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Adsorption of Organic Pollutants in Microplastic in the Arctic Ocean

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Unni Mette Nordang

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Preface

This thesis was carried out at the Norwegian Institute for Air Research (NILU) located at FRAM - High North Research Centre for Climate and the Environment (The Fram Centre) in Tromsø from March 2018 – May 2019. Sampling in Ny-Ålesund was performed by the Norwegian Polar Institute, and in Longyearbyen by NILU. The project was founded by The Fram Centre, flagship for "Hazardous compounds", by the project "POPs adsorbing to Marine plastic litter in the Arctic marine environment acting as a new vector of exposure" (#312018) and the JPI OCEAN project "Direct and indirect ecotoxicological impacts of microplastics on marine organisms" (PLASTOX).

An additional educational project, the NFR INPART project PlastPoll, focusing on plastic pollution as a global challenge, founded expenses in connection with a trip to China from 12 – 24 February 2019. Topics for the trip was "towards harmonised understanding, education and methodology in Europe, USA and China".

Tromsø, 2019-05-13

signature

Unni Mette Nordang

Acknowledgements

Abstract

Oceans all over the world are housing large quantities of plastic pollution and persistent organic pollutants (POPs). Concerns regarding both of them having lipophilic characteristic that allows a successful partitioning of POPs to plastic if in contact in an aqueous medium, led to this study where the relationship between different types of plastic and POPs in the Arctic ocean are looked into. In two seasons, respectively summer and winter, pellets of polyethylene high-density (PE-HD), polyethylene low-density (PE-LD), polyethylene terephthalate (PET) and polypropylene (PP) have been located in Kongsfjorden, the Arctic ocean outside Ny-Ålesund, Svalbard. The concentration of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in plastics have been analysed before entering the ocean and during the seasons. Also, a selection of marine plastic garbage collected in Longyearbyen, Svalbard, was identified and analysed. The POPs adsorb more to rubbery polymers (PH-HD, PE-LD, PP) than glassy polymers (PET). A clear variation between type of plastic and concentration was found, from highest to lowest: PE-HD > PE-LD > PP > PET. The plastics stability in regard to chemical structure and possible surface changes was investigated with Fourier-transform infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM) respectively. All plastics were chemically stable after being in the ocean. Among the garbage samples, differences concerning how and how many particles breaking of as microplastics and type of plastic were discovered. Based on results in this study, PE-HD is classified as the most harmful and PET the least harmful type of plastic if entering the Arctic marine environment, both regarding adsorption of POPs and degree of degradation.

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Abbreviations

ATR	Attenuated total reflectance
DCM	Dichloromethane
e.g	For example
FTIR	Fourier-transform infrared spectroscopy
GC-MS	Gas chromatography – Mass spectrometry
GPC	Gel permeation chromatography
HCB	Hexachlorobenzene
HOC	Hydrophobic organic chemicals
LOD	Limit of detection
LRAT	Long-range atmospheric transport
NILU	Norwegian Institute for Air Research
PA	Polyamide
PBDE	Polybrominated diphenyl ether
PC	Polycarbonate
PCB	Polychlorinated biphenyl
PE	Polyethylene
PE-HD	Polyethylene high-density
PE-LD	Polyethylene low-density
PET	Polyethylene terephthalat
PHA	Polyhydroxyalkanoate
PHB	Polyhydroxybutyrate
PLA	Polyactic acid
POPs	Persistent organic pollutants
PP	Polypropylene
PS	Polystyrene
RRF	Relative response factor
SEM	Scanning electron microscopy
SIM	Selected ion monitoring
SPE	Solid phase extraction
UiT	University of Tromsø - The Arctic University of Norway
UPVC	Unplasticized polyvinyl chloride
UV	Ulraviolet

1 Introduction

1.1 Plastic

Plastic is a term derived from the Latin "plasticus" which is derived from the Greek "plastikos" that was used to describe something able to be molded or fit for molding. This terminology was actually used already in the 17ᵗʰ century, long before the first plastic material, Parkesine, was invented (PlasticsEurope, 2018, p. 16).

During the end of World War II in 1945 plastic producers investigated new consumer markets to support the war effort by substituting traditional materials with plastic, and since then the use of plastic has grown exponentially. Figure 1 illustrates the global plastic production since 1950 (red line) and future trends to 2050 (yellow line). In 2017 the world plastic production reached 348 million tonnes. Only 14 % of plastics are effectively recycled, while approximately 67% of all plastic ever produced has been released into the environment, where it still remains (Azoulay et al., 2019, pp. 5-6).
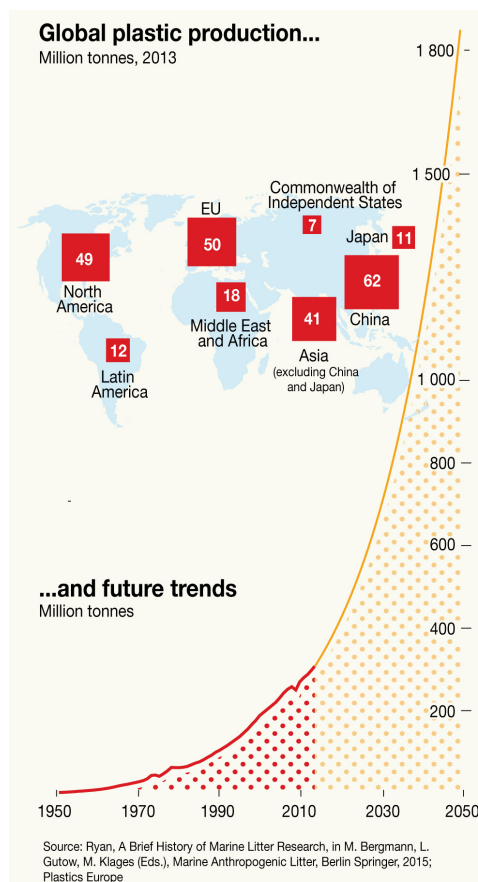
Figure 1: Global plastic production from 1950 to 2013 (red line) and estimated future trends until 2050 (yellow line) (Azoulay et al., 2019, p. 6).

According to United Nations environmental Programme UNEP, the ubiquitous plastic debris in the world's oceans is one of the world largest growing problems. If the future plastic production continues as estimated, there will by weight be more plastic than fish in the oceans by 2050 (Hallanger and Gabrielsen, 2018, p. 5).

The largest producer of plastics is China, followed by Europe and North America. In 2017 Europe used 40% of produced plastic in packaging, 20% in building and constructions, 10% in automotive, 6% in electrical and electronics, 4% in household, leisure and sports, 3% in agriculture and the remaining 17% was used for other applications (PlasticsEurope, 2018, p. 24). In other words, in today's society plastics are widely used in thousands of different end products and in a broad range of applications.

Plastics are divided in two categories: thermosets and thermoplastics. When <u>thermoset</u> plastics are heated a chemical change occur, and a three-dimensional network is created. After being heated and formed it is not possible to re-melt and reform the plastic material. Examples of thermosets plastics are silicone, vinyl ester and epoxy resin. When <u>thermoplastics</u> are heated they melt, and when cooled they hardened. These characteristics are reversible, and the plastics can be reheated, reshaped and frozen repeatedly. Typical thermoplastics are polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polyethylene terephthalat (PET) and polystyrene (PS) (PlasticsEurope, 2018, p. 17).

The polymeric backbone structure, which are made from a diverse suite of polymer types, constitutes the fundamental differences between plastic types. These polymers are augmented with an array of additives in production to give the plastic desired properties. Examples of additives are flame retardants (often used in building materials and electronics), stabilizers (increases the stability and longevity of an end product), colorants (gives product wanted colour), reinforcements and fillers (improves the plastics mechanical properties) and plasticizers (amends for example hard, glassy plastic into a soft, rubbery plastic) (Rochman et al., 2019, pp. 703-706).

Plastic composed by different polymers with different additives leads to a range of products with diverse morphologies and colours. The morphology/shape of small plastic products (< 5 mm) are often categorized as foams (compressible, soft, cloud-like), spheres (round), pellets (cylindrical, rounded), films (thin, flat, malleable), fragments (rigid structure in many

shapes), fibers (flexible, looks like small threads) and fiber bundles (20 or more fibers compromised completely together). Plastic can adsorb pollutants, and polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) may therefore be present in plastics found in nature. (Rochman et al., 2019, pp. 703-706).

1.1.1 Microplastic

Scientists do not always degree on what size microplastic should be defined as, but most often it is defined as plastic particles < 5 mm in one dimension. Scientific publications, media articles and policy reports often incorrectly introduce microplastics as if they are a single compound or one type of material. The fact is that microplastics is a catch-all term for a variety of unique chemical compounds, and every piece of plastic is a complex chemical cocktail, illustrated in Figure 2 (Rochman et al., 2019, pp. 703-704).
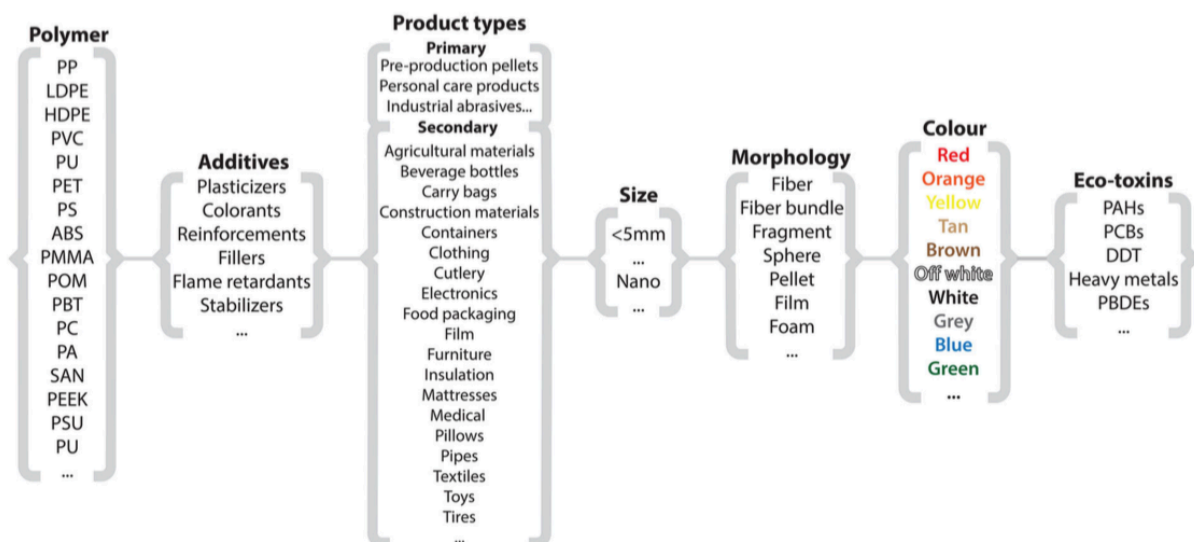
Figure 2: Microplastics are made with a variety of polymers that are added different additives, leading to a multitude of products in a lot of sizes, morphologies and colours. When these plastic products are found in nature, they can adsorb and leak numerous environmental chemical contaminants, including persistent organic pollutants (POPs) and heavy metals. Please note that none of the lists are complete (Rochman et al., 2019, p. 704).

Primary microplastics are plastic products that are produced to be < 5 mm, like microbeads used as abrasives in personal care products or for industrial use and preproduction pellets used to manufacture other plastic products, while secondary microplastics are by-products from breakup and fragmentation of bigger plastic products (Rochman et al., 2019, pp. 703-706).

1.1.2 Degradation of plastic in to microplastic in the marine environment

In the marine environment plastic can be degraded through many different pathways including photodegradation (occurs when exposed to ultraviolet (UV) radiation and oxygen), hydrolysis (reacts with water and results in a physical change by splitting the polymer chains into smaller pieces) and mechanical degradation (fragmentation by external forces and abrasion from sand and stones due to tidal and wave forces). The dominant process is photodegradation through solar UV radiation. Polymer composition and presence of additives highly influences the rate of plastic degradation, together with several other environmental parameters such as temperature, amount of sunlight, oxygen levels and water. The plastic typically undergoes surface changes, discolours and becomes weak and brittle during the degradation process. Figure 3 shows estimated decomposition rates of common marine debris items. Degradation of plastic occurs very slowly, and in general will lower temperatures, less oxygen, less light and less biota slow down the process.

Figure 3: Estimated rates for decomposition of common debris items often found in the marine environment (Booth et al., 2017, p. 61).

The marine environment is divided in three compartments: the sea surface, the shoreline and the seabed, which all are having different conditions with respect to temperature, light, oxygen and biota. When plastics are immersed in seawater, its surface rapidly becomes coated with organic and inorganic compounds and biofilms, leading floating plastic objects to sink to the bottom where they due to low temperatures, low UV-radiation and absence of wave forces can persist for centuries (Booth et al., 2017, pp. 43-51) (Hallanger and Gabrielsen, 2018, p. 6). Plastic debris and microplastic in the ocean can harm the marine life as animals in all sizes from large fishes and birds to small zooplanktons are ingesting it. It is expected, depending on size, that microplastics leaves the gut and enters organs, tissues and cells in living organisms. The increasing amount of decreasingly sized microplastics in the oceans rise concerns for the increasing potential to be transferred outside the gut in living organisms, and that it might even enter the food webs (Rochman et al., 2019, p. 709)

1.1.3 How are plastics entering the marine environment and do we find it in the Arctic?
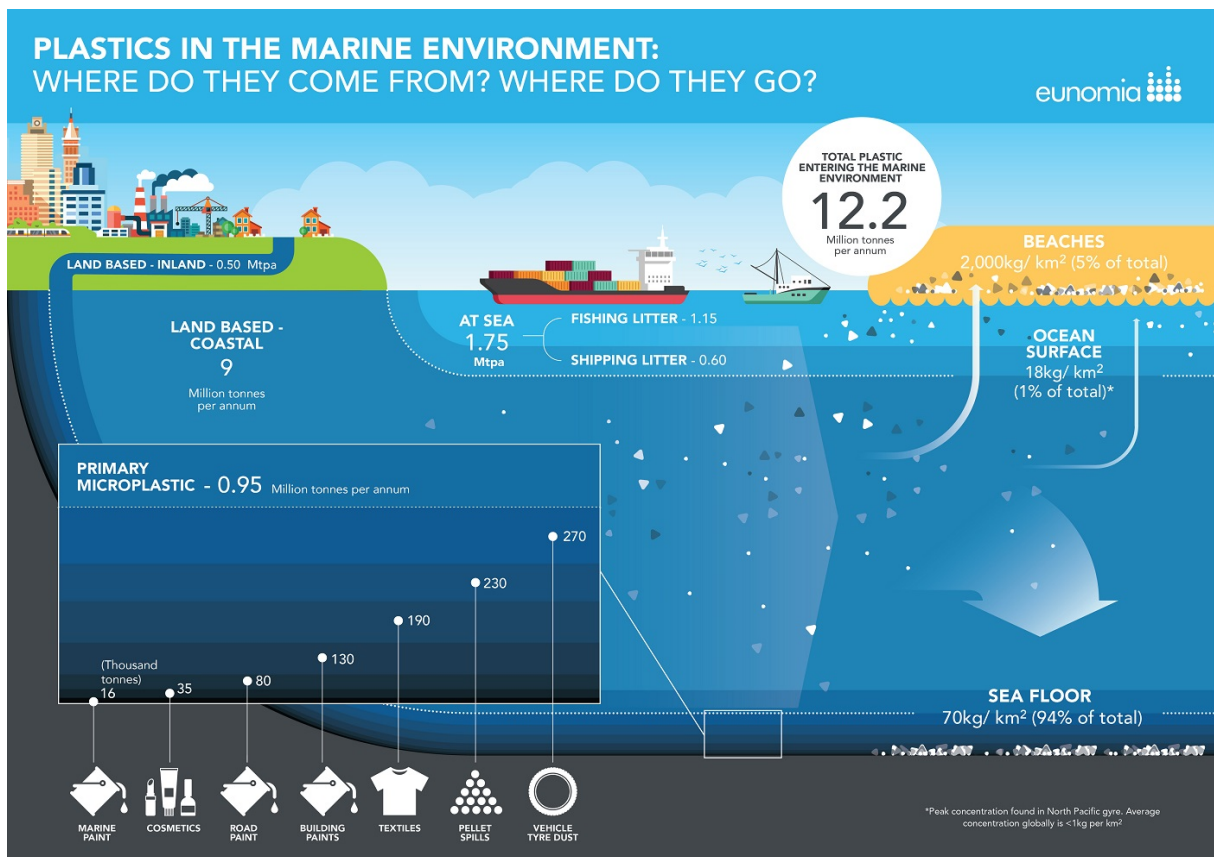
Figure 4: A summary of depositions and principal sources of plastics and microplastics entering the marine environment (Sherrington, 2016).

Figure 4 illustrates several scenarios for how microplastics enters the marine environment and where they are deposited. In total 12.2 million tonnes of plastics enter the marine environment per annum, where land-based sources accounts for more than 80 % of it. Larger plastic litter such as drink bottles and other types of packaging is the main contributor, however emission of primary microplastics are also of importance. The remaining 20 % are released from the sea, mostly due to fishing activities. As much as 94 % of ocean entered plastics ends up on the sea floor, which makes sense regarding surface coating that leads to sinking (Sherrington, 2016).

Plastic has been observed in all abiotic environments within the European Arctic, also in remote areas with low human impact (Hallanger and Gabrielsen, 2018, p. 6) Most of the microplastic found in Svalbard are mainly fibers. Parts of these have spent a long period at sea and are transported long distances before arriving the Arctic, others arise from local sources as fishing, commercial activities, textile washing and sewage. Several inflowing systems from the North Atlantic brings microplastics to the Arctic, as well as winds are picking up lighter plastic particles and transport them far by air (Lusher et al., 2015, pp. 2-6) (Rochman et al., 2019, p. 709).

1.2 Plastic types analysed in the project

This master project is focusing on four of the most common plastic types PE high-density (PE-HD), PE low-density (PE-LD), PP and PET, produced from three different polymers.
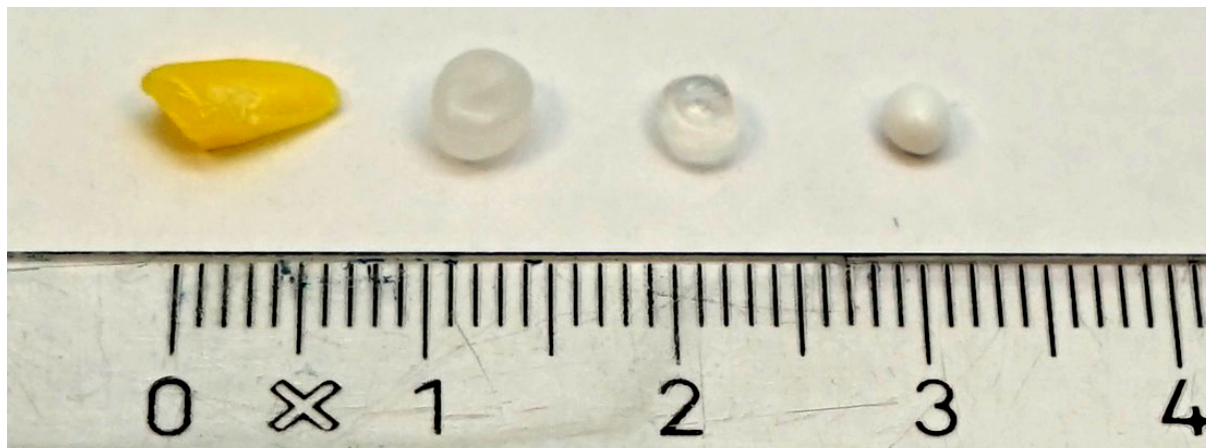
Figure 5: Plastic pellets analysed in the project, from left to right: PE-HD (≈ 5 mm), PE-LD (≈ 4 mm), PP (≈ 3 mm) and PET (≈ 2 mm).

1.2.1 PE-LD and PE-HD
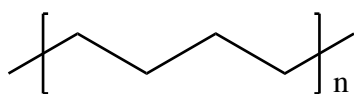
Figure 6: Chemical structure of PE, created in ChemDraw.

PE is the worlds most manufactured plastic polymer, and from 1950 to 2015 it constituted 36% of all plastic (Azoulay et al., 2019, p. 27). It is a rubbery polymer and its chemical structure consists of a -CH_2- chain (Rochman et al., 2013, p. 1651) (Rochman et al., 2019, p. 707). Due to its ability to be made with density variating between 0.88 g/cm^3 – 0.97 g/cm^3, PE exists in several versions having distinct characteristics. PE-LD are usually used in reusable bags, agricultural films, food packing films, trays and containers. PE-HD are normally used in shampoo bottles, milk bottles, toys, pipes and general houseware products. PE has mechanical functions including low strength and high flexibility, does not absorb water and has melting point from 105–180 °C depending on its quality. PE is not easily affected by oxidising or reducing agents, strong acid or bases because it has a high chemical resistance. Photo-initiated oxidative degradation initiated by UV radiation is the main degradation process of PE in the marine environment (Booth et al., 2017, pp. 54-55) (PlasticsEurope, 2018, p. 27).

1.2.2 PP
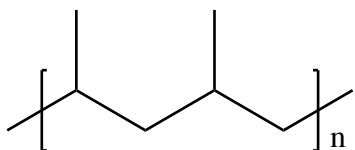
Figure 7: Chemical structure of PP, created in ChemDraw.

PP is the second most produced polymer and represented 21% of the World´s produced plastic from 1950 – 2015 (Azoulay et al., 2019, p. 27). It is also a rubbery polymer, and its chemical structure is similar to PE plus additional methyl groups (Rochman et al., 2013, p. 1651) (Rochman et al., 2019, p. 707). The density of PP is 0.90 g/cm^3 – 0.92 g/cm^3. It is commonly used in textiles, automotive parts, pipes, ropes, reusable plastic containers, packing and labelling. The mechanical functions of PP are tougher than PE, but it is still flexible and has melting point from 160 – 170 °C depending on degree of crystallinity. As for PE, PP has high chemical resistance, and is mainly degraded by UV initiated photo-initiated oxidative degradation in the marine environment (Booth et al., 2017, p. 56).

1.2.3 PET
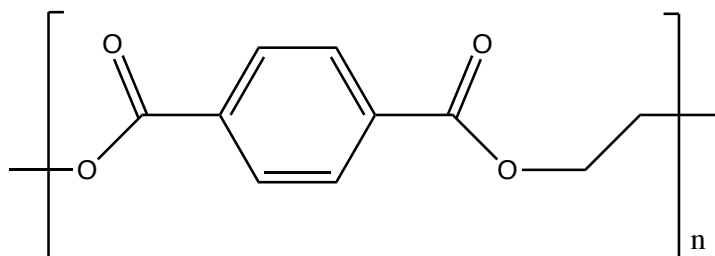
Figure 8: Chemical structure of PET, created in ChemDraw.

PET is among the six types of plastics most produced between 1950 and 2015 and constitutes about 10 % of all plastic (Azoulay et al., 2019, p. 27). It is a glassy polymer and has a chemical structure with heteroatoms in its main chain, consisting of carbon, hydrogen and oxygen (Rochman et al., 2013, p. 1651) (Rochman et al., 2019, p. 707). The density of PET is around 1.4 g/cm^3 and it has melting point at 244 °C. It is generally used in bottles for soft drinks, juices, water and cleaners. PET is normally degraded by photo-oxidative and hydrolytic degradation in the marine environment. It is not that chemical resistant as PE and PP, and under acidic and basic conditions the rate of degradation increases (Booth et al., 2017, p. 58).

1.3 Persistent organic pollutants (POPs)

Persistent organic pollutants (POPs) are stable, anthropogenic organic chemicals produced both deliberately like industrial chemicals and pesticides, and by accident as for example by-products from industrial or combustion processes (Eljarrat and Barcelo, 2003, p. 655) (Girard, 2014, pp. 410-411). They are resistant to environmental degradation due to their physical and chemical properties, therefore persistent once released to the environment. By bioconcentration, POPs enter living organisms, and by bioaccumulation the POP concentrations increase at higher levels in the food chain. They are toxic to humans and wildlife, and health problems like hormone disruptions, allergies, suppressed immune system, reproduction disorders, neurologic disorders and increasing cancer risk are suspected effects (StockholmConvention, 2008c). Figure 9 gives an brief overview how POPs moves in the environment and finally enters the food chain (Nair, 2018).
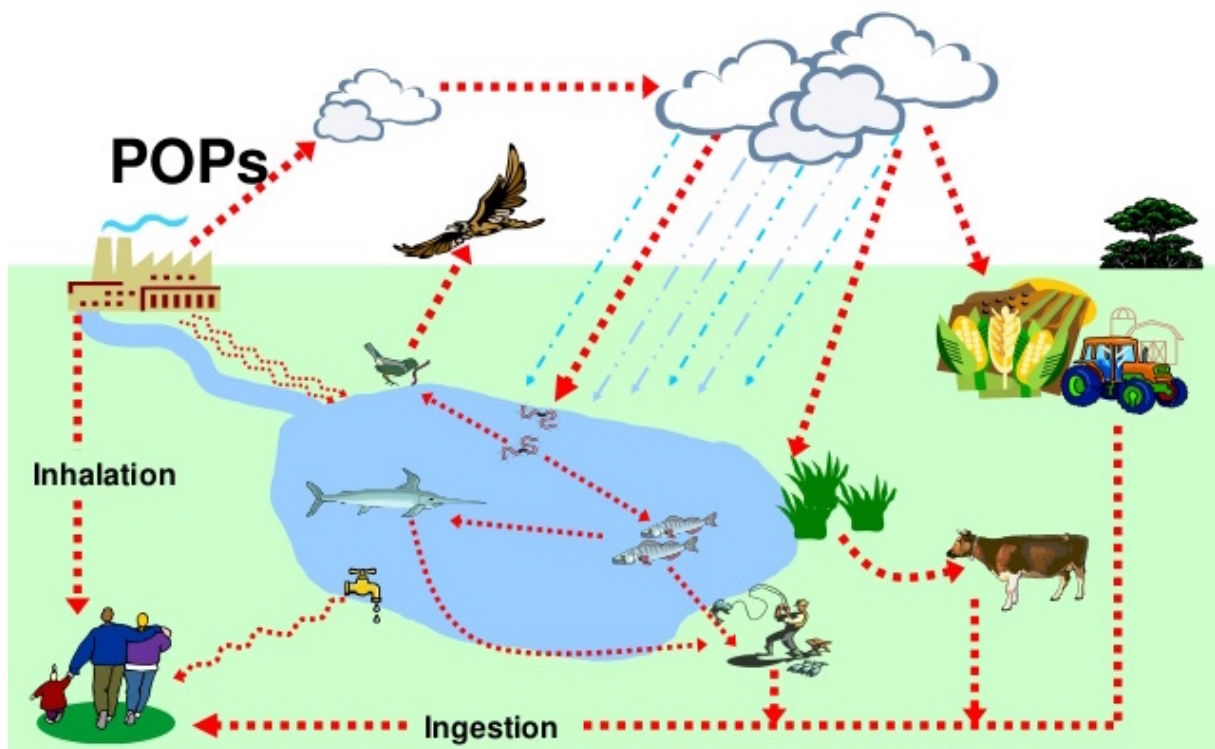
Figure 9: Toxic POPs circulates in the environment and may enter the food chain and living organisms (Nair, 2018).

