 48 hours in a shaking incubator at room temp and 150 rpm. Extracts were preserved until analysis by ICP-MS.

- B: Non-bioaccessible fraction

  Washed residue (pellets) following the SBET and acid extraction procedures were subjected to cold leaching extraction in 20 % *aqua regia* cold digestion as described in step A.

An indication of the quality of the applied procedures was obtained by comparing the sum of the bioaccessible and non-bioaccessible fractions with the result of the separate aqua regia digestion i.e. A = B + (results of modified SBET or HCl extraction).

7.2.3 Bioaccessible PTE concentrations in beached plastic pellets

Polyethylene and PP pellets collected from Limekilns, Scotland were extracted in glycine and HCl. The aim was to assess the bioaccessible arsenic, cadmium, chromium and lead to simulated solution of fish stomach, by estimating the PTE released from each type of plastic pellet by modified SBET and acid extraction methods. Table 7-1 shows the mean concentrations of PTE released from beached pellets using SBET extraction and HCl extraction methods, together with the non-bioaccessible fraction after SBET and HCl test and the *aqua regia* soluble PTE concentrations. Individual concentrations of the triplicates after the extraction and mass balance of cold leaching are presented in Appendix 10.

Table 7-1 Concentrations of bioaccessible and non-bioaccessible PTE released from beached pellets using SBET glycine extraction and HCl extraction methods, and the parallel extraction of equivalent pellets (n = 3)

SBET- method				**Acid extraction-method**				**The parallel extraction**
Elements	**Type of pellets**	**Bioaccessible concentration ($\mu g\ g^{-1}$)**	**Non-bioaccessible concentration ($\mu g\ g^{-1}$)**	**Elements**	**Type of pellets**	**Bioaccessible concentration ($\mu g\ g^{-1}$)**	**Non-bioaccessible concentration ($\mu g\ g^{-1}$)**	**Cold aqua regia soluble ($\mu g\ g^{-1}$)**
As	PE			**As**	PE			
Mean		0.975	2.81	Mean		0.278	2.67	3.52
SD		± 0.017	±0.16	SD		± 0.019	± 0.09	0.128
RSD		1.74	5.69	RSD		6.83	3.37	3.63
Mean	PP	0.904	2.51	Mean	PP	0.263	2.98	3.24
SD		± 0.001	± 0.138	SD		± 0.0009	± 0.06	0.097
RSD		0.11	5.49	RSD		0.342	2.01	3.00
Cd	PE			**Cd**	PE			
Mean		0.0021	0.00788	Mean		0.000383	0.0041	0.00951
SD		± 0.0001	± 0.006	SD		± 0.00008	± 0.0008	0.0013
RSD		4.76	76.1	RSD		20.8	19.5	13.6
Mean	PP	< LOD	0.00246	Mean	PP	< LOD	0.00328	0.00439
SD			± 0.0009	SD			± 0.0005	0.0005
RSD			36.5	RSD			1.52	11.3
Cr	PE			**Cr**	PE			
Mean		0.051	0.278	Mean		0.0267	0.252	0.564
SD		± 0.003	± 0.08	SD		± 0.006	± 0.001	0.44
RSD		5.88	**28.7**	RSD		22.4	0.396	78.0
Mean	PP	0.021	0.266	Mean	PP	0.0172	0.264	0.309
SD		± 0.014	± 0.024	SD		± 0.003	± 0.008	0.018
RSD		66.6	9.02	RSD		17.4	3.03	5.82
Pb	PE			**Pb**	PE			
Mean		0.242	0.0496	Mean		0.184	0.074	0.296
SD		± 0.083	± 0.032	SD		± 0.011	± 0.006	0.055
RSD		34.3	64.5	RSD		5.97	8.1	18.5
Mean	PP	0.15	0.026	Mean	PP	0.131	0.0266	0.194
SD		± 0.005	± 0.0009	SD		± 0.004	± 0.003	0.052
RSD		3.3	3.46	RSD		3.05	11.2	26.8

7.2.3.1 Discussion of the results

All results obtained for SBET and acid extractions methods were above the procedure limit of detection, which was 0.00178, 0.000366, 0.000732 and 0.000899 μg g^{-1} for arsenic, cadmium, chromium and lead respectively, except for the cadmium in PP in both methods, whilst cadmium in PE extracted by the HCl method (0.000383 μg g^{-1}) was very close to the limit of detection (0.000366 μg g^{-1}). The RSD of triplicates were mostly less than 10 % and showing a good precision for the PTE studied. However some RSD values were larger, particularly for cadmium in PE using the HCl method (20.8 %), chromium in PE using the HCl method (22.4 %), chromium in PP using the SBET method (66.6 %), chromium in PP using the HCl method (17.4 %), and lead in PE using the SBET method (34.3 %). Such variation was expected as PTE are not equally present in pellets as seen in beached pellets results obtained in Section 6-3-2.

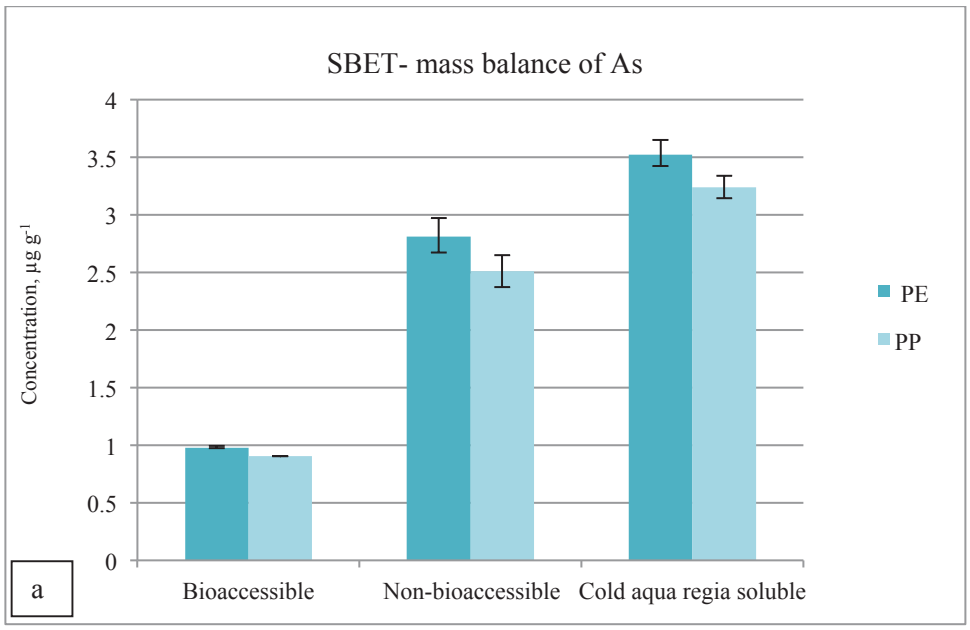
Bioaccessible concentrations obtained using SBET and HCl extraction methods showed that all PTE studied were bioaccessible from plastic pellets, especially arsenic and lead. The highest concentrations were for the arsenic whereas the lowest were for cadmium. This can be attributed to the concentrations of total PTE present in beached pellets (mass balance will be discussed later). All PTE concentrations released from PE pellets were higher than the concentrations released from PP type of pellets. This was expected as beached PE pellets adsorb more PTE on the surface than the PP, and it is in agreement with results obtained in section 6-3-2, Table 6-3.

For all elements studied, the bioaccessible concentrations released were lower than the non-bioaccessible concentrations using SBET and HCl-extraction methods except for lead where the bioaccessible concentrations in PE and PP were greater than the non-bioaccessible concentrations obtained. This indicated that most of the lead present in pellets would be bioaccessible to the simulated solution of fish stomach when ingested and so may accumulate in fish tissue and enter the human food chain. This was in agreement with bioaccessible lead reported in literature[260] where ~70% of total lead was soluble in simulated gastric solutions of pH 1.5 and pH 1.7.

Comparison between results obtained using SBET and HCl methods revealed that the bioaccessible PTE concentrations using modified SBET method were greater than those obtained using the HCl method. For example, arsenic released from PE pellets to the glycine extractant was 3.5 times more than the arsenic released in HCl extractant, showing that modified SBET method was more effective in releasing PTE than the HCl extraction method proposed by Pena-Icart *et al*.[259] indicating that glycine have higher affinity for PTE than HCl.

The new method worked and was more appropriate. According to Getachew[258], the pH used in modified SBET method (1.5) was more representative of real conditions (pH 1.4 – 1.5). The glycine solution was also more representative to the organic legends present in real stomach which bind with PTE and bring to the solution.

The total mass balance of all bioaccessible concentrations of arsenic, cadmium, chromium and lead from PE and PP pellets to fish was assessed by comparing the sum of the bioaccessible and non-bioaccessible fractions with results for equivalent pellets (collected from the same place, at the same time) after cold digestion by 20 % *aqua regia*. This is visualised in Figures 7-3 to 7-6.



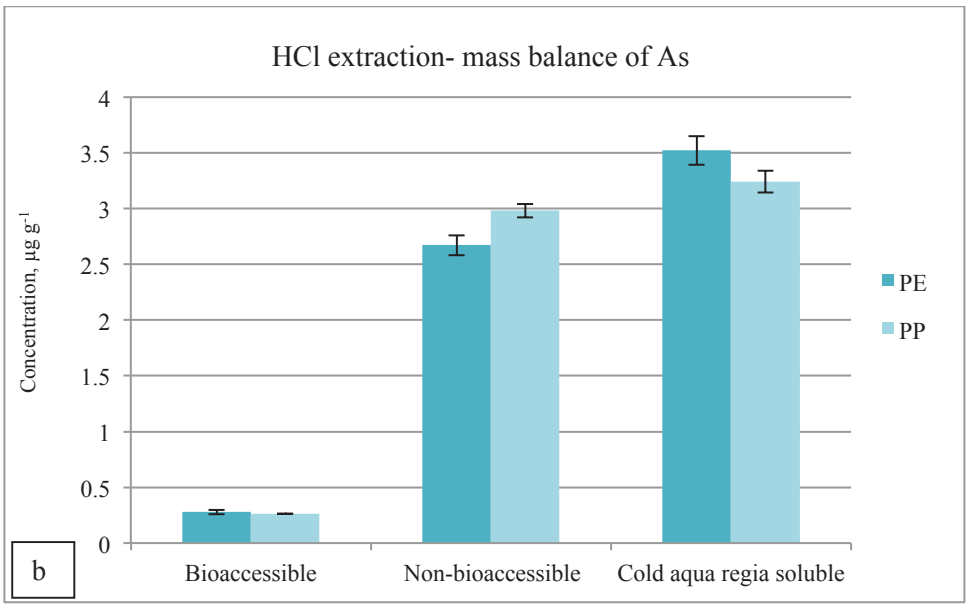
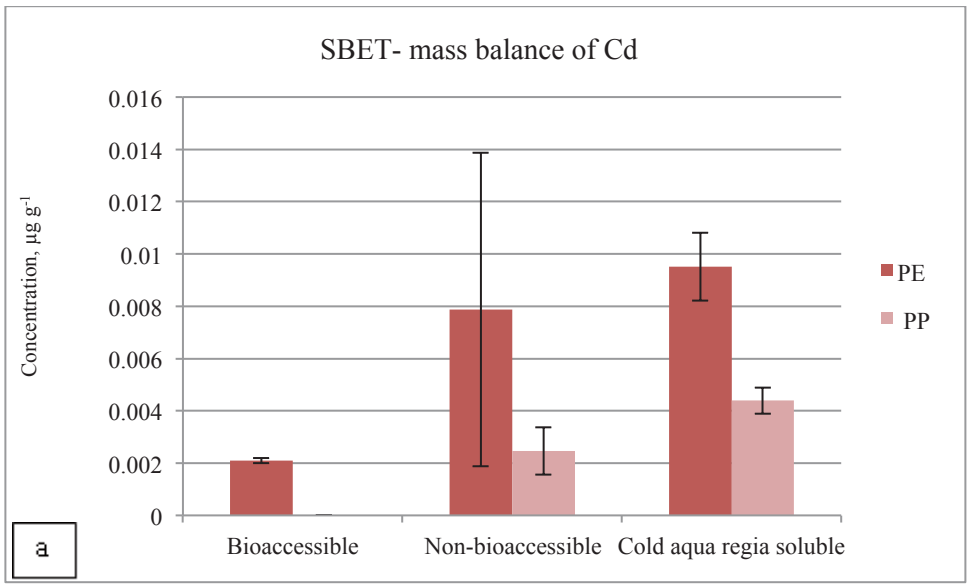


Figure 7-3 Bioaccessible concentrations of As from PE and PP beached plastic pellets to fish and the non-bioaccessible As extracted from the same pellets using cold digestion by 20 % aqua regia after bioaccessibility test, comparing to the cold aqua regia soluble of equivalent pellets collected from the same location at the same time after cold digestion by 20 % aqua regia. a: after modified SBET method and b: after acid (HCl) extraction method (n=3).



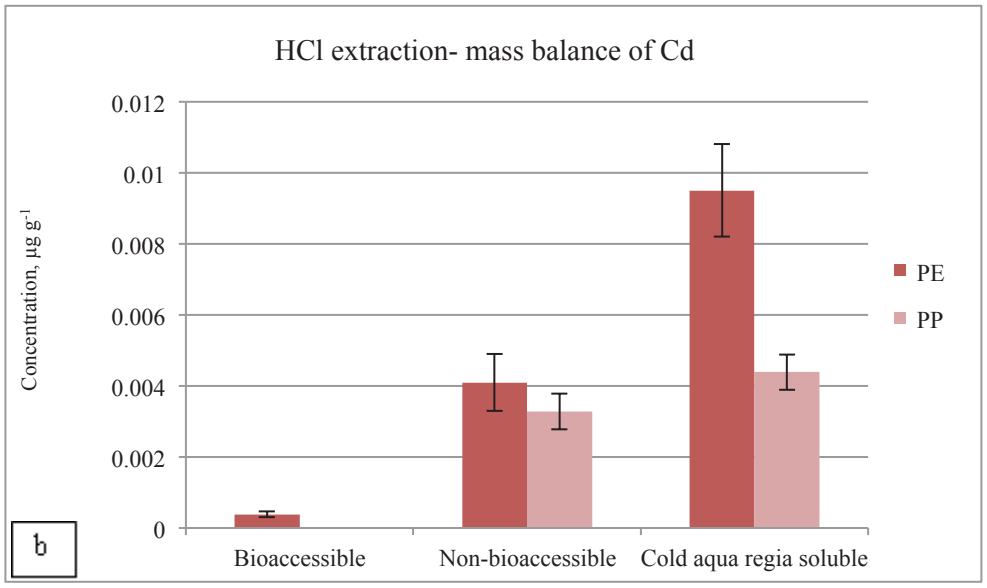
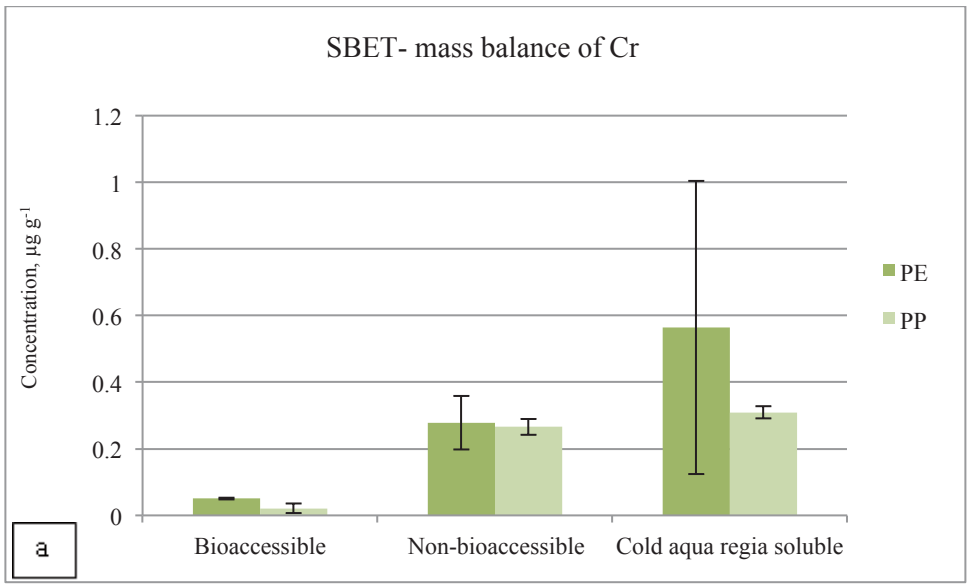


Figure 7-4 Bioaccessible concentrations of Cd from PE and PP beached plastic pellets to fish and the non-bioaccessible Cd extracted from the same pellets using cold digestion by 20 % aqua regia after bioaccessibility test, comparing to the cold aqua regia soluble of equivalent pellets collected from the same location at the same time after cold digestion by 20 % aqua regia. a: after modified SBET method and b: after acid (HCl) extraction method (n=3).



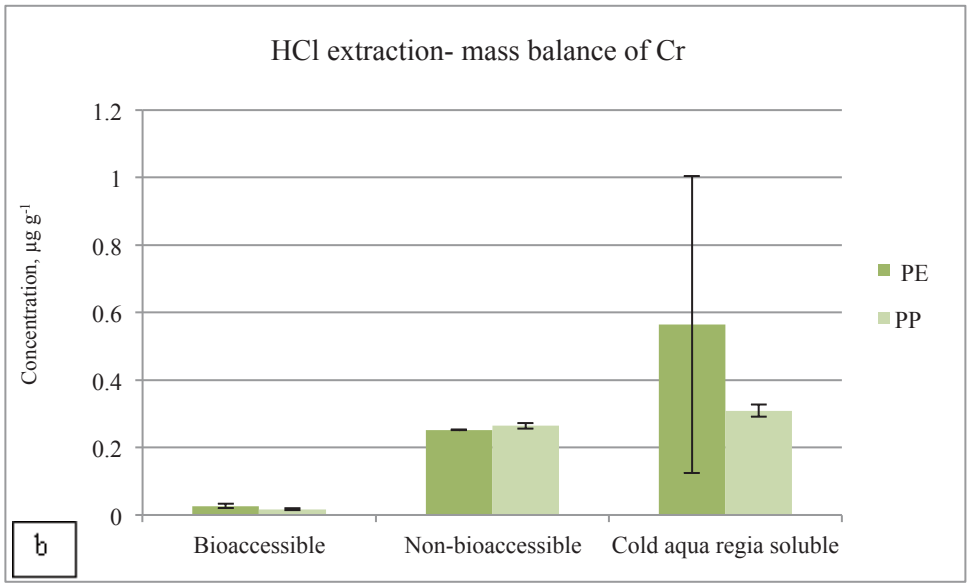
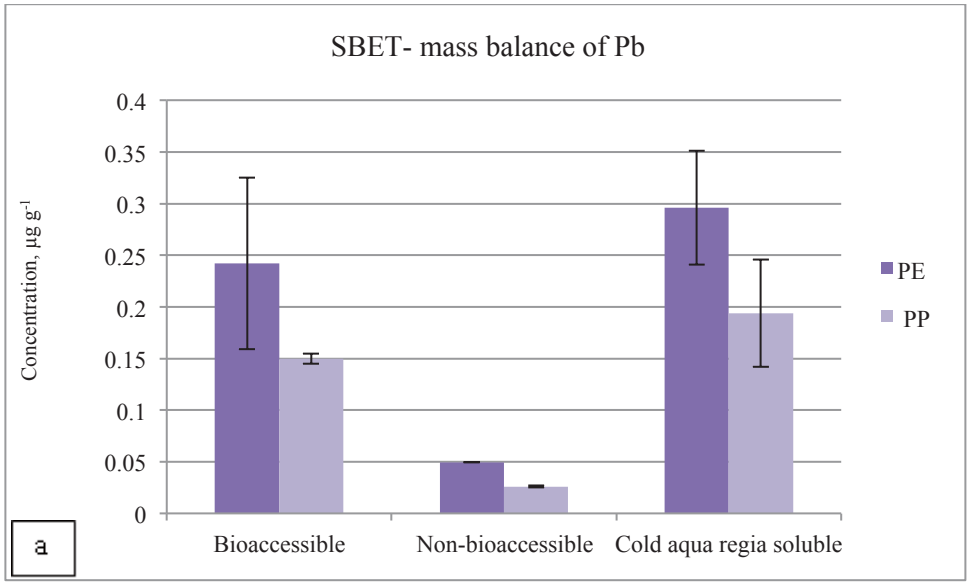


Figure 7-5 Bioaccessible concentrations of Cr from PE and PP beached plastic pellets to fish and the non-bioaccessible Cr extracted from the same pellets using cold digestion by 20 % aqua regia after bioaccessibility test, comparing to the cold aqua regia soluble of equivalent pellets collected from the same location at the same time after cold digestion by 20 % aqua regia. a: after modified SBET method and b: after acid (HCl) extraction method (n=3).



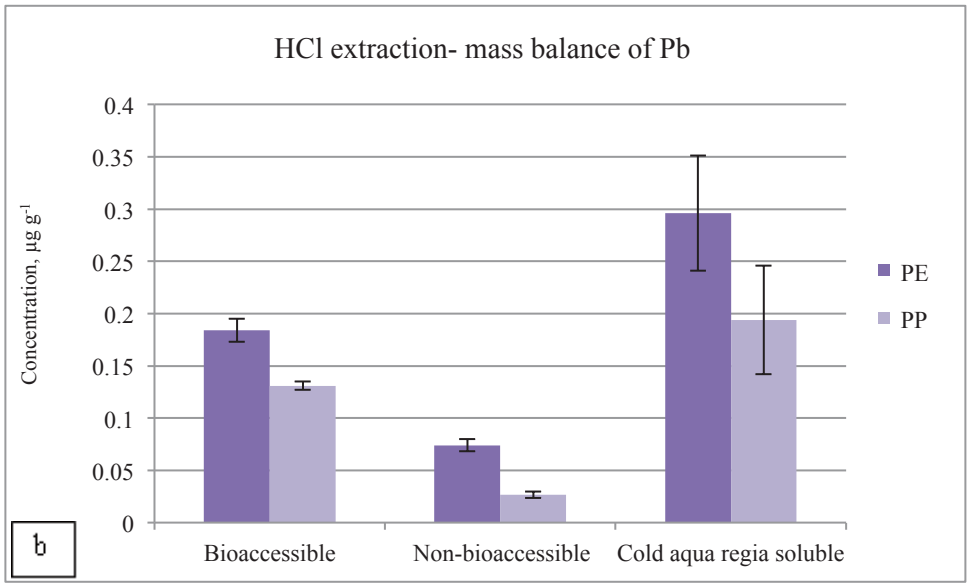


Figure 7-6 Bioaccessible concentrations of Pb from PE and PP beached plastic pellets to fish and the non-bioaccessible Pb extracted from the same pellets using cold digestion by 20 % aqua regia after bioaccessibility test, comparing to the cold aqua regia soluble of equivalent pellets collected from the same location at the same time after cold digestion by 20 % aqua regia. a: after modified SBET method and b: after acid (HCl) extraction method (n=3).

Quantitative results of analysis of the pellets collected from the same location at the same time, as a feature of starting concentration, showed that arsenic concentration was the highest, then, in decreasing concentration order, chromium, lead and cadmium. This result can explain the results of bioaccessibility test where arsenic was accessible in greater concentration than other PTE studied, and the cadmium showed the lowest accessible concentration.

The sum of the amounts of PTE released by the bioaccessibility test and cold leaching of the same pellets following extraction (bioaccessible + non-bioaccessible) were generally close to the concentrations obtained for parallel *aqua regia* extraction of equivalent pellets except for cadmium in PP and chromium in PE as seen in Table 7-2. For example, the sum of arsenic concentrations in PE and arsenic concentration in equivalent pellets were 2.94 μg g^{-1} and 3.52 μg g^{-1}, respectively whilst the concentrations were 3.24 μg g^{-1} and 3.24 μg g^{-1} for arsenic from the PP, respectively (using SBET method). The mass balance check revealed that average recoveries of PTE using modified SBET method and HCl extraction method were 93.7 % and 77.4 % respectively. In literature the HCl extraction method had more than 90 % recovery for elements including As, Cd, Cr and Pb for bioaccessibility test from sediment to fish[259].

Table 7-2 Average bioaccessible and non-bioaccessible concentration of PTE comparing to the total concentration of 20 % cold *aqua regia* soluble of parallel extraction of pellets collected from the same location at the same time in μg g^{-1}.

Elements	Pellets type	SBET- method bioaccessible + non-bioaccessible concentration	Parallel extraction of cold *aqua regia* soluble	HCl - method bioaccessible + non-bioaccessible concentration
As	PE	3.785	3.52 ± 0.128	2.948
	PP	3.414	3.24 ± 0.097	3.243
Cd	PE	0.00998	0.00951 ± 0.0013	0.00448
	PP	0.00246	0.00439 ± 0.0005	0.00328
Cr	PE	0.329	0.564 ± 0.44	0.278
	PP	0.287	0.309 ± 0.018	0.281
Pb	PE	0.2916	0.296 ± 0.055	0.258
	PP	0.176	0.194 ± 0.052	0.157

The % bioaccessibility was expressed relative to the concentrations obtained by cold 20 % *aqua regia* digestion of the equivalent pellets as:

% BA = (bioaccessible concentration / *aqua regia* soluble concentration) x 100

Table 7-3 summarises the percentage PTE released (hence bioaccessible to simulated solution of fish stomach) using SBET and HCl extraction methods.

Table 7-3 Bioaccessible concentrations expressed as a percentage using modified SBET and HCl extraction methods

Elements	**Pellets type**	**%BA* SBET-method**	**%BA* HCl extraction-method**
Arsenic	PE	27.6	7.89
	PP	27.9	8.11
Cadmium	PE	22.1	4.03
Chromium	PE	9.04	4.73
	PP	6.80	5.57
Lead	PE	81.8	62.2
	PP	77.3	67.5

* % BA = (bioaccessible concentration / *aqua regia* soluble concentration) x 100

Bioaccessibility of arsenic: arsenic bioaccessible concentration from PE using SBET method was 27.6 % of the total arsenic recovered after the cold leaching of the equivalent pellets, whereas it was 7.89 % using HCl method. Using SBET method, the concentration was 27.9 % of total arsenic recovered from PP pellets, and it was 8.11 % using HCl method. More arsenic was released by SBET over the HCl method. This can be attributed to the glycine mechanism of amino acid extraction over the HCl acid. Bioaccessible percentage from the total PE and the PP were similar, within each method, which indicates that different pellets has the same effect and release relatively the same percentage of arsenic in simulated fish stomach when ingested.

Bioaccessibility of cadmium: using SBET method, Bioaccessible cadmium released from PE was 22.1 % of the total cadmium obtained after the cold leaching of the equivalent pellets, whereas it was 4.03 % using HCl method, showing that more cadmium was released by SBET compared with the HCl method. The percentage of bioaccessible cadmium was lower than arsenic bioaccessible percentage released in the same conditions. This can be attributed to the PTE-pellet binding strength.

Bioaccessibility of chromium: the bioaccessible concentration of chromium obtained from the PE using SBET method was 9.04 % of the total chromium, and was 6.80 % from the PP. Using HCl method, the bioaccessible concentration was lower, it was 4.73 % from the PE, and 5.57 % from the PP. In agreement to arsenic, bioaccessible concentration from the PE was relatively close to the PP within each method. Bioaccessible concentrations were clearly lower than the arsenic and cadmium bioaccessible concentrations. This was in agreement with the results obtained and discussed in Section 6-3-2 where chromium release was notably low after cold digestion suggesting that the chromium was more tightly incorporated into pellets and a longer leaching time may be required.

Bioaccessibility of lead: lead had a greatest % bioaccessible concentration amongst the PTE studied. It was 81.8 % and 77.3 % of total lead from PE and PP respectively using SBET method, and 62.2 % and 67.5% of total lead from PE and PP respectively using HCl method. Bioaccessible concentrations from the PE and the PP were relatively close in each method. Lead was released more by SBET method than it was released by the HCl method. However, both methods showed high bioaccessible concentrations of lead compared to other PTE studied. This was in agreement with bioaccessible lead reported in literature[260] as mentioned in Section 7-2-3-1.

In general, different PTE studied showed different extractability as follows: using SBET method: average Pb (79.5 %) > As (27.8 %) > Cd (22.1 %) > Cr (7.92 %) and using HCl method average Pb (64.8 %) > As (8.0 %) > Cr (5.15 %) > Cd (4.03 %) showing that ingested pellets, that carry PTE on the surface, can convey PTE to

simulated fish stomach, notably lead. Further study is requiring to determine how much of the bioaccessible PTE are incorporated into fish tissue; and ultimately to assess risk to humans from fish ingestion.

In literature, bioaccessibility of PTE from sediment to fish[259, 261] and from fish to human[262, 263] were reported. However, no studies were found to cover the bioaccessibility and bioavailability from plastic pellets to fish (simulated fish stomach).

7.3 Conclusions

In vitro bioaccessibility of PTE to simulated solution of fish stomach from beached PE and PP plastic pellets were successfully estimated using a new modified SBET method and HCl extraction method proposed by Pena-Icart *et al*.[259].

Both methods showed bioaccessible concentrations of arsenic, cadmium, chromium and lead to fish. However, the new modified SBET method was successfully worked and showed notably greater release of PTE studied than the HCl extraction method.

Correlation between the total concentration of PTE present in pellets and concentrations of bioaccessible PTE was found. Therefore pellets that carry greater concentrations of PTE can pass greater amounts to simulated fish by ingestion. This was in agreement with T. Tongesayi *et al*.[255] study where a positive correlation was found between total metal content and bioaccessibility of cadmium, copper, iron, lead, manganese and zinc in biosolids.

Generally, PTE concentrations released from PE pellets were higher than the concentrations released from PP type of pellets. However, when comparing to the total PTE levels in equivalent pellets, the percent bioaccessibility of PTE from PE and PP were close, for the same extraction method. This indicated that all pellets studied were likely to have relatively the same effect once ingested by simulated fish stomach.

Extractability of PTE studied was assessed by mass balance recovery, and it was: Pb (79.5 %) > As (27.8 %) > Cd (22.1 %) > Cr (7.92 %) using SBET method, and

Pb (64.8 %) > As (8.0 %) > Cr (5.15 %) > Cd (4.03 %) using HCl method. Lead always had a greater release from plastic surface in simulated fish stomach than arsenic, cadmium and chromium.

8 Conclusions and future work

8.1 Conclusions

Potentially toxic elements were investigated in virgin plastic pellets by microwave-assisted digestion with nitric acid followed by analysis with ICP-MS. The majority of the elements detected in virgin plastic were associated with one or more aspect of plastic production. It was found that pellets were not uniform and each individual pellet was different with regards to the PTE concentration and distribution.

The sorption pattern and transport potential of four types of petroleum-based plastic pellets (high density polyethylene, low density polyethylene, polypropylene and polyethylene terephthalate) and one bio-based poly(hydroxybutyrate-co-hydroxyvalerate) plastic for arsenic, cadmium, chromium and lead were estimated in different media. As the pH and TDS increased — by the use of deionised, fresh (drinking) and then artificial seawater — arsenic uptake increased whereas the level of cadmium and lead uptake decreased. Chromium results fluctuated, but with a similar trend to arsenic. Equilibrium time was achieved between 24 and 35 hours. Results suggested that all types of petroleum-based and bio-based plastic pellets studied have an affinity to adsorb the selected PTE in the marine environment. Further, all type of pellets used showed similar properties regarding the adsorption of different PTE. The overall amounts of PTE taken up were in the order: Pb > As > Cd ≥ Cr.

Sorption profiles of virgin and laboratory-weathered pellets in artificial seawater revealed that weathered plastic pellets showed higher uptake of PTE compared with virgin pellets, this behaviour can be attributed to surface erosion by abiotic effects such as oxidation under UV light, which occurs at room temperature, or due to the chlorination mechanism in artificial seawater.

Bio-based pellets are considered environmental friendly. However, the results of this study revealed that biopellets can act as a vector of PTE, and their adsorption of

cadmium and chromium was higher, particularly in weathered pellets, compared with petroleum-based pellets.

The PTE adsorption capacities of the plastics were studied in multi-element spiked seawater. It was found that lead had the highest adsorption, then cadmium, chromium and arsenic for all types.

In chapter 5, surface morphology and elemental composition of virgin and laboratory-weathered pellets were studied using analytical scanning electron microscope SEM with energy-dispersive EDS analyser. As observed, the surface imaging of pellets generally indicated that virgin pellets used in this study did not have a smooth surface. Roughness was apparent to different degrees. Weathered pellets showed changes in surface characteristics. The PET and BIO pellets with functional groups (ester) were more eroded compared to the pellets with only a C-C backbone. In PE pellets, the LD type was more eroded than the HD ones.

Elemental scanning of virgin and laboratory-weathered plastic indicated that the surface of each pellet was not uniform i.e. each individual pellet was different and even different spots on the same pellet differed from one another. It was hypothesised that pellets were affected by their surrounding environment and were carrying elements on the surface sorbed from the ambient environment.

Internal reference spectra for different plastic pellets used in current study was established to use along with other means such as spectra library and typical spectra region for polymers to identify pellets.

The next stage of this investigation, covered in chapter 6, involved studying beached (naturally-weathered) pellets collected from Shuwaikh beach, Kuwait and Limekilns, Scotland. Most of the pellets collected were classified by infrared spectroscopy (ATR-FTIR) as PE and PP. Analysis by SEM revealed roughness and accumulation of layers likely attributed to the biofilms in real seawater. Elemental analysis of beached pellets revealed that pellets were carrying elements from the surrounding seawater environment

and beach sand, where pellets eventually settled, such as calcium and silicon and can act as a vector of PTE exist and carried from ambient environment.

Sequential acid digestion (cold digestion followed by microwave assisted digestion) of beached PE and PP indicated the PTE studied were mainly released in the first stage of digestion, except for chromium, indicating they are relatively labile and weakly bound to the pellets surface. In contrast the sequential acid digestion of a plastic reference material showed the reverse, with greater release of PTE in the microwave acid digestion step rather than the cold leaching. This is expected since the PTE in the RM were incorporated during manufacturing rather than sorbed on pellet surfaces showing that only weakly bound PTE were extracted in this stage. Higher concentrations of PTE were recovered from PE than from PP pellets collected from Kuwait and Scotland. Lead was released in highest concentration whereas cadmium concentration was the lowest among the PTE studied. Pellets collected from Kuwait had generally higher concentrations of PTE than the pellets collected from Scotland, especially arsenic. Pellets collected from the same location at different times varied in PTE concentrations, reflecting changes in the surrounded environment.

Bioaccessibility estimation of the selected PTE to simulated solution of fish stomach from the dominant PE and PP beached pellets was conducted using modified SBET and HCl extraction methods. Results indicated that all PTE studied were bioaccessible in the simulated (*in vitro*) fish stomach. The new modified SBET method was appropriate and successfully worked, it generally showed greater release of PTE compared with the HCl extraction, probably due to differences in pH of the extractants.

A correlation between the acid-soluble PTE present in pellets and the bioaccessible concentration of the same PTE was observed, suggesting that the higher the concentration of PTE in pellets, the greater amount of PTE may pass to simulated fish stomach following ingestion.

Comparing the bioaccessible PTE concentrations with acid-soluble PTE concentrations in equivalent pellets, it was found that the percentage bioaccessibility of PTE in PE and

PP by each method was similar, indicating that different types of pellets act similarly when ingested by simulated fish. Extractability of PTE was as follows: Pb > As > Cd > Cr and Pb >As > Cr > Cd using modified SBET and HCl extraction methods, respectively.

Overall, this study has shown that both petroleum-based and bio-based plastic pellets can act as a vector of arsenic, cadmium, chromium and lead in the marine environment. The adsorption capacity for cadmium and lead was higher than arsenic and chromium in simulated sea environment. Weathering caused different degrees of morphology changes in plastic pellet surfaces but, in all cases, it contributed to uptaken of higher concentrations of PTE than virgin pellets. All pellets appeared to be affected by the ambient environment, with marked differences between individual pellets. Of the beached pellets collected from Kuwait and Scotland, PE and PP were dominant. Surfaces were clearly eroded, PTE levels present reflected the ambient environment and all PTE studied were found to be potentially bioaccessible when ingested by marine organisms.

8.2 Future work

- A complete analysis of PTE concentrations in virgin plastic pellets from different producers is recommended to investigate if characteristic profiles exist that could be used to establish a database to help in identifying spillage sources. Also it is important for quantifying variability across pellet and plastic types.
- In this study, pH and TDS were both changed simultaneously in each different media. For some elements, the effect of one was clearly dominant on the sorption behaviour. However, this was not the case for chromium. Therefore a follow up study of the effects of pH and TDS changes separately is worth doing to better understand the chromium profiles.
- Further study of the pellets such as density, particle size distribution, surface area is recommended to compare like with like and overcome the limitation of only using the pellets weight in this study.