Combination of persistent and toxic was and still are of high concern. The discovery of POPs in the Arctic, an area thousands of miles away from where POPs are manufactured and used, became the major impetus for the Stockholm Convention. In May 2001, 90 countries signed the Convention, promising to reduce or eliminate the production, use and release of 12 key POPs, and in May 2004 it entered into force (StockholmConvention, 2008b) (Girard, 2014, p. 411).

1.3.1 POPs in the Arctic

The presence of POPs in the Arctic, unable to relate to known use and/or release from sources within the area, are due to long-range transport. Water currents, Arctic rivers, sea-ice drift and atmosphere are transport routes to and within the Arctic. A lot of parameters effects how they move, including geographic location, weather conditions and physical-chemical properties such as volatility, water solubility and ability to adsorb to particles (Burkow and Kallenborn, 2000, pp. 87-88). Under environmental temperatures POPs can enter the gas phase and volatilise into the atmosphere from water bodies, soils and vegetation. Depending on temperature in the atmosphere, POPs partition between aerosols and particles, and they can travel long distances owing to resistance against breakdown reactions in air, before deposition appears (Jones and De Voogt, 1999, p. 209). Figure 10 is from the theses *"Study of Long Range Transported Pollutants in Arctic Soil"* by Carolin Huber and explains two ways of long range atmospheric transport (LRAT) of pollutants from lower latitudes to the Arctic.
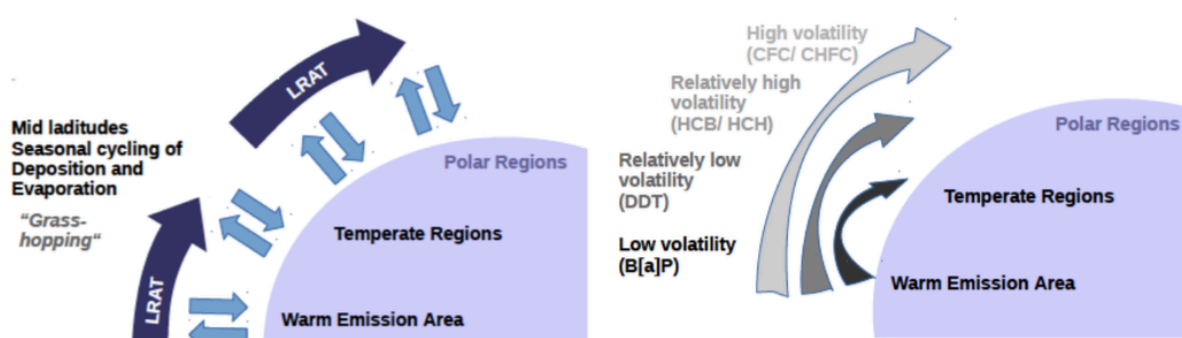
Figure 10: Schematic description of POPs can be transported over long distances by grasshopper effect (left) and global fractionation (right) (Huber et al., 2017, p. 11).

The grasshopper effect (left) is based on the tendency POPs have to undergo several evaporation and deposition steps between air, soil, water, snow, ice and other environmental media on its way to the Arctic. The equilibrium concentrations of POPs in sea waters, which are a large reservoir for them, are higher than in air, and of the total amount of POPs is only a tiny fraction present in the atmosphere (Burkow and Kallenborn, 2000, p. 88). Depending on temperature and volatility, pollutants are transported and deposited at different latitudes, referred to as the global fractionation (right). Pollutants with low volatility such as benzo(a)pyrene (B[a]P) evaporate very slowly and tend to remain close to their sources and deposit locally, while semi-volatile POPs like dichlorodiphenyltrichloroethane (DDT), hexachlorobenzene (HCB) and hexachlorocyclohexane (HCH) undergo long-range transport

and deposits at higher latitudes. The higher volatility, the longer transported before deposited. High volatile compound as chlorofluorocarbon (CFC) and chlorinated hydrofluorocarbons (CHFC) are preferentially deposited in polar regions by reason that they condense at around -30 °C (Wania and Mackay, 1996, p. 393).

Pollutants tend to of partition more easily from air at cooler temperatures, and concentrations seems to increase with distance from source (Wania and Mackay, 1996, p. 392). The rate of re-release from surface to atmosphere are slower in colder areas, and concern that Arctic and polar regions may be acting as "global sinks" for POPs has been expressed (Jones and De Voogt, 1999, p. 215). Owing to the Stockholm Convention the concentration of many POPs in the Arctic air have decreased during the past few decades (Ma et al., 2011, p. 255).

1.4 POPs of interests in the project

1.4.1 HCB
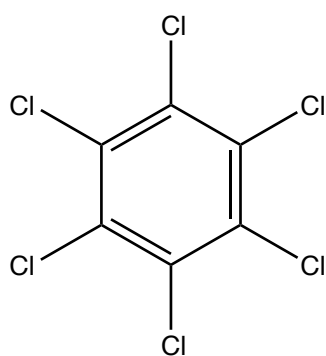
Figure 11: Chemical structure of HCB, created in ChemDraw.

HCB is an industrial by-product formed during the production of several pesticides and chlorinated compounds. It was first introduced in 1945 and in 1960 it had limited use as a fungicide. Due to long half-life in biota (2.7 - 5.7 years) and high lipophilicity is it relative bioaccumulate, and higher doses of HCB in living organisms is lethal. It is listed as one of the 12 key POPs in the Stockholm Convention (de March et al., 1998, p. 186) (StockholmConvention, 2008a).

1.4.2 PCBs
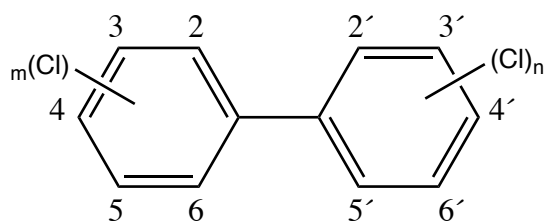
Figure 12: Chemical structure of PCBs, created in ChemDraw.

PCBs is a family of POPs consisting of 209 different compounds depending on chlorine substitutions on the biphenyl rings. They are chemically stable and heat resistant industrial products that were introduced in 1929 and used worldwide as e.g. hydraulic and heat exchange fluids and oils for lubricating, cutting, in capacitor and transformer, and as additives in paint, carbonless copy paper and plastics. Most PCBs are extremely persistent in the environment, having half-lives variating from 10 days to 2 years depending on the degree of chlorination. They are toxic to fish and harmful to humans. A large number of peoples have been exposed to PCBs through food contamination. Like HCB, the group of PCBs are listed as a key POP in the Stockholm Convention. Open use is banned, but there are still equipment in use contaminated or containing PCBs (de March et al., 1998, p. 187) (StockholmConvention, 2008a).

1.4.3 PBDEs
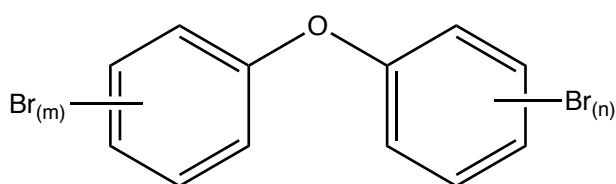
Figure 13: Chemical structure of PBDEs, created in ChemDraw.

PBDEs are brominated flame retardants structurally related to PCBs, but with bromines substituted instead of chlorines and an oxygen between the two phenyl rings (de March et al., 1998, p. 188). Production of PBDEs began in the 1970s. They are industrial compounds used to make materials more fire resistant such as electric and electronic equipment, textile back-coating in furniture, curtains, carpets, rubber for coating wire, building sectors, and plastics. PBDE additives are mixed with the product directly during manufacturing and do not

react with the material, therefore may migration from product and releasement into the environment occur. Negative effect on sex hormones, reproduction and neurological functions are some of the toxicology of PBDEs (de Wit et al., 2010, pp. 2886-2887). In 2009, tetra-, penta-, hexa- and hepta-BDEs were added to the Stockholm Convention, and in 2013 was also deca-BDE included (StockholmConvention) (Sindiku et al., 2015).

1.5 Adsorption of POPs in microplastic in the marine environment

Because both POPs and plastics are relative lipophilic, a successful partitioning of POPs to plastic through Van der Waals forces tend to happen if in contact with each other in an aqueous medium (Pascall et al., 2005, p. 164). Also, the hydrophobic/"water-hating" characterization of POPs makes them favour adsorption to plastic instead of being in the water phase (Jones and De Voogt, 1999, p. 209).

1.5.1 Octanol/Water Partition Coefficient (K_{ow})

The octanol/water partition coefficient (K_{ow}) has turned out as a key parameter in the study of the environmental fate of organic compounds such as POPs. It can be used to estimate water solubility, which is an important property as it affects both the fate and transport of chemicals. Increase in size of organic molecules leads to decrease in polarity and water solubility, which results in the molecules are becoming more hydrophobic. This characteristic can be measured and expressed with K_{ow}, and is defined as the ratio of the molar concentrations of a chemical in n-octanol and water. It is constant at a certain temperature for a given compound and expresses an organic contaminants tendency to move from water phase to the immiscible n-octanol phase. K_{ow} values are normally reported in the base 10 logarithm, log K_{ow}, by reason that values for important environmental contaminants can be in the millions (Girard, 2014, pp. 419-420). A greater K_{ow} value represents greater presence in octanol than in water, and a lower K_{ow} value represents greater presence in water than in octanol (Cicilio, 2013, p. 4).

1.5.2 Influencing factors

Uptake of POPs (sorbate) by plastics (sorbent) are influenced by several factors including the physical and chemical nature of POPs, the physical and chemical nature of the plastic, the POP

concentrations in contact with the plastic, the characteristics of the phase in contact with the absorbent, the contact time of the system and the environmental temperature (Pascall et al., 2005, p. 164). Higher surface area to volume ratio on plastic are also affecting as it results in higher capacity of adsorbing POPs (Rochman et al., 2019, p. 709). Figure 14 illustrates mass of different environmental media in the oceans (A) and percentage of hydrophobic organic chemicals (HOC) bound to these media (B). HOC represents here PCBs, PBDEs and perfluorooctanoic acid (PFOA) (Koelmans et al., 2016, pp. 3318-3319).
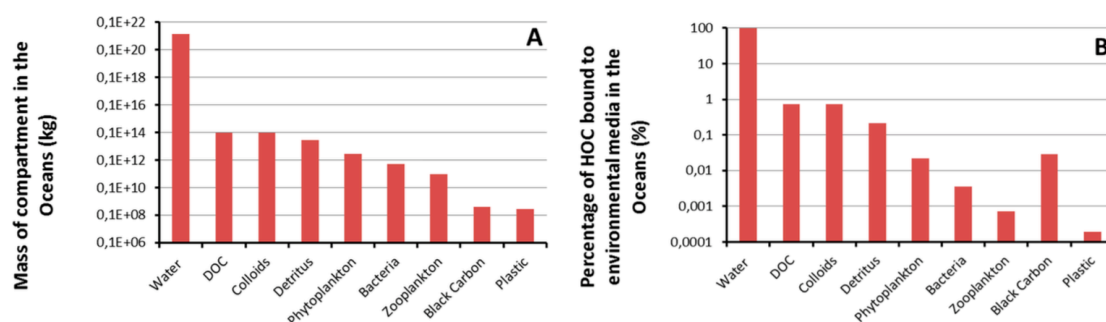
Figure 14: Abundances of environmental media in the oceans (Panel A) and distribution of hydrophobic organic chemicals (HOC) across these environmental media (Panel B). DOC = dissolved organic carbon (Koelmans et al., 2016, p. 3319).

HOC distribution is dominated by water that holds 98.3% of it, whereas plastic holds 0.0002%. In other words: There are a lot of HOC in the oceans that never will come in contact with plastic debris.

1.5.3 Harmful?

Additives such as POPs in plastics indicate that recycling of plastic is not strait forward. These POPs can be transferred to new plastic products during the recycling process, as seen for e.g. toys (Azoulay et al., 2019, p. 40), where as humans can be exposed to these compounds. The ability of microplastics to be transported long distances, and also leach additives and/or leak (already adsorbed) POPs to the environment, makes it act as a source of chemical contaminants that may are having potential harmful effects (Schoolmeester et al., 2019, p. 25). If exposure to microplastics have negative or neutral effect on organisms are debated by many researches. The study *"A meta-analysis of the effects of exposure to microplastics on fish and aquatic invertebrates"* (Foley et al., 2018) provides evidence supporting both sides. Exposure to microplastics has been found to negatively affect an organism in many studies, while in others, biological effects from microplastics are not detected. The great diversity of physical and

chemical characteristics in microplastics to which organisms are being exposed might be the reason for this discrepancy (Rochman et al., 2019, p. 709).

1.6 Clean-up

Separation, identification and measurement of one or more components from a complex mixture have to be done in the vast majority of real analytical problems (Harris, 2010, p. 538). Environmental samples are no excuse, as they generally contain a complex mixture of organic compounds (Medeiros and Simoneit, 2007, p. 272). Some of these compounds can interfere with the determination of specific analytes in further analysis, as for example in gas chromatography – mass spectroscopy (GC-MS), it is therefore desirable to remove these. By performing one or more clean-up steps, which takes advantage of the difference in chemical or physical properties of the components, can unwanted matrix be removed. There are a lot of different clean-up techniques available, and which one to choose depends on several criteria such as: what type of matrix do you want to remove, which degree of purification is required, laboratory constraints, cost of setup and execution relative to other candidate clean-ups, appropriate capacity for the sample size to be used, and previous experience in the laboratory (Erickson, 1997, pp. 186-187, 228-232). Gel Permeation Chromatography (GPC) and Solid Phase Extraction (SPE) are two examples of clean-up techniques and used in this study.

1.6.1 Gel Permeation Chromatography (GPC)

GPC is a molecular exclusion chromatography technique used for separation of molecules according to their size and/or shape. An ideal exclusion has no interactions between the solute and the stationary phase. Molecules within a sample are separated by a liquid (mobile phase) passing through a column packed with porous gel (stationary phase). Figure 15 illustrates how pores in the gel will allow molecules that are small enough to penetrate into them, while larger molecules will be excluded. Small molecules must therefore pass an effectively larger volume before leaving the column than larger molecules, resulting in elution of larger molecules first. Resolution gets greater and flow rate slower the finer the particle size of the gel is (Harris, 2010, pp. 542-543, 647-648).
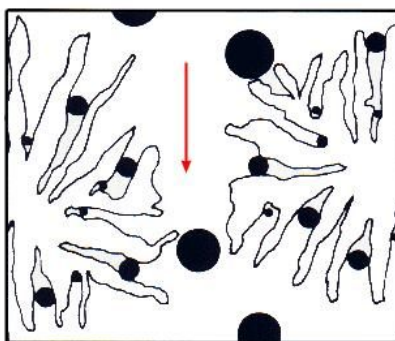
Figure 15: Illustration how porous gel (stationary phase) inside a GPC column works. Molecules (black dots in the figure) small enough can penetrate into gel pores, the larger ones will float with the solvent (mobile phase), go directly through the column and be eluted first (Waters, 2018b).

System setup

A GPC system is illustrated in Figure 16. The solvent is led through the system by a pump, and the sample of interest enters the system via an injector. As the molecules are separated and leaves the column, they are detected and by a detector. UV-detector is often used. A connected screen visualizes a chromatogram created by the detector signals, where each peak in the chromatogram represents an eluted compound, and the height/area of the peaks corresponds to amount. Portions of the column eluent that contains components of interest are collected by a fraction collector, rest goes to waste (Waters, 1999) (Waters, 2018a) (Waters, 2018b).
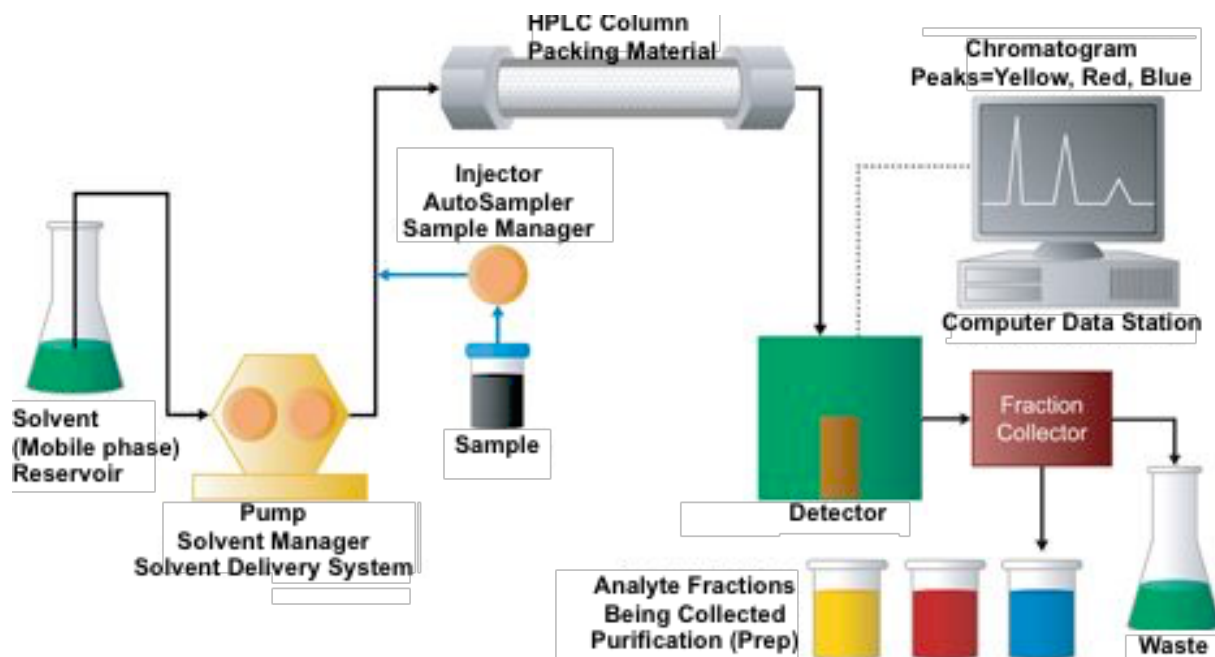
Figure 16: Schematic setup of a gel chromatography system (Waters, 2018c)

Column calibration

In order to decide at what time and for how long the fraction collector should collect eluent, information of how the columns work is needed. Injection of a test/calibration solution with known amounts of known compounds gives a sample calibration chromatogram (Figure 17), that illustrates at what time the different components are passing out from the column.
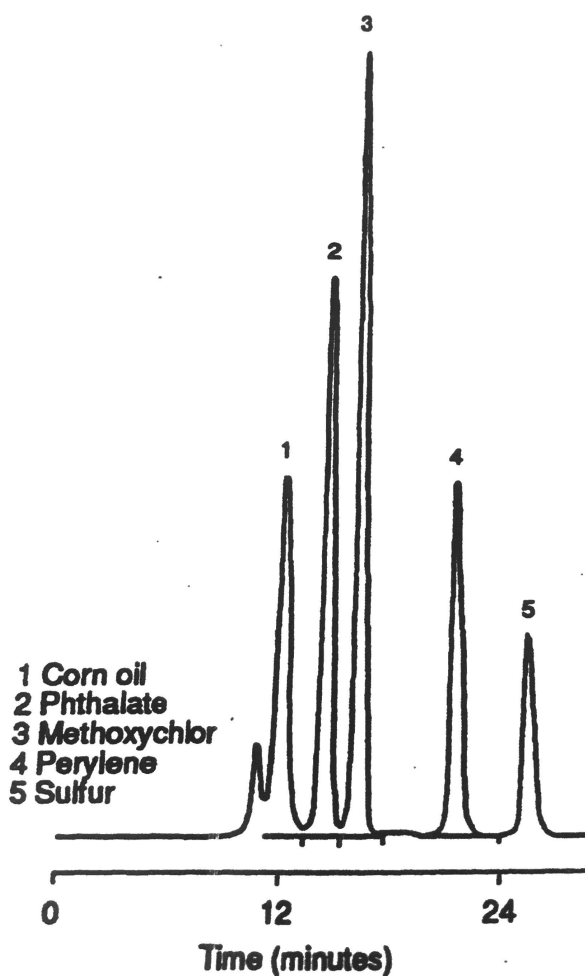
Figure 17: Sample Calibration Chromatogram (Waters, 2007).

Depending on which types of components it is desirable to collect/exclude, the time on the fraction collector is set up based on the calibration chromatogram. The elution time can vary after running several samples, as possible air, dirt and contamination may get inside the column. A good routine is to run the calibration solution on the beginning of each day the system will be used, in case adjustments are needed. Since the flow rate of the mobile phase affects the time different components uses to pass through the column, is it important to set the flow rate to the same rate as for the samples, before injecting the calibration solution (Waters, 2007).

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1.6.2 Solid Phase Extraction (SPE)

In SPE analytes are isolated from a sample by using a small volume of a chromatographic stationary phase or a molecular imprinted polymer (Harris, 2010, pp. 713-714). Small, porous particles with a bonded organic phase, such as silica or florisil, are typically solid phase materials. The extraction itself can be carried out in different ways, and for chemical analysis it is common to pack the solid phase material between two frits in a small tube and pass the liquid sample through the tube. Substances within the sample are extracted by solid phase particles and eluted by washing with an appropriate liquid solvent (Fritz, 1999, p. 2). Figure 18 illustrates steps involved in SPE: conditioning, sample addition and elution.
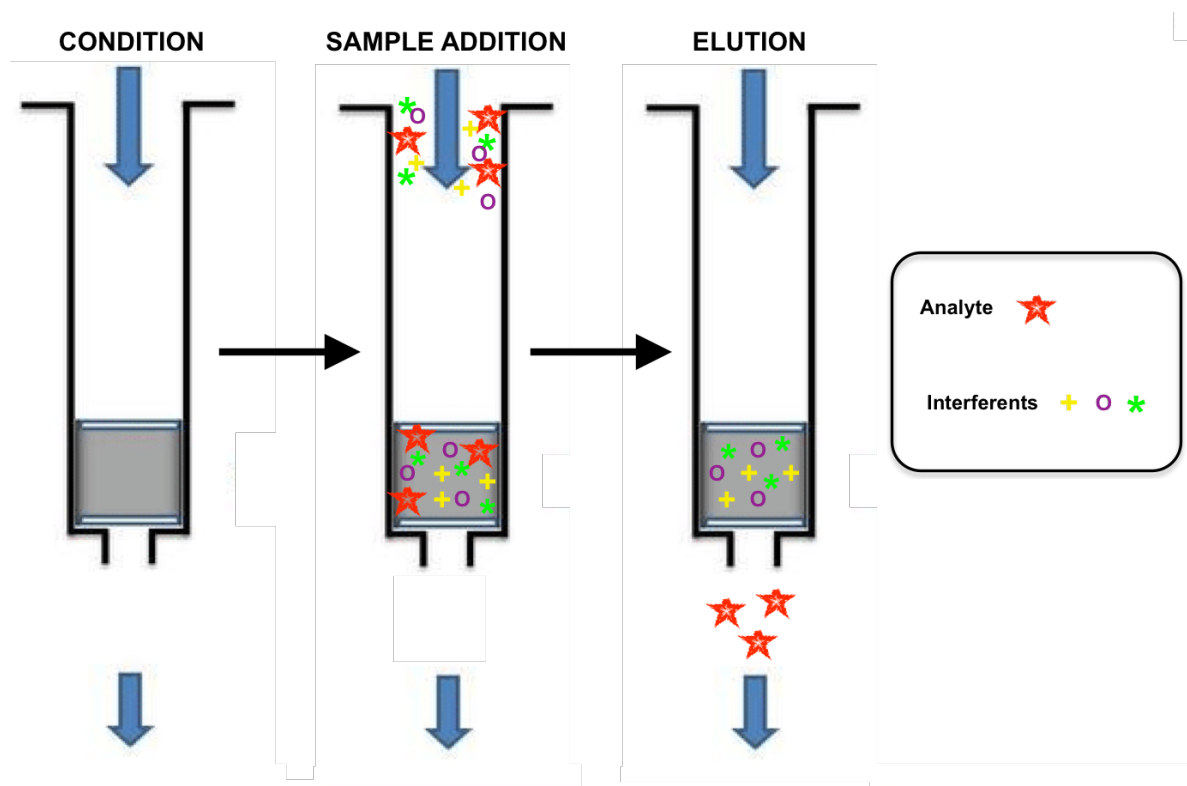
Figure 18: Schematic drawing of solid phase extraction steps. In the last step analyte is released while interferents remain bonded with the stationary phase. Figure is created with inspiration from (Dheyaa, 2016).