- Further investigation is recommended on the adsorption capacity of different types of plastic for PTE to determine which substrates are most efficient transporters of which elements. Once controlled, this may lead to the use of micro plastic as an adsorbent for removal of PTE from contaminated waters in optimum conditions.
- Further study of the link between the weathering time, accumulation of layers on weathered plastic pellets and PTE sorption is required plus more characterisation of the supposed biofilms layer found on beached pellets.
- Further monitoring of plastic pellets in the environment (repeatedly collected from multiple locations) and their analysis for PTE is recommended in the next stage. Plus a comparison with other surrounded materials (such as soil and water) in the same locations.
- Further study of bioavailability of PTE to marine life is required along with measurement of bioaccessible PTE incorporated into fish (mainly the edible parts) to be able to assess risk to humans from fish or seafood ingestion. Additional PTE should to be investigated for their bioaccessibility and availability to fish through ingestion of not only PE and PP plastics but also bio-based plastic by using pre contaminated pellets.
- Recommendations and legislations are required for decision makers concerning the use of plastic, and their recycling, and to reduce or prevent spillage of plastic pellets from manufacturing and during transport. Also for the use of certain additives after studying their effect to marine life.
- Better public communications to introduce problems associated with plastic in marine environment to society, and especially to school pupils as a new generation who will be facing and dealing with the use of plastic consequences, to increase public awareness regarding this issue.

Whilst the current study has shown that plastic pellets can act as a vector for arsenic, cadmium, chromium and lead, further information is required about the ability of plastic pellets to sorb other PTE and to investigate the optimum conditions for

remediation and removal of the PTE. Research effort should also be pointed toward bioaccessibility and bioavailability testing, so as to assess the availability and ultimately the possible risk to marine life and humans posed by PTE associated with plastic pellets in the marine environment.

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Appendix

Appendix 1

Semi-quantitative analysis results of virgin plastic pellets

Elements	HDPE	LDPE	PP	PET	BIO	Inclusion or exclusion in quantitative analysis
Ag (ng L^{-1})	84.8	770	32.7	578	3.54	
Al (µg L^{-1})	5.56	44.8	9.25	9.02	12.1	✔
As (ng L^{-1})	0.032	0.033	0.025	19.5	0.026	✔
B (µg L^{-1})	558	199	200	638	42	
Ba (µg L^{-1})	1.79	2.98	1.74	1.78	5.87	✔
Be (µg L^{-1})	125	125	125	125	125	
Ca (ng L^{-1})	51.2	73.6	55.8	40.4	62.2	
Cd (ng L^{-1})	21.9	18.3	21.9	14.6	23.7	✔
Co (µg L^{-1})	16.4	55.7	45.9	54.0	53.0	✔
Cr (ng L^{-1})	0.061	0.061	0.068	0.0603	0.0581	✔
Cu (µg L^{-1})	5.34	7.41	5.28	5.13	6.11	
Fe (µg L^{-1})	9.26	23.9	62.2	8.37	27.7	✔
K (ng L^{-1})	38.6	50.4	53.4	152	37.1	
Li (µg L^{-1})	333	599	599	333	333	
Mg (mg L^{-1})	1.12	1.55	1.12	0.868	1.07	✔
Mn (µg L^{-1})	2.19	3.18	2.26	1.85	4.61	
Mo (ng L^{-1})	8.21	77.6	18.2	28.1	41.3	
Na (µg L^{-1})	744	1002	740	629	650	✔
Ni (ng L^{-1})	0.0241	0.0234	0.0201	0.0221	0.0233	
P (µg L^{-1})	11.3	12.6	1.74	197	223	
Pb (ng L^{-1})	7.25	1.13	7.37	1.61	603	✔
S (µg L^{-1})	358	636	437	416	595	
Sb (ng L^{-1})	58.8	36.5	6.36	812	302	✔
Si (µg L^{-1})	28.3	58.7	36.3	76.8	101	✔
Sn (µg L^{-1})	249	450	244	407	308	✔
U (ng L^{-1})	121	170	118	99.8	151	
V (ng L^{-1})	25.6	0.712	0.722	0.176	0.144	
W (ng L^{-1})	68.9	66.5	22.4	73.4	57.3	
Zn (µg L^{-1})	11.4	168	5.79	8.74	41.3	✔
Zr (ng L^{-1})	93.5	155	101	543	107	

Appendix 2

Quantitative analysis results of virgin plastic pellets by ICP-MS

Element	HDPE	LDPE	PP	PET	BIO	LOD_p $\mu g\ g^{-1}$
Al						
1	21.5	3.71	5.01	5.08	6.50	
2	3.66	4.0	4.26	5.31	6.1	
3	44.5	10.8	13.2	4.36	7.11	
Mean	23.2	6.18	7.48	4.92	6.57	
SD	± 20.5	±4.04	± 4.94	± 0.494	± 0.5082	0.02423
RSD	88.3	65.3	66.1	10.0	7.73	
As						
1	0.00378	0.00212	0.000675	0.0157	0.00577	
2	0.00387	0.00101	0.000876	0.0133	0.00595	
3	0.00556	0.00116	0.000101	0.0151	0.00567	
Mean	0.00441	0.00143	0.000551	0.0147	0.0058	0.00102
SD	± 0.001	± 0.000602	0.000402	± 0.00124	± 0.000145	
RSD	22.8	42.1	73.0	8.46	2.50	
Ba						
1	0.657	0.626	0.577	0.713	2.02	
2	0.682	0.605	0.583	0.748	2.02	
3	0.723	0.662	0.508	0.631	2.16	
Mean	0.687	0.631	0.556	0.697	2.07	
SD	± 0.0329	± 0.02904	± 0.0413	± 0.06029	± 0.0816	0.0062
RSD	4.79	4.59	7.43	8.64	3.94	
Cd						
1	0.00421	0.00338	0.00527	0.00572	0.00726	
2	0.00246	0.00288	0.00344	0.00341	0.00753	
3	0.00401	0.00273	0.00227	0.00341	0.00859	
Mean	0.00356	0.00299	0.00366	0.00418	0.00779	
SD	± 0.000958	± 0.000339	± 0.00151	± 0.00133	± 0.000703	0.00055
RSD	26.9	11.2	41.2	31.8	9.0	
Co						
1	0.0148	0.0125	0.0170	11.1	0.0198	
2	0.0103	0.0132	0.0248	10.6	0.0164	
3	0.0141	0.0153	0.0115	10.8	0.0192	
Mean	0.0131	0.0136	0.0178	10.8	0.0185	
SD	± 0.00243	± 0.00144	± 0.00668	± 0.249	± 0.00182	0.00037
RSD	18.5	10.5	37.5	2.29	9.82	
Cr						
1	0.111	0.112	0.0862	0.149	0.165	
2	0.077	0.127	0.0932	0.154	0.227	
3	0.159	0.122	0.0998	0.923	0.185	
Mean	0.115	0.120	0.0931	0.409	0.192	
SD	± 0.0414	± 0.00761	± 0.0068	± 0.445	± 0.0316	0.01097
RSD	35.6	6.29	7.30	108	16.4	
Fe						
1	12.3	12.1	12.1	12.8	19.0	
2	10.9	20.3	11.5	12.0	20.1	
3	16.7	16.8	34.1	13.2	22.2	
Mean	13.3	16.4	19.2	12.6	20.4	
SD	± 3.00	± 4.12	± 12.8	± 0.605	± 1.61	0.01122
RSD	22.5	25.0	67.0	4.77	7.88	

Element	HDPE	LDPE	PP	PET	BIO	DL_p µg g^{-1}
Mg						
1	277	308	255	267	263	
2	257	315	312	311	267	
3	327	289	278	272	316	
Mean	287	304	281	284	282	
SD	± 35.8	± 13.4	± 28.6	± 24.1	± 29.6	0.13295
RSD	12.4	4.41	10.1	8.51	10.5	
Na						
1	508	571	521	550	450	
2	489	579	585	603	466	
3	593	531	449	523	552	
Mean	530	560	519	559	489	
SD	± 55.6	± 25.4	± 68.05	± 40.6	± 54.8	0.04737
RSD	10.4	4.54	13.1	7.27	11.2	
Ni						
1	0.138	0.172	0.28	0.227	0.213	
2	0.112	0.374	0.261	0.178	0.163	
3	0.136	0.261	0.474	0.154	0.254	
Mean	0.129	0.269	0.338	0.187	0.210	
SD	± 0.015	± 0.101	± 0.117	± 0.036	± 0.045	0.00171
RSD	11.6	37.5	34.8	19.7	21.5	
Pb						
1	0.302	0.265	0.244	0.526	0.201	
2	0.141	0.180	0.203	0.228	0.224	
3	0.201	0.173	0.144	0.197	0.215	
Mean	0.214	0.206	0.197	0.317	0.213	0.01981
SD	± 0.0812	± 0.05102	± 0.0505	± 0.182	± 0.0117	
RSD	37.7	24.7	25.6	57.3	5.51	
Sb						
1	0.00907	0.00517	0.00436	47.2	0.0324	
2	0.00388	0.00497	0.00391	46.7	0.0137	
3	0.00528	0.00490	0.00799	48.2	0.0139	
Mean	0.00607	0.00501	0.00542	47.3	0.02	
SD	± 0.00268	± 0.00014	± 0.00223	± 0.770	± 0.0107	0.001
RSD	44.1	2.79	41.1	1.62	53.5	
Si						
1	13.4	10.4	10.3	15.3	28.9	
2	12.1	11.4	10.7	12.2	31.9	
3	52.3	17.0	11.2	15.0	32.0	
Mean	25.9	12.9	10.7	14.2	30.9	
SD	± 22.8	± 3.55	± 0.424	± 1.68	± 1.76	4.495
RSD	88.0	27.3	3.95	11.8	5.71	
Sn						
1	0.172	0.0613	0.0227	0.0645	0.0886	
2	0.0603	0.0565	0.0125	0.0322	0.0857	
3	0.107	0.0689	0.0333	0.0732	0.0254	
Mean	0.113	0.0622	0.0228	0.0566	0.0666	
SD	± 0.0562	± 0.00624	± 0.0103	± 0.0216	± 0.0356	0.00069
RSD	49.6	10.0	45.4	38.1	53.5	
V						
1	0.0334	0.0273	0.0281	0.0221	0.0304	
2	0.0227	0.0267	0.0271	0.0284	0.0264	
3	0.0445	0.0345	0.0246	0.0257	0.0297	
Mean	0.0335	0.0295	0.0266	0.0254	0.0288	
SD	± 0.0109	± 0.00434	± 0.00179	± 0.00315	± 0.00215	0.00058
RSD	32.5	14.7	6.74	12.3	7.46	

Element	HDPE	LDPE	PP	PET	BIO	DL_p $\mu g\ g^{-1}$
Zn						
1	41.9	3.77	1.37	3.07	24.7	
2	3.51	6.48	2.16	6.72	12.6	
3	61.7	20.8	1.61	5.58	13.1	
Mean	35.7	10.3	1.71	5.12	16.84	
SD	± 29.6	± 9.14	± 0.401	± 1.86	± 6.82	0.02361
RSD	82.9	88.3	23.3	36.4	40.5	

Appendix 3

As uptake- 5 types of pellets in 3 different media.

Table A-1: As uptake (μg L^{-1}) by virgin plastic resin pellets in deionised water, pH 5.8

Time/hr	HDPE	LDPE	PP	PET	BIO	CONT
0	4.953	4.953	4.953	4.953	4.953	4.953
1	4.848	4.773	4.814	4.811	4.913	4.911
3	4.831	4.732	4.797	4.768	4.903	4.951
7	4.803	4.715	4.727	4.687	4.796	4.957
12	4.747	4.704	4.75	4.578	4.734	4.955
24	4.734	4.665	4.753	4.705	4.741	4.931
29	4.702	4.709	4.75	4.686	4.791	4.948
44	4.691	4.714	4.693	4.770	4.752	4.931
48	4.626	4.836	4.836	4.636	4.787	4.917
53	4.628	4.760	4.754	4.859	4.783	4.943
59	4.738	4.755	4.704	4.715	4.779	4.948
77	4.795	4.767	4.732	4.810	4.717	4.964
100	4.730	4.713	4.739	4.766	4.712	4.951

Table A-2: As uptake (μg L^{-1}) by virgin plastic resin pellets in fresh water, pH 7.8

Time/hr	HDPE	LDPE	PP	PET	BIO	CONT
0	4.999	4.999	4.999	4.999	4.999	4.9997
1	4.713	4.627	4.589	4.698	4.789	4.816
3	4.711	4.529	4.539	4.678	4.611	4.907
7	4.669	4.464	4.522	4.607	4.586	5.047
11	4.696	4.425	4.513	5.563	4.592	4.999
24	4.544	4.352	4.420	4.586	4.598	4.993
29	4.476	4.365	4.487	4.494	4.487	4.846
34	4.442	4.497	4.468	4.421	4.480	5
47	4.552	4.485	4.467	4.560	4.482	4.893
52	4.591	4.480	4.543	4.409	4.518	4.895
58	4.570	4.430	4.528	4.503	4.524	5
76	4.517	4.479	4.530	4.527	4.561	4.929
100	4.52	4.482	4.530	4.521	4.522	4.932

Table A-3: As uptake (μg L^{-1}) by virgin plastic resin pellets in seawater, pH 8.5

Time/hr	HDPE	LDPE	PP	PET	BIO	CONT
0	5.200	5.200	5.200	5.200	5.200	5.2
1	5.173	5.051	4.988	5.09	5.111	5.16
3	5.242	5.013	4.979	5.119	5.070	5.17
7	5.093	4.438	4.679	5.121	4.949	5.22
11	4.471	4.578	4.687	4.703	4.789	5.193
23	4.448	4.317	4.440	4.768	4.429	5.099
28	4.203	4.121	4.420	4.576	4.220	5.2003
34	4.671	4.149	4.469	4.473	4.244	5.095
47	4.864	4.093	4.633	4.629	4.406	5.193
52	5.528	4.252	4.475	4.510	4.689	5.1293
58	4.642	4.305	4.516	4.553	4.579	5.1923
76	4.645	4.097	4.494	4.673	4.421	5.0463
100	4.746	4.375	4.517	4.687	4.655	5.13

Table A-4: As uptake (μg L^{-1}) by weathered plastic resin pellets in seawater

Time/hr	HDPE	LDPE	PP	PET	BIO	CONT
0	5.428	5.428	5.428	5.428	5.428	5.2
1	5.222	5.267	4.955	5.207	5.247	5.16
3	5.126	5.232	4.892	4.898	4.988	5.17
7	5.023	5.068	4.810	4.745	4.858	5.22
11	4.908	4.699	4.939	4.663	4.783	5.193
23	4.894	4.737	4.904	4.371	4.848	5.099
28	4.865	4.467	4.938	4.307	4.570	5.2003
34	4.866	4.233	4.761	4.449	4.347	5.095
47	4.974	4.141	4.620	4.693	4.286	5.193
52	5.059	4.157	4.803	4.552	4.497	5.129
58	5.042	3.925	4.714	4.546	4.778	5.192
76	4.984	4.167	4.810	4.565	4.929	5.046
100	5.077	4.226	4.782	4.666	4.882	5.13

Appendix 4

Cd uptake- 5 types of pellets in 3 different media.

Table A-1: Cd uptake (μg L^{-1}) by virgin plastic resin pellets in deionised water

Time/hr	HDPE	LDPE	PP	PET	BIO	CONT
0	4.92	4.92	4.92	4.92	4.92	4.92
1	4.704	5.03	4.631	4.587	4.482	4.93
2	4.683	4.65	4.591	4.52	4.487	4.89
5	4.652	4.65	4.577	4.49	4.457	4.96
8	4.64	4.58	4.515	4.5	4.453	4.94
12	4.645	4.508	4.524	4.49	4.604	4.86
23	4.50	4.066	3.949	3.92	3.96	4.87
28	4.097	4.061	3.956	3.96	3.98	4.94
33	3.891	4.063	3.994	3.97	4.01	4.87
48	4.023	4.064	4.022	4.05	3.99	4.876
56	4.101	4.048	4.035	4.0	4.06	4.86
73	4.088	4.051	4.05	4.0	4.04	4.79
100	4.019	4.12	4.061	4.01	4.01	4.9

Table A-2: Cd uptake (μg L^{-1}) by virgin plastic resin pellets in fresh water

Time/hr	HDPE	LDPE	PP	PET	BIO	CONT
0	4.96	4.96	4.96	4.96	4.96	4.96
1	4.849	4.778	4.786	4.782	4.784	4.87
3	4.727	4.704	4.779	4.685	4.683	4.95
8	4.725	4.653	4.685	4.685	4.5802	5.02
13	4.606	4.595	4.683	4.563	4.582	4.98
23	4.649	4.622	4.692	4.501	4.595	4.893
28	4.654	4.548	4.662	4.516	4.578	4.96
35	4.652	4.551	4.669	4.545	4.586	4.94
48	4.628	4.582	4.673	4.548	4.678	4.894
58	4.625	4.596	4.677	4.566	4.662	4.945
71	4.646	4.578	4.662	4.568	4.667	4.94
80	4.664	4.594	4.677	4.57	4.667	4.963
100	4.657	4.592	4.67	4.58	4.66	4.943

Table A-3: Cd uptake (μg L^{-1}) by virgin plastic resin pellets in seawater

Time/hr	HDPE	LDPE	PP	PET	BIO	CONT
0	4.9179	4.9179	4.9179	4.9179	4.9179	4.918
1	4.822	4.8169	4.7972	4.7027	4.4995	4.73
3	4.7492	4.7636	4.7191	4.6775	4.6914	4.73
7	4.6628	4.4766	4.7921	4.5525	4.684	4.96
11	4.6424	4.5512	4.7726	4.5808	4.6822	4.95
23	4.5949	4.5132	4.6776	4.5239	4.6874	4.85
28	4.6735	4.6967	4.7633	4.7332	4.7436	4.76
34	5.6512	4.7139	4.8508	4.7059	4.9814	4.94
48	4.6618	4.7598	4.8078	4.7681	4.7168	4.78
52	4.6614	4.7359	4.7973	4.7214	4.7166	4.81
58	4.7782	4.7211	4.7753	4.6462	4.7003	4.92
76	4.6827	4.7624	4.7721	4.7353	4.6867	4.84
100	4.7786	4.7236	4.7086	4.7705	4.7325	4.82

Table A-4: Cd uptake (μg L^{-1}) by weathered plastic resin pellets in seawater

Time/hr	HDPE	LDPE	PP	PET	BIO	CONT
0	4.811	4.811	4.811	4.811	4.811	4.918
1	4.683	4.512	4.501	4.509	4.199	4.73
3	4.656	4.244	4.341	4.321	4.125	4.73
7	4.603	4.189	4.335	4.321	4.043	4.96
11	4.518	4.114	4.466	4.401	4.102	4.95
23	4.611	4.054	4.060	4.260	4.177	4.85
28	4.476	4.338	4.019	4.026	3.759	4.76
34	4.584	4.488	4.311	4.269	4.188	4.94
47	4.566	4.396	4.395	4.192	4.132	4.78
52	4.646	4.392	4.364	4.134	4.164	4.81
58	4.525	4.412	4.451	4.241	4.218	4.92
76	4.558	4.474	4.378	4.191	4.178	4.84
100	5.242	4.481	4.380	4.110	4.174	4.82

Appendix 5

Cr uptake- 5 types of pellets in 3 different media.