1.7 Gas Chromatography - Mass Spectrometry (GC-MS)

In order to analyse different components in a sample, they need to be separated and identified. This can be done with GC-MS, an instrument consisting of the combination of a gas chromatograph and a mass spectrometer. Schematic of a typical GC-MS is shown in Figure 19.
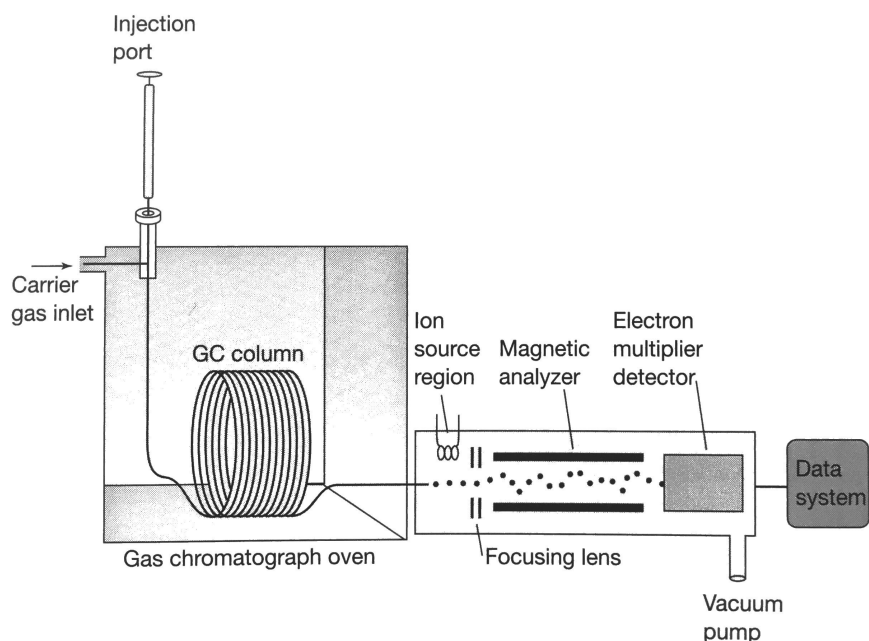
Figure 19: Schematic of a GC-MS (Girard and Girard, 2013, p. 436).

1.7.1 GC

The GC part of the instrument consists of an injection port surrounded by a heated liner, a carrier gas (mobile phase) and a capillary separation column inner coated with a stationary phase, which is placed inside an oven. When a small amount of a liquid environmental sample is injected through the injection port, heat from the liner makes it vaporize rapidly over to gas phase. The carrier gas swipes the gaseous sample from the injection port and leads it through the separation column at a constant rate of flow. Here components are separated. There are several types of columns with differences in lengths, internal diameter and type and thickness of stationary phase. The choice of which one to use is based on the "like dissolves like" rule, and most commonly used is silicone stationary phase because of its thermally stability at high temperatures. Separation of components is not only based on how they bond to the stationary phase, but also on boiling point. A good general rule is that organic components elutes from GC in order of increasing boiling points. GC can be run with a temperature programmed separation. The oven surrounding the column is having a relatively low temperature when the

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sample is injected and then increases with time. This will increase the vapor pressure of the components and more quickly bring them out of the column (Girard, 2014, pp. 428-430).

1.7.2 MS

The MS part of the instrument detects and identifies components as they sequentially are eluted from the GC column. It consists of an ion source, a focusing lens, an analyser/mass spectrometer, a detector and a data system. When the gaseous components are introduced to the ion source, they are converted into ions. Electron ionization is one of two commonly used ionization methods: Electrons are emitted from a hot filament and forms an electron beam with an energy of usually 70 eV that interacts with the incoming components M (M for molecule) and forms positively charged radical ions ($M^{\cdot+}$) : $M + e^- \rightarrow M^{\cdot+} + 2e^-$ (Harris, 2010, pp. 502-505). To prevent ions to encounter collision with background gas molecules, the whole MS system is kept at high vacuum. The positively charged ions are accelerated into the mass spectrometer by a very negative charged focusing lens. There are several types of MS, in this project an orbitrap was used. It consists of a central and outer electrode making an electric field that pushes the ions into an orbital motion around the centre of the orbitrap, illustrated in Figure 20.
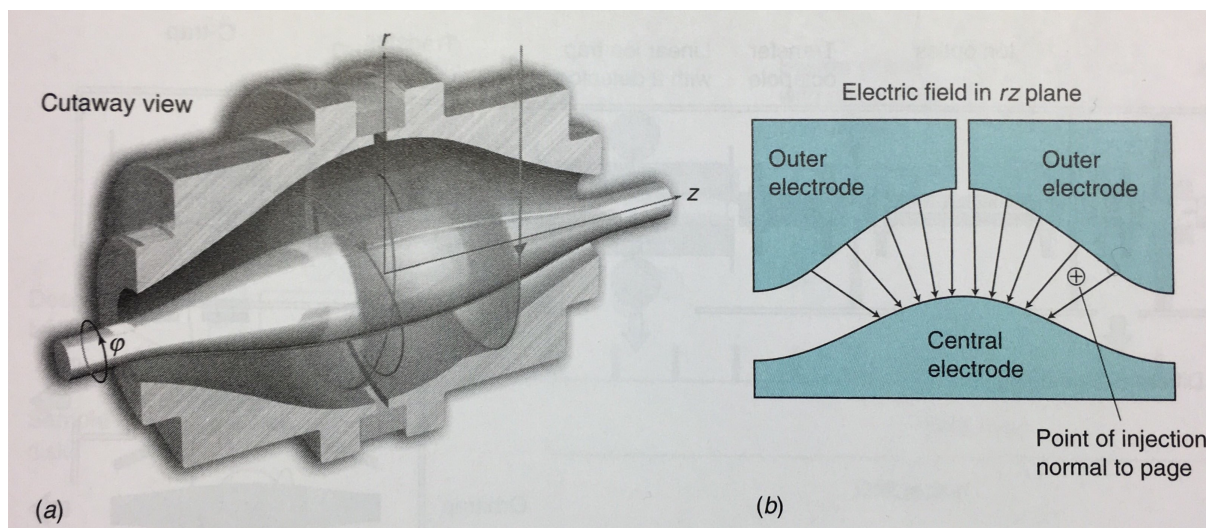
Figure 20: (a) Cutway drawing of an orbitrap and (b) Electric field in one longitudinal plane of an orbitrap (Harris, 2010, p. 517).

The ions are creating components of current with different frequencies. These are recorded for a predetermined time before a computer decomposes the currents into the components frequencies and hence m/z values through a Fourier transform (Harris, 2010, p. 517) (Girard, 2014, pp. 433-436).

1.7.3 Quantification

Selected ion monitoring (SIM) is a MS technique often used in quantitative analysis. Instead of scanning over a range of masses, SIM only scans for masses of interest, one at a time. The sensitivity is 100 to 1000 times greater since the instrument can spend more time monitoring selected ions instead of scanning for all. The concentration of analytes in a sample is found by converting the peak areas of the measured masses. This is achieved by using analytical standards (Girard, 2014, pp. 436-437).

Standards

Internal Standard

Sample loss can occur during sample preparation, and the intension of using an internal standard is to correct for these losses. The internal standard consists of a known quantity of a compound, different from the analyte, that is added to the sample prior to sample preparation. If losses appear, the ratio of internal standard to analyte remain constant, because same fraction of each is lost in any operation. To find out how much analyte that is present in a sample, signal from analyte is compared with signal from the internal standard (Harris, 2010, p. 109). Good internal standards are chemically very similar to the analyte, and the very best ones, which is used in this project, are isotopically labelled versions of the analyte (Girard, 2014, p. 437).

Quant standard

A quant standard is a mixture consisting of the internal standard added to samples (^{13}C) and known amounts of ^{12}C compounds. The mixture is analysed on the GC-MS instrument now and then in between samples and is used to decide the relative response factor (RRF) between internal standard and ^{12}C compound, see equation nr 1. When RRF is known the unknown amount of ^{12}C in sample can be found by equation nr. 2 (Rome and McIntyre, 2012).

$$RRF = \frac{(Area\ 12\ C\ qaunt\ standard)x\ (Amount\ 13\ C\ quant\ standard)}{(Area\ 13\ C\ qaunt\ standard)x\ (Amount\ 12\ C\ quant\ standard)} \tag{1}$$

$$Amount\ 12C\ in\ sample = \frac{(Area\ 12C\ sample)\ x\ (Amount\ 13C\ sample)}{RRF\ x\ (Area\ 13C\ sample)} \tag{2}$$

Recovery Standard

Recovery relate to the extraction efficiency of an analytical method within the limits of variability. Recovery of analyte does not need to be 100 %, but the extent of recovery of the internal standard and of an analyte should be consistent, precise and reproducible. (Boyd et al., 2008, p. 563). At NILU, the recovery standard is added to the samples as the last step before analysis on instrument (e.g. GC-MS) and consist of a known amount of a ^{13}C compound that is not present in the internal standards. It can be seen as an internal standard for the internal standards. A RRF_2 between the internal standard and the recovery standard is found with equation (1) by replacing ^{12}C in quant standard with ^{13}C in internal standard, and ^{13}C in quant standard with ^{13}C recovery standard:

$$RRF_2 = \frac{(Area\ 13\ C\ internal\ standard)x\ (Amount\ 13\ C\ recovery\ standard)}{(Area\ 13\ C\ recovery\ standard)x\ (Amount\ 12\ C\ internal\ standard)} \tag{3}$$

The amount of internal standard left in sample after analysis can then be found:

$$Amount\ 13C\ internal\ standard_{end} = \frac{(Area\ 13C\ internal\ standard)\ x\ (Amount\ 13C\ recovery\ standard)}{RRF\ x\ (Area\ 13C\ recovery\ standard)} \tag{4}$$

Since the amount of internal standard added to the samples prior to analysis is known, can the recovery easily be calculated with equation nr 5:

$$Recovery\ (\%) = \frac{Amount\ 13\ C\ internal\ standard}{Amount\ 13C\ internal\ standar d_{end}} * 100 \tag{5}$$

Limit of detection (LOD)

The limit of detection (LOD) is generally defined as the smallest concentration or amount of analyte that can be detected with reasonable certainty for a given analytical procedure (Foley and Dorsey, 1984, p. 503). There are several ways to decide LOD, one is:

$$LOD = \overline{Xb} + k\ Sb \tag{6}$$

Where $\overline{Xb}$ is the mean of the blank measurements, Sb is the standard deviation of the blank measurement, and k is a numerical factor chosen according to the confidence level desired. k is often set to 3 (A. D. McNaught, 1997).

1.8 Fourier Transform Infrared Spectroscopy (FTIR)

An infrared spectrometer is an instrument that determines a compounds absorption spectrum. In organic laboratories is it common to use a type of infrared spectrometer named Fourier transform (FTIR), which rapidly provides spectra of a compound in the common range of 4000 - 400 cm^{-1} carried out with a computer-interfaced instrument. A spectrum of the background is always collected before and between every sample. The sample of interest is placed on the instrument and an infrared light source is passing through it onto the detector, where the amount of absorbed light is precisely measured. The software automatically subtracts the background spectrum from the sample spectrum, implements the mathematical process Fourier transform that extracts the individual frequencies absorbed, reconstructs the raw data and plots the sample´s infrared spectrum on the computer screen, all in just a few seconds. It operates in a single-beam mode, which is convenient for higher absorbing samples such as polymers (Pavia, 2015, pp. 22-25) (Technologies, 2011). Figure 21 shows the FTIR instrument located at UiT, equipped with diamond attenuated total reflectance (ATR).
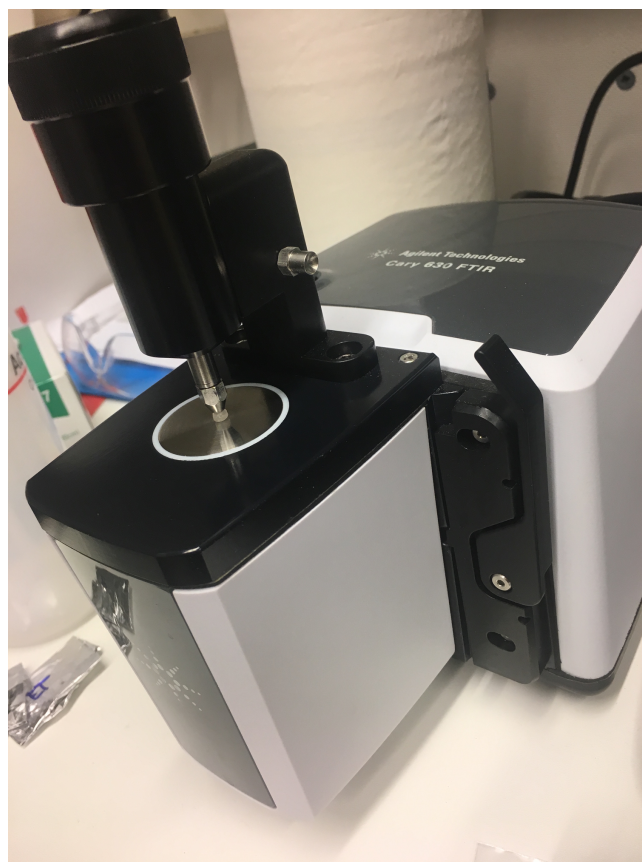
Figure 21: Agilent Technologies Cary 630 FTIR spectrometer with Diamond ATR at UiT, analysing a pristine poly-propylene pellet.

1.8.1 Diamond ATR sampling accessory

Diamond ATR is a sampling accessory taking advantage of the physical properties of light when two materials with differences in index of refraction meet. Figure 22 illustrates how an ATR sampling accessory works. The sample is placed on a cut and precisely mounted diamond, where an infrared source beam bounces back and forth off the crystal internal surfaces, slightly penetrating the sample when it reflects off the diamond´s surface where the sample is applied. The penetration attenuates the infrared beam before it exits the crystal and hits the detector.
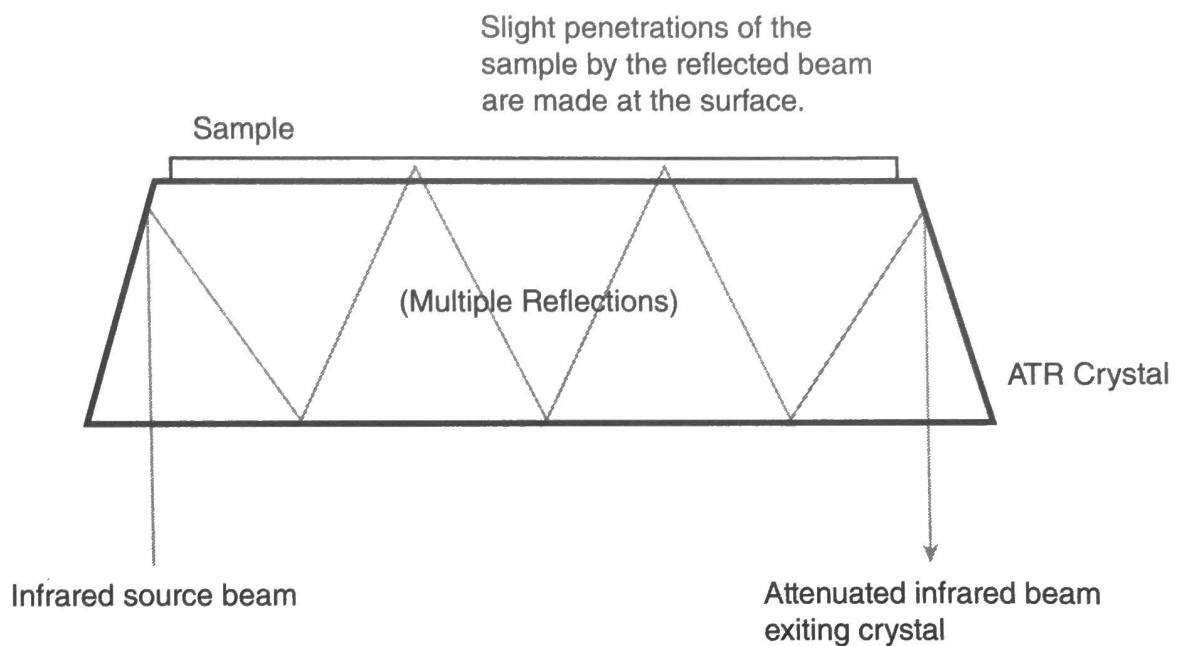
Figure 22: Closeup and description of how an ATR sampling accessory works (Pavia, 2015, p. 26).

The ATR method eliminates sample preparation, conducing rapid analysis (Pavia, 2015, pp. 25-26). The extreme hardness and chemical resistivity of the diamond crystal makes it suitable for analysing hard plastic samples, where making good contact between the sample and the crystal is the key to obtain good results (Technologies, 2011).

1.8.2 What information can an infrared spectrum provide?

No molecules of different structure have the exact same infrared spectrum. The reason is different, natural, characteristic frequencies of vibration in every type of bond, see Figure 23. Even though the same type of bond can be present in two different molecules, the environment around is diverse and prevents identical infrared spectra.
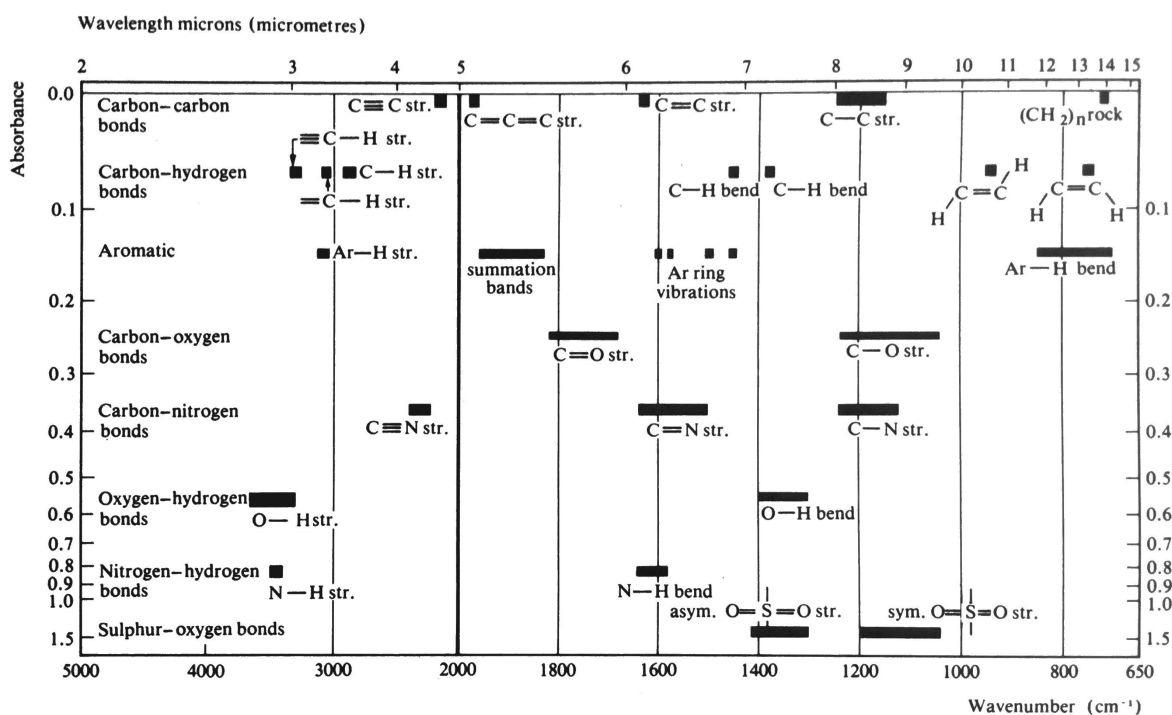
Figure 23: Absorption regions for common bonding types (Vogel et al., 1989, p. 270).

An infrared spectrum can be used to obtain structural information of a compound, and is a useful tool when comparing two compounds thought to be identical (Pavia, 2015, p. 16). A given IR-spectrum can automatically be compared to a database of IR spectra to quickly identify analytes.

1.9 Scanning Electron Microscope (SEM)

When working with weathered plastic samples that have stayed in the marine environment over a certain time, it is of huge interest to investigate possible physical changes at the sample surface during the period. Both since the surface is where adsorption of POPs happens, and it may explain how plastic fragmentation occur. With a Scanning Electron Microscope (SEM) the surface is scanned by an electron probe, and the reflected electrons that bounce back from the sample are recorded by a detector in relation to the moving point of the probe. The process takes place in vacuum, and a schematic drawing is shown in Figure 24.
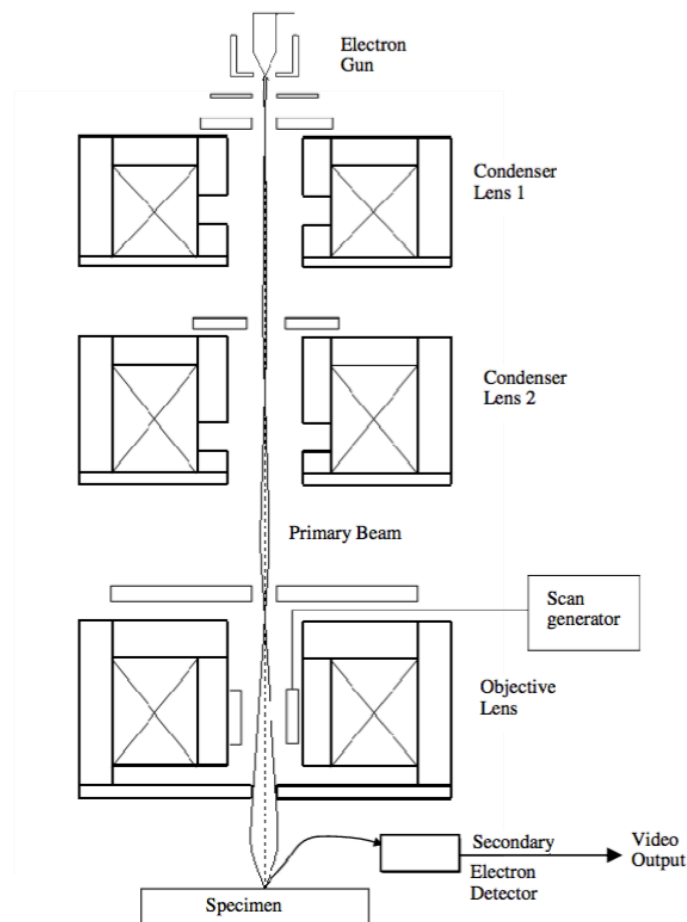
Figure 24: Schematic drawing of a SEM. The three-stage lens system subsequently demagnifies the electron probe provided by the electron gun, so it has a diameter of 1 to 10 nm when hitting the sample surface (Khursheed, 2010, p. 3).

The detector translates the incoming electrons into a high resolution, topographical, 3D image of the sample surface and sends it to a video screen (Khursheed, 2010, pp. 1-3) (Griffiths, 2006, p. 3). Sample preparation in form of surface coating by a conducting material is needed in order to localize the signal on the sample and to enhance electrical conductivity (Griffiths, 2006, p. 47).

2 Design and aim of study

Inspired by the study "Long-Term Field Measurement of Sorption of Organic Contaminants to Five Types of Plastic Pellets: Implications for Plastic Marine Debris" (Rochman et al., 2013) done in San Diego, curiosity surrounding this topic regarding the Arctic ocean arose.

Plastic pellets of secondary PE-HD and primary PE-LD, PP and PET have been placed in Kongsfjorden, the Arctic ocean outside Ny-Ålesund, Svalbard, for two seasons, respectively summer and winter. A time trend was achieved by having five intervals of sampling within each season. In addition, plastic garbage samples that already spent time in the Arctic ocean were collected from the shore in Longyearbyen.

Extraction of POPs was done by using a standard method including use of internal standard (quantitative analysis). Purification and analysis were conducted using SPE, GPC and different setups of GC-MS. The weathered plastics chemical structure was investigated using FTIR, and their surface was looked into using a SEM.

The aim of this study was to investigate if:
- Adsorption rate and concentration of POPs to marine plastic in the Arctic vary by type of plastic.
- Concentration of POPs adsorbed to plastic in the Arctic ocean are likewise as in San Diego.
- The stability of plastics is affected over time in the Arctic ocean.
- Surface changes can answer if/how process and rate of degradation vary by plastic type.
- Random garbage samples can be identified with respect to type of plastic.
- Some plastic types are more harmful than others when in the Arctic marine environment.

3   Experimental Section

Please note that this is a simplified experimental description. A complete version and additional information can be found in Appendix. Information regarding chemicals, standards and materials/instruments are detailed in Appendix 1.