Table A-1: Cr uptake (µg L^{-1}) by virgin plastic resin pellets in deionised water

Time/hr	HDPE	LDPE	PP	PET	BIO	CONT
0	4.94	4.94	4.94	4.94	4.94	4.94
1	4.82	4.84	4.89	4.89	4.78	4.85
2	4.8	4.78	4.84	4.84	4.79	4.89
4	4.78	5.17	4.86	4.77	4.82	4.93
8	4.82	4.84	4.86	4.81	4.47	4.95
12	4.82	4.88	4.82	4.78	4.86	4.93
22	4.75	4.8	4.84	4.73	4.81	4.87
28	4.76	4.78	4.86	4.85	4.78	4.88
33	4.75	4.72	4.89	4.82	4.83	4.95
46	4.7	4.64	4.82	4.78	4.75	4.88
60	4.533	4.77	4.95	5.19	4.78	4.88
80	5.21	4.63	4.83	4.86	4.69	4.93
100	4.81	4.68	4.86	4.66	4.71	4.89

Table A-2: Cr uptake (µg L^{-1}) by virgin plastic resin pellets in fresh water

Time/hr	HDPE	LDPE	PP	PET	BIO	CONT
0	5.337	5.337	5.337	5.337	5.337	5.337
1	5.172	5.336	5.391	5.328	5.401	5.258
3	5.172	5.26	5.492	5.309	5.277	5.325
7	5.158	5.963	5.373	5.409	5.122	5.385
11	5.234	5.247	5.369	5.249	4.993	5.082
23	5.134	5.175	5.362	5.223	5.077	5.65
28	5.227	5.129	5.31	5.284	5.022	5.362
34	5.196	5.107	5.336	5.235	4.874	5.347
47	5.271	5.111	5.208	5.168	4.879	5.37
57	5.322	5.023	5.363	5.229	4.876	5.246
71	5.19	4.968	5.184	5.404	4.875	5.309
80	5.171	5.002	5.188	5.196	4.873	5.23
100	5.2	5.00	5.18	5.21	4.87	5.241

Table A-3: Cr uptake (µg L^{-1}) by virgin plastic resin pellets in seawater

Time/hr	HDPE	LDPE	PP	PET	BIO	CONT
0	5.217	5.217	5.217	5.217	5.217	5.217
1	4.777	4.859	4.821	4.873	4.817	5.138
3	4.824	4.762	4.744	4.799	4.897	5.205
7	4.864	4.797	4.617	4.883	4.581	5.265
11	4.710	4.305	4.492	4.746	4.864	5.43
23	4.564	4.204	4.116	4.565	4.194	5.29
28	4.629	4.269	4.503	4.587	4.137	5.242
34	4.657	4.382	4.738	4.580	4.151	5.227
47	4.600	4.432	4.677	4.471	4.416	4.962
52	4.705	4.563	4.722	4.483	4.466	5.126
58	8.249	4.691	4.788	4.694	4.394	5.189
76	4.609	4.671	4.625	4.698	4.460	5.11
100	4.810	4.709	4.754	4.514	4.487	5.14

Table A-4: Cr uptake (µg L^{-1}) by weathered plastic resin pellets in seawater

Time/hr	HDPE	LDPE	PP	PET	BIO	CONT
0	5.048	5.048	5.048	5.048	5.048	5.217
1	4.630	4.678	4.540	4.453	4.527	5.138
3	4.574	4.530	4.507	4.407	4.526	5.205
7	4.55	4.549	4.677	4.212	4.748	5.265
11	4.509	4.196	4.527	4.347	4.412	5.43
23	4.331	4.103	4.437	4.159	4.265	5.29
28	4.375	0.397	4.288	4.091	4.128	5.242
34	4.539	4.316	4.151	4.277	4.298	5.227
47	4.380	4.483	4.205	4.281	4.208	4.962
52	4.543	4.517	4.384	4.398	4.399	5.126
58	4.496	4.412	4.459	4.372	4.367	5.189
76	4.383	4.413	4.434	4.364	4.400	5.11
100	4.492	4.369	4.357	4.364	4.433	5.14

Appendix 6

Lead uptake- 5 types of pellets in 3 different media.

Table A-1: Pb uptake (μg L^{-1}) by virgin plastic resin pellets in deionised water

Time/hr	HDPE	LDPE	PP	PET	BIO	CONT
0	4.85	4.85	4.85	4.85	4.85	4.85
1	3.974	4.310	3.869	3.745	4.327	4.667
3	3.240	3.383	3.659	3.008	3.579	4.658
7	2.901	3.278	3.393	3.224	3.361	4.898
11	3.442	3.194	3.258	3.182	3.194	4.976
23	3.372	2.975	3.305	3.462	3.158	4.781
28	3.125	2.965	3.469	3.469	3.065	4.696
34	3.220	3.155	3.110	3.566	3.247	4.877
47	3.305	3.207	3.195	3.635	3.471	4.713
52	3.425	3.450	3.606	3.463	3.425	4.745
58	3.668	3.440	3.482	3.616	3.660	4.895
76	3.728	3.6476	3.676	3.695	4.130	4.769
100	3.775	3.707	3.641	3.682	3.975	4.743

Table A-2: Pb uptake (μg L^{-1}) by virgin plastic resin pellets in fresh water

Time/hr	HDPE	LDPE	PP	PET	BIO	CONT
0	5.4	5.4	5.4	5.4	5.4	5.4
1	5.21	5.15	5.39	5.05	5.13	5.61
3	5.21	5.04	5.45	4.71	5.03	5.32
7	5.2	4.82	5.33	4.71	4.72	5.46
11	5.1	4.58	5.27	4.23	4.95	5.26
23	5.1	4.35	5.13	3.95	4.69	5.32
28	4.89	4.09	5.16	4.0	4.65	5.44
34	4.83	3.54	4.92	3.71	4.47	5.41
47	4.8	3.76	4.58	3.36	4.38	5.28
52	4.9	3.73	5.1	3.72	4.43	5.24
58	4.8	3.59	4.55	3.61	4.41	5.28
76	4.83	3.74	4.6	3.7	4.41	5.33
100	4.81	3.73	4.59	3.71	4.42	5.32

Table A-3: Pb uptake (μg L^{-1}) by virgin plastic resin pellets in seawater

Time/hr	HDPE	LDPE	PP	PET	BIO	CONT
0	5.037	5.037	5.037	5.037	5.037	5.031
1	4.445	4.243	4.469	4.57	4.782	5.084
3	4.592	4.179	4.424	4.127	4.45	5.077
7	4.429	4.27	4.398	4.136	4.585	5.062
11	4.18	4.182	4.437	4.102	4.406	4.937
22	4.118	3.975	4.501	4.101	4.268	4.849
27	4.145	3.928	4.415	4.082	4.268	5.047
33	4.442	3.55	4.116	3.873	4.232	4.893
44	4.454	3.756	3.919	4.186	4.37	5.0005
49	4.392	3.974	4.384	4.1	4.495	4.943
55	4.173	4.061	4.544	4.534	4.206	5.049
73	4.228	4.088	4.156	4.517	4.295	5.024
100	4.351	3.982	4.233	4.265	4.232	5.055

Table A-4: Pb uptake (μg L^{-1}) by weathered plastic resin pellets in seawater

Time/hr	HDPE	LDPE	PP	PET	BIO	CONT
0	5.031	5.031	5.031	5.031	5.031	5.031
1	4.42	4.169	3.962	4.192	4.071	5.084
3	3.98	4.175	4.149	4.188	3.931	5.077
7	4.364	6.93	4.031	4.227	4.016	5.062
11	4.069	4.156	3.742	4.095	3.918	4.937
22	4.024	3.98	4.227	3.993	3.866	4.849
27	3.914	3.86	3.92	3.991	3.942	5.047
33	3.497	3.236	4.281	3.663	4.943	4.893
44	3.513	3.577	4.226	4.051	4.978	5.0005
49	4.162	4.356	4.145	4.112	4.201	4.943
55	4.203	4.304	4.081	4.187	4.169	5.049
73	4.172	4.337	3.609	4.252	4.178	5.024
100	4.173	4.323	4.001	4.309	4.217	5.055

Appendix 7

Calculation: As (µg kg^{-1}) in deionised water, fresh water and seawater

- Concentration loss (µg L^{-1}) = initial concentration – concentration determined by ICP-MS

- Mass loss to pellets present in vial (µg) = concentration loss x volume

- % Mass uptake = (Concentration loss µg L^{-1} / initial concentration µg L^{-1}) x 100

- Uptake (µg kg^{-1}) = (mass loss µg / wt of pellets in vial g) x 1000 = Uptake (ng g^{-1})

HDPE virgin pellets results in deionised water

Shaking time/hr	As in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- As in present pellets (µg)	% Mass uptake	As uptake by pellets (µg/kg)
0	4.953	0	0	0	0
1	4.848	0.105	0.00525	2.119	11.78
3	4.831	0.122	0.0061	2.463	13.69
7	4.803	0.15	0.0075	3.028	16.84
12	4.747	0.206	0.0103	4.159	23.13
24	4.734	0.219	0.01095	4.421	24.59
29	4.702	0.251	0.01255	5.067	28.18
44	4.691	0.262	0.0131	5.289	29.41
48	4.626	0.327	0.01635	6.602	36.71
53	4.628	0.325	0.01625	6.561	36.49
59	4.738	0.215	0.01075	4.340	24.14
77	4.795	0.158	0.0079	3.189	17.74
100	4.73	0.223	0.01115	4.502	25.03
Average			0.01067	4.312	23.98
Sum					287.7

LDPE virgin pellets results in deionised water

Shaking time/hr	As in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- As in present pellets (µg)	% Mass uptake	As uptake by pellets (µg/kg)
0	4.953	0	0	0	0
1	4.773	0.18	0.009	3.634	19.85
3	4.732	0.221	0.01105	4.461	24.37
7	4.715	0.238	0.0119	4.805	26.25
12	4.704	0.249	0.01245	5.027	27.46
24	4.665	0.288	0.0144	5.814	31.76
29	4.709	0.244	0.0122	4.926	26.91
44	4.714	0.239	0.01195	4.825	26.36
48	4.836	0.117	0.00585	2.362	12.90
53	4.76	0.193	0.00965	3.896	21.28
59	4.755	0.1971	0.009855	3.979	21.74
77	4.767	0.186	0.0093	3.755	20.51
100	4.713	0.24	0.012	4.845	26.47
Average			0.0108	4.361	23.82
Sum					285.9

PP virgin pellets results in deionised water

Shaking time/hr	As in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- As in present pellets (µg)	% Mass uptake	As uptake by pellets (µg/kg)
0	4.953	0	0	0	0
1	4.814	0.139	0.00695	3.815	15.21
3	4.797	0.156	0.0078	4.199	17.07
7	4.727	0.226	0.0113	6.319	24.73
12	4.75	0.203	0.01015	5.128	22.21
24	4.753	0.2	0.01	5.087	21.88
29	4.75	0.203	0.01015	5.148	22.21
44	4.693	0.26	0.013	6.299	28.45
48	4.836	0.117	0.00585	3.412	12.80
53	4.754	0.199	0.00995	5.067	21.77
59	4.704	0.249	0.01245	6.077	27.24
77	4.732	0.221	0.01105	5.511	24.18
100	4.739	0.214	0.0107	5.370	23.41
Average			0.00994	5.119	21.76
Sum					261.2

PET virgin pellets results in deionised water

Shaking time/hr	As in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- As in present pellets (µg)	% Mass uptake	As uptake by pellets (µg/kg)
0	4.953	0	0	0	0
1	4.811	0.142	0.0071	2.866	15.25
3	4.768	0.185	0.00925	3.735	19.87
7	4.687	0.266	0.0133	5.370	28.58
12	4.578	0.375	0.01875	7.571	40.29
24	4.705	0.248	0.0124	5.007	26.64
29	4.686	0.267	0.01335	5.390	28.69
44	4.77	0.183	0.00915	3.694	19.66
48	4.636	0.317	0.01585	6.400	34.06
53	4.859	0.094	0.0047	1.897	10.10
59	4.715	0.238	0.0119	4.805	25.57
77	4.81	0.143	0.00715	2.887	15.36
100	4.766	0.187	0.00935	3.775	20.09
Average			0.01102	4.450	23.68
Sum					284.2

BIO virgin pellets results in deionised water

Shaking time/hr	As in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- As in present pellets (µg)	% Mass uptake	As uptake by pellets (µg/kg)
0	4.953	0	0	0	0
1	4.913	0.04	0.002	0.807	4.386
3	4.903	0.05	0.0025	1.009	5.483
7	4.796	0.157	0.00785	3.169	17.21
12	4.734	0.219	0.01095	4.421	24.01
24	4.741	0.212	0.0106	4.280	23.25
29	4.791	0.162	0.0081	3.270	17.76
44	4.752	0.201	0.01005	4.058	22.04
48	4.787	0.166	0.0083	3.351	18.20
53	4.783	0.17	0.0085	3.432	18.64
59	4.779	0.174	0.0087	3.513	19.08
77	4.717	0.236	0.0118	4.764	25.88
100	4.712	0.2409	0.012045	4.863	26.42
Average			0.00845	3.411	18.53
Sum					222.4

HDPE virgin pellets results in fresh water*

Shaking time/hr	As in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- As in present pellets (µg)	% Mass uptake	As uptake by pellets (µg/kg)
0	4.9997	0	0	0	0
1	4.7135	0.2861	0.0143	5.722	31.56
3	4.7111	0.2885	0.0144	5.770	31.83
7	4.6696	0.3300	0.0165	6.602	36.41
11	4.6968	0.3028	0.0151	6.056	33.40
24	4.5448	0.4548	0.0227	9.098	50.18
29	4.4766	0.5230	0.0261	10.46	57.70
34	4.4429	0.5567	0.0278	11.13	61.42
47	4.5529	0.4467	0.0223	8.935	49.29
52	4.5913	0.4083	0.0204	8.166	45.04
58	4.5701	0.4295	0.0214	8.591	47.39
76	4.5173	0.4823	0.0241	9.646	53.21
100	4.5201	0.4796	0.0239	9.581	52.84
Average			0.020496	8.19902	45.86
Sum					550.32

LDPE virgin pellets results in fresh water*

Shaking time/hr	As in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- As in present pellets (µg)	% Mass uptake	As uptake by pellets (µg/kg)
0	4.9997	0	0	0	0
1	4.6271	0.3726	0.0186	7.452	40.40
3	4.5296	0.4701	0.0235	9.402	50.97
7	4.4644	0.5353	0.0267	10.70	58.04
11	4.4258	0.5739	0.0286	11.47	62.23
24	4.3527	0.647	0.0323	12.94	70.15
29	4.365	0.6347	0.0317	12.69	68.82
34	4.4979	0.5018	0.0250	10.03	54.41
47	4.4853	0.5144	0.0257	10.28	55.77
52	4.4802	0.5195	0.0259	10.39	56.33
58	4.4306	0.5691	0.0284	11.38	61.71
76	4.4793	0.5204	0.0260	10.40	56.43
100	4.482	0.5177	0.0258	10.35	56.13
Average			0.0266	10.65	57.62
Sum					691.44

PP virgin pellets results in fresh water*

Shaking time/hr	As in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- As in present pellets (µg)	% Mass uptake	As uptake by pellets (µg/kg)
0	4.9997	0	0	0	0
1	4.5894	0.4102	0.0205	8.204	43.95
3	4.5393	0.4603	0.0230	9.206	49.32
7	4.5223	0.4773	0.0238	9.547	51.14
11	4.5130	0.4866	0.0243	9.734	52.15
24	4.4204	0.5792	0.0289	11.58	62.07
29	4.4872	0.5124	0.0256	10.24	54.91
34	4.4683	0.5313	0.0265	10.62	56.94
47	4.4676	0.5320	0.0266	10.64	57.00
52	4.5433	0.4563	0.0228	9.126	48.89
58	4.5283	0.4713	0.0235	9.427	50.50
76	4.5304	0.4692	0.0234	9.386	50.28
100	4.5300	0.4697	0.0234	9.394	50.33
Average			0.0244	9.796	52.29
Sum					627.54

PET virgin pellets results in fresh water*

Shaking time/hr	As in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- As in present pellets (µg)	% Mass uptake	As uptake by pellets (µg/kg)
0	4.999	0	0	0	0
1	4.698	0.3009	0.0150	6.018	32.50
3	4.678	0.3216	0.0160	6.432	34.74
7	4.607	0.3924	0.0196	7.848	42.39
11	5.563	-0.5635	-0.02818	-11.27	-60.87
24	4.586	0.4134	0.0206	8.269	44.66
29	4.494	0.5054	0.0252	10.10	54.60
34	4.421	0.5782	0.0289	11.56	62.47
47	4.560	0.4389	0.0219	8.780	47.42
52	4.409	0.5904	0.0295	11.80	63.78
58	4.503	0.4966	0.0248	9.933	53.65
76	4.527	0.4726	0.0236	9.454	51.06
100	4.521	0.4786	0.0239	9.573	51.70
Average			0.0225	9.023	48.94
Sum					538.8

BIO virgin pellets results in fresh water*

Shaking time/hr	As in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- As in present pellets (µg)	% Mass uptake	As uptake by pellets (µg/kg)
0	4.9997	0	0	0	0
1	4.7894	0.2102	0.0105	4.205	22.49
3	4.6119	0.3877	0.0193	7.754	41.48
7	4.5869	0.4127	0.0206	8.255	44.16
11	4.5920	0.4076	0.0203	8.154	43.62
24	4.5986	0.4010	0.0200	8.021	42.90
29	4.4875	0.5121	0.0256	10.24	54.79
34	4.4809	0.5187	0.0259	10.37	55.50
47	4.4827	0.5170	0.0258	10.34	55.31
52	4.5187	0.4809	0.0240	9.620	51.46
58	4.5240	0.4756	0.0237	9.513	50.89
76	4.5610	0.4386	0.0219	8.772	46.93
100	4.5220	0.4770	0.0238	9.541	51.03
Average			0.0216	8.660	46.70
Sum					560

HDPE virgin pellets results in seawater

Shaking time/hr	As in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- As in present pellets (µg)	% Mass uptake	As uptake by pellets (µg/kg)
0	5.2	0	0	0	0
1	5.173	0.027	0.00135	0.519	2.95
3	5.242	-0.042	-0.0021	-0.807	-4.60
7	5.093	0.107	0.00535	2.057	11.71
11	4.471	0.729	0.0364	14.01	79.84
23	4.448	0.752	0.0376	14.46	82.36
28	4.203	0.997	0.0498	19.17	109.2
34	4.671	0.529	0.0264	10.17	57.94
47	4.864	0.336	0.0168	6.461	36.80
52	5.528	-0.328	-0.0164	-6.307	-35.92
58	4.642	0.558	0.0279	10.73	61.11
76	4.645	0.555	0.0277	10.67	60.78
100	4.746	0.454	0.0227	8.730	49.72
Average			0.0252	9.7	55.22
Sum					552.2

LDPE virgin pellets results in seawater

Shaking time/hr	As in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- As in present pellets (µg)	% Mass uptake	As uptake by pellets (µg/kg)
0	5.2	0	0	0	0
1	5.051	0.149	0.00745	2.865	16.05
3	5.013	0.187	0.00935	3.596	20.15
7	4.438	0.762	0.0381	14.65	82.11
11	4.578	0.622	0.0311	11.96	67.02
23	4.317	0.883	0.0441	16.98	95.15
28	4.121	1.079	0.0539	20.75	116.2
34	4.149	1.051	0.0525	20.21	113.2
47	4.093	1.107	0.0553	21.28	119.2
52	4.252	0.948	0.0474	18.23	102.1
58	4.305	0.895	0.0447	17.21	96.44
76	4.097	1.103	0.0551	21.21	118.8
100	4.375	0.825	0.0412	15.86	88.90
Average			0.04004	15.40	86.26
Sum					1035

PP virgin pellets results in seawater

Shaking time/hr	As in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- As in present pellets (µg)	% Mass uptake	As uptake by pellets (µg/kg)
0	5.2001	0	0	0	0
1	4.9888	0.2112	0.0105	4.061	22.70
3	4.979	0.221	0.0110	4.25	23.76
7	4.679	0.521	0.0260	10.01	56.02
11	4.687	0.513	0.0256	9.865	55.16
23	4.4405	0.7595	0.0379	14.60	81.66
28	4.4206	0.7794	0.0389	14.98	83.80
34	4.469	0.731	0.0365	14.05	78.60
47	4.6339	0.5661	0.02830	10.88	60.87
52	4.475	0.725	0.0362	13.94	77.95
58	4.516	0.684	0.0342	13.15	73.54
76	4.494	0.706	0.0353	13.57	75.91
100	4.517	0.683	0.0341	13.13	73.44
Average			0.0337	12.98	63.61
Sum					763.41

PET virgin pellets results in seawater

Shaking time/hr	As in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- As in present pellets (µg)	% Mass uptake	As uptake by pellets (µg/kg)
0	5.2001	0	0	0	0
1	5.09	0.11	0.0055	2.115	11.83
3	5.119	0.081	0.00405	1.557	8.717
7	5.121	0.079	0.00395	1.519	8.501
11	4.703	0.497	0.02485	9.557	53.48
23	4.768	0.432	0.0216	8.307	46.49
28	4.576	0.624	0.0312	12	67.15
34	4.473	0.727	0.03635	13.98	78.23
47	4.629	0.571	0.02855	10.98	61.45
52	4.51	0.69	0.0345	13.26	74.25
58	4.553	0.647	0.03235	12.44	69.62
76	4.673	0.527	0.02635	10.13	56.71
100	4.687	0.513	0.02565	9.865	55.20
Average			0.0229	8.810	49.30
Sum					591.6

BIO virgin pellets results in seawater

Shaking time/hr	As in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- As in present pellets (µg)	% Mass uptake	As uptake by pellets (µg/kg)
0	5.2	0	0	0	0
1	5.111	0.089	0.00445	1.711	9.684
3	5.0706	0.1294	0.00647	2.488	14.08
7	4.949	0.251	0.0125	4.826	27.31
11	4.789	0.411	0.0205	7.903	44.72
23	4.429	0.771	0.0385	14.82	83.89
28	4.2208	0.9792	0.0489	18.83	106.5
34	4.244	0.956	0.0478	18.38	104.0
47	4.406	0.794	0.0397	15.26	86.39
52	4.689	0.511	0.0255	9.826	55.60
58	4.579	0.621	0.0310	11.94	67.57
76	4.421	0.779	0.0389	14.98	84.76
100	4.655	0.545	0.0272	10.48	59.30
Average			0.0284	10.95	61.99
Sum					743.9

HDPE weathered pellets results in seawater

Shaking time/hr	As in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- As in present pellets (µg)	% Mass uptake	As uptake by pellets (µg/kg)
0	5.4283	0	0	0	0
1	5.2224	0.2059	0.010295	3.793	22.48
3	5.126	0.3023	0.015115	5.569	33.01
7	5.0239	0.4044	0.02022	7.450	44.16
11	4.9087	0.5196	0.02598	9.572	56.74
23	4.8945	0.5338	0.02669	9.834	58.30
28	4.865	0.5633	0.028165	10.37	61.52
34	4.866	0.5623	0.028115	10.35	61.41
47	4.9748	0.4535	0.022675	8.354	49.53
52	5.0599	0.3684	0.01842	6.787	40.23
58	5.0427	0.3856	0.01928	7.103	42.11
76	4.9841	0.4442	0.02221	8.183	48.51
100	5.0771	0.3512	0.01756	6.470	38.35
Average			0.0212	7.821	46.36
Sum					556.4

LDPE weathered pellets results in seawater

Shaking time/hr	As in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- As in present pellets (µg)	% Mass uptake	As uptake by pellets (µg/kg)
0	5.4283	0	0	0	0
1	5.2671	0.1611	0.00805	2.967	17.22
3	5.2329	0.1953	0.00976	3.598	20.88
7	5.0688	0.3594	0.0179	6.621	38.42
11	4.6994	0.7288	0.0364	13.42	77.91
23	4.7376	0.6906	0.0345	12.72	73.83
28	4.4676	0.9606	0.0480	17.69	102.6
34	4.2334	1.1948	0.0597	22.01	127.7
47	4.1415	1.2867	0.0643	23.70	137.5
52	4.1577	1.2705	0.0635	23.40	135.8
58	3.9251	1.5031	0.0751	27.69	160.6
76	4.1677	1.2605	0.0630	23.22	134.7
100	4.2263	1.2019	0.0601	22.14	128.4
Average			0.045	16.602	96.33
Sum					1156

PP weathered pellets results in seawater

Shaking time/hr	As in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- As in present pellets (µg)	% Mass uptake	As uptake by pellets (µg/kg)
0	5.4283	0	0	0	0
1	4.9558	0.4724	0.0236	8.703	50.82
3	4.8926	0.5356	0.0267	9.868	57.63
7	4.8102	0.6180	0.0309	11.38	66.50
11	4.9396	0.4886	0.0244	9.002	52.57
23	4.9040	0.5242	0.0262	9.658	56.40
28	4.9383	0.4899	0.0244	9.026	52.72
34	4.7615	0.6667	0.0333	12.28	71.73
47	4.6205	0.8077	0.0403	14.88	86.91
52	4.8034	0.6248	0.0312	11.51	67.22
58	4.7143	0.7139	0.0356	13.15	76.82
76	4.8100	0.6182	0.0309	11.39	66.52
100	4.7821	0.6461	0.0323	11.90	69.51
Average			0.0300	11.06	64.61
Sum					775.4

PET weathered pellets results in seawater

Shaking time/hr	As in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- As in present pellets (µg)	% Mass uptake	As uptake by pellets (µg/kg)
0	5.4283	0	0	0	0
1	5.2070	0.2212	0.0111	4.076	24.00
3	4.8988	0.5294	0.0264	9.754	57.45
7	4.7457	0.6825	0.0341	12.57	74.05
11	4.6638	0.7644	0.0382	14.08	82.94
23	4.3711	1.0571	0.0528	19.47	114.7
28	4.3076	1.1206	0.0560	20.64	121.5
34	4.4498	0.9784	0.0489	18.02	106.1
47	4.6933	0.7349	0.0367	13.54	79.75
52	4.5529	0.8753	0.0437	16.1	94.97
58	4.5461	0.8821	0.0441	16.25	95.72
76	4.5652	0.8630	0.0431	15.90	93.65
100	4.6663	0.7619	0.0380	14.03	82.67
Average			0.0394	14.54	85.64
Sum					1027.7

BIO weathered pellets results in seawater

Shaking time/hr	As in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- As in present pellets (µg)	% Mass uptake	As uptake by pellets (µg/kg)
0	5.4283	0	0	0	0
1	5.2470	0.1812	0.00906	3.339	19.87
3	4.9886	0.4396	0.0219	8.099	48.19
7	4.8588	0.5694	0.0284	10.49	62.42
11	4.7834	0.6448	0.0322	11.87	70.68
23	4.8484	0.5798	0.0289	10.68	63.56
28	4.5704	0.8578	0.0428	15.80	94.04
34	4.3478	1.0804	0.0540	19.90	118.4
47	4.2865	1.1417	0.0570	21.03	125.1
52	4.4970	0.9312	0.0465	17.15	102.0
58	4.7781	0.6501	0.0325	11.97	71.27
76	4.9293	0.4989	0.0249	9.191	54.69
100	4.8820	0.5463	0.0273	10.06	59.88
Average			0.0338	12.46	74.19
Sum					890.3

Calculation: Cd (µg kg^{-1}) in deionised water, fresh water and seawater

HDPE virgin pellets results in deionised water

Shaking time/hr	Cd in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cd in present pellets (µg)	% Mass uptake	Cd uptake by pellets (µg/kg)
0	4.92	0	0	0	0
1	4.704	0.216	0.0108	4.390	24.30
2	4.683	0.237	0.0118	4.817	26.66
5	4.652	0.268	0.0134	5.447	30.15
8	4.64	0.28	0.0140	5.691	31.50
12	4.645	0.275	0.0137	5.589	30.94
23	4.5	0.42	0.0210	8.536	47.25
28	4.097	0.823	0.0411	16.72	92.59
33	3.891	1.029	0.0514	20.91	115.7
48	4.023	0.897	0.0448	18.23	100.9
56	4.101	0.819	0.0409	16.64	92.14
73	4.088	0.832	0.0416	16.91	93.60
100	4.019	0.901	0.0450	18.31	101.3
Average			0.029	11.85	65.60
Sum					787.2

LDPE virgin pellets results in deionised water

Shaking time/hr	Cd in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cd in present pellets (µg)	% Mass uptake	Cd uptake by pellets (µg/kg)
0	4.92	0	0	0	0
1	5.03	-0.11	-0.0055	-2.235	-12.32
2	4.65	0.27	0.0135	5.487	30.24
5	4.65	0.27	0.0135	5.487	30.24
8	4.58	0.34	0.017	6.910	38.09
12	4.508	0.412	0.0206	8.373	46.15
23	4.066	0.854	0.0427	17.35	95.67
28	4.061	0.859	0.0429	17.45	96.23
33	4.063	0.857	0.0428	17.41	96.01
48	4.064	0.856	0.0428	17.39	95.89
56	4.048	0.872	0.0436	17.72	97.69
73	4.051	0.869	0.0434	17.66	97.35
100	4.12	0.8	0.04	16.26	89.62
Average			0.0329	13.41	73.93
Sum					813.24

PP virgin pellets results in deionised water

Shaking time/hr	Cd in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cd in present pellets (µg)	% Mass uptake	Cd uptake by pellets (µg/kg)
0	4.92	0	0	0	0
1	4.631	0.289	0.0144	5.873	32.30
2	4.591	0.329	0.0164	6.686	36.77
5	4.577	0.343	0.0171	6.971	38.34
8	4.515	0.405	0.0202	8.231	45.27
12	4.524	0.396	0.0198	8.048	44.26
23	3.949	0.971	0.0485	19.73	108.5
28	3.956	0.964	0.0482	19.59	107.7
33	3.994	0.926	0.0463	18.82	103.5
48	4.022	0.898	0.0449	18.25	100.3
56	4.035	0.885	0.0442	17.98	98.92
73	4.05	0.87	0.0435	17.68	97.25
100	4.061	0.859	0.0429	17.45	96.02
Average			0.0338	13.77	75.77
Sum					909.33

PET virgin pellets results in deionised water

Shaking time/hr	Cd in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cd in present pellets (µg)	% Mass uptake	Cd uptake by pellets (µg/kg)
0	4.92	0	0	0	0
1	4.587	0.333	0.0166	6.768	36.01
2	4.52	0.4	0.020	8.130	43.26
5	4.49	0.43	0.0215	8.739	46.50
8	4.5	0.42	0.0210	8.536	45.42
12	4.49	0.43	0.0215	8.739	46.50
23	3.92	1.00	0.050	20.32	108.1
28	3.96	0.96	0.048	19.51	103.8
33	3.97	0.95	0.0475	19.30	102.7
48	4.05	0.87	0.0435	17.68	94.09
56	4	0.92	0.046	18.69	99.50
73	4	0.92	0.046	18.69	99.50
100	4.01	0.91	0.0455	18.49	98.42
Average			0.0355	14.46	76.99
Sum					923.9

BIO virgin pellets results in deionised water

Shaking time/hr	Cd in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cd in present pellets (µg)	% Mass uptake	Cd uptake by pellets (µg/kg)
0	4.92	0	0	0	0
1	4.482	0.438	0.0219	8.902	48.76
2	4.487	0.433	0.0216	8.800	48.20
5	4.457	0.463	0.0231	9.410	51.54
8	4.453	0.467	0.0233	9.491	51.99
12	4.604	0.316	0.0158	6.422	35.18
23	3.96	0.960	0.0480	19.51	106.8
28	3.98	0.940	0.0470	19.10	104.6
33	4.01	0.910	0.0455	18.49	101.3
48	3.99	0.930	0.0465	18.90	103.5
56	4.06	0.860	0.0430	17.47	95.74
73	4.04	0.880	0.0440	17.88	97.97
100	4.01	0.910	0.0455	18.49	101.3
Average			0.0354	14.40	78.92
Sum					947.112

HDPE virgin pellets results in fresh water

Shaking time/hr	Cd in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cd in present pellets (µg)	% Mass uptake	Cd uptake by pellets (µg/kg)
0	4.96	0	0	0	0
1	4.849	0.111	0.00555	2.237	12.44
3	4.727	0.233	0.0116	4.697	26.13
8	4.725	0.235	0.0117	4.737	26.35
13	4.606	0.354	0.0177	7.137	39.70
23	4.649	0.311	0.0155	6.270	34.88
28	4.654	0.306	0.0153	6.169	34.32
35	4.652	0.308	0.0154	6.209	34.54
48	4.628	0.332	0.0166	6.693	37.23
58	4.625	0.335	0.0167	6.754	37.57
71	4.646	0.314	0.0157	6.330	35.21
80	4.664	0.296	0.0148	5.967	33.19
100	4.657	0.303	0.0151	6.108	33.98
Average			0.014325	3.980	32.13
Sum					385.5

LDPE virgin pellets results in fresh water

Shaking time/hr	Cd in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cd in present pellets (µg)	% Mass uptake	Cd uptake by pellets (µg/kg)
0	4.96	0	0	0	0
1	4.778	0.182	0.0091	3.669	19.98
3	4.704	0.256	0.0128	5.161	28.10
8	4.653	0.307	0.0153	6.189	33.70
13	4.595	0.365	0.0182	7.358	40.07
23	4.622	0.338	0.0169	6.814	37.11
28	4.548	0.412	0.0206	8.306	45.23
35	4.551	0.409	0.0204	8.245	44.90
48	4.582	0.378	0.0189	7.620	41.50
58	4.596	0.364	0.0182	7.338	39.96
71	4.578	0.382	0.0191	7.701	41.94
80	4.594	0.366	0.0183	7.379	40.18
100	4.592	0.368	0.0184	7.419	40.40
Average			0.0171	6.889	35.51
Sum					426.11

PP virgin pellets results in fresh water

Shaking time/hr	Cd in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cd in present pellets (µg)	% Mass uptake	Cd uptake by pellets (µg/kg)
0	4.96	0	0	0	0
1	4.786	0.174	0.0087	3.508	18.99
3	4.779	0.181	0.00905	3.649	19.75
8	4.685	0.275	0.0137	5.544	30.02
13	4.683	0.277	0.0138	5.584	30.24
23	4.692	0.268	0.0134	5.403	29.25
28	4.662	0.298	0.0149	6.008	32.53
35	4.669	0.291	0.0145	5.866	31.76
48	4.673	0.287	0.0143	5.786	31.33
58	4.677	0.283	0.0141	5.705	30.89
71	4.662	0.298	0.0149	6.008	32.53
80	4.677	0.283	0.0141	5.705	30.89
100	4.670	0.290	0.0145	5.846	31.65
Average			0.0132	5.342	26.72
Sum					320.64

PET virgin pellets results in fresh water

Shaking time/hr	Cd in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cd in present pellets (µg)	% Mass uptake	Cd uptake by pellets (µg/kg)
0	4.96	0	0	0	0
1	4.782	0.178	0.0089	3.588	19.35
3	4.685	0.275	0.0137	5.544	29.89
8	4.685	0.275	0.0137	5.544	29.89
13	4.563	0.397	0.0198	8.004	43.16
23	4.501	0.459	0.0229	9.254	49.90
28	4.516	0.444	0.0222	8.951	48.27
35	4.545	0.415	0.0207	8.366	45.11
48	4.548	0.412	0.0206	8.306	44.79
58	4.566	0.394	0.0197	7.943	42.83
71	4.568	0.392	0.0196	7.903	42.61
80	4.57	0.39	0.0195	7.862	42.40
100	4.58	0.38	0.0190	7.661	41.31
Average			0.0183	7.388	39.96
Sum					479.5

BIO virgin pellets results in fresh water

Shaking time/hr	Cd in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cd in present pellets (µg)	% Mass uptake	Cd uptake by pellets (µg/kg)
0	4.96	0	0	0	0
1	4.784	0.176	0.0088	3.548	19.54
3	4.683	0.277	0.0138	5.584	30.76
8	4.580	0.379	0.0189	7.657	42.09
13	4.582	0.378	0.0189	7.620	41.98
23	4.595	0.365	0.0182	7.358	40.53
28	4.578	0.382	0.0191	7.701	42.42
35	4.586	0.374	0.0187	7.540	41.53
48	4.678	0.282	0.0141	5.685	31.09
58	4.662	0.298	0.0149	6.008	33.09
71	4.667	0.293	0.0146	5.907	32.54
80	4.667	0.293	0.0146	5.907	32.54
100	4.661	0.299	0.0149	6.008	33.09
Average			0.0158	6.411	35.10
Sum					421.25