3.1   Sampling

Time series samples

Four different types of plastic pellets, virgin PP, virgin PE-LD, virgin PET and pieces PE-HD from a beached fisher box, were positioned in four separated teabags, making each tea bag containing only one type of plastic. Each of these tea bags were gathered in a washing net for underwear which represented a time interval in the experiment. A total of ten nets were made, divided in to two batches and sent to Svalbard. The tea bag itself was made of polyamide (PA), however these were not analysed in this project.

Employees from Norwegian Polar Institute handled the batches and located them in the Arctic ocean for two different time periods, respectively summer and winter. The batches were placed three meters below sea level from a floating dock in Ny-Ålesund. Within each period, the five washing nets were collected at different time intervals. For additional information regarding sampling see Appendix 2.

Back at the laboratory in Tromsø the samples (tea bags) were prepared for analysis by dipping them shortly in a beaker of Milli-Q water for removal of possible dust and salt particles from the ocean. The tea bags were then opened and set out on alumina foil in clean cabinet to dry overnight. Using a clean cabinet prevented the samples from being contaminated with air and dust from the surrounding area.

Figure 25: Weathered time series plastic samples left to dry in clean cabinet overnight. The tea bags colour got darker and dirtier for each month it stayed in the ocean. Please note that samples are placed in random order in the picture.

Garbage samples

28 plastic garbage items collected along the shoreline in Longyearbyen were cut into microplastic pieces, transferred to vials and randomly named.

Figure 26: 18 out of 28 plastic garbage items collected along the shoreline in Longyearbyen. These were cut into microplastic pieces and analysed for POPs. Random sample id name can be seen in lower, right corner at each aluminium sheet. Colour and density varies among samples.

3.2 Chemical analysis

Blank samples (vial without plastic pellets) were made for circa every fourth plastic sample and processed likewise as them. Two replicates of approximately 0.4 g of each time series sample, and 0.4 g of the garbage samples, one replicate, were spiked with internal standard mix, extracted three times by sonication in cyclohexane and concentrated with RapidVap. Afterwards samples were filtered, followed by solvent shift from cyclohexane to dichloromethane (DCM) with use of nitrogen gas. Sample clean-up number 1 was carried out with GPC. The sample containing fractions were concentrated with TurboVap. A small amount of DCM was used to wash possible remaining's on the fraction glass walls back to the sample. The sample was transferred to a round bottom tube that fit the SPE performing robot. Sample remaining was washed with hexane, and further concentration and solvent shift from DCM to hexane was done with MiVac. For sample clean-up number 2, SPE with florisil as solid phase was used. Sample analytes were eluted with 1:9 DCM:hexane and 100% hexane.

Figure 27: SPE robot. In the modules (3 and 4) fraction collection tubes are placed to the left and samples to the right. Florisil packed columns are stored above the modules, and a cannula transfers solvents and sample through the column to the fraction collector. The robot worked over night, and this picture was taken next morning. The sample fractions (left in modules) have at this point evaporated a little.

Concentration and solvent shift to isooctane was carried out with RapidVap and nitrogen flow. Final extracts were spiked with recover standard and run on GC-MS. Target SIM acquisition was used to detect HCB, 12 PCBs (CB#28/31, 52, 101, 99, 118, 153, 105, 138, 187, 183, 180, 170) and 25 PBDEs (BDE#17, 28, 49, 71, 47, 66, 77, 100, 119, 99, 85, 126, 154, 153, 138, 156, 184, 183, 191, 202, 197, 196, 207, 206, 209). Further GC-MS details are described in Appendix 6.

Internal standard calibration with isotopic dilution was used for quantification, and data processing carried out with Tracefinder. LOD for time series samples was set as 3 times standard deviation of blank. Blank correction was done, and results < LOD were replaced with ½ LOD. Since garbage samples only had one blank, their LOD was set to 2 times their blank value, and results < LOD replaced with LOD.

3.3 FTIR

A triplicate of unextracted plastic pellets form each time series sample and the garbage samples from Svalbard were analysed with Diamond (ATR) FTIR. A library of IR-spectra was achieved by taking FTIR of a selection of pristine, known plastic pellets. The unidentified garbage samples were identified by comparing their IR-spectra to those in the achieved library.
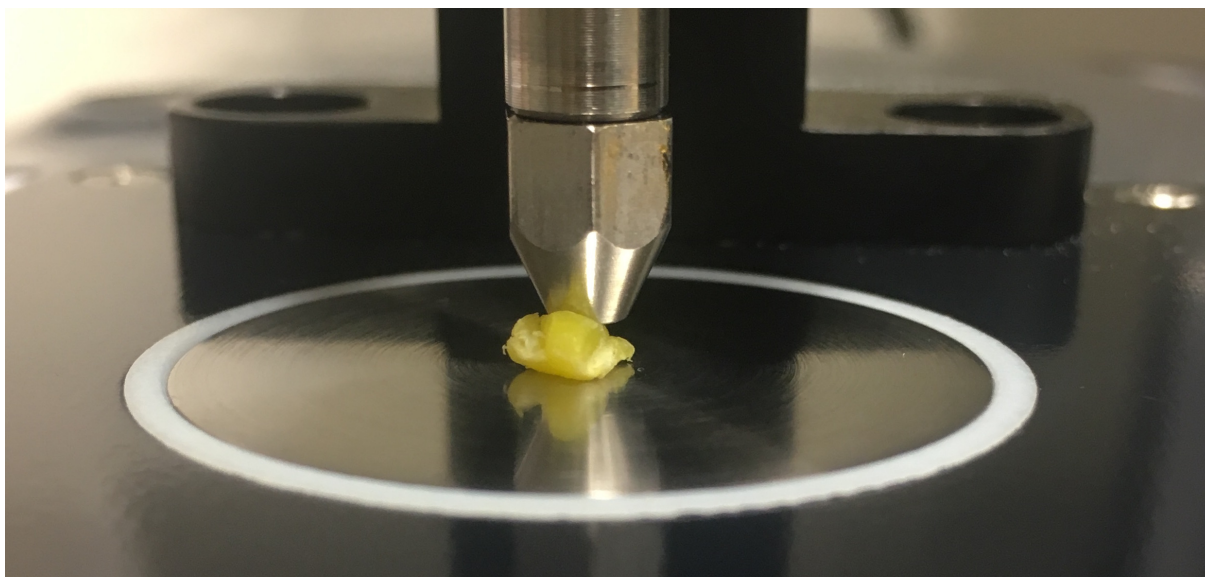
Figure 28: A pellet of PE-HD squeezed against the diamond on FTIR instrument. Good contact between the sample and the crystal is the key to obtain good IR-spectra. Adjustment of the pellet was done now and then during the analysis.

3.4 SEM

Due to cost and time, only 12 time series samples and 4 garbage samples were analysed on the SEM. It was very important to always wear gloves when working with equipment and samples positioned inside the scanning electron microscope, because oil from hands could contaminate and make the inside of the chamber dirty in vacuum. Each sample was mounted on double-sided carbon sticker on an aluminium pin. A small amount of conductive silver paste was attached to a little part of the plastic, over to the carbon sticker and down to the pin. The non-conducting plastic samples were surface coated with gold/palladium (conducting material).
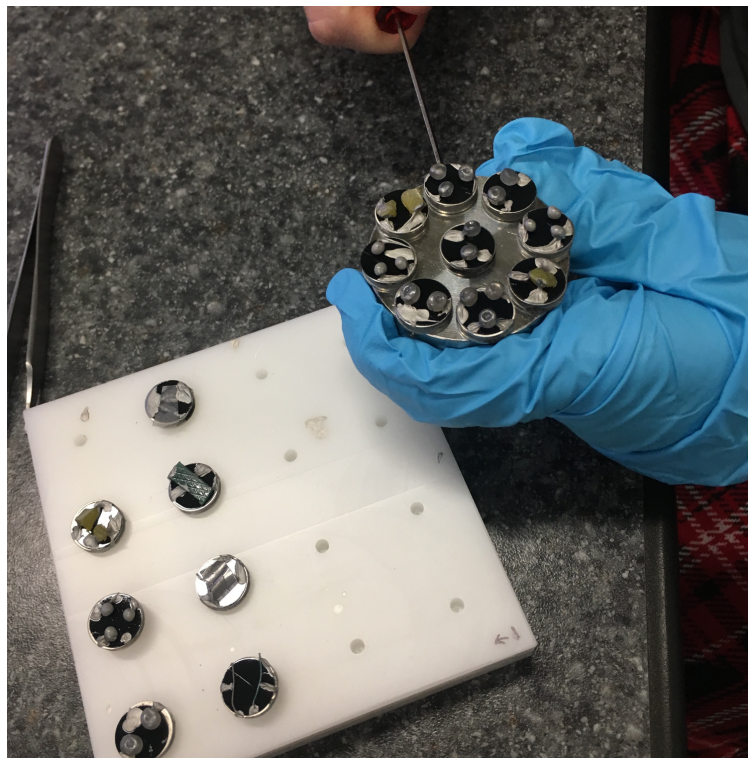
Figure 29: Surface coated plastic samples mounted on carbon sticker and aluminium pin. The light grey spots at each pin are silver conductive paste. The pins are getting properly attached before entering the SEM chamber.

The surface coting allows the electrons from the electron beam to reflect when they hit the sample surface inside the vacuum achieved microscope chamber. A detector translated the reflected electrons into high resolution pictures. Scale bars were added to the pictures using data software ImageJ (http://imagej.nih.gov).

4 Results

4.1 Sampling

Sampling of the two last time intervals in the winter batch, supposed to be collected in February and March 2018, did not go as planned. The container holding the plastic samples loosened from the harbour in Ny-Ålesund and disappeared under sea ice. Luckily divers found it again in the in the early autumn 7 months later, resulting that these samples spent longer time in the ocean than planned. Complete overview of actual sample dates can be found in Appendix 2. The picture below shows both samples holding containers, respectively the summer container to the left and the winter container to the right. Strong forces from the sea ice had pressed the winter container completely together and help from workers at "Akvaplan-niva" was needed in order to be able to open it and get the samples out.

Figure 30: Sample holding containers from the summer batch (left) and the winter batch(right). The green fabric that can be seen in the winter container belongs to the washing net holding the samples inside the container, which was completely stuck.

4.2 Concentrations of POPs in time series samples

The samples were analysed on a GC-Orbitrap and analysed for a wide range of PBDEs, PCBs and HCB. LOD values can be found in Appendix 9.

4.2.1 Time trend of PBDEs

The results for the pristine plastic pellets showed that only PBDE-47 and PBDE-49 were above LOD. Concentration of PBDE-47 and PBDE-99 in the four plastic types each month during its period in the ocean are shown in the next two figures (Figure 31 and Figure 32), respectively at summer and winter time. Samples where values < LOD were replaced with ½ LOD value and are marked with an asterisk *. A table with results is also presented in Appendix 8. PBDE-47 was detected in 38% of all samples, PBDE-99 in 33%. Detection varied among type of plastic and are visualized with asterisks *.
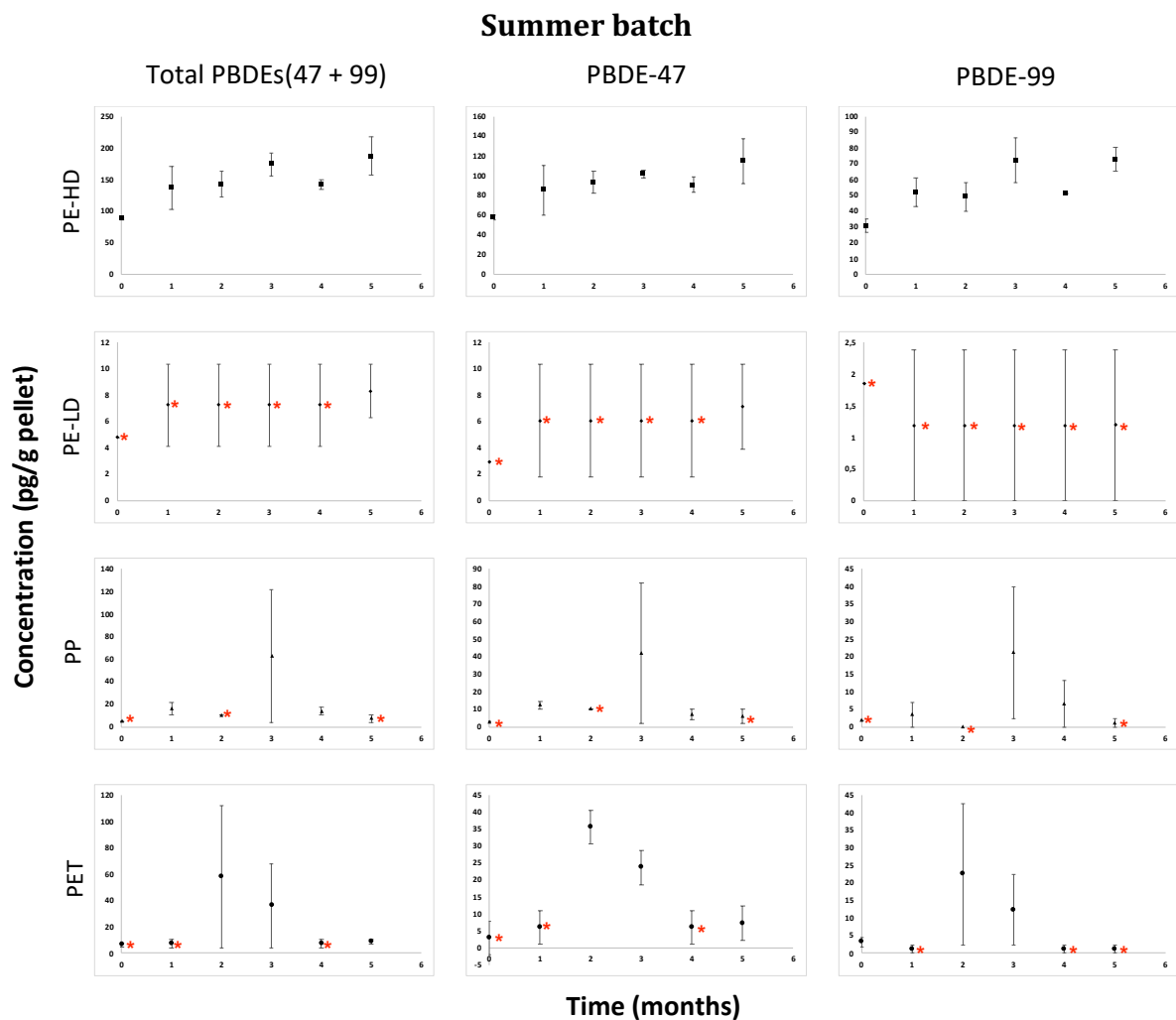
*Figure 31: Concentration of PBDEs (pg/g pellet) (y-axis) vs time (x-axis) in each type of plastic in the summer batch from May (time = 0) until October 2017 (time = 5). Standard deviations are included (vertical lines). Columns represent PBDEs: Total PBDEs (47 and 99), PBDE-47 and PBDE-99 (in order from left to right). Rows represent plastic types: PE-HD, PE-LD, PP and PET (in order from top to bottom). Asterisks * represents cases where minimum one of the two replicates had values < LOD. Please note that the vertical axes differ among graphs.*

Winter batch
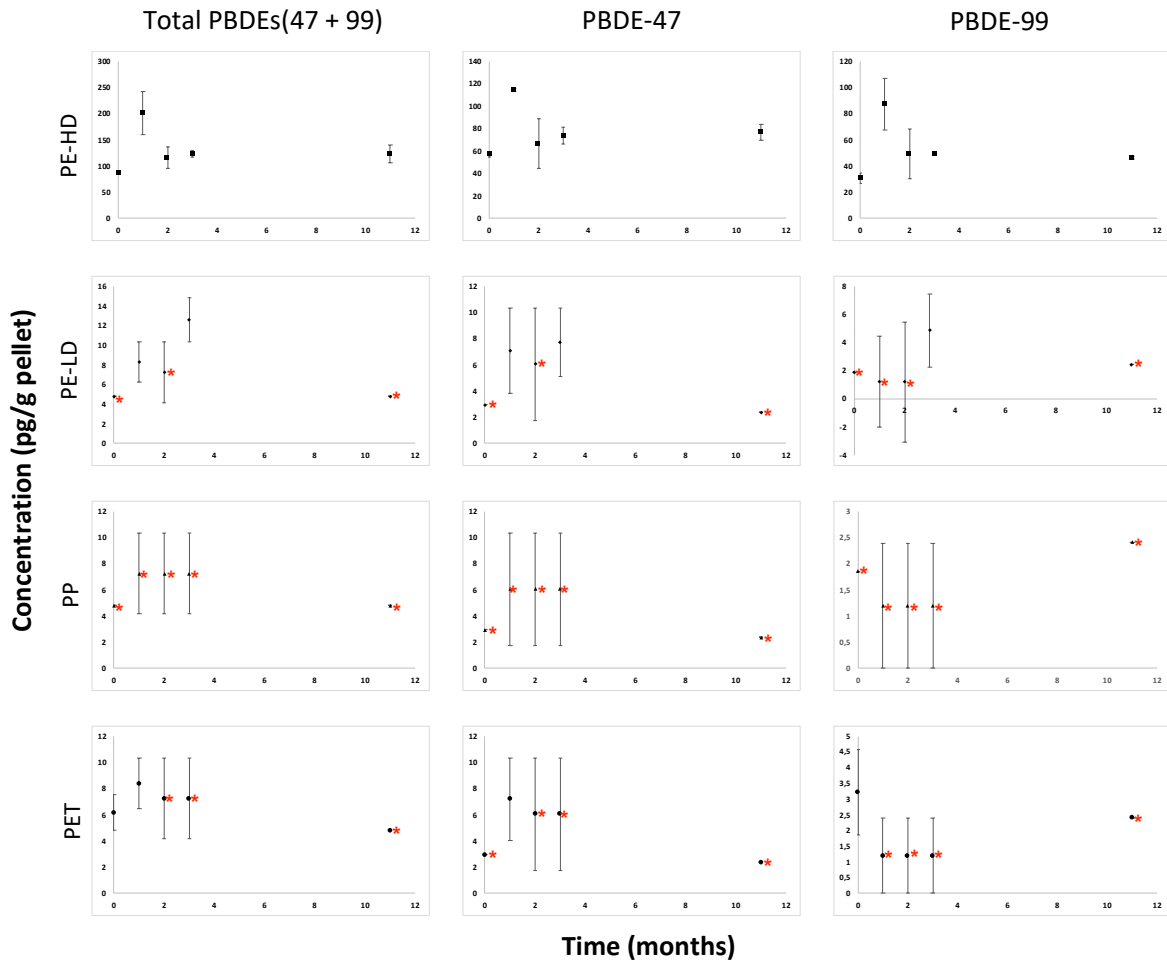
*Figure 32: Concentration of PBDEs (pg/g pellet) (y-axis) vs time (x-axis) in each type of plastic in the winter batch from October 2017 (time = 0) – January 2018 (time = 3) plus September 2018 (time = 11). Standard deviations are included (vertical lines). Columns represent PBDEs: Total PBDEs (47 and 99), PBDE-47 and PBDE-99 (in order from left to right). Rows represent plastic types: PE-HD, PE-LD, PP and PET (in order from top to bottom). Asterisks * represents cases where minimum one of the two replicates had values < LOD. Please note that the vertical axes differ among graphs.*

4.2.2 Time trend of HCB and PCBs

Total PCB (CB#28/31, 52, 101, 99, 118, 153, 105, 138, 187, 183, 180, 170 and HCB), HCB and PCB 28/31 concentration in the plastics during summer and winter time are shown in the next two figures (Figure 33 and Figure 34). Several of the Total PCB components were detected, however HCB and PCB 28/31 were detected most frequently. Concentrations < LOD were replaced with ½ LOD. PCB 28 and PCB 31 coelutes and based on the GC-MS setup used in this study they could not be separated. They are therefore analysed as one component (PCB 28/31). A table with results is also presented in Appendix 8. HCB was detected in 84% of all samples, PCB 28/31 in 75%. PET stood out among the other plastic types by detecting fewest of the components.
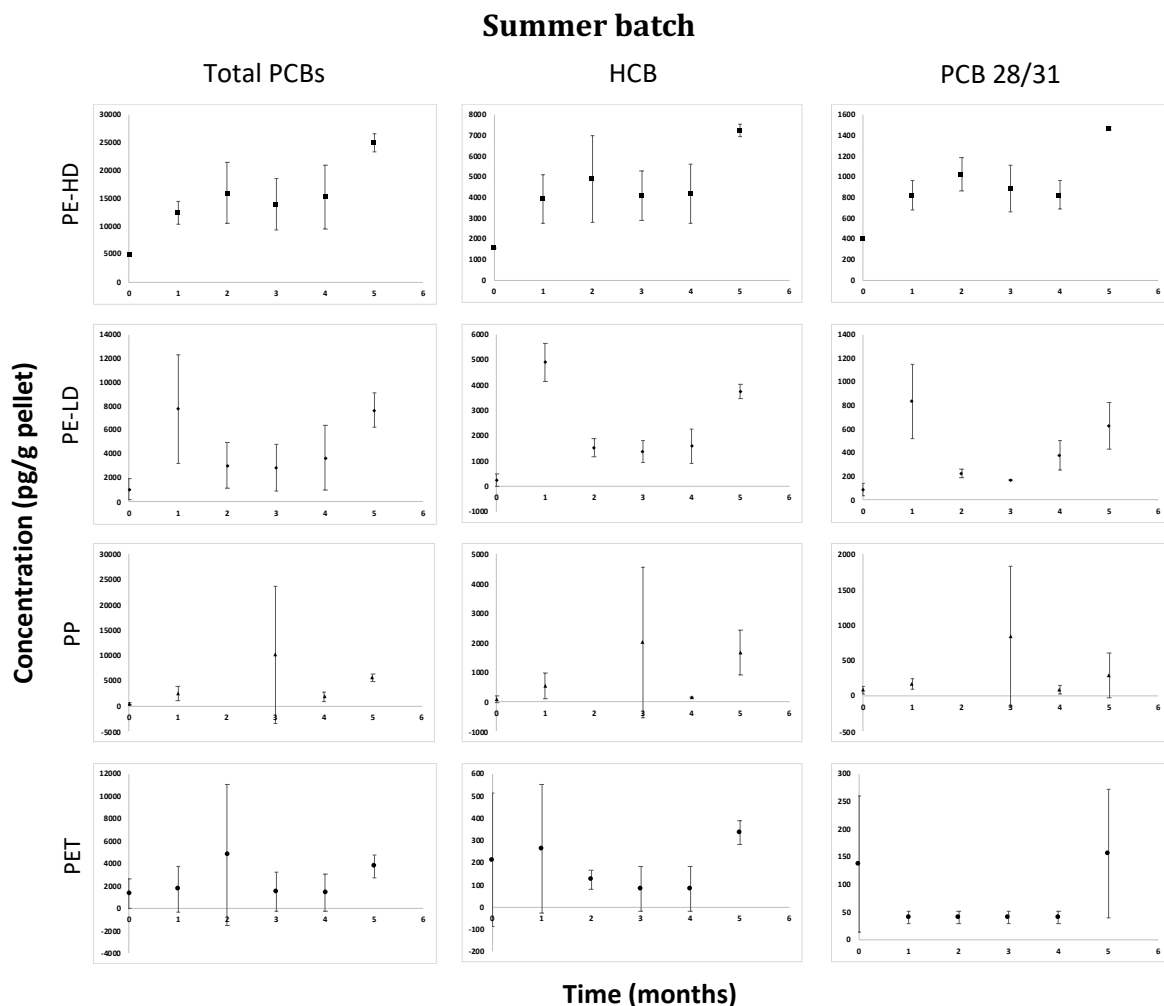
Figure 33: Concentration of PCBs (pg/g pellet) (y-axis) vs time (x-axis) for each type of plastic in the summer batch from May until October 2017. Standard deviations are included (vertical lines). Columns represent PCBs: Total PCBs (including HCB), HCB and PCB 28/31 (in order from left to right). Rows represent plastic types: PE-HD, PE-LD, PP and PET (in order from top to bottom). Please note that the vertical axes differ among graphs, and that the value of PP at month number 2 is missing.
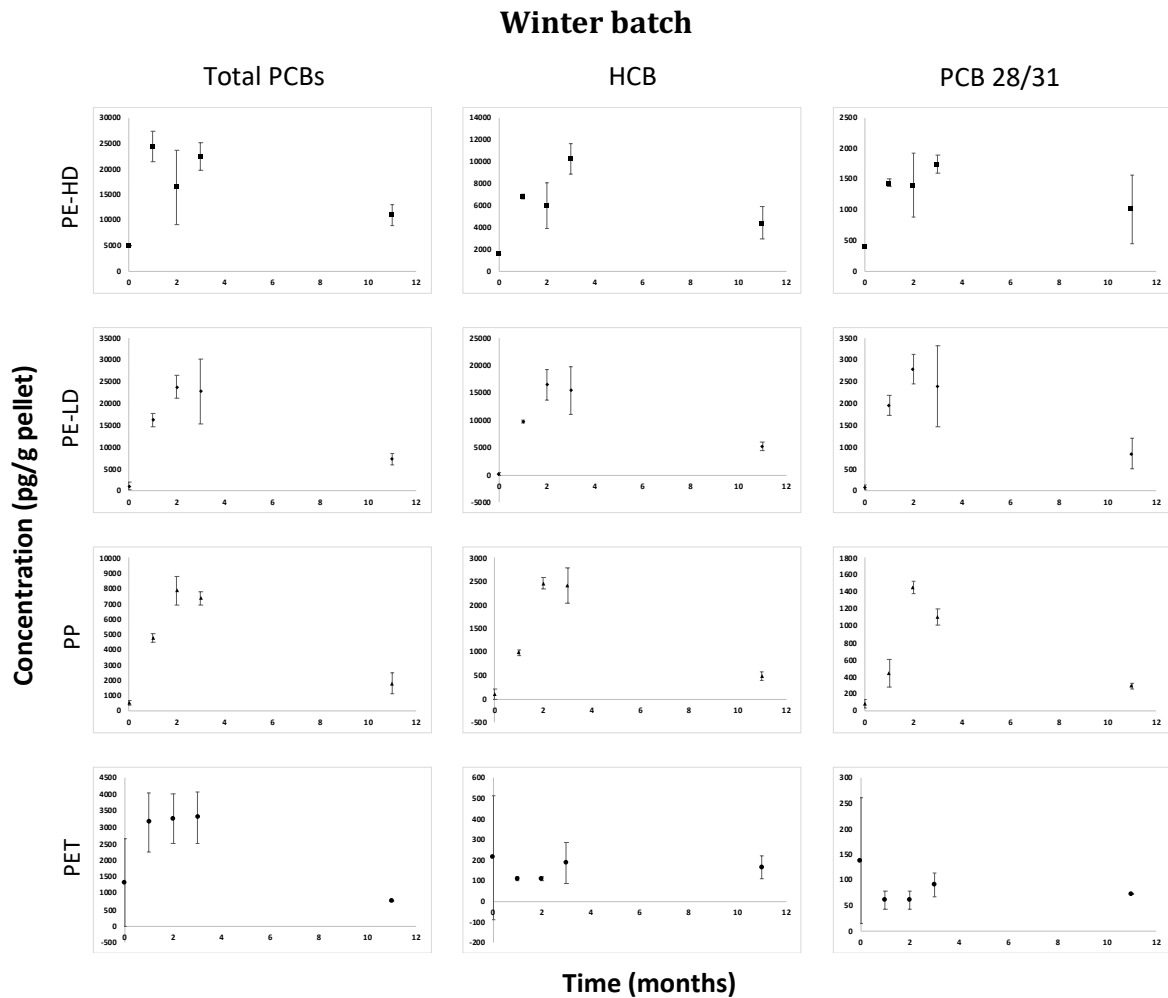
Winter batch

Figure 34: Concentration of PCBs (pg/g pellet) (y-axis) vs time (x-axis) for each type of plastic in the winter batch from October 2017 – January 2018 plus September 2018. Standard deviations are included (vertical lines). Columns represent PCBs: Total PCBs (including HCB), HCB and PCB 28/31 (in order from left to right). Rows represent plastic types: PE-HD, PE-LD, PP and PET (in order from top to bottom). Please note that the vertical axes differ among graphs.