HDPE virgin pellets results in seawater

Shaking time/hr	Cd in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cd in present pellets (µg)	% Mass uptake	Cd uptake by pellets (µg/kg)
0	4.918	0	0	0	0
1	4.822	0.096	0.0048	1.952	10.27
3	4.7492	0.1688	0.00844	3.432	18.06
7	4.6628	0.2552	0.0127	5.189	27.31
11	4.6424	0.2756	0.0137	5.603	29.50
23	4.5949	0.3231	0.0161	6.569	34.58
28	4.6735	0.2445	0.0122	4.971	26.17
34	5.6512	-0.7332	-0.0366	-14.90	-78.48
48	4.6618	0.2562	0.0128	5.209	27.42
52	4.6614	0.2566	0.0128	5.217	27.46
58	4.7782	0.1398	0.00699	2.842	14.96
76	4.6827	0.2353	0.0117	4.784	25.18
100	4.7786	0.1394	0.00697	2.834	14.92
Average			0.0116	4.418	23.26
Sum					255.88

LDPE virgin pellets results in seawater

Shaking time/hr	Cd in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cd in present pellets (µg)	% Mass uptake	Cd uptake by pellets (µg/kg)
0	4.918	0	0	0	0
1	4.8169	0.1011	0.00505	2.055	10.91
3	4.7636	0.1544	0.00772	3.139	16.67
7	4.4766	0.4414	0.02207	8.975	47.65
11	4.5512	0.3668	0.0183	7.458	39.60
23	4.5132	0.4048	0.0202	8.230	43.70
28	4.6967	0.2213	0.01106	4.499	23.89
34	4.7139	0.2041	0.0102	4.150	22.03
48	4.7598	0.1582	0.00791	3.216	17.08
52	4.7359	0.1821	0.00910	3.702	19.66
58	4.7211	0.1969	0.00984	4.003	21.25
76	4.7624	0.1556	0.00778	3.163	16.79
100	4.7236	0.1944	0.00972	3.952	20.98
Average			0.0115	4.712	25.02
Sum					300.26

PP virgin pellets results in seawater

Shaking time/hr	Cd in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cd in present pellets (µg)	% Mass uptake	Cd uptake by pellets (µg/kg)
0	4.918	0	0	0	0
1	4.7972	0.1208	0.00604	2.456	12.90
3	4.7191	0.1989	0.00994	4.044	21.25
7	4.7921	0.1259	0.00629	2.559	13.45
11	4.7726	0.1454	0.00727	2.956	15.53
23	4.6776	0.2404	0.0120	4.888	25.68
28	4.7633	0.1547	0.00773	3.145	16.53
34	4.8508	0.0672	0.00336	1.366	7.181
48	4.8078	0.1102	0.00551	2.240	11.77
52	4.7973	0.1207	0.00603	2.454	12.89
58	4.7753	0.1427	0.00713	2.901	15.24
76	4.7721	0.1459	0.00729	2.966	15.59
100	4.7086	0.2094	0.01047	4.257	22.37
Average			0.0074	3.019	15.87
Sum					190.44

PET virgin pellets results in seawater

Shaking time/hr	Cd in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cd in present pellets (µg)	% Mass uptake	Cd uptake by pellets (µg/kg)
0	4.918	0	0	0	0
1	4.7027	0.2153	0.01076	4.377	23.38
3	4.6775	0.2405	0.01202	4.890	26.12
7	4.5525	0.3655	0.01827	7.431	39.70
11	4.5808	0.3372	0.01686	6.856	36.62
23	4.5239	0.3941	0.01970	8.013	42.81
28	4.7332	0.1848	0.00924	3.757	20.07
34	4.7059	0.2121	0.01060	4.312	23.03
48	4.7681	0.1499	0.00749	3.047	16.28
52	4.7214	0.1966	0.00983	3.997	21.35
58	4.6462	0.2718	0.01359	5.526	29.52
76	4.7353	0.1827	0.00913	3.714	19.84
100	4.7705	0.1475	0.00737	2.999	16.02
Average			0.0121	4.911	26.23
Sum					314.7

BIO virgin pellets results in seawater

Shaking time/hr	Cd in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cd in present pellets (µg)	% Mass uptake	Cd uptake by pellets (µg/kg)
0	4.918	0	0	0	0
1	4.4995	0.4185	0.0209	8.509	45.14
3	4.6914	0.2266	0.0113	4.607	24.44
7	4.684	0.234	0.0117	4.758	25.24
11	4.6822	0.2358	0.0117	4.794	25.43
23	4.6874	0.2306	0.0115	4.688	24.87
28	4.7436	0.1744	0.0087	3.546	18.81
34	4.9814	-0.0634	-0.00317	-1.289	-6.839
48	4.7168	0.2012	0.01006	4.091	21.70
52	4.7166	0.2014	0.01007	4.095	21.72
58	4.7003	0.2177	0.01088	4.426	23.48
76	4.6867	0.2313	0.01156	4.703	24.95
100	4.7325	0.1855	0.00927	3.771	20.01
Average			0.0116	4.726	25.07
Sum					275.83

HDPE weathered pellets results in seawater

Shaking time/hr	Cd in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cd in present pellets (µg)	% Mass uptake	Cd uptake by pellets (µg/kg)
0	4.8116	0	0	0	0
1	4.6839	0.1277	0.00638	2.654	14.00
3	4.6567	0.1549	0.00774	3.219	16.99
7	4.6033	0.2083	0.0104	4.329	22.84
11	4.5181	0.2935	0.0146	6.099	32.19
23	4.6116	0.2	0.010	4.156	21.93
28	4.4768	0.3348	0.0167	6.958	36.72
34	4.5843	0.2273	0.0113	4.724	24.93
47	4.5664	0.2452	0.0122	5.096	26.89
52	4.6462	0.1654	0.00827	3.437	18.14
58	4.5257	0.2859	0.0142	5.941	31.36
76	4.5589	0.2527	0.0126	5.251	27.72
100	5.2428	-0.4312	-0.0215	-8.961	-47.30
Average			0.0113	4.715	24.88
Sum					273.76

LDPE weathered pellets results in seawater

Shaking time/hr	Cd in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cd in present pellets (µg)	% Mass uptake	Cd uptake by pellets (µg/kg)
0	4.8116	0	0	0	0
1	4.5129	0.2987	0.0149	6.207	32.20
3	4.2441	0.5675	0.0283	11.79	61.17
7	4.189	0.6226	0.0311	12.93	67.11
11	4.1149	0.6967	0.0348	14.47	75.10
23	4.0546	0.757	0.0378	15.73	81.60
28	4.3381	0.4735	0.0236	9.840	51.04
34	4.4886	0.323	0.0161	6.712	34.82
47	4.3965	0.4151	0.0207	8.627	44.74
52	4.3927	0.4189	0.0209	8.706	45.15
58	4.4121	0.3995	0.0199	8.302	43.06
76	4.474	0.3376	0.0168	7.016	36.39
100	4.481	0.3306	0.0165	6.870	35.64
Average			0.0214	8.903	46.18
Sum					554.18

PP weathered pellets results in seawater

Shaking time/hr	Cd in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cd in present pellets (µg)	% Mass uptake	Cd uptake by pellets (µg/kg)
0	4.8116	0	0	0	0
1	4.5019	0.3097	0.0154	6.436	33.45
3	4.3416	0.47	0.0235	9.768	50.76
7	4.3357	0.4759	0.0237	9.890	51.40
11	4.4666	0.345	0.0172	7.170	37.26
23	4.0604	0.7512	0.0375	15.61	81.14
28	4.0197	0.7919	0.0395	16.45	85.53
34	4.311	0.5006	0.0250	10.40	54.07
47	4.3955	0.4161	0.0208	8.647	44.94
52	4.3646	0.447	0.0223	9.290	48.28
58	4.4519	0.3597	0.0179	7.475	38.85
76	4.3788	0.4328	0.0216	8.994	46.74
100	4.3805	0.4311	0.0215	8.959	46.56
Average			0.0238	9.925	51.58
Sum					619.03

PET weathered pellets results in seawater

Shaking time/hr	Cd in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cd in present pellets (µg)	% Mass uptake	Cd uptake by pellets (µg/kg)
0	4.8116	0	0	0	0
1	4.5098	0.3018	0.0150	6.272	32.58
3	4.3218	0.4898	0.0244	10.17	52.88
7	4.3218	0.4898	0.0244	10.17	52.88
11	4.4018	0.4098	0.0204	8.516	44.24
23	4.2605	0.5511	0.0275	11.45	59.50
28	4.0264	0.7852	0.0392	16.31	84.77
34	4.2695	0.5421	0.0271	11.26	58.52
47	4.1926	0.619	0.0309	12.86	66.83
52	4.1349	0.6767	0.0338	14.06	73.06
58	4.2414	0.5702	0.0285	11.85	61.56
76	4.1915	0.6201	0.0310	12.88	66.95
100	4.1107	0.7009	0.0350	14.56	75.674
Average			0.0281	11.70	60.79
Sum					729.49

BIO weathered pellets results in seawater

Shaking time/hr	Cd in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cd in present pellets (µg)	% Mass uptake	Cd uptake by pellets (µg/kg)
0	4.8116	0	0	0	0
1	4.1991	0.6125	0.0306	12.72	66.17
3	4.1259	0.6857	0.0342	14.25	74.08
7	4.0434	0.7682	0.0384	15.96	82.99
11	4.1024	0.7092	0.0354	14.73	76.62
23	4.1778	0.6338	0.0316	13.17	68.47
28	3.7592	1.0524	0.0526	21.87	113.6
34	4.1888	0.6228	0.0311	12.94	67.28
47	4.1325	0.6791	0.0339	14.11	73.36
52	4.1646	0.647	0.0323	13.44	69.90
58	4.2181	0.5935	0.0296	12.33	64.12
76	4.1782	0.6334	0.0316	13.16	68.43
100	4.1747	0.6369	0.0318	13.23	68.80
Average			0.0344	14.33	74.49
Sum					893.9

Calculation: Cr (µg kg^{-1}) in deionised water, fresh water and seawater

HDPE virgin pellets results in deionised water

Shaking time/hr	Cr in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cr in present pellets (µg)	% Mass uptake	Cr uptake by pellets (µg/kg)
0	4.94	0	0	0	0
1	4.82	0.12	0.006	2.429	13.53
2	4.8	0.14	0.007	2.834	15.79
4	4.78	0.16	0.008	3.238	18.05
8	4.82	0.12	0.006	2.429	13.53
12	4.82	0.12	0.006	2.429	13.53
22	4.75	0.19	0.0095	3.846	21.43
28	4.76	0.18	0.009	3.643	20.30
33	4.75	0.19	0.0095	3.846	21.43
46	4.7	0.24	0.012	4.858	27.07
60	4.533	0.407	0.0203	8.238	45.91
80	5.21	-0.27	-0.0135	-5.465	-30.46
100	4.81	0.13	0.0065	2.631	14.66
Average			0.009	3.675	20.48
Sum					225.3

LDPE virgin pellets results in deionised water

Shaking time/hr	Cr in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cr in present pellets (µg)	% Mass uptake	Cr uptake by pellets (µg/kg)
0	4.94	0	0	0	0
1	4.84	0.1	0.005	2.024	11.21
2	4.78	0.16	0.008	3.238	17.93
4	5.17	-0.23	-0.0115	-4.655	-25.78
8	4.84	0.1	0.005	2.024	11.21
12	4.88	0.06	0.003	1.214	6.726
22	4.8	0.14	0.007	2.834	15.69
28	4.78	0.16	0.008	3.238	17.93
33	4.72	0.22	0.011	4.453	24.66
46	4.64	0.3	0.015	6.072	33.63
60	4.77	0.17	0.0085	3.441	19.05
80	4.63	0.31	0.0155	6.275	34.75
100	4.68	0.26	0.013	5.263	29.14
Average			0.009	3.644	20.18
Sum					222.01

BIO virgin pellets results in deionised water

Shaking time/hr	Cr in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cr in present pellets (µg)	% Mass uptake	Cr uptake by pellets (µg/kg)
0	4.94	0	0	0	0
1	4.78	0.16	0.008	3.238	18.21
2	4.79	0.15	0.0075	3.036	17.08
4	4.82	0.12	0.006	2.429	13.66
8	4.47	0.47	0.0235	9.514	53.51
12	4.86	0.08	0.004	1.619	9.109
22	4.81	0.13	0.0065	2.631	14.80
28	4.78	0.16	0.008	3.238	18.21
33	4.83	0.11	0.0055	2.226	12.52
46	4.75	0.19	0.0095	3.846	21.63
60	4.78	0.16	0.008	3.238	18.21
80	4.69	0.05	0.0025	1.012	5.693
100	4.71	0.13	0.0065	2.631	14.80
Average			0.0079	3.221	18.12
Sum					217.48

PP virgin pellets results in deionised water

Shaking time/hr	Cr in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cr in present pellets (µg)	% Mass uptake	Cr uptake by pellets (µg/kg)
0	4.94	0	0	0	0
1	4.89	0.05	0.0025	1.012	5.351
2	4.84	0.1	0.005	2.024	10.70
4	4.86	0.08	0.004	1.619	8.561
8	4.86	0.08	0.004	1.619	8.561
12	4.82	0.12	0.006	2.429	12.84
22	4.84	0.1	0.005	2.024	10.70
28	4.86	0.08	0.004	1.619	8.561
33	4.89	0.05	0.0025	1.012	5.351
46	4.82	0.12	0.006	2.429	12.84
60	4.95	-0.01	-0.0005	-0.202	-1.070
80	4.83	0.11	0.0055	2.226	11.77
100	4.86	0.08	0.004	1.619	8.561
Average			0.0044	1.785	9.437
Sum					103.8

PET virgin pellets results in deionised water

Shaking time/hr	Cr in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cr in present pellets (µg)	% Mass uptake	Cr uptake by pellets (µg/kg)
0	4.94	0	0	0	0
1	4.89	0.05	0.0025	1.012	5.624
2	4.84	0.1	0.005	2.024	11.24
4	4.77	0.17	0.0085	3.441	19.12
8	4.81	0.13	0.0065	2.631	14.62
12	4.78	0.16	0.008	3.238	17.99
22	4.73	0.21	0.0105	4.251	23.62
28	4.85	0.09	0.0045	1.821	10.12
33	4.82	0.12	0.006	2.429	13.49
46	4.78	0.16	0.008	3.238	17.99
60	5.19	-0.25	-0.0125	-5.060	-28.12
80	4.86	0.08	0.004	1.619	8.998
100	4.66	0.28	0.014	5.668	31.49
Average			0.007	2.852	15.85
Sum					174.35

HDPE virgin pellets results in fresh water

Shaking time/hr	Cr in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cr in present pellets (µg)	% Mass uptake	Cr uptake by pellets (µg/kg)
0	5.337	0	0	0	0
1	5.172	0.165	0.00825	3.091	18.46
3	5.172	0.165	0.00825	3.091	18.46
7	5.158	0.179	0.00895	3.353	20.03
11	5.234	0.103	0.00515	1.929	11.52
23	5.134	0.203	0.01015	3.803	22.72
28	5.227	0.11	0.0055	2.061	12.31
34	5.196	0.141	0.00705	2.641	15.78
47	5.271	0.066	0.0033	1.236	7.387
57	5.322	0.015	0.00075	0.2810	1.678
71	5.19	0.147	0.00735	2.754	16.45
80	5.171	0.166	0.0083	3.110	18.58
100	5.21	0.127	0.00635	2.379	14.21
Average			0.0071	2.664	14.80
Sum					177.63

LDPE virgin pellets results in fresh water

Shaking time/hr	Cr in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cr in present pellets (µg)	% Mass uptake	Cr uptake by pellets (µg/kg)
0	5.337	0	0	0	0
1	5.336	0.001	0.00005	0.0187	0.109
3	5.26	0.077	0.00385	1.442	8.468
7	5.963	-0.626	-0.0313	-11.72	-68.85
11	5.247	0.09	0.0045	1.686	9.898
23	5.175	0.162	0.0081	3.035	17.81
28	5.129	0.208	0.0104	3.897	22.87
34	5.107	0.23	0.0115	4.309	25.29
47	5.111	0.226	0.0113	4.234	24.85
57	5.023	0.314	0.0157	5.883	34.53
71	4.968	0.369	0.0184	6.913	40.58
80	5.002	0.335	0.0167	6.276	36.84
100	5.00	0.337	0.0168	6.314	37.06
Average			0.1117	4.186	23.48
Sum					258.35

PP virgin pellets results in fresh water

Shaking time/hr	Cr in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cr in present pellets (µg)	% Mass uptake	Cr uptake by pellets (µg/kg)
0	5.337	0	0	0	0
1	5.391	-0.054	-0.0027	-1.011	-5.964
3	5.492	-0.155	-0.00775	-2.904	-17.11
7	5.373	-0.036	-0.0018	-0.6745	-3.976
11	5.369	-0.032	-0.0016	-0.5995	-3.534
23	5.362	-0.025	-0.00125	-0.4684	-2.761
28	5.31	0.027	0.00135	0.5059	2.982
34	5.336	0.001	0.00005	0.0187	0.1104
47	5.208	0.129	0.00645	2.4170	14.24
57	5.363	-0.026	-0.0013	-0.4871	-2.871
71	5.184	0.153	0.00765	2.8667	16.89
80	5.188	0.149	0.00745	2.7918	16.45
100	5.184	0.153	0.00765	2.8667	16.89
Average			0.005	2.145	11.26
Sum					67.58

PET virgin pellets results in fresh water

Shaking time/hr	Cr in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cr in present pellets (µg)	% Mass uptake	Cr uptake by pellets (µg/kg)
0	5.337	0	0	0	0
1	5.328	0.009	0.00045	0.168	0.969
3	5.309	0.028	0.0014	0.524	3.017
7	5.409	-0.072	-0.0036	-1.349	-7.758
11	5.249	0.088	0.0044	1.648	9.482
23	5.223	0.114	0.0057	2.136	12.28
28	5.284	0.053	0.00265	0.993	5.711
34	5.235	0.102	0.0051	1.911	10.99
47	5.168	0.169	0.00845	3.166	18.21
57	5.229	0.108	0.0054	2.023	11.63
71	5.404	-0.067	-0.00335	-1.255	-7.219
80	5.196	0.141	0.00705	2.641	15.19
100	5.211	0.126	0.00635	2.360	13.68
Average			0.005	1.881	10.11
Sum					101.18

BIO virgin pellets results in fresh water

Shaking time/hr	Cr in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cr in present pellets (µg)	% Mass uptake	Cr uptake by pellets (µg/kg)
0	5.337	0	0	0	0
1	5.401	-0.064	-0.0032	-1.199	-7.068
3	5.277	0.06	0.003	1.124	6.626
7	5.122	0.215	0.0107	4.028	23.74
11	4.993	0.344	0.0172	6.445	37.99
23	5.077	0.26	0.013	4.871	28.71
28	5.022	0.315	0.0157	5.902	34.79
34	4.874	0.463	0.0231	8.675	51.13
47	4.879	0.4577	0.0228	8.575	50.55
57	4.8764	0.4605	0.0230	8.629	50.86
71	4.8756	0.4613	0.0230	8.644	50.95
80	4.8731	0.4639	0.0231	8.692	51.23
100	4.871	0.466	0.0233	8.731	51.46
Average			0.0175	6.558	39.82
Sum					438.089