Due to challenges during sampling (see chapter 4.1) only the first three months are common intervals of sampling for both seasons. Results from Figure 33 and Figure 34 at these months are summarized in Figure 35, where different colours represent different plastic types, solid line represents summer time and dotted line represents winter time.
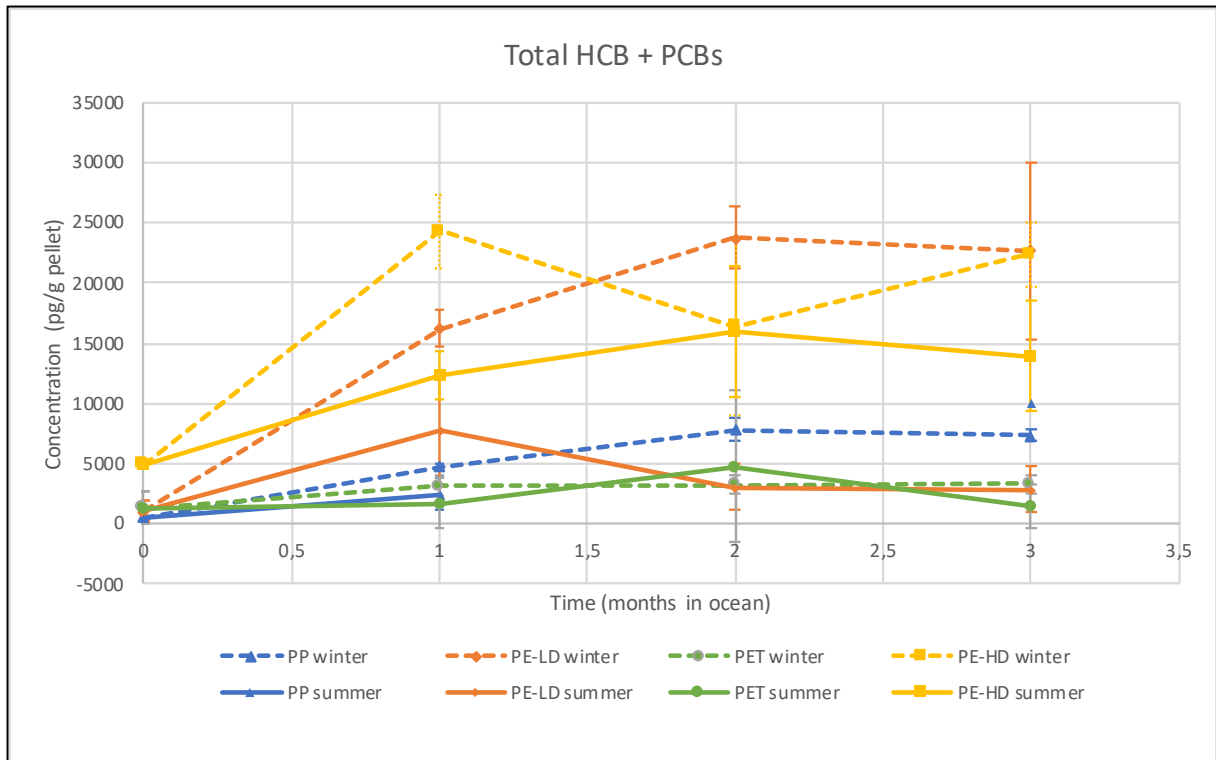
Figure 35: Total HCB and PCB concentrations (pg/g pellet) (y-axis) in PP, PE-LD, PET and PE-HD the three first months (x-axis) in ocean during summer and winter time. Standard deviations are included (vertical lines). Please note that the values of summer PP at month number 2 is missing.

Summer versus winter time

Total PCB and HCB concentration in PE-HD after 1 month in the ocean was significant higher at winter time compared to summer time (p = 0.039, α = 0.05). None other significant differences between summer and winter were found.

Types of plastic

Relative differences between the plastic types and total HCB and PCB concentrations in each season are seen in Figure 35, while Table 1 presents significant differences.

Table 1: 95 % CI simple t-test between different plastic types concentration in each season. S = summer, W = winter, number 1-3 donating months.

	PE-HD	PE-LD	PET
PP	0.03 (S1)	0.04 (W1) 0.04 (W2)	0.02 (W2) 0.04 (W3)
PE-LD			0.04 (W2) 0.04 (W3)
PET	0.01 (S1) 0.04 (S2) 0.04 (W3)		

4.2.3 Reproducibility between plastic pellets

Figure 36 and Figure 37 visualizes how concentrations of PCBs and HCB within the same plastic type and the same time spend in the ocean may vary between two replicates.
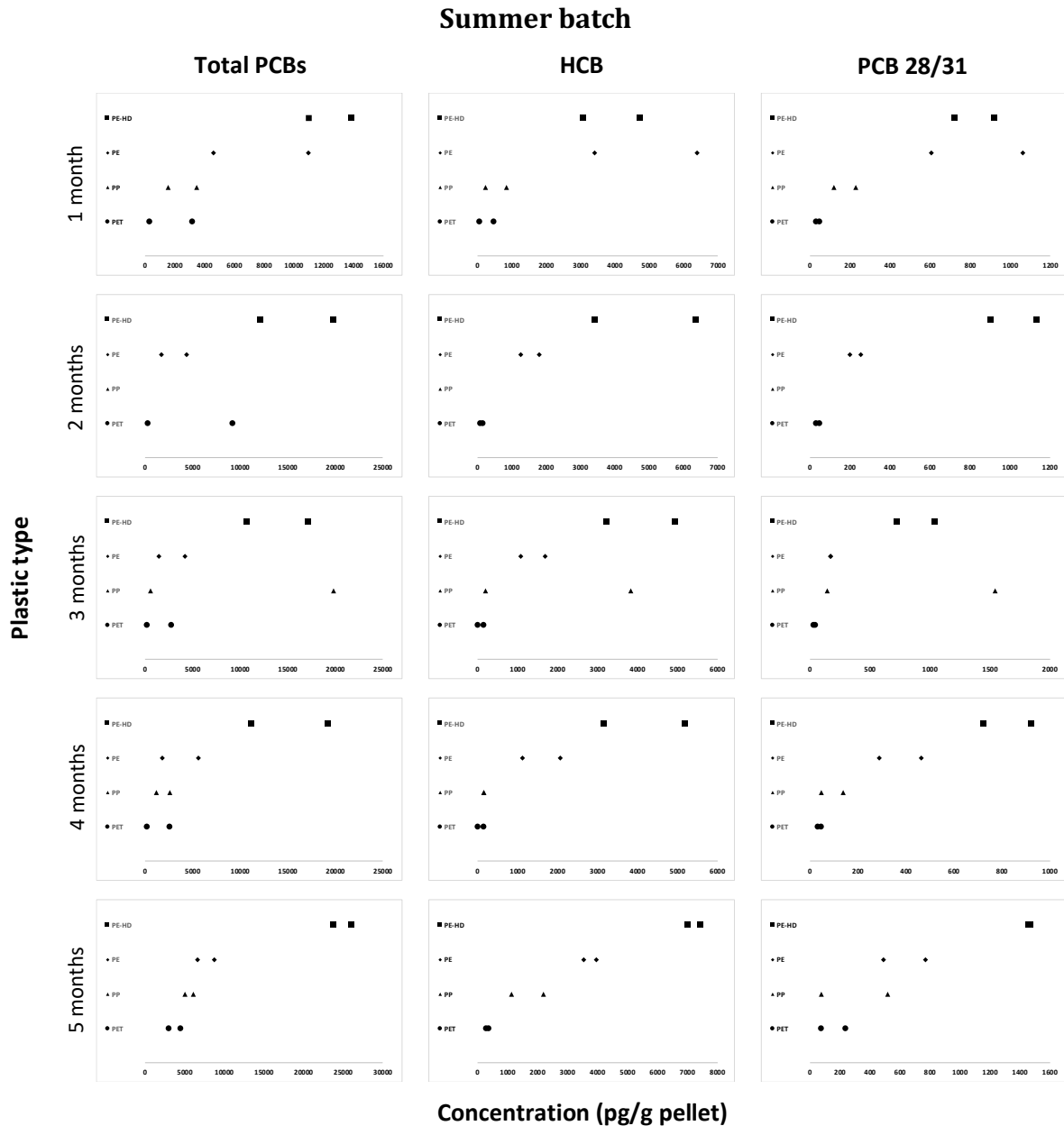
Figure 36: Plastic type (y-axis) vs adsorbed PCB and HCB concentrations (pg/g pellet) (x-axis) during the summer period (n = 2 replicates). Columns represents: Total PCBs (including HCB), HCB and PCB 28/31 (in order from left to right). Rows represent number of months the plastic samples have been in the ocean: 1, 2, 3, 4 and 5 months (in order from top to bottom). Plastic types are listed within each graph (y-axis): PE-HD, PE, PP and PET (in order from top to bottom). OBS, typing error: every PE in the figure should be PE-LD. Please note that the vertical axes differ among graphs, and that the value of PP at month number 2 is missing.

Winter batch
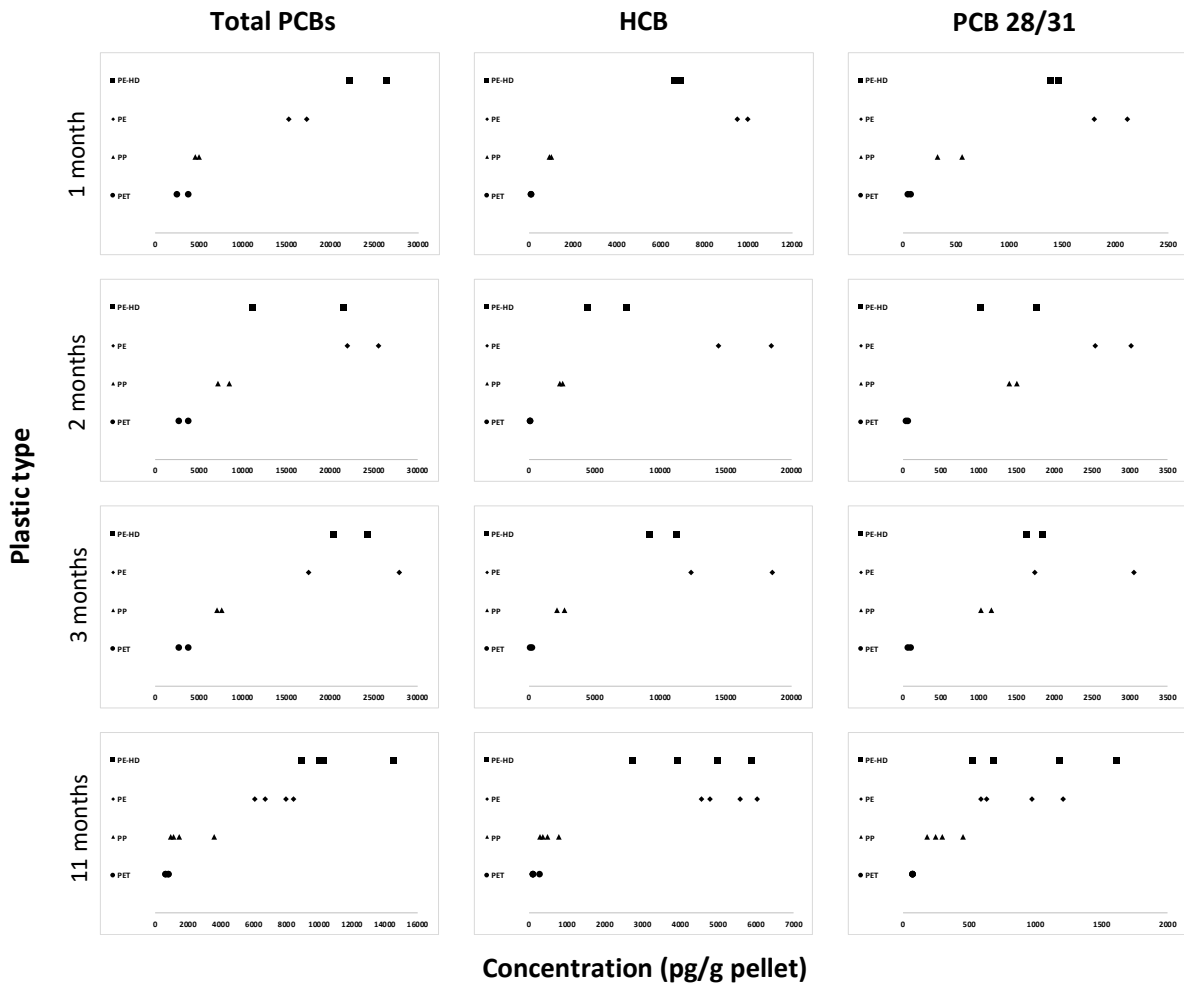
Figure 37: Plastic type (y-axis) vs adsorbed PCB and HCB concentrations (pg/g pellet) (x-axis) during the winter period (n = 2 replicates for months 1-3, n = 4 replicates for month 11). Columns represents: Total PCBs (including HCB), HCB and PCB 28/31 (in order from left to right. Rows represent number of months the plastic samples have been in the ocean: 1, 2, 3 and 11 months (in order from top to bottom). Plastic types are listed within each graph (y-axis): PE-HD, PE, PP and PET (in order from top to bottom). OBS, typing error: every PE in the figure should be PE-LD. Please note that the horizontal axes differ among graphs.

4.3 Concentrations of POPs in garbage samples

4.3.1 PBDE concentration

Figure 38 visualises total PBDE concentrations divided by component in each garbage sample. Value of each PBDE in garbage sample B1, B6, B8, G14 and Y2 was below LOD and thereby replaced with 2 x LOD. Garbage sample G1 are excluded from the figure owing to much higher total PBDE concentrations compared to the rest. Results for G1 are shown in Figure 39.
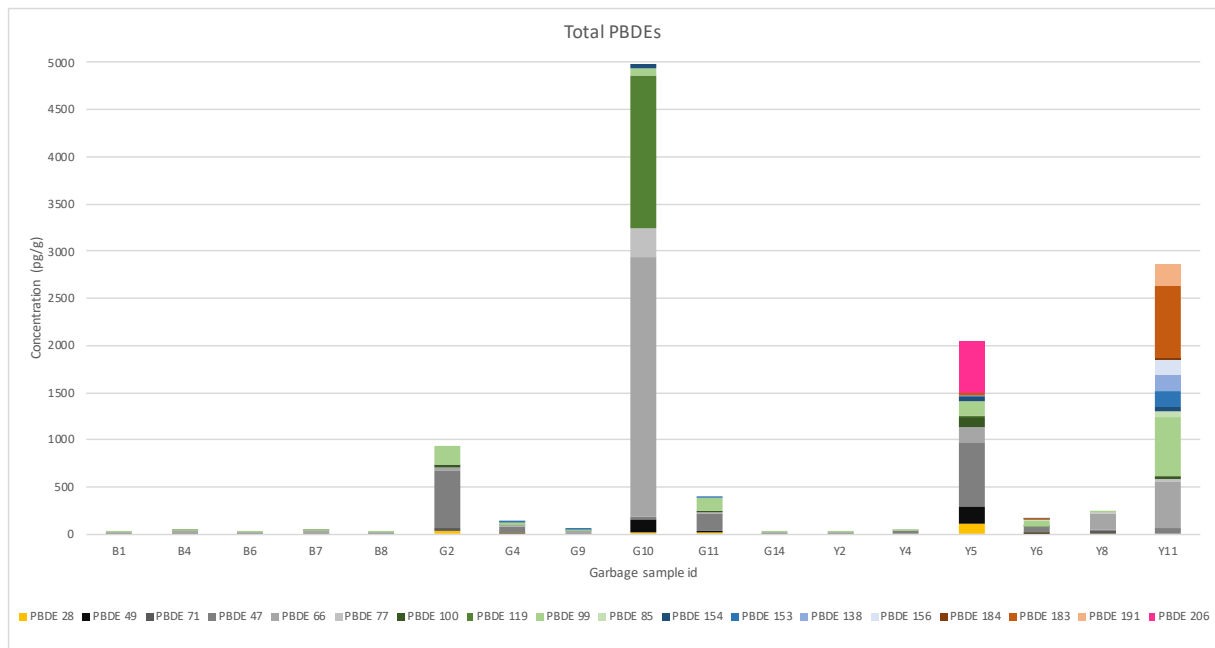
Figure 38: Total PBDEs concentration (pg/g) in garbage samples divided by component. The different types of colours represent similar numbers of substituted Br (yellow = tri, black/grey = tetra, green = penta, blue = hexa, orange = hepta, pink = nona) and different colour strength represents different PBDEs. Samples B1, B6, B8, G14 and Y12 represents 2xLOD.
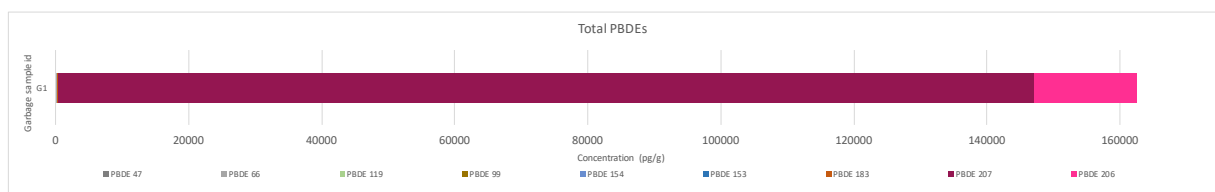
Figure 39: Total PBDEs concentration (pg/g) in garbage sample G1, divided by component. The different types of colours represent similar numbers of substituted Br (black/grey = tetra, green = penta, blue = hexa, orange = hepta, purple/pink = nona) and different colour strength represents different PBDEs. Please note that axes are switched compared to Figure 38.

4.3.2 HCB and PCB concentration

One or more PCB concentrations were detected above LOD in every garbage sample, except sample G9, which is replaced with 2 x LOD. Figure 40 visualises total HCB and PCB concentrations divide by component in each garbage sample. Total concentration in sample Y11 was so high that it was excluded from the figure, and instead visualised in Figure 41.
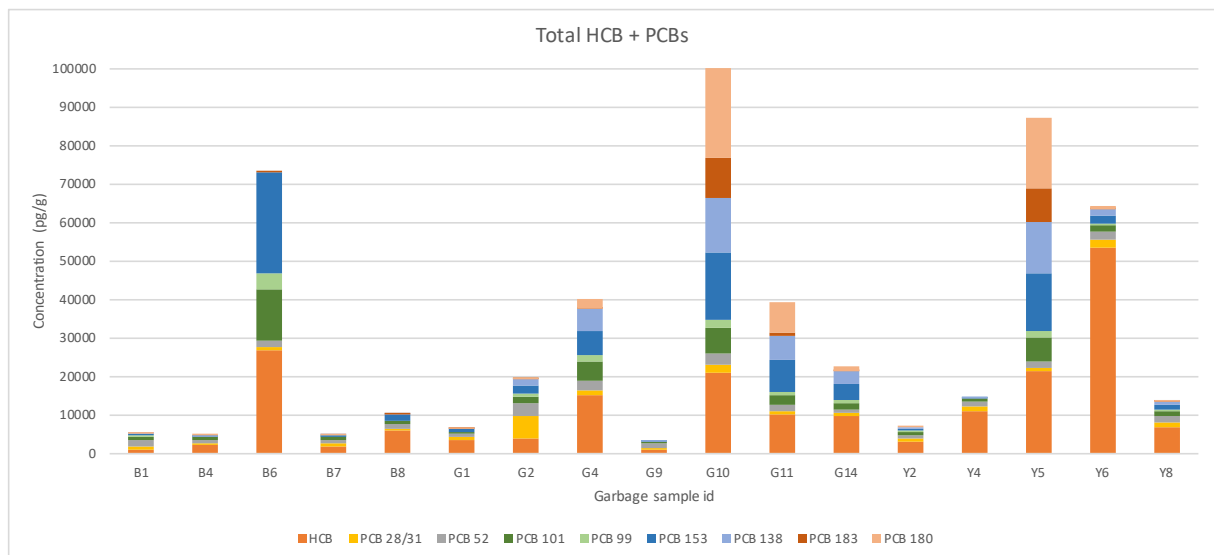
Figure 40: Total HCB and PCBs concentration (pg/g) in garbage samples divided by component. The different types of colours represent similar numbers of substituted Cl (yellow = tri, black/grey = tetra, green = penta, blue = hexa, orange = hepta) and different colour strength represents different HCB/PCBs. Sample G9 represents 2xLOD.
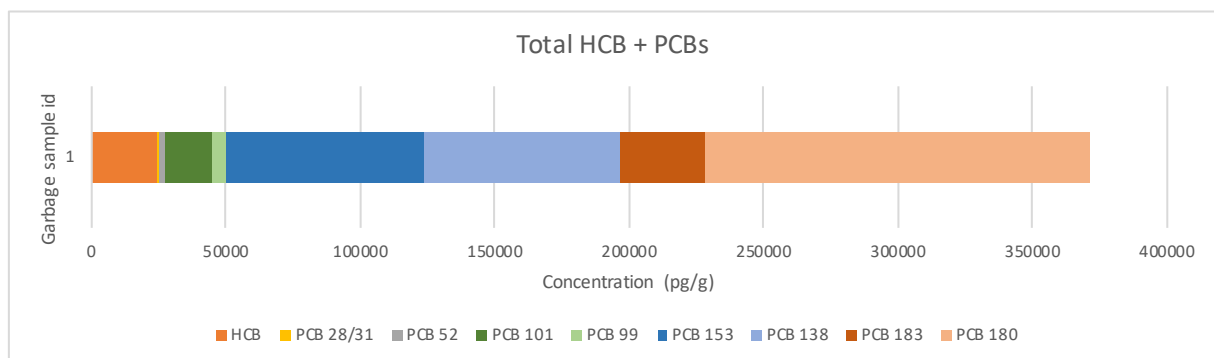
Figure 41: Total HCB and PCBs concentration (pg/g) in garbage sample Y11, divided by component. The different types of colours represent similar numbers of substituted Cl (yellow = tri, black/grey = tetra, green = penta, blue = hexa, orange = hepta) and different colour strength represents different HCB/PCBs. Please note that axes are switched compared to Figure 40.

4.4 FTIR

4.4.1 Explanation of IR-spectra

Figure 42, 43, 44 and 45 shows chemical structure and FTIR-spectra to pristine plastic pellets of respectively PET, PP and PE-HD and PE-LD. Table 2, 3 and explains what the different absorbance frequencies in the spectra represents regarding to their structure (Pavia, 2015, pp. 32-36,64-66).