HDPE virgin pellets results in seawater

Shaking time/hr	Cr in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cr in present pellets (µg)	% Mass uptake	Cr uptake by pellets (µg/kg)
0	5.217	0	0	0	0
1	4.777	0.44	0.022	8.433	47.76
3	4.824	0.393	0.0196	7.533	42.66
7	4.864	0.353	0.0176	6.766	38.31
11	4.71	0.507	0.0253	9.718	55.03
23	4.564	0.653	0.0326	12.51	70.88
28	4.629	0.588	0.0294	11.27	63.82
34	4.657	0.56	0.028	10.73	60.79
47	4.60	0.617	0.0308	11.82	66.97
52	4.705	0.512	0.0256	9.814	55.57
58	8.249	-3.032	-0.1516	-58.11	-329.1
76	4.609	0.608	0.0304	11.65	66.00
100	4.81	0.407	0.0203	7.801	44.18
Average			0.0256	9.824	55.63
Sum					612.018

LDPE virgin pellets results in seawater

Shaking time/hr	Cr in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cr in present pellets (µg)	% Mass uptake	Cr uptake by pellets (µg/kg)
0	5.217	0	0	0	0
1	4.859	0.358	0.0179	6.862	38.60
3	4.762	0.455	0.0227	8.721	49.06
7	4.797	0.42	0.021	8.050	45.28
11	4.305	0.912	0.0456	17.48	98.33
23	4.204	1.013	0.0506	19.41	109.2
28	4.269	0.948	0.0474	18.17	102.2
34	4.382	0.835	0.0417	16.00	90.03
47	4.432	0.785	0.0392	15.04	84.64
52	4.563	0.654	0.0327	12.53	70.51
58	4.691	0.526	0.0263	10.08	56.71
76	4.671	0.546	0.0273	10.46	58.87
100	4.709	0.508	0.0254	9.737	54.77
Average			0.0331	12.71	71.52
Sum					858.31

PP virgin pellets results in seawater

Shaking time/hr	Cr in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cr in present pellets (µg)	% Mass uptake	Cr uptake by pellets (µg/kg)
0	5.217	0	0	0	0
1	4.821	0.396	0.0198	7.590	43.32
3	4.744	0.473	0.0236	9.066	51.75
7	4.617	0.6	0.03	11.50	65.64
11	4.492	0.725	0.0362	13.89	79.32
23	4.116	1.101	0.0550	21.10	120.4
28	4.503	0.714	0.0357	13.68	78.11
34	4.738	0.479	0.0239	9.181	52.40
47	4.677	0.54	0.027	10.35	59.08
52	4.722	0.495	0.0247	9.488	54.15
58	4.788	0.429	0.0214	8.223	46.93
76	4.625	0.592	0.0296	11.34	64.77
100	4.754	0.463	0.0231	8.874	50.65
Average			0.029	11.19	63.88
Sum					766.6

PET virgin pellets results in seawater

Shaking time/hr	Cr in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cr in present pellets (µg)	% Mass uptake	Cr uptake by pellets (µg/kg)
0	5.217	0	0	0	0
1	4.873	0.344	0.0172	6.593	36.98
3	4.799	0.418	0.0209	8.012	44.93
7	4.883	0.334	0.0167	6.402	35.90
11	4.746	0.471	0.0235	9.028	50.63
23	4.565	0.652	0.0326	12.49	70.09
28	4.587	0.63	0.0315	12.07	67.72
34	4.58	0.637	0.0318	12.21	68.47
47	4.471	0.746	0.0373	14.29	80.19
52	4.483	0.734	0.0367	14.06	78.90
58	4.694	0.523	0.0261	10.02	56.22
76	4.698	0.519	0.0259	9.948	55.79
100	4.514	0.703	0.0351	13.47	75.57
Average			0.027	10.71	60.12
Sum					721.45

BIO weathered pellets results in seawater

Shaking time/hr	Cr in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cr in present pellets (µg)	% Mass uptake	Cr uptake by pellets (µg/kg)
0	5.217	0	0	0	0
1	4.817	0.4	0.02	7.667	43.11
3	4.897	0.32	0.016	6.133	34.49
7	4.581	0.636	0.0318	12.19	68.54
11	4.864	0.353	0.0176	6.766	38.04
23	4.194	1.023	0.0511	19.60	110.2
28	4.137	1.08	0.054	20.70	116.4
34	4.151	1.066	0.0533	20.43	114.8
47	4.416	0.801	0.04005	15.35	86.33
52	4.466	0.751	0.0375	14.39	80.94
58	4.394	0.823	0.0411	15.77	88.70
76	4.46	0.757	0.0378	14.51	81.59
100	4.487	0.73	0.0365	13.99	78.68
Average			0.036	13.96	78.50
Sum					942.012

HDPE weathered pellets results in seawater

Shaking time/hr	Cr in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cr in present pellets (µg)	% Mass uptake	Cr uptake by pellets (µg/kg)
0	5.048	0	0	0	0
1	4.63	0.418	0.0209	8.280	45.62
3	4.574	0.474	0.0237	9.389	51.73
7	4.55	0.498	0.0249	9.865	54.35
11	4.509	0.5385	0.0269	10.66	58.77
23	4.331	0.7168	0.0358	14.19	78.23
28	4.375	0.6725	0.0336	13.32	73.40
34	4.539	0.5089	0.0254	10.08	55.54
47	4.380	0.6677	0.0333	13.22	72.87
52	4.543	0.5049	0.0252	10.00	55.10
58	4.496	0.5516	0.0275	10.92	60.20
76	4.383	0.6645	0.0332	13.16	72.52
100	4.492	0.5555	0.0277	11.00	60.63
Average			0.028	11.17	61.58
Sum					739.02

LDPE weathered pellets results in seawater

Shaking time/hr	Cr in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cr in present pellets (µg)	% Mass uptake	Cr uptake by pellets (µg/kg)
0	5.048	0	0	0	0
1	4.678	0.3701	0.0185	7.331	39.71
3	4.530	0.518	0.0259	10.26	55.57
7	4.549	0.4986	0.0249	9.877	53.49
11	4.196	0.852	0.0426	16.87	91.41
23	4.103	0.9447	0.0472	18.71	101.3
28	3.977	1.0713	0.0535	21.22	114.9
34	4.316	0.7319	0.0365	14.49	78.53
47	4.483	0.5652	0.0282	11.19	60.64
52	4.517	0.5307	0.0265	10.51	56.94
58	4.412	0.6362	0.0318	12.60	68.26
76	4.413	0.635	0.0317	12.57	68.13
100	4.3690	0.679	0.0339	13.45	72.88
Average			0.03064	12.13	71.82
Sum					861.9

PP weathered pellets results in seawater

Shaking time/hr	Cr in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cr in present pellets (µg)	% Mass uptake	Cr uptake by pellets (µg/kg)
0	5.048	0	0	0	0
1	4.540	0.5073	0.0253	10.04	54.83
3	4.5078	0.5401	0.0270	10.70	58.38
7	4.6774	0.3706	0.0185	7.341	40.05
11	4.5275	0.5205	0.0260	10.31	56.25
23	4.4372	0.6108	0.0305	12.09	66.01
28	4.2889	0.7591	0.0379	15.03	82.04
34	4.1519	0.8961	0.0448	17.75	96.85
47	4.2052	0.8428	0.0421	16.69	91.09
52	4.3847	0.6633	0.0331	13.13	71.69
58	4.4592	0.5888	0.0294	11.66	63.64
76	4.4346	0.6134	0.0306	12.15	66.29
100	4.3574	0.6906	0.0345	13.68	74.64
Average			0.0316	12.55	68.48
Sum					821.8

PET weathered pellets results in seawater

Shaking time/hr	Cr in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cr in present pellets (µg)	% Mass uptake	Cr uptake by pellets (µg/kg)
0	5.048	0	0	0	0
1	4.453	0.5949	0.0297	11.78	63.11
3	4.407	0.6406	0.0320	12.69	67.96
7	4.212	0.8357	0.0417	16.55	88.65
11	4.347	0.7002	0.0350	13.87	74.28
23	4.159	0.889	0.0444	17.61	94.31
28	4.091	0.956	0.0478	18.95	101.5
34	4.277	0.771	0.0385	15.27	81.79
47	4.281	0.7665	0.0383	15.18	81.31
52	4.398	0.6493	0.0324	12.86	68.88
58	4.372	0.6755	0.0337	13.38	71.66
76	4.364	0.6838	0.0341	13.54	72.54
100	4.364	0.6837	0.0341	13.54	72.53
Average			0.0368	14.60	78.21
Sum					938.58

BIO virgin pellets results in seawater

Shaking time/hr	Cr in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Cr in present pellets (µg)	% Mass uptake	Cr uptake by pellets (µg/kg)
0	5.048	0	0	0	0
1	4.527	0.520	0.0260	10.30	56.74
3	4.526	0.521	0.0260	10.32	56.85
7	4.748	0.30	0.015	5.942	32.72
11	4.412	0.635	0.0317	12.58	69.29
23	4.265	0.783	0.0391	15.51	85.42
28	4.128	0.919	0.0459	18.21	100.3
34	4.298	0.749	0.0374	14.83	81.72
47	4.208	0.839	0.0419	16.63	91.59
52	4.399	0.648	0.0324	12.84	70.76
58	4.367	0.680	0.0340	13.48	74.26
76	4.400	0.647	0.0323	12.83	70.67
100	4.433	0.614	0.0307	12.16	67.01
Average			0.0327	12.97	71.44
Sum					857.39

Calculation: Pb (µg kg^{-1}) in deionised water, fresh water and seawater

HDPE virgin pellets results in deionised water

Shaking time/hr	Pb in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Pb in present pellets (µg)	% Mass uptake	Pb uptake by pellets (µg/kg)
0	4.85	0	0	0	0
1	3.974	0.876	0.0438	18.06	96.90
3	3.240	1.609	0.0804	33.18	178.0
7	2.901	1.948	0.0974	40.16	215.4
11	3.442	1.407	0.0703	29.01	155.6
23	3.372	1.477	0.0738	30.45	163.3
28	3.125	1.724	0.0862	35.55	190.7
34	3.22	1.63	0.0815	33.60	180.3
47	3.305	1.545	0.0772	31.85	170.9
52	3.425	1.425	0.0712	29.38	157.6
58	3.668	1.182	0.0591	24.37	130.7
76	3.728	1.122	0.0561	23.13	124.1
100	3.7754	1.074	0.0537	22.15	118.8
Average			0.0709	29.24	156.90
Sum					1882.86

LDPE virgin pellets results in deionised water

Shaking time/hr	Pb in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Pb in present pellets (µg)	% Mass uptake	Pb uptake by pellets (µg/kg)
0	4.85	0	0	0	0
1	4.310	0.539	0.0269	11.12	60.76
3	3.383	1.466	0.0733	30.23	165.1
7	3.278	1.571	0.0785	32.40	176.9
11	3.194	1.655	0.0827	34.13	186.4
23	2.975	1.874	0.0937	38.64	211.0
28	2.965	1.884	0.0942	38.86	212.2
34	3.155	1.694	0.0847	34.92	190.7
47	3.207	1.643	0.0821	33.87	185.0
52	3.450	1.399	0.0699	28.85	157.6
58	3.44	1.41	0.0705	29.07	158.7
76	3.647	1.202	0.0601	24.79	135.4
100	3.707	1.143	0.0571	23.56	128.7
Average			0.0728	30.04	164.07
Sum					1968.93

PP virgin pellets results in deionised water

Shaking time/hr	Pb in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Pb in present pellets (µg)	% Mass uptake	Pb uptake by pellets (µg/kg)
0	4.85	0	0	0	0
1	3.869	0.980	0.0490	20.21	111.4
3	3.659	1.191	0.0595	24.55	135.3
7	3.393	1.456	0.0728	30.03	165.5
11	3.258	1.591	0.0795	32.81	180.8
23	3.305	1.544	0.0772	31.84	175.5
28	3.469	1.381	0.0690	28.47	156.9
34	3.110	1.739	0.0869	35.87	197.7
47	3.195	1.655	0.0827	34.12	188.0
52	3.606	1.244	0.0622	25.64	141.3
58	3.482	1.367	0.0683	28.19	155.3
76	3.676	1.173	0.0586	24.20	133.3
100	3.641	1.208	0.0604	24.91	137.3
Average			0.068891	28.40859	156.570
Sum					1878.84

PET virgin pellets results in deionised water

Shaking time/hr	Pb in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Pb in present pellets (µg)	% Mass uptake	Pb uptake by pellets (µg/kg)
0	4.85	0	0	0	0
1	3.745	1.104	0.0552	22.77	119.2
3	3.008	1.842	0.0921	37.97	198.9
7	3.224	1.625	0.0812	33.51	175.5
11	3.182	1.667	0.0833	34.38	180.0
23	3.462	1.387	0.0693	28.60	149.8
28	3.469	1.381	0.0690	28.47	149.1
34	3.566	1.283	0.0641	26.47	138.6
47	3.635	1.214	0.0607	25.03	131.1
52	3.463	1.386	0.0693	28.58	149.7
58	3.616	1.233	0.0616	25.43	133.2
76	3.695	1.154	0.0577	23.80	124.6
100	3.682	1.167	0.0583	24.07	126.1
Average			0.0694	28.64	150.01
Sum					1800.19

BIO virgin pellets results in deionised water

Shaking time/hr	Pb in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Pb in present pellets (µg)	% Mass uptake	Pb uptake by pellets (µg/kg)
0	4.85	0	0	0	0
1	4.327	0.522	0.0261	10.78	59.55
3	3.579	1.270	0.0635	26.18	144.6
7	3.361	1.488	0.0744	30.69	169.5
11	3.194	1.656	0.0828	34.14	188.6
23	3.158	1.692	0.0846	34.88	192.7
28	3.065	1.784	0.0892	36.79	203.2
34	3.247	1.603	0.0801	33.05	182.5
47	3.471	1.378	0.0689	28.41	156.9
52	3.425	1.425	0.0712	29.38	162.3
58	3.660	1.189	0.0594	24.53	135.5
76	4.130	0.719	0.0359	14.82	81.90
100	3.975	0.875	0.0437	18.04	99.65
Average			0.0650	26.81	148.10
Sum					1777.28

HDPE virgin pellets results in fresh water

Shaking time/hr	Pb in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Pb in present pellets (µg)	% Mass uptake	Pb uptake by pellets (µg/kg)
0	5.40	0	0	0	0
1	5.21	0.19	0.0095	3.518	21.33
3	5.21	0.19	0.0095	3.518	21.33
7	5.20	0.2	0.01	3.703	22.45
11	5.10	0.3	0.015	5.555	33.68
23	5.10	0.3	0.015	5.555	33.68
28	4.89	0.51	0.0255	9.444	57.26
34	4.83	0.57	0.0285	10.55	64.00
47	4.80	0.6	0.03	11.11	67.37
52	4.90	0.5	0.025	9.259	56.14
58	4.80	0.6	0.03	11.11	67.37
76	4.83	0.57	0.0285	10.55	64.00
100	4.81	0.59	0.0295	10.92	66.24
Average			0.02059	7.626	47.90
Sum					574.886

*Avg wt = 0.4453

LDPE virgin pellets results in fresh water

Shaking time/hr	Pb in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Pb in present pellets (µg)	% Mass uptake	Pb uptake by pellets (µg/kg)
0	5.4	0	0	0	0
1	5.15	0.25	0.0125	4.629	28.18
3	5.04	0.36	0.018	6.666	40.58
7	4.82	0.58	0.029	10.74	65.38
11	4.58	0.82	0.041	15.18	92.44
23	4.35	1.05	0.0525	19.44	118.3
28	4.09	1.31	0.0655	24.25	147.6
34	3.54	1.86	0.093	34.44	209.6
47	3.76	1.64	0.082	30.37	184.8
52	3.73	1.67	0.0835	30.92	188.2
58	3.59	1.81	0.0905	33.51	204.0
76	3.74	1.66	0.083	30.74	187.1
100	3.73	1.67	0.0835	30.92	188.2
Average			0.059136	21.9023	137.91
Sum					1654.9

PP virgin pellets results in fresh water

Shaking time/hr	Pb in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Pb in present pellets (µg)	% Mass uptake	Pb uptake by pellets (µg/kg)
0	5.4	0	0	0	0
1	5.39	0.01	0.0005	0.185	1.125
3	5.45	-0.05	-0.0025	-0.925	-5.626
7	5.33	0.07	0.0035	1.296	7.877
11	5.27	0.13	0.0065	2.407	14.62
23	5.13	0.27	0.0135	5.0	30.38
28	5.16	0.24	0.012	4.444	27.00
34	4.92	0.48	0.024	8.888	54.01
47	4.58	0.82	0.041	15.18	92.27
52	5.1	0.3	0.015	5.555	33.76
58	4.55	0.85	0.0425	15.74	95.65
76	4.6	0.8	0.04	14.81	90.02
100	4.59	0.81	0.0405	15.0	91.15
Average			0.022	8.148	48.90
Sum					537.91

PET virgin pellets results in fresh water

Shaking time/hr	Pb in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Pb in present pellets (µg)	% Mass uptake	Pb uptake by pellets (µg/kg)
0	5.40	0	0	0	0
1	5.05	0.35	0.0175	6.481	38.06
3	4.71	0.69	0.0345	12.77	75.04
7	4.71	0.69	0.0345	12.77	75.04
11	4.23	1.17	0.0585	21.66	127.2
23	3.95	1.45	0.0725	26.85	157.7
28	4.00	1.4	0.07	25.92	152.2
34	3.71	1.69	0.0845	31.29	183.8
47	3.36	2.04	0.102	37.77	221.8
52	3.72	1.68	0.084	31.11	182.7
58	3.61	1.79	0.0895	33.14	194.6
76	3.70	1.7	0.085	31.48	184.9
100	3.72	1.68	0.084	31.11	182.7
Average			0.066591	24.66	148
Sum					1776.11