PET
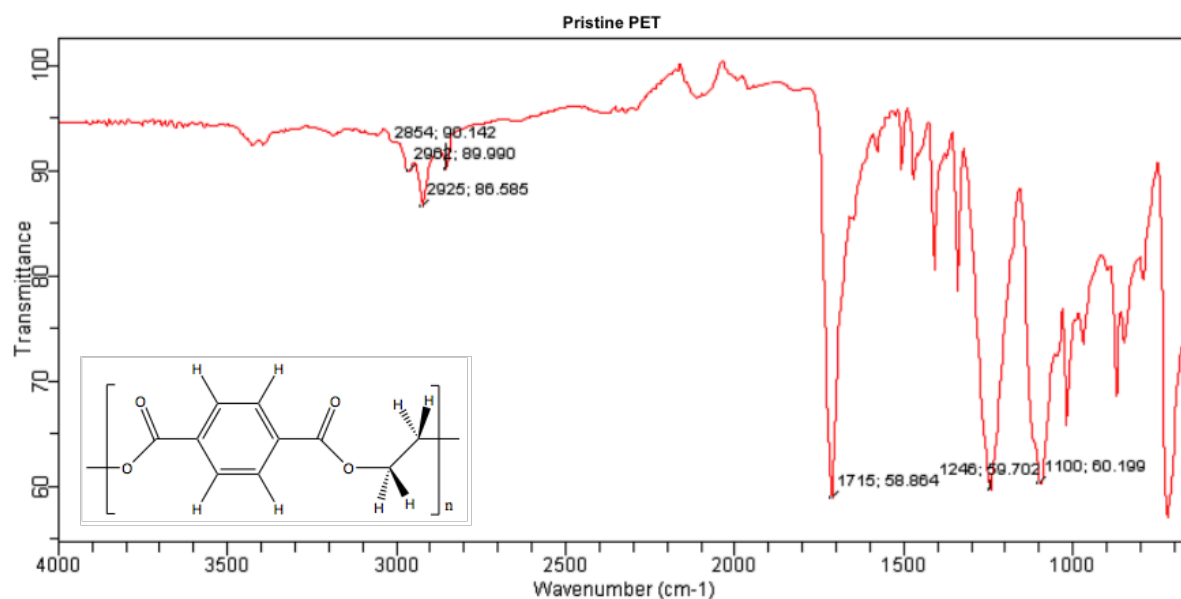
Figure 42: IR-spectra to pristine PET.

Table 2: Explanation of what the different absorbance frequencies in IR-spectra to PET represents.

PET	
Absorbance frequency (cm^{-1})	**Represents**
3400	C=O overtone
3050 - 3010	sp^2 C-H (aromatic rings)
3000 - 2840	sp^3 C-H (alkanes)
1715	Conj. C=O
1600 - 1400	C=C (aromatic)
1300 – 1000	C-O (esters)
850 - 800	para-Disubstituted Rings

PP
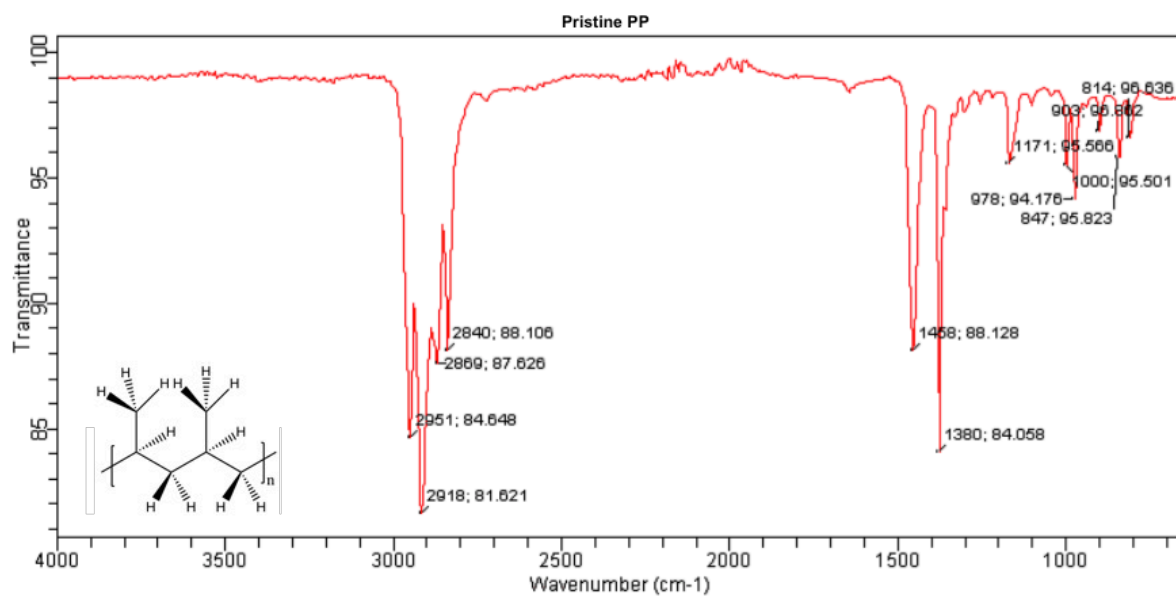
Figure 43: IR spectra to pristine PP.

Table 3: Explanation of what the different absorbance frequencies in IR-spectra to PP represents.

PP	
Absorbance frequency (cm^{-1})	**Represents**
3000 - 2840	sp^3 C-H (alkanes)
Approximately 1465	CH$_2$ bend
Approximately 1375	CH$_3$ bend
Approximately 720	long-chain band

PE-HD and PE-LD

As PE-HD and PE-LD consists of the same type of polymer, they have identical chemical structure and thereby similar IR-spectra.
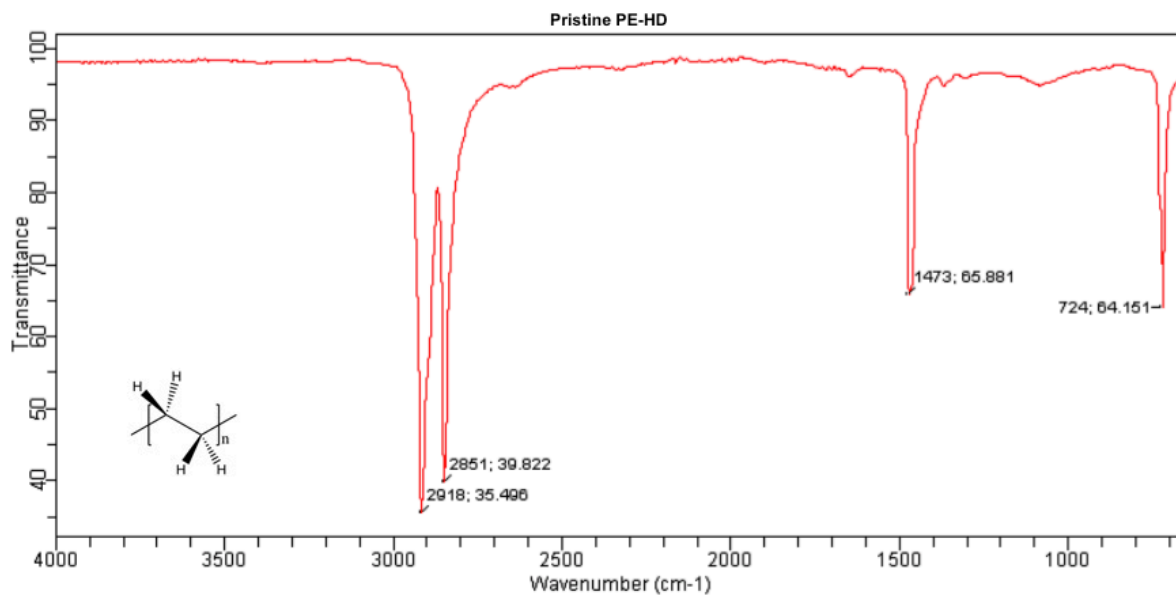
Figure 44: IR-spectra to pristine PE-HD.
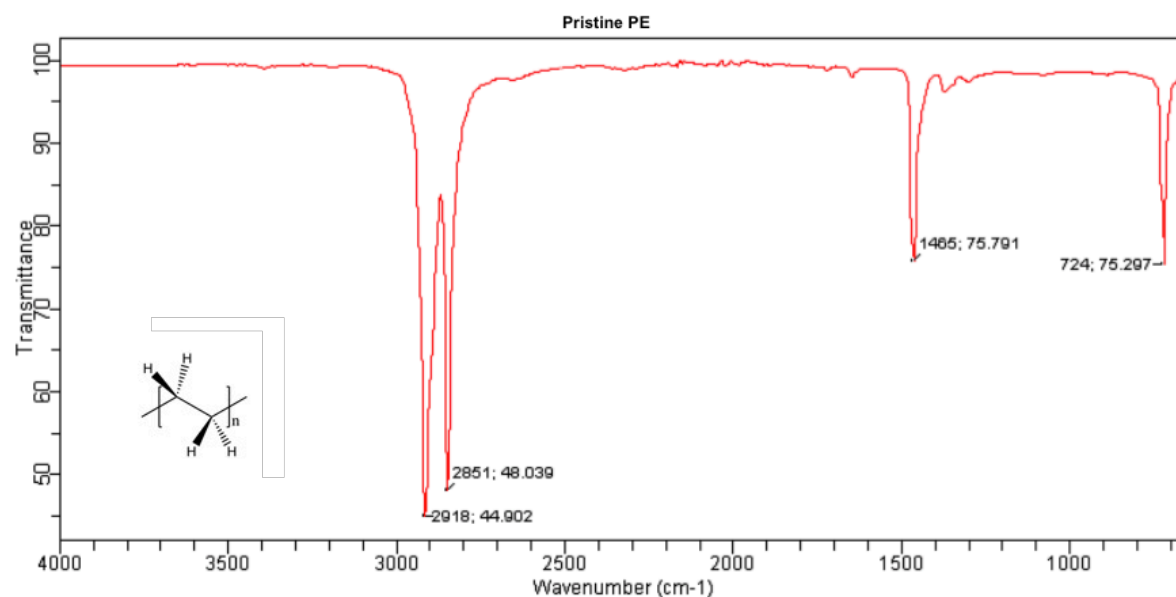
Figure 45: IR-spectra to pristine PE-LD.

Table 4: Explanation of what the different absorbance frequencies in IR-spectra to PE-HD and PE-LD represents.

PE-HD and PE-LD	
Absorbance frequency (cm⁻¹)	**Represents**
3000 - 2840	sp^3 C-H (alkanes)
Approximately 1465	CH_2 bend
Approximately 720	long-chain band *

*Long-chain band represents four or more CH_2 groups in an open chain

4.4.2 Time series samples

Figure 46 compares IR-spectra from the summer batch at time (t) = 0 months and time (t) = 5 months (October 2017). For PE-HD and PE-LD an absorption frequency around 1000 cm⁻¹ has occurred over time, while for PET the absorption frequency around 3000 cm⁻¹ are weakened.
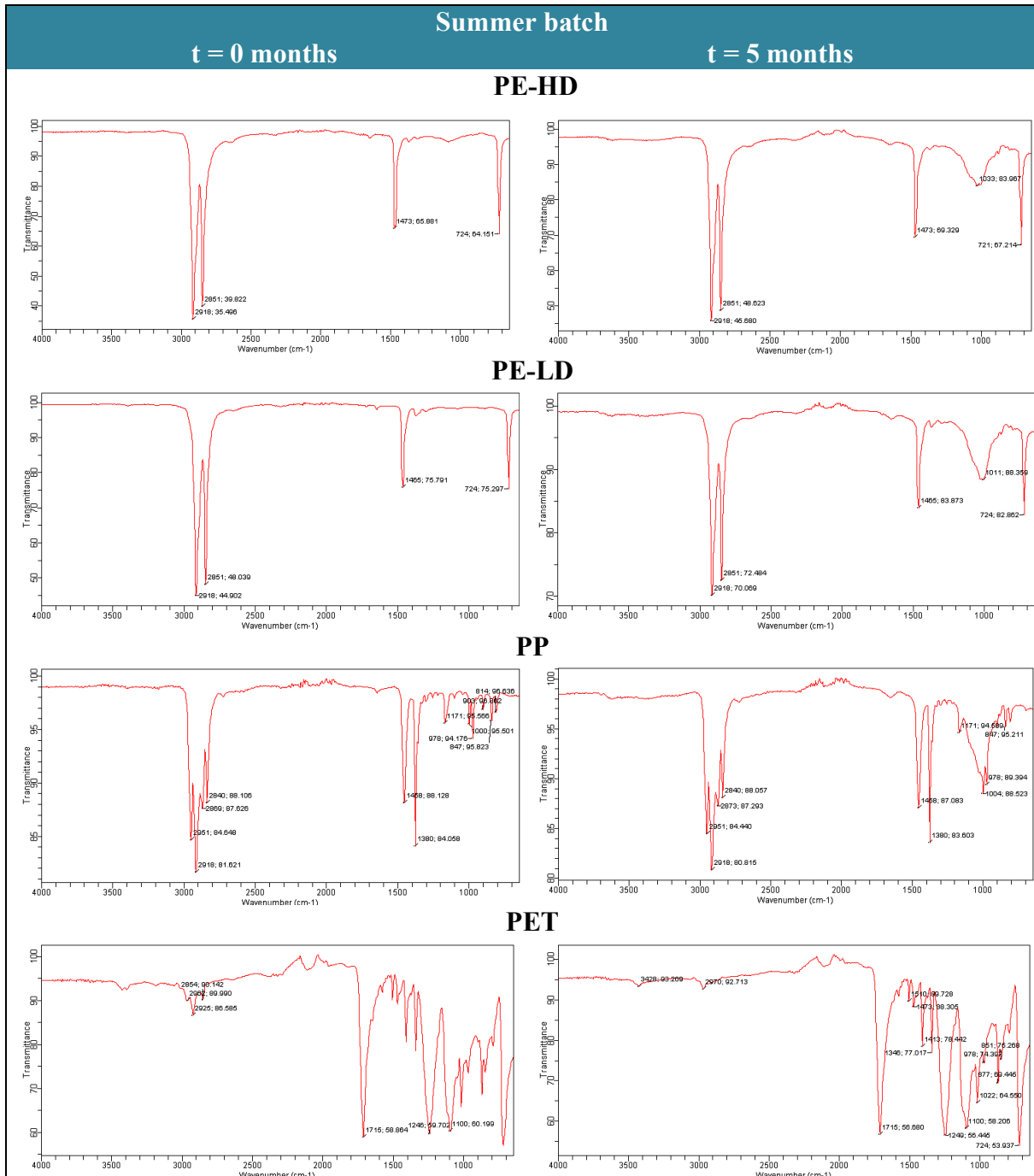
Figure 46: Comparison of IR-spectra to all four plastic types bellowing to the summer batch at time = 0 months and time = 5 months.

Figure 47 compares IR-spectra from the winter batch at time (t) = 0 months and time (t) = 11 months (September 2018). Here as well has an absorption frequency around 1000 cm^{-1} occurred over time for PE-HD and PE-LD, and PET has a weakened absorption frequency around 3000 cm^{-1}.
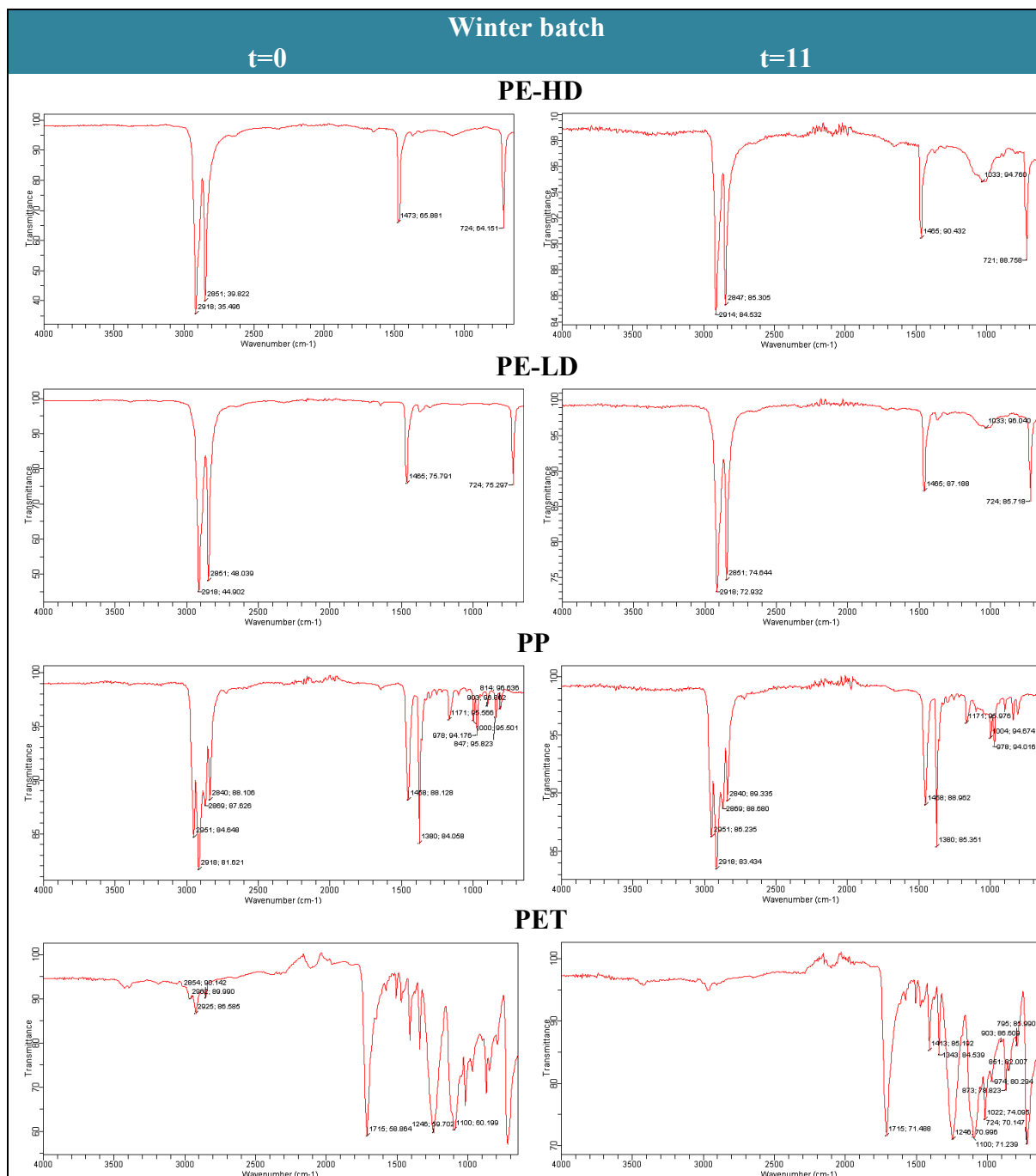
Figure 47: Comparison of IR-spectra to all four plastic types bellowing to the winter batch at time = 0 months and time = 11 months.

4.4.3 Identification of garbage samples with FTIR

A library of IR-spectra was achieved by performing FTIR on 11 different types of known plastic types, respectively PP, PE-LD, PE-HD, PET, PA, UPVC, PC, PS, PHA, PHB and PLA. Full name of each plastic types is listed in abbreviations. The unknown garbage samples were identified by comparing their IR-spectra to those in the library, and Figure 48 visualizes the distribution of plastic types within the garbage samples. Achieved FTIR library, garbage samples IR-spectra and suggestion of their plastic type are listed in Appendix 11 and 12.
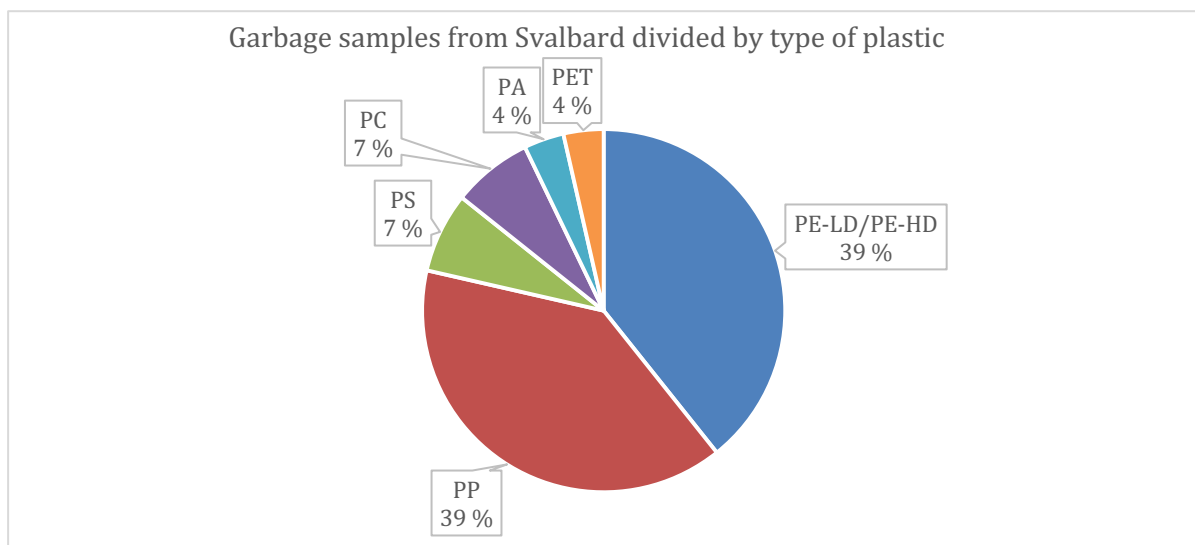
Figure 48: Plastic type distribution of 28 random garbage samples collected along the shoreline in Longyearbyen.

Total 11 out of 28 samples ended up in the PE-LD/PE-HD category, Figure 49 compares IR-spectra to three of them. Left spectra represent "B1", which is a piece of a fishing net, "B6" in the middle is a hard piece of plastic, and "G10" to the right is a soft plastic net.
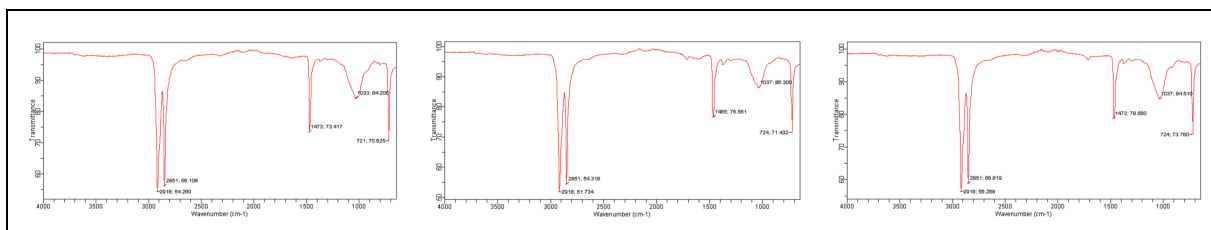
Figure 49: IR-spectra of garbage samples B1(left), B6(middle) and G10(right).

To increase the quality of the qualitative determination of the garbage samples, three measurements of IR-spectra was sampled for each sample. Table 5 contains detailed information from all spectra that belongs to the PE-LD/PE-HD garbage samples. Variations in absorption frequencies around 1000 cm^{-1} within the same sample can be seen in several cases.

Table 5: Detailed FTIR-spectra information from PE-LD/PE-HD garbage samples.

Sample	Parallel	Absorption frequency (cm-1)					Type of product
PE		2918	2851	1465	-	724	Pristine
PEHD		2918	2851	1473	-	724	Pristine
B1	A	2918	2851	1473	1033	721	Fishing net
	B	2918	2851	1473	1033	721	
	C	2918	2851	1473	1041	721	
B2	A	2918	2851	1473	1037	721	Fishing net
	B	2918	2851	1473	1033	721	
	C	2918	2851	1473	1033	721	
B4	A	2918	2851	1473	1037	721	Hard
	B	2918	2851	1473	1033	721	
	C	2918	2851	1473	1033	721	
B6	A	2918	2851	1465	1037	724	Hard
	B	2918	2851	1473	1037	724	
	C	2918	2851	1465	1030	724	
B7	A	2918	2851	1473	1033	721	Fishing net
	B	2918	2851	1473	1037	721	
	C	2918	2851	1473	1037	721	
B8	A	2914	2851	1473	1033	721	Fishing net
	B	2918	2851	1473	1037	721	
	C	2918	2851	1473	1033	721	
G1	A	2914	2851	1473	1030	721	Fishing net
	B	2918	2851	1473	1037	721	
	C	2918	2851	1473	1037	721	
G10	A	2918	2851	1473	1037	724	Soft
	B	2918	2851	1473	1037	724	
	C	2918	2851	1473	1033	724	
G11	A	2918	2851	1469	1037	724	Soft
	B	2918	2851	1473	1033	724	
	C	2918	2851	1473	1037	724	
Y5	A	2918	2851	1473	1037	724	Soft
	B	2918	2851	1473	1037	724	
	C	2918	2851	1473	1033	724	
Y11	A	2918	2851	1473	1033	724	Soft
	B	2918	2851	1473	1033	724	
	C	2918	2851	1473	1037	724	

4.5 SEM
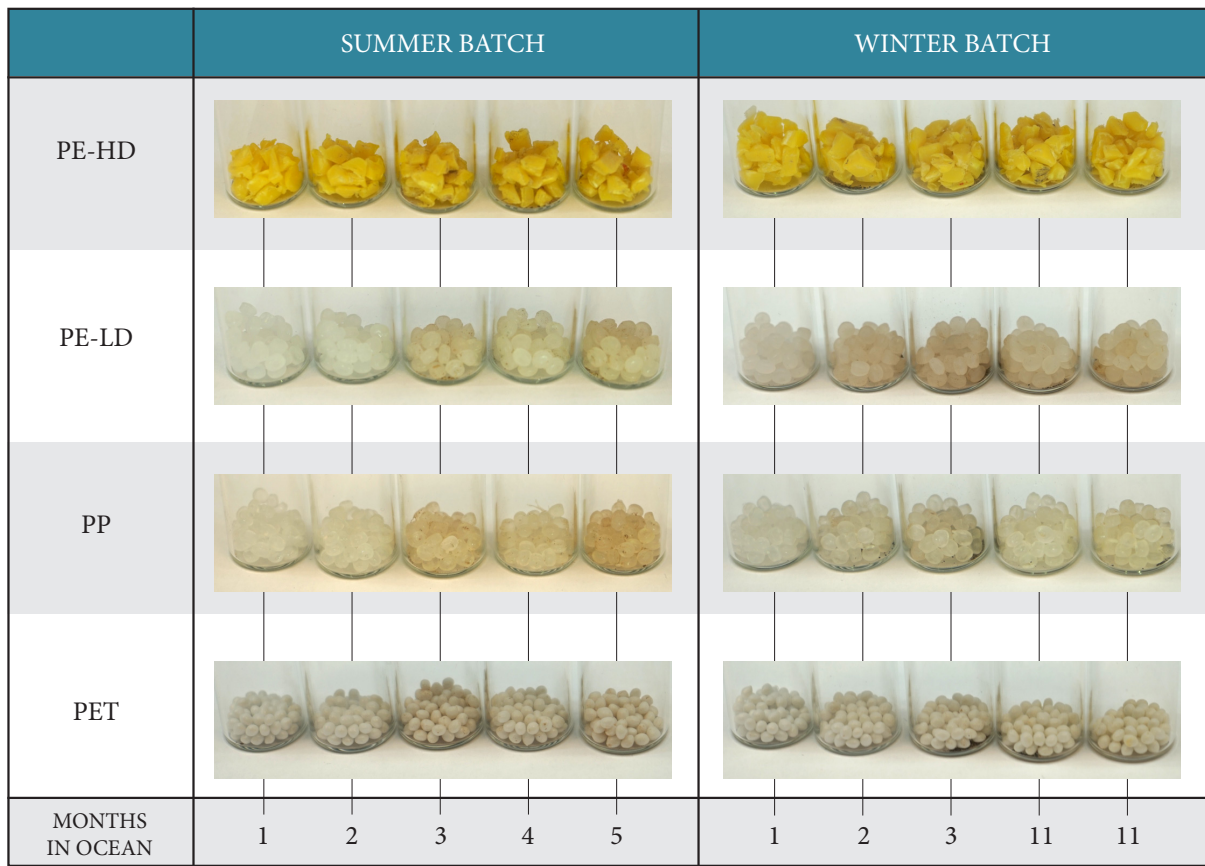
Figure 50: Time trend picture of the plastic pellets after being in the ocean, from the summer batch (left) and winter batch (right). For the white pellet, colour changes over time can be seen.

This section is divided in two parts. The first part compares SEM pictures from the time series samples (Figure 50). Each plastic type (PE-HD, PE-LD, PP and PET) at three stages in the experiment are shown: pristine pellets that have not been in the ocean, pellets from the summer batch after 5 months in the ocean and pellets from the winter batch after 11 months in the ocean. Each pellet is captured at two different magnitudes. The white spots that can be observed in several of the next pictures, especially at those with magnitude ≈ 100, are the conductive silver paste and should not be taken in account as a part of the plastic pellet.

In part two SEM pictures of four garbage samples are presented. To get a better understanding about what these pictures actually shows, a picture of the relevant garbage sample in normal size is placed above each SEM picture.

4.5.1 Time series samples

PE-LD
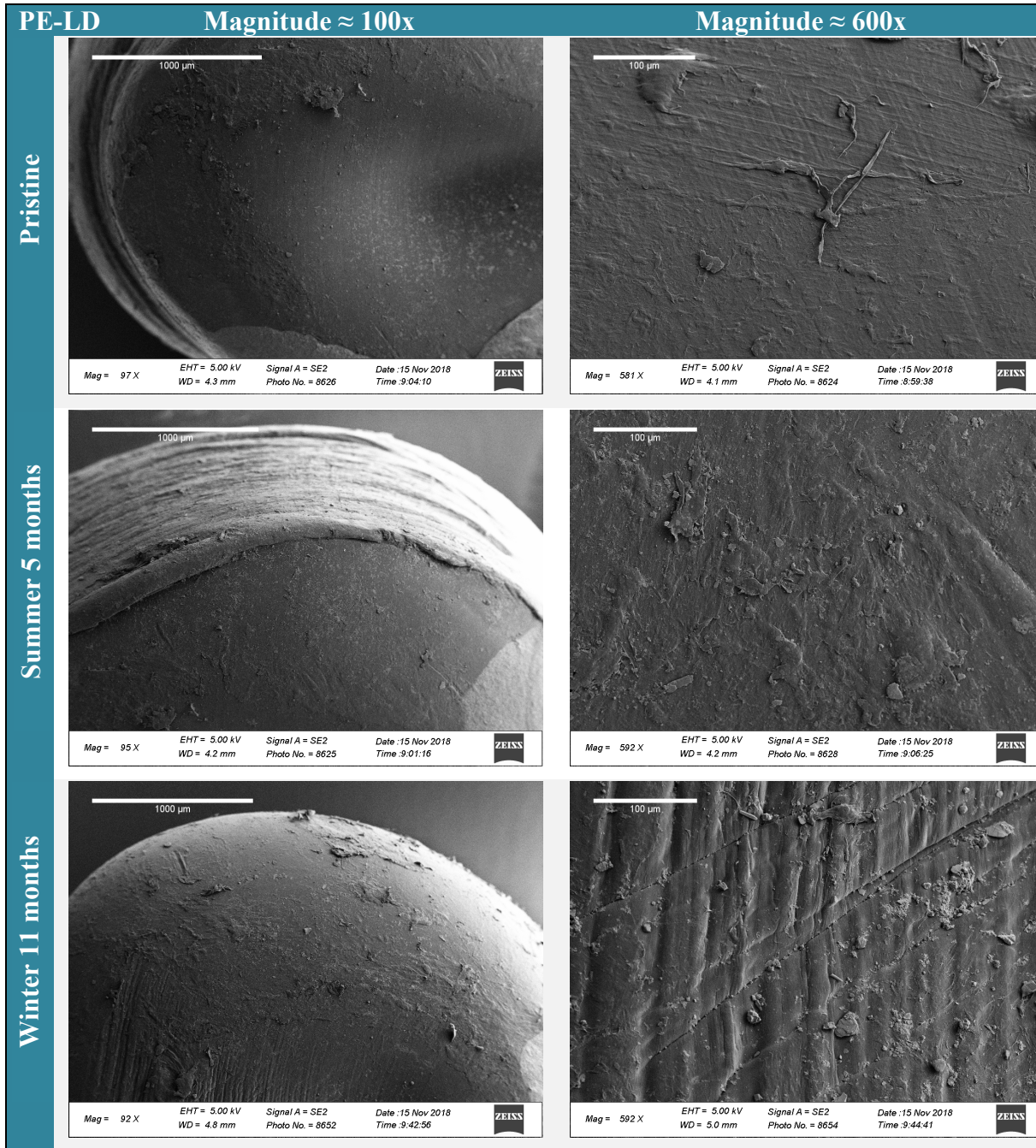
Figure 51: SEM pictures of PE-LD. Columns represents magnitudes: ≈ 100x, ≈ 600x (in order from left to right). Rows represents different stages in the time series experiment: Pristine before entering the ocean, summer after 5 months in the ocean and winter after 11 months in the ocean (in order from top to bottom).

The pristine PE-LD pellet looks quite slippery at both magnitudes, while the pellet at summer 5 months is a bit rougher, and pellet at winter 11 months is even more rough. Distinct scratches at winter 11 months (magnitude ≈ 600x) are clearly seen.

PE-HD
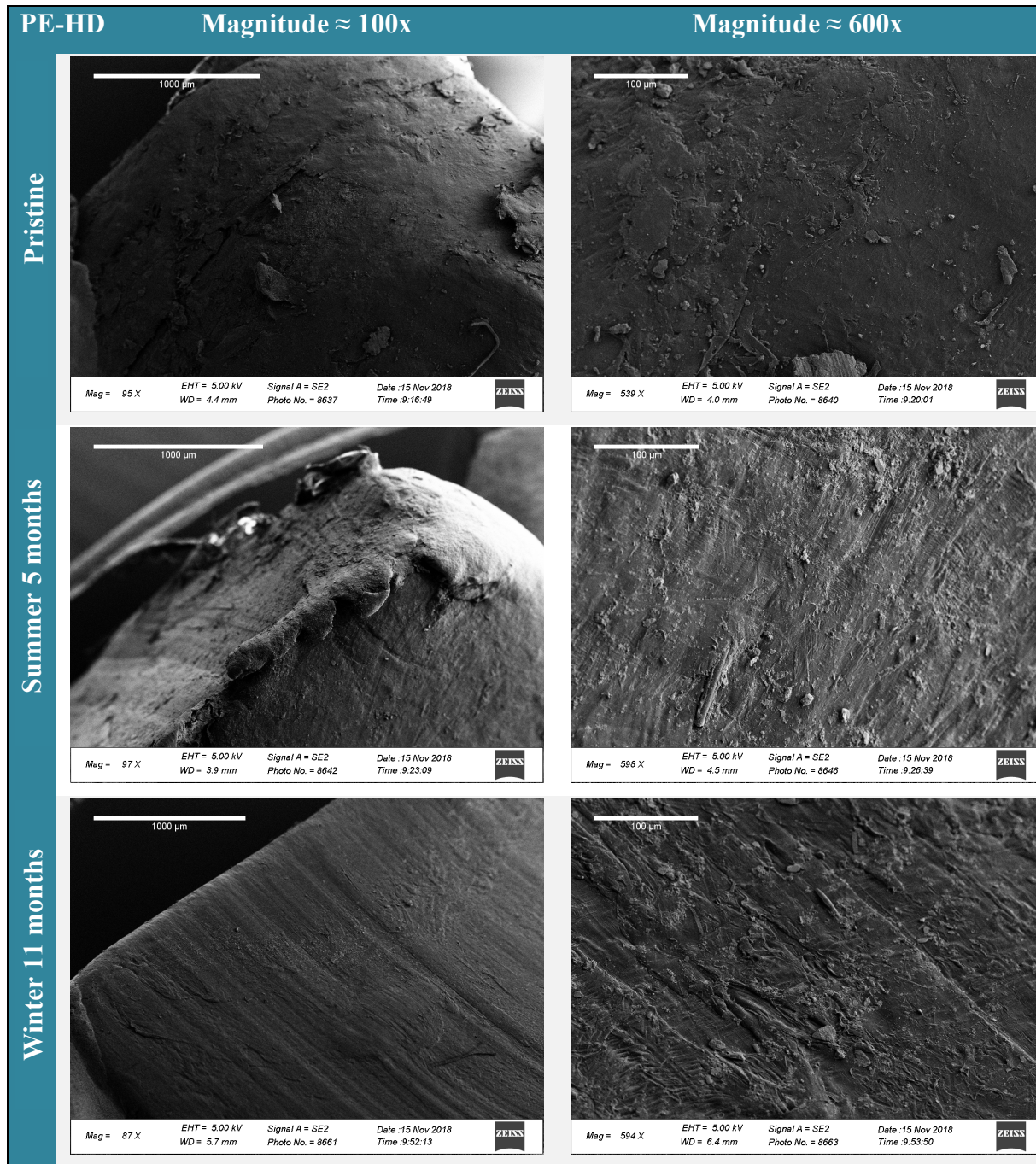
Figure 52: SEM pictures of PE-HD. Columns represents magnitudes: ≈ 100x, ≈ 600x (in order from left to right). Rows represents different stages in the time series experiment: Pristine before entering the ocean, summer after 5 months in the ocean and winter after 11 months in the ocean (in order from top to bottom).

In the pictures to the left (magnitude ≈ 100x) of pristine and summer 6 months the surface of PE-HD is rough, while it looks polished in winter 11 months. Right side pictures (magnitude ≈ 600x) shows the same. However, in winter 11 months is the surface is a bit rough, but it is still polished compared to the pristine and summer 5 months pellets.

PP
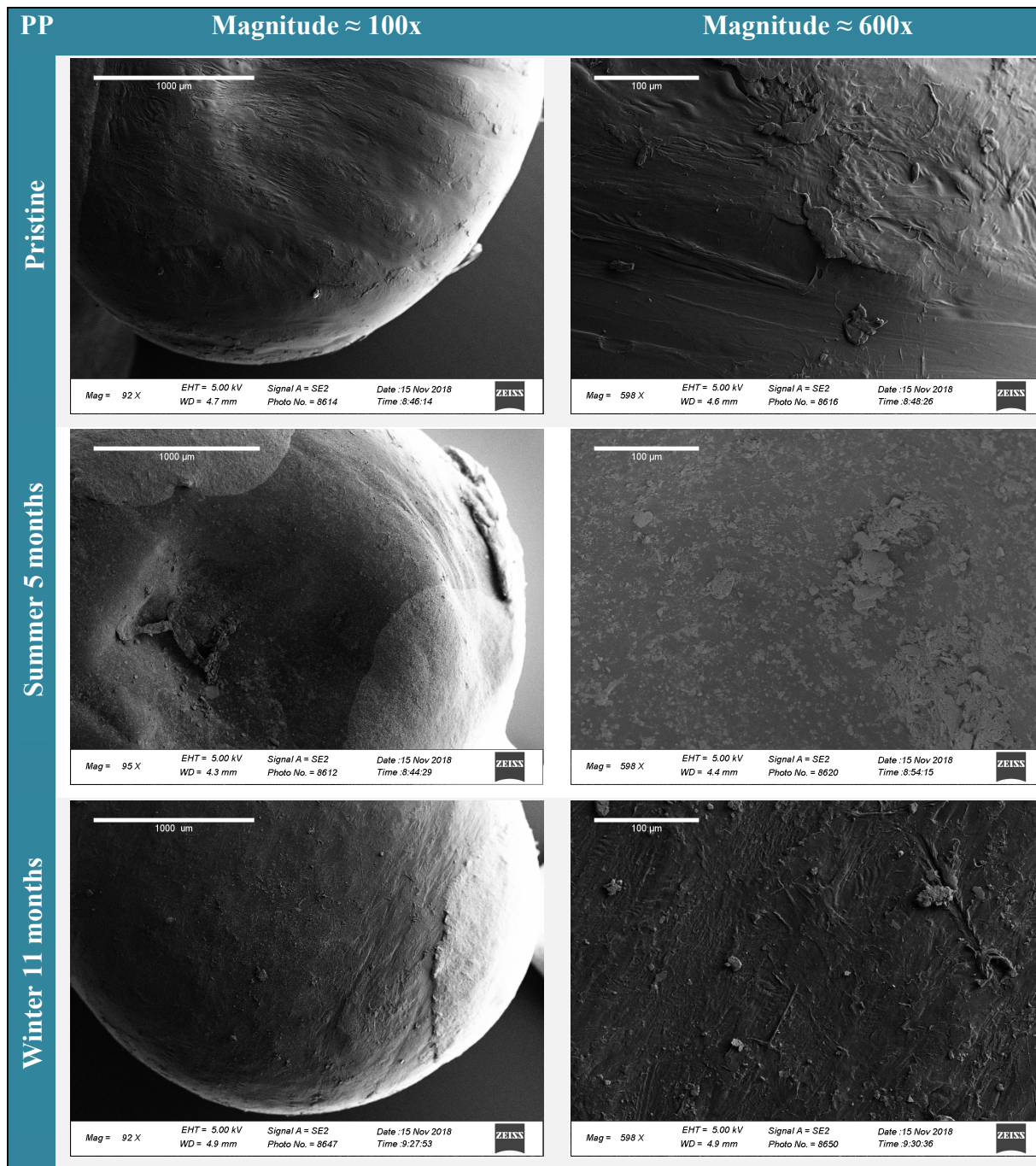
Figure 53: SEM pictures of PP. Columns represents magnitudes: ≈ 100x, ≈ 600x (in order from left to right). Rows represents different stages in the time series experiment: Pristine before entering the ocean, summer after 5 months in the ocean and winter after 11 months in the ocean (in order from top to bottom)

Unfortunately, the pictures at magnitude ≈ 600 of PP are taken with different brightness settings, making them a bit difficult to compare. At both magnitudes, the pristine pellet looks slippery, while summer 5 months and winter 11 months looks a bit rougher. A scratch and several particles are observed on the surface at winter 11 months (magnitude ≈ 600x).

PET
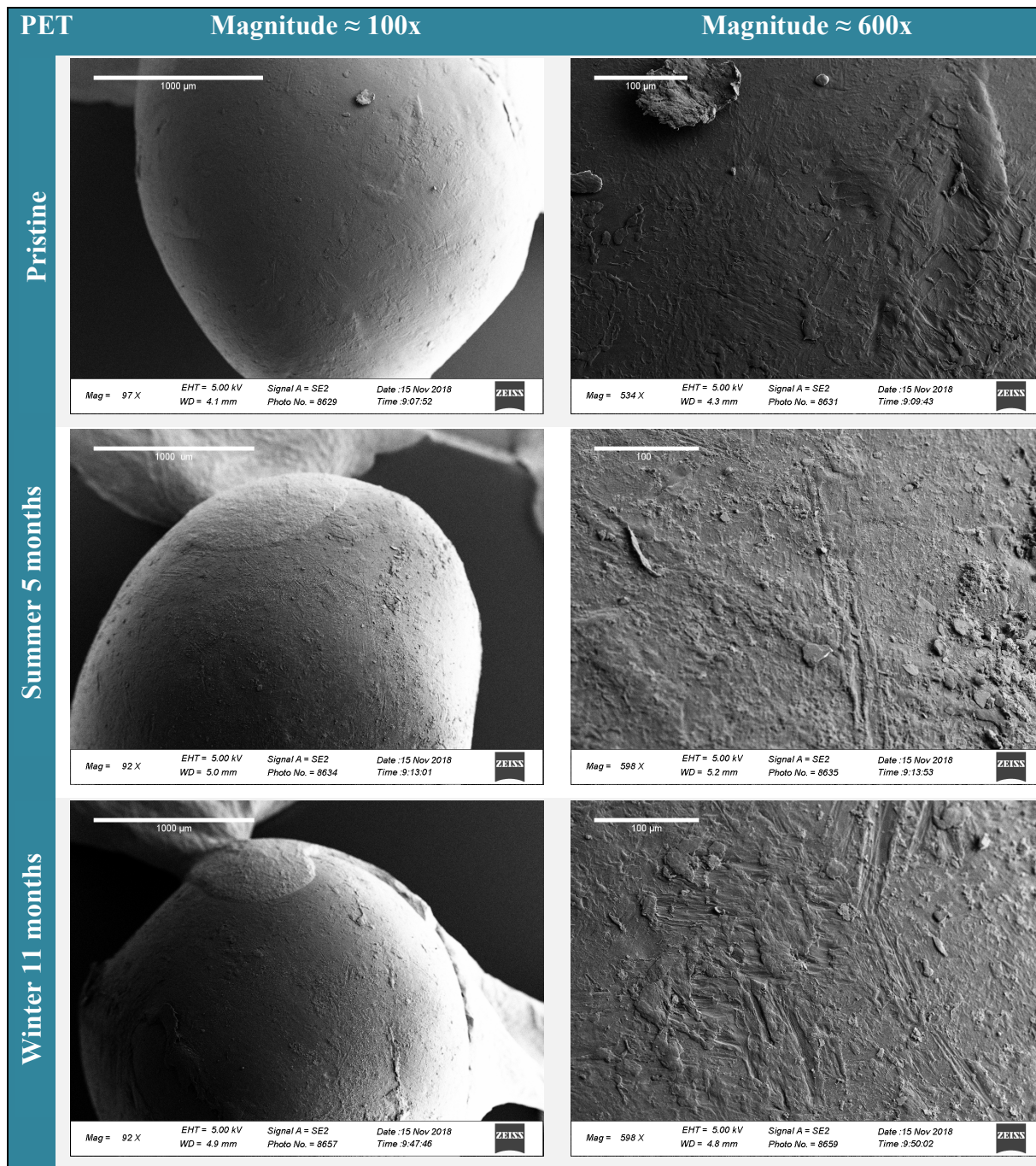
Figure 54: SEM pictures of PET. Columns represents magnitudes: ≈ 100x, ≈ 600x (in order from left to right). Rows represents different stages in the time series experiment: Pristine before entering the ocean, summer after 5 months in the ocean and winter after 11 months in the ocean (in order from top to bottom). The particle (≈100 μm) seen in pristine, magnitude ≈ 600x picture is leftovers from the conductive silver tape.

The surface of PET looks kind of smooth in all pictures above. Several scratches in winter 11 months (magnitude ≈ 600x) and some in summer 5 months (magnitude ≈ 600x) are observed.

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4.5.2 Garbage samples

B1
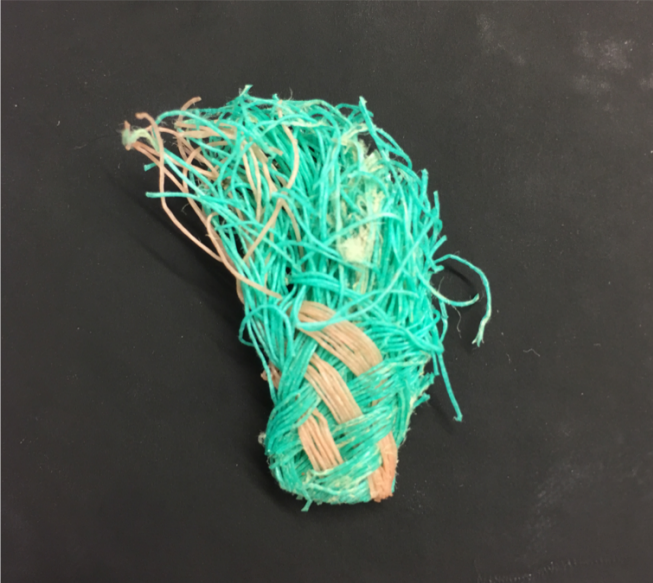
Figure 55: Garbage sample B1.
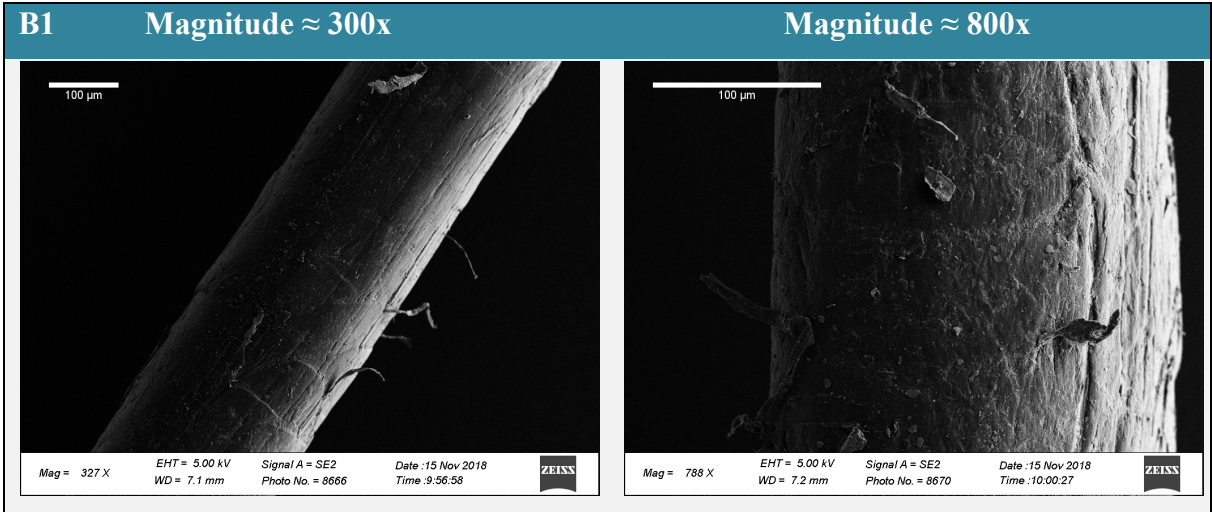
Figure 56: SEM pictures of garbage sample B1 at magnitude ≈ 300x (left) and ≈ 800x (right).

Garbage sample B1 is a piece of a green and orange rope, consisting of many, thinner threads. SEM pictures are focusing at one of these threads. Small fibers sticking out and several scratches in the thread are observed in both SEM pictures.

G4
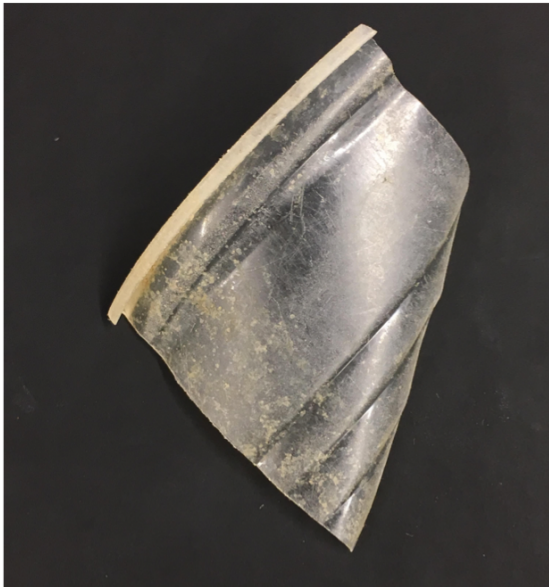
Figure 57: Garbage sample G4.
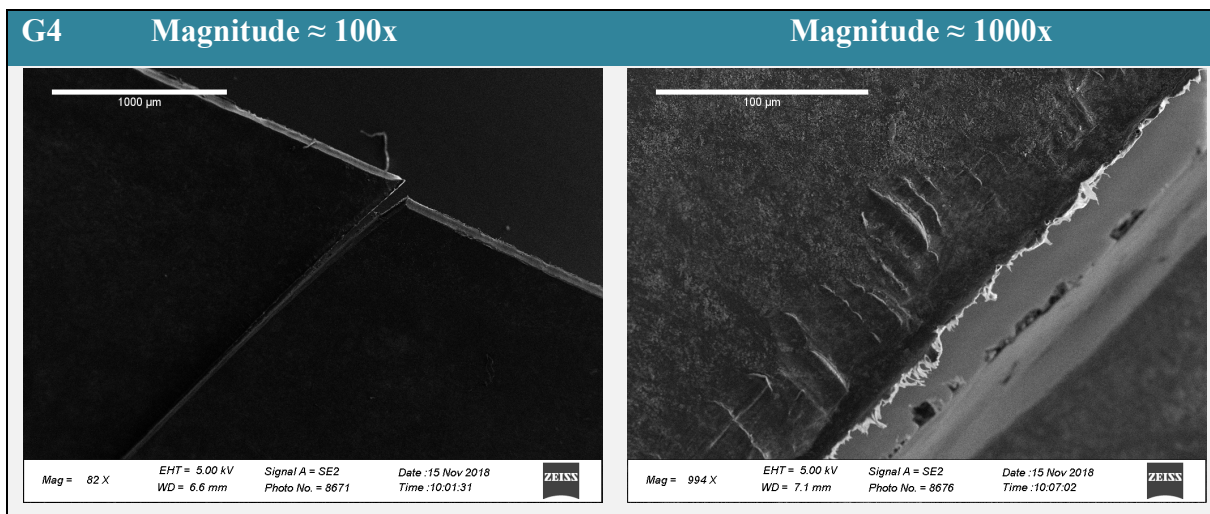
Figure 58: SEM pictures of garbage sample G4 at magnitude ≈ 100x (left) and ≈ 1000x (right).

Garbage sample G4 is a piece of a white/transparent, single use plastic cup. In left SEM picture (magnitude ≈ 100x) is an out sticking fibre and a breakage in the plastic seen. Right SEM picture (magnitude ≈ 1000x) focus on this breakage, and uprising fibers along the edge are observed.

G9
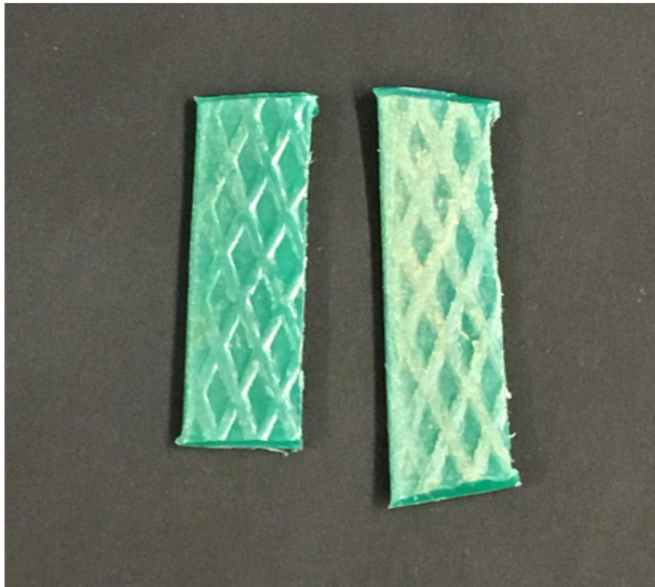
Figure 59: Garbage sample G9.
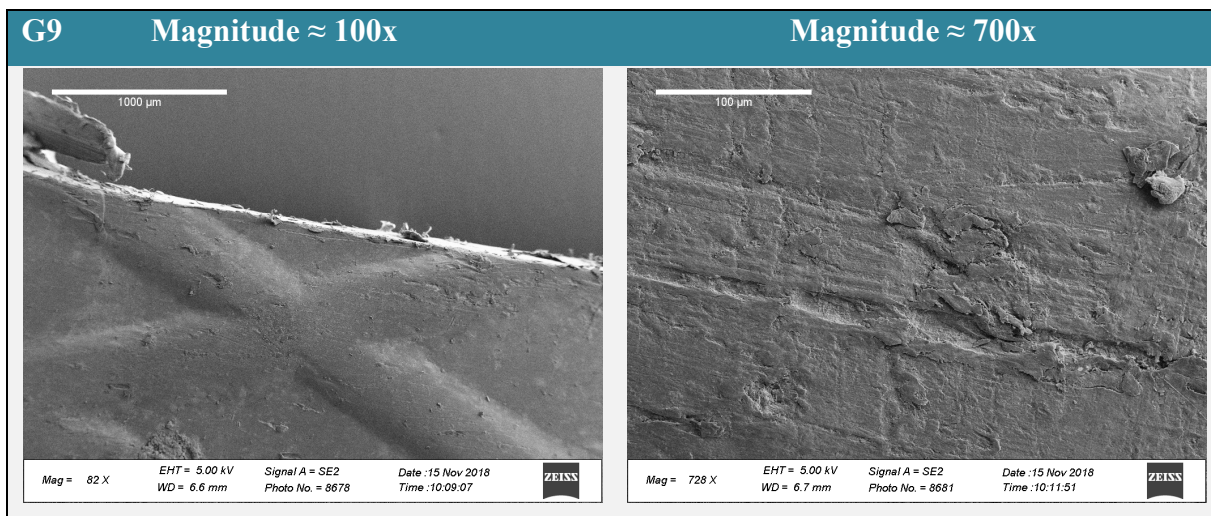
Figure 60: SEM pictures of garbage sample G9 at magnitude ≈ 100x (left) and ≈ 700x (right).

Garbage sample G9 is a piece of a green strips. Left SEM picture (magnitude ≈ 100x) shows outstanding particles along the edge of the strips. Also, a part of the pattern (seen in Figure 59) is recognised here. In right SEM picture (magnitude ≈ 700x) a quite smooth surface with some scratches is seen.

G10
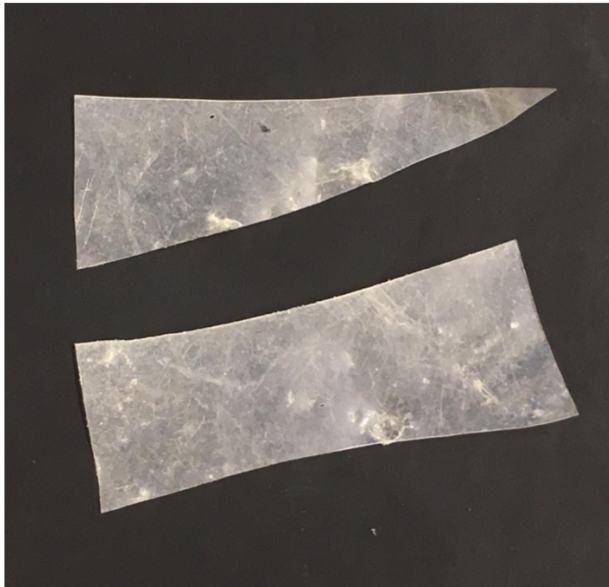
Figure 61: Garbage sample G10.
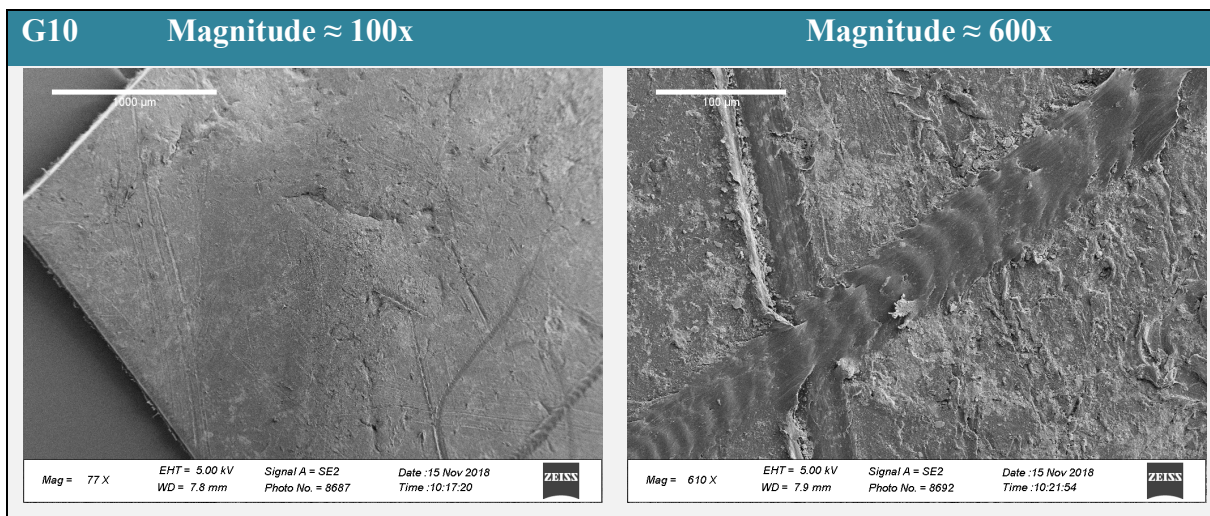
Figure 62: SEM pictures of garbage sample G10 at magnitudes ≈ 100x (left) and ≈ 600x (right).

Garbage sample G10 is a piece of a thick, white/persistent trash bag. Several scratches are observed in all three pictures, also in normal size (Figure 61). In right SEM picture (magnitude ≈ 600x) a wave-like surface is seen.

5 Discussion

5.1 Concentration of POPs in time series samples

5.1.1 Time trend of PBDEs

For the time series samples PBDE-47 and PBDE-99 were the only two PBDEs that had results and/or LOD > 0. For the values replaced with ½ LOD (marked with red * in Figure 31 and 32) is it not possible to say wheatear or not if the actual PBDE are present. Only that none concentration above LOD are detected here.

In the majority of the virgin pellets (PE-LD, PP and PET) the PBDE concentrations were close to LOD or not detected, both for summer and winter batch. This indicate that the water concentration of PBDEs in Ny-Ålesund is very low, and also that minor variations among the influencing factors (see chapter 1.5.2) have an impact. There are none reported values for PBDEs in water measurements from Ny-Ålesund, however air measurements from the Zeppelin Observatory located in a distance of circa 1.7 km from this study´s sampling location have detected both PBDE-47 and PBDE-99 (Hung et al., 2016).

PBDE concentrations in PE-HD samples (weathered fish box) indicate a trend where concentrations increase the first month. At summer time the concentration increases slightly and stabilizes the following months, while it decreases before being stabilized at winter time. Concentrations at summer tends to be higher than at winter. This probably due to the summer having warmer water temperatures and 24 hours of daylight, while the winter has colder water temperatures and complete absent of daylight. The PBDE-47 (log K_{ow} = 6.8) concentration is higher than PBDE-99 (log K_{ow} = 7.3), which can be explained by to water-solubility. The lower log K_{ow} value, the more water-soluble component and the greater presence in water, and more available to adsorb to particles, here represented by plastic. Compared to virgin pellets, there was also detected several other PBDEs in PE-HD. Two reasons for that can be:

1. The pellets of PE-HD are secondary pieces of a weathered, yellow fisher box, while PE-LD, PP and PET are pellets of none coloured, virgin, primarily plastic. PE-HD may therefore contain unknow additives from production, possible PBDEs. This is confirmed by a total PBDE concentration at 500 pg/g in PE-HD before being placed in the ocean (time = 0).

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2. The PE-HD pellets were of greater size then the others, as shown in Figure 5. A greater surface area for POPs to adsorb into the plastic are therefore be available.

As observed in this study, concentration of total PBDEs was found to be higher at summer than winter time, and the PBDE-47 concentration was higher than PBDE-99 concentration. In an unpublished study *"Kinetics of POP sorption and additive release of a variety of polymers under Arctic conditions"* presented by Dorte Herzke (NILU) at the Arctic Frontiers conference in Tromsø January 2019 (https://www.arcticfrontiers.com), the pellets of PE-HD from exact same fish box as in this study been in the ocean in close to a dock in Tromsø. Similar observations were done here, however, concentration of PBDE-47 are 4 times higher in Tromsø then in Ny-Ålesund and PBDE-99 6 times higher. Tromsø has a population of 75 600, while Ny-Ålesund has 130 inhabitants in summer time and 30 in winter time. Considering that Tromsø lies within the Arctic as well, also having low sea water temperature and absent of sun at winter time, suggest that human activity impact PBDE concentrations.

5.1.2 Time trend of HCB and PCBs

The detection frequency for PCBs/HCB > LOD varied between type of plastic. HCB was detected in all four plastics. The virgin plastic pellets PET, PP and PE-HD detected respectively 1, 2 and 4 PCB components, while in PE-HD all of the 12 monitored PCBs were detected. The degree of chlorination impacts the water solubility. PCB 28/31 are among the most water-soluble PCB, it has 3 substituted Cl-atoms and a log K_{ow} = 5.7, and in this study the most frequently detected PCB component. HCB, with log K_{ow} = 5.5, is even more water-soluble than PCB 28/31, explaining its presence in all types of plastic in the project. The more water-soluble, the more detected. Complete list of degree of chlorination and log K_{ow} values to HCB and PCBs can be found in Appendix 13.

The PCB and HCB concentration varied between plastic type. PE-HD has the highest total concentration, and a simple t-test confirmed significant differences between the virgin plastics: PE-LD > PP > PET. As frequencies of components detected varies from plastic to plastic, it makes sense that total concentration does it as well. However, concentration of HCB and PCB28/31 also differs individually between type of plastic. Presence of HCB and PCB 28/31 in PE-HD and PE-LD are more or less within same concentration range, while PP has lower

concentration and PET clearly the lowest. Similarities in a component's concentration between weathered PE-HD and pristine PE-LD suggest that PCBs probably are taken up from the environment, not from production.

PET stood out by being the plastic with lowest concentrations. This result is also found in a similar study from San Diego (Rochman et al., 2013) and is explained by that rubbery polymers like PE-HD, PE-LD and PP are expected to demonstrate greater diffusion (e.g., permeability and greater free volume) than the glassy PET polymer.

Relative difference between concentration of HCB/PCBs and season is seen in Figure 35, being higher at winter time. A possible explanation is presence of sea ice, preventing PCBs in the ocean to evaporate. This is the opposite as for the PBDEs, where the concentrations were highest in the summer season. The difference might be related to differences regarding chemical structure, water-solubility and volatility between PCBs and PBDEs, however this needs to be future studied.

Comparing our results with the study from San Diego (Rochman et al., 2013), where they had a 12 month time trend of 5 plastic types (including those in this project) located in San Diego Bay, shows that concentration of PCB 28/31 in marine plastics are lower in Arctic. The total PCB concentration in PE-HD tends to be similar both places, however numbers of PCBs monitored for were 27 in San Diego compared to 12 in Arctic, whereas 10 are common. Based on this can no conclusion be made. However, an indication that several PCBs are present in Arctic compared to San Diego is given, probably owing to different chemical properties and environmental behaviour between components.

5.1.3 Reproducibility between plastic pellets

None of the plastic pellets are identical in shape and form, explaining PCB concentration variations within same type of plastic. Based on size (in concentration) between replicates within each plastic type (Figure 36 and 37), PET seems to have the most identical pellets while PE-HD seems to have the greatest variations between its pellets. PET is also having a greater number of extracted pellets compared to PE-HD (see Appendix 2), amplifying this suggestion. Reproducibility divided by plastic type from best to least good: PET > PP > PE-LD > PE-HD. This order is the same order as pellet size from smallest to greatest (Figure 5), and opposite

order regarding concentration of HCB/PCBs. PE-HD is secondary plastic from a fragmented fisher box and has the biggest variations between it pellets, while the other plastic pellets are primary produced plastic.

5.2 Concentrations of POPs in garbage samples

5.2.1 PBDE concentrations

Among the garbage samples were several PBDEs detected, where tetra, penta and nona PBDEs constituted the majority. ΣPBDE concentrations varied from < LOD – 162 448 pg/g. Considering that few PBDEs were detected in the virgin pellets, and that several samples were < LOD, it is suggested that most of the PBDEs detected here are additives, and not from the environment.

5.2.2 HCB and PCB concentrations

There is a trend between detection frequency of HCB/PCB and total concentration within each sample. However, ΣHCB+PCB concentrations varies from < LOD – 371 415 pg/g. Since only one sample were < LOD, and a trend between the other samples is seen, it is suggested that HCB/PCBs are absorbed into plastics from the environment, and not from production. Based on the results from the time trend of HCB and PCBs, the variance in total concentration among garbage samples can be explained with them being different types of plastics.

5.3 FTIR

5.3.1 Time series samples

Study of Figure 23 (Absorption regions for common bonding types) and Figure 46 and 47 indicates that the type of bonding occurring over time in PE-HD and PE-LD at 1000 cm^{-1} is a bend C-H, and that the absorption frequency around 3000 cm^{-1} that weakened in PET over time is representing a planar C-H.

Beside this, very few changes in IR-spectra have occurred over time. Spectra from winter batch at 11 months are quite similar to those from summer batch at 5 months, even these plastics have stayed in the ocean 6 months longer. After 11 months in the Arctic ocean are negligible changes regarding their chemical structure found. These results confirm that plastics are stable products, resistant to environmental degradation.

5.3.2 Identification of garbage samples with FTIR

Most spectra were surprisingly easy to identify, but to distinguish between PE-LD and PE-HD was challenging. 39% of garbage samples ended up in this category and most of these had an absorption frequency around 1000 cm^{-1}, which neither pristine PE-LD or pristine PE-HD has. For the time series spectra, it was observed that this frequency occurs over time in PE-HD and PE-LD, it is therefore likely to expect that the case has been the same for these garbage samples.

Even though the physical properties vary between PE-LD/PE-HD garbage samples B1, B6 and G10, their spectra look quite similar (Figure 49). The result is not surprising as they do have the same chemical structure, which is exactly the information an IR-spectra provides (see chapter 1.8.2).

IR-spectra are used to provide structural information about a sample and does not give any information regarding density, which is the main difference between PE-HD and PE-LD. A closer study of their physical properties, and some kind of density test might make it possible to determine if samples are PE-LD or PE-HD. A possible explanation for absorption frequency variations within same sample and same type of plastic (Table 5) is copolymers. With intent to give products specific properties, plastic can consist of more than one type of polymer from

production. However, the IR-spectra should likely have been more affected if several polymers are present.

5.4 SEM

5.4.1 Time series samples

The weathered PE-HD pellets are rough in its "pristine" form, and the surface are polished as it spends time in the ocean. For the pristine PE-LD and PP were opposite observations founds. Their surfaces seem to be quite smooth before being placed in the ocean, while scratches and roughness formed over time, and PE-LD are more changes over time than PP. The surface of pristine PET is also smooth. After spending time in the ocean are very few changes found, just a few scratches are formed. PET seems to be plastic type being most resistant to environmental degradation.

A combination of sea ice (at winter time), other pellets being in contact with each other inside the teabag and ocean waves are probably main reasons for both forming scratches and polishing pellets. That opposite surface changes occurred in this experiment gives an idea that this might be a repetitious process, and as a consequence are microplastic fragmented and released to the environment.

During sampling, some of the pellets were in contact with both the teabag plus and other pellets, while some of them might have been in the middle of the bag and only in contact with other pellets, which might affect regarding surface changes. The samples were not scrubbed and properly cleaned before SEM, just shortly dipped in Milli-Q water. It is therefore a chance that some of the particles about to break, observed in several SEM pictures might be salt and impurities.

A disadvantage is that samples are lost for further studies other than SEM after being coated. Considering that none pellets are identical in shape and form, it would be even more interesting to investigate changes in exact same pellet over time.

5.4.2 Garbage samples

Common for samples B1 and G10 is that both are identified as PE, and microplastics seems to be released from anywhere of it surface. For G4 (PP) and G9 (PET) microplastic tends to break off along the edges of the products. It must be taken in account that the SEM pictures might have been taken from different angles according to garbage sample, possible affecting the visualization of particles about to break off. Also, how many days, months, maybe even years the garbage samples have been in the environment is unknown, probably variating from sample to sample. Considering that the rope (Figure 55) consists of probably 100 threads like the one in SEM Figure 56, and that this kind of ropes are widely used by fishermen, is this a huge source of released microplastic at sea.

5.5 Evaluation of study

Average recovery for ΣPBDE = 106 % and ΣHCB+PCB = 112 %. Further details regarding recovery can be found in Appendix 10. The were no control samples available for this matrix (plastic), however the method used has previously been used for biological matrices were certified reference material are available, and shown acceptable results. It is therefore assumed that it works for plastic as well, and the analysis is controlled at all times through internal standards.

It was desirable to indicate how long the plastic garbage collected in Longyearbyen have stayed in the environment based on its POP concentration. However, to fit reasonable linear/exponential trend lines with respect to POP concentrations in the time trend samples were not able. Another challenge to consider, as plastics are complex chemical cocktails (see chapter 1.1.1), POPs detected in a random plastic samples may come from production.

It is important to remember that result of each of these environmental samples is a snapshot. A lot of factors influence, not only out in the environment but also inside at the laboratory, including how samples are treated, cross contamination on equipment and instruments, condition of the GC column etc. Variations in LOD can also matter. Result in this study could been improved by increasing number of replicates.

If this time series experiment is ethical correct can be discussed, as the opportunity of releasing microplastic to the environment during sampling exists. On the other hand, plastics are very persistent, also, the pellets were stored inside a teabag which hopefully collected microplastic particles if any released from the pellets.

6 Conclusions and future perspectives

This is the first study to report POPs adsorption to pristine plastic under Arctic conditions. Summer and winter time trend study of PE-HD, PE-LD, PP and PET in the ocean (Kongsfjorden) outside Ny-Ålesund showed that adsorption rate and concentration of POPs vary by type of plastic and season. The POPs adsorb more to rubbery polymers (PH-HD, PE-LD, PP) than glassy polymers (PET). Trend regarding POP concentration and plastic type from greatest to least are PE-HD > PE-LD > PP > PET. Stability in weathered plastics chemical structure was affirmed by FTIR, confirming plastics as persistent products. Surface investigation with SEM showed that microplastics are fragmented into smaller microplastics in the marine environment, and that degradation rate and process vary by type of plastics. Rough pellets become smoother by time, smooth pellets become rougher. PCB concentrations adsorbed to plastic are considerably lower in the Arctic compared to San Diego, and PBDE concentrations considerably lower in Ny-Ålesund compared to Tromsø.

This study shows that there is a ubiquitous presence of POPs in garbage samples. Plastic garbage samples collected along the shore in Longyearbyen was identified by IR-spectra, and most plastic were either PE or PP. Analysis of these samples showed that POP concentration was highest in PE plastics. This allows to conclude that marine plastic litter carries and transports pollutants. Surface investigation of four of the samples showed that fragmentation of PE tends to happen anywhere on its surface, while along edges of PP and PET.

Based on results in this study, PE-HD is classified as the most harmful and PET the least harmful type of plastic if entering the Arctic marine environment, both regarding adsorption of POPs and degree of degradation.

For future perspective would a study of why the total concentrations of PBDE and PCBs are highest in opposite seasons be of interest. Also, making a 12-month time trend, expanding the list of plastic types, POPs analysed for and the number of sampling locations within the Arctic, and a closer study of if/how much the sea ice is influencing concentration of POPs in the Arctic ocean.

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Appendix

Appendix 1: Chemicals, Materials and Standards

Chemicals

Substance	Purity/Quality	CAS number	Supplier
Acetone	Suprasolv	67-64-1	Merck
Bis(2-ethylhexyl)phthalate	≥ 96 %	117-81-7	Alfa Aesar
Corn oil	-	8001-30-7	MP Biomedicals
Cyclohexane	Suprasolv	110-82-7	Merck
Dichloromethane	Suprasolv	75-09-2	Merck
Florisil (0,150 – 0,250 mm)	-	1343-88-0	Merck
Isooctane	Suprasolv	540-84-1	Merck
Metanol	Suprasolv	67-56-1	Merck
Methoxychlor		72-43-5	Merck
n-hexane	Suprasolv	110-54-3	Merck
Perylene	≥ 98 %	198-55-0	Merck
Sulfur	≥ 99 %	7704-34-9	Merck
Nitrogen (g)	5.0	7727-37-9	Nippon gases (Praxair)
Helium (g)	5.0	7440-59-7	Nippon gases (Praxair)

Materials

Usage/description	Product name/nr	Supplier
Analytical balance	Sartorius	Mettler Toledo, Colombus, Ohio, USA
Analytical balance	Sartorius	Mettler Toledo, Colombus, Ohio, USA
Auto sampler (CG-MS)	TriPlus RSH^{TM} Autosampler	Thermo Fisher Scientific, Waltham, Massachusetts, USA
Auto sampler (CG-MS)	TriPlus RSH^{TM} Autosampler	Thermo Fisher Scientific, Waltham, Massachusetts, USA
Balance	PG802	Mettler Toledo