BIO virgin pellets results in fresh water

Shaking time/hr	Pb in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Pb in present pellets (µg)	% Mass uptake	Pb uptake by pellets (µg/kg)
0	5.40	0	0	0	0
1	5.13	0.27	0.0135	5	30.67
3	5.03	0.37	0.0185	6.851	42.03
7	4.72	0.68	0.034	12.59	77.25
11	4.95	0.45	0.0225	8.333	51.12
23	4.69	0.71	0.0355	13.14	80.66
28	4.65	0.75	0.0375	13.88	85.20
34	4.47	0.93	0.0465	17.22	105.6
47	4.38	1.02	0.0510	18.88	115.8
52	4.43	0.97	0.0485	17.96	110.2
58	4.41	0.99	0.0495	18.33	112.4
76	4.41	0.99	0.0495	18.33	112.4
100	4.42	0.98	0.0490	18.14	111.3
Average			0.0369	13.686	86.24
Sum					1034.9

*Avg wt = 0.440127

HDPE weathered pellets results in seawater

Shaking time/hr	Pb in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Pb in present pellets (µg)	% Mass uptake	Pb uptake by pellets (µg/kg)
0	5.031	0	0	0	0
1	4.42	0.611	0.0305	12.14	68.40
3	3.98	1.051	0.0525	20.89	117.6
7	4.364	0.667	0.0333	13.25	74.67
11	4.069	0.962	0.0481	19.12	107.7
22	4.024	1.007	0.0503	20.01	112.7
27	3.914	1.117	0.0558	22.20	125.0
33	3.497	1.534	0.0767	30.49	171.7
44	3.513	1.518	0.0759	30.17	169.9
49	4.162	0.869	0.0434	17.27	97.29
55	4.203	0.828	0.0414	16.45	92.70
73	4.172	0.859	0.0429	17.07	96.17
100	4.173	0.858	0.0429	17.05	96.05
Average			0.0495	19.67	110.8
Sum					1330

LDPE weathered pellets results in seawater

Shaking time/hr	Pb in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Pb in present pellets (µg)	% Mass uptake	Pb uptake by pellets (µg/kg)
0	5.031	0	0	0	0
1	4.169	0.862	0.0431	17.13	94.64
3	4.175	0.856	0.0428	17.01	93.98
7	6.93	-1.899	-0.0949	-37.74	-208.4
11	4.156	0.875	0.0437	17.39	96.06
22	3.98	1.051	0.0525	20.89	115.3
27	3.86	1.171	0.0585	23.27	128.5
33	3.236	1.795	0.0897	35.67	197.0
44	3.577	1.454	0.0727	28.90	159.6
49	4.356	0.675	0.0337	13.41	74.11
55	4.304	0.727	0.0363	14.45	79.81
73	4.337	0.694	0.0347	13.79	76.19
100	4.323	0.708	0.0354	14.07	77.73
Average			0.0494	19.63	108.4
Sum					1193

PP weathered pellets results in seawater

Shaking time/hr	Pb in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Pb in present pellets (µg)	% Mass uptake	Pb uptake by pellets (µg/kg)
0	5.031	0	0	0	0
1	3.962	1.069	0.0534	21.24	117.8
3	4.149	0.882	0.0441	17.53	97.2
7	4.031	1	0.05	19.87	110.2
11	3.742	1.289	0.0644	25.62	142.0
22	4.227	0.804	0.0402	15.98	88.60
27	3.92	1.111	0.0555	22.08	122.4
33	4.281	0.75	0.0375	14.90	82.65
44	4.226	0.805	0.0402	16.00	88.71
49	4.145	0.886	0.0443	17.61	97.64
55	4.081	0.95	0.0475	18.88	104.6
73	3.609	1.422	0.0711	28.26	156.7
100	4.001	1.03	0.0515	20.47	113.5
Average			0.0480	19.11	105.9
Sum					1271.4

PET weathered pellets results in seawater

Shaking time/hr	Pb in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Pb in present pellets (µg)	% Mass uptake	Pb uptake by pellets (µg/kg)
0	5.031	0	0	0	0
1	4.192	0.839	0.0419	16.67	90.09
3	4.188	0.843	0.0421	16.75	90.52
7	4.227	0.804	0.0402	15.98	86.34
11	4.095	0.936	0.0468	18.60	100.5
22	3.993	1.038	0.0519	20.63	111.4
27	3.991	1.04	0.052	20.67	111.6
33	3.663	1.368	0.0684	27.19	146.9
44	4.051	0.98	0.049	19.47	105.2
49	4.112	0.919	0.0459	18.26	98.68
55	4.187	0.844	0.0422	16.77	90.63
73	4.252	0.779	0.0389	15.48	83.65
100	4.309	0.722	0.0361	14.35	77.53
Average			0.0463	18.40	99.44
Sum					1193.29

BIO weathered pellets results in seawater

Shaking time/hr	Pb in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Pb in present pellets (µg)	% Mass uptake	Pb uptake by pellets (µg/kg)
0	5.031	0	0	0	0
1	4.071	0.96	0.048	19.08	105.4
3	3.931	1.1	0.055	21.86	120.7
7	4.016	1.015	0.0507	20.17	111.4
11	3.918	1.113	0.0556	22.12	122.2
22	3.866	1.165	0.0582	23.15	127.9
27	3.942	1.089	0.0544	21.64	119.5
33	4.943	0.088	0.0044	1.749	9.663
44	4.978	0.053	0.0026	1.053	5.820
49	4.201	0.83	0.0415	16.49	91.14
55	4.169	0.862	0.0431	17.13	94.66
73	4.178	0.853	0.0426	16.95	93.67
100	4.217	0.814	0.0407	16.17	89.39
Average			0.0411	16.46	90.98
Sum					1091.8

HDPE virgin pellets results in seawater

Shaking time/hr	Pb in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Pb in present pellets (µg)	% Mass uptake	Pb uptake by pellets (µg/kg)
0	5.037	0	0	0	0
1	4.445	0.592	0.0296	11.75	65.18
3	4.592	0.445	0.0222	8.834	48.99
7	4.429	0.608	0.0304	12.07	66.94
11	4.18	0.857	0.0428	17.01	94.36
22	4.118	0.919	0.0459	18.24	101.1
27	4.145	0.892	0.0446	17.70	98.21
33	4.442	0.595	0.0297	11.81	65.51
44	4.454	0.583	0.0291	11.57	64.19
49	4.392	0.645	0.0322	12.80	71.01
55	4.173	0.864	0.0432	17.15	95.13
73	4.228	0.809	0.0404	16.06	89.07
100	4.351	0.686	0.0343	13.61	75.53
Average			0.0353	14.05	77.94
Sum					935.36

LDPE virgin pellets results in seawater

Shaking time/hr	Pb in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Pb in present pellets (µg)	% Mass uptake	Pb uptake by pellets (µg/kg)
0	5.037	0	0	0	0
1	4.243	0.794	0.0397	15.76	86.11
3	4.179	0.858	0.0429	17.03	93.05
7	4.27	0.767	0.0383	15.22	83.18
11	4.182	0.855	0.0427	16.97	92.73
22	3.975	1.062	0.0531	21.08	115.1
27	3.928	1.109	0.0554	22.01	120.2
33	3.55	1.487	0.0743	29.52	161.2
44	3.756	1.281	0.0640	25.43	138.9
49	3.974	1.063	0.0531	21.10	115.2
55	4.061	0.976	0.0488	19.37	105.8
73	4.088	0.949	0.0474	18.84	102.9
100	3.982	1.055	0.0527	20.94	114.4
Average			0.0511	20.27	110.7
Sum					1329.2

PP virgin pellets results in seawater

Shaking time/hr	Pb in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Pb in present pellets (µg)	% Mass uptake	Pb uptake by pellets (µg/kg)
0	5.037	0	0	0	0
1	4.469	0.568	0.0284	11.27	60.91
3	4.424	0.613	0.0306	12.16	65.74
7	4.398	0.639	0.0319	12.68	68.53
11	4.437	0.6	0.03	11.91	64.35
22	4.501	0.536	0.0268	10.64	57.48
27	4.415	0.622	0.0311	12.34	66.70
33	4.116	0.921	0.0460	18.28	98.77
44	3.919	1.118	0.0559	22.19	119.9
49	4.384	0.653	0.0326	12.96	70.03
55	4.544	0.493	0.0246	9.787	52.87
73	4.156	0.881	0.0440	17.49	94.48
100	4.233	0.804	0.0402	15.96	86.22
Average			0.0352	13.97	75.50
Sum					906.04

PET virgin pellets results in seawater

Shaking time/hr	Pb in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Pb in present pellets (µg)	% Mass uptake	Pb uptake by pellets (µg/kg)
0	5.037	0	0	0	0
1	4.57	0.467	0.0233	9.271	50.06
3	4.127	0.91	0.0455	18.06	97.55
7	4.136	0.901	0.0450	17.88	96.59
11	4.102	0.935	0.0467	18.56	100.2
22	4.101	0.936	0.0468	18.58	100.3
27	4.082	0.955	0.0477	18.95	102.3
33	3.873	1.164	0.0582	23.10	124.7
44	4.186	0.851	0.0425	16.89	91.23
49	4.1	0.937	0.0468	18.60	100.4
55	4.534	0.503	0.0251	9.986	53.92
73	4.517	0.52	0.026	10.32	55.74
100	4.265	0.772	0.0386	15.32	82.76
Average			0.041	16.29	88.00
Sum					1056.0

BIO virgin pellets results in seawater

Shaking time/hr	Pb in soln. (µg/l)	Concentration loss in soln.(µg/l)	mass loss- Pb in present pellets (µg)	% Mass uptake	Pb uptake by pellets (µg/kg)
0	5.037	0	0	0	0
1	4.782	0.255	0.0127	5.062	27.75
3	4.45	0.587	0.0293	11.65	63.88
7	4.585	0.452	0.0226	8.973	49.19
11	4.406	0.631	0.0315	12.52	68.67
22	4.268	0.769	0.0384	15.26	83.69
27	4.268	0.769	0.0384	15.26	83.69
33	4.232	0.805	0.0402	15.98	87.61
44	4.37	0.667	0.0333	13.24	72.59
49	4.495	0.542	0.0271	10.76	58.98
55	4.206	0.831	0.0415	16.49	90.44
73	4.295	0.742	0.0371	14.73	80.75
100	4.232	0.805	0.0402	15.98	87.61
Average			0.0327	12.99	71.24
Sum					854.91

Appendix 8

Residual PTE concentrations in multi element solution.

Elements	HDPE	LDPE	PET	PP	BIO
As					
1	5.0827	4.9015	5.0113	5.0066	4.9241
2	4.9791	5.0291	4.9641	5.1743	4.9156
3	5.0509	5.1367	5.0035	5.0419	4.9334
Mean	5.0376	5.0225	4.9930	5.0743	4.9244
SD	0.0531	0.1177	0.0253	0.0883	0.0088
RSD	1.0538	2.3442	0.5070	1.7417	0.1805
Cd					
1	4.6245	4.7604	4.7152	4.9549	4.5709
2	4.5688	4.6258	4.3704	4.7052	4.6327
3	4.7445	4.7237	4.4564	4.7992	4.4194
Mean	4.6459	4.7033	4.5140	4.8198	4.5410
SD	0.0897	0.0696	0.1794	0.1261	0.1097
RSD	1.9325	1.4798	3.976	2.6166	2.4159
Cr					
1	5.8730	6.0350	5.7996	6.1567	5.8249
2	5.7306	5.9594	5.6678	5.7278	5.8379
3	5.7834	5.8090	5.8714	5.7556	5.8794
Mean	5.7946	5.9345	5.7796	5.8801	5.8474
SD	0.0722	0.1150	0.1035	0.2400	0.0284
RSD	1.2474	1.9386	1.7866	4.0817	0.4871
Pb					
1	4.4434	4.3131	4.4403	4.3230	4.3526
2	4.3298	4.4672	4.3344	4.3714	4.4130
3	4.4517	4.4968	4.4005	4.2162	4.1362
Mean	4.4083	4.4257	4.3917	4.3035	4.3006
SD	0.0681	0.0986	0.0534	0.0793	0.1455
RSD	1.5451	2.2288	1.2180	1.8444	3.3838

Appendix 9

Zirconium concentration in plastic resin pellets in µg g^{-1}.

Type of pellets	**Zr in µg g^{-1}**
HDPE	
1	2.2791
2	0.0334
3	4.3997
Avg.	2.2374
SD.	2.1834
LDPE	
1	0.0236
2	0.0218
3	0.0519
Avg.	0.0324
SD.	0.0168
PET	
1	13.524
2	0.9122
3	6.8552
Avg.	7.0974
SD.	6.3097
PP	
1	0.7144
2	0.0271
3	0.0121
Avg.	0.2512
SD.	0.4011
BIO	
1	0.3641
2	2.5959
3	0.0909
Avg.	1.0170
SD.	1.3742

Appendix 10

Recovery of two sequential steps

location	Kuwait		Scotland		Scotland		Scotland	
Type	PE	PP	PE	PP	PE	PP	PE	PP
Year	2013	2013	2013	2013	2014	2014	2015	2015
Total As ($\mu g\ g^{-1}$)	18.15	7.71	9.37	1.90	5.45	2.52	4.35	1.23
% step 1*	68.9	72.5	70.3	99.4	59.8	49.6	100	100
% step 2*	31.1	27.5	29.7	0.57	40.2	50.4	0	0
Total Cd ($\mu g\ g^{-1}$)	0.411	0.1156	0.2618	0.098	0.428	0.248	0.649	0.313
% step 1	90.3	58.5	92.4	72.4	73.8	46.4	73.0	49.8
% step 2	9.7	41.5	7.6	27.6	26.2	53.6	27.0	50.2
Total Cr ($\mu g\ g^{-1}$)	96.3	29.25	24.86	11.63	23.0	5.17	17.22	10.42
% step 1	19.8	17.6	59.9	25.9	52.6	19.5	84.2	95.2
% step 2	80.2	82.4	40.1	74.0	47.4	80.5	15.8	4.8
Total Pb ($\mu g\ g^{-1}$)	35.41	29.26	35.76	17.83	19.7	13.17	53.66	25.55
% step 1	80.2	65.9	71.8	43.3	90.3	40.4	89.0	70.0
% step 2	19.8	34.0	28.1	56.6	55.3	59.5	10.9	29.9

Appendix 11

Bioaccessibility and mass balance

SBET- method				Acid extraction-method			
Elements	**Type of pellets**	**Bioaccessible ($\mu g\ g^{-1}$)**	**Non-bioaccessible ($\mu g\ g^{-1}$)**	**Elements**	**Type of pellets**	**Bioaccessible ($\mu g\ g^{-1}$)**	**Non-bioaccessible ($\mu g\ g^{-1}$)**
As	PE	0.975 ± 0.017	2.81 ± 0.15	As	PE	0.278 ± 0.019	2.67 ± 0.09
1		0.9865	2.8631			0.2636	2.6290
2		0.9551	2.9441			0.2706	2.6190
3		0.9845	2.6355			0.3003	2.7875
Avg		0.9754	2.8143			0.2782	2.6785
SD		0.0175	0.1599			0.0194	0.0945
RSD		1.8	5.65			6.97	3.54
	PP	0.904 ± 0.001	2.51 ± 0.138		PP	0.263 ± 0.0009	2.98 ± 0.06
1		0.9060	2.6488			0.2695	2.9219
2		0.9032	2.5284			0.2672	2.9874
3		0.9031	2.3720			0.2523	3.0428
Avg		0.9041	2.5164			0.2630	2.9840
SD		0.0016	0.1388			0.0093	0.0605
RSD		0.183	5.49			3.539	2.03
Cd	PE	0.0021 ± 0.0001	0.00788 ± 0.006	Cd	PE	$0.000383 \pm 8x10^{-5}$	0.0041 ±0.0008
1		0.002196	0.011681			0.000297	0.003454
2		0.001918	0.011104			0.000395	0.003805
3		0.002196	0.000860			0.000458	0.005042
Avg		0.002103	0.007882			0.000383	0.004100
SD		0.000160	0.006087			0.0000808	0.000833
RSD		7.305	77.1			21	20.3
	PP	< DL	0.00246 ± 0.001		PP	< DL	0.000328 ± 0.0005
1			0.00210				0.00388
2			0.00176				0.00273
3			0.00352				0.00322
Avg			0.00246				0.00328
SD			0.00093				0.00057
RSD			37.8				17.5
Cr	PE	0.051 ± 0.003	0.278 ± 0.08	Cr	PE	0.0267 ± 0.006	0.252 ± 0.001
1		0.0506	0.3065			0.0291	0.2519
2		0.0540	0.1864			0.0312	0.2536
3		0.0472	0.3429			0.0197	0.2511
Avg		0.0506	0.2786			0.0267	0.2522
SD		0.00343	0.0818			0.0061	0.0012
RSD		6.77	29.4			22.9	0.5

	PP	0.021 ± 0.014	0.266 ± 0.024		PP	0.0172 ± 0.003	0.264 ± 0.008
1		0.0384	0.2698			0.0187	0.2542
2		0.0111	0.2895			0.0191	0.2661
3		0.01556	0.2409			0.0137	0.271
Avg		0.02172	0.2668			0.0172	0.2640
SD		0.01468	0.0244			0.003002	0.00898
RSD		67.2	9.17			17.4	3.40
Pb	PE	0.242 ± 0.083	0.0496 ± 0.0319	Pb	PE	0.184 ± 0.011	0.074 ± 0.006
1		0.3256	0.0858			0.1910	0.0680
2		0.1581	0.0254			0.1714	0.0759
3		0.2423	0.0375			0.1895	0.0804
Avg		0.2420	0.0496			0.1840	0.0748
SD		0.0837	0.0319			0.0108	0.0062
RSD		34.5	64.3			5.86	8.34
	PP	0.15 ± 0.005	0.026 ± 0.001		PP	0.131 ± 0.004	0.0266 ± 0.003
1		0.1503	0.0270			0.1256	0.0264
2		0.1553	0.0251			0.1312	0.0229
3		0.1435	0.0257			0.1355	0.0304
Avg		0.1497	0.0260			0.1307	0.0266
SD		0.0059	0.00099			0.0049	0.00378
RSD		3.97	3.807			3.79	14.2

Mass balance reference

Elements	PE	PP
As	3.538	3.326
1	3.528	3.327
2	3.335	3.188
3	3.192	3.136
4	**3.398**	**3.244**
Avg	**0.166**	**0.0971**
SD	**4.89**	**2.99**
RSD		
Cd	0.00419	0.00856
1	0.00418	0.00819
2	0.00401	0.01036
3	0.00518	0.01092
4	**0.004392**	**0.00951**
Avg	**0.000534**	**0.00133**
SD	**12.1**	**13.9**
RSD		
Cr	1.230	0.322
1	0.325	0.320
2	0.378	0.310
3	0.324	0.283
4	**0.564**	**0.309**
Avg	**0.444**	**0.0180**
SD	**78.7**	**5.83**
RSD		
Pb	1.187	0.223
1	0.360	0.223
2	0.260	0.214
3	0.268	0.115
4	**0.296**	**0.194**
Avg	**0.055**	**0.052**
SD	**18.6**	**27.2**
RSD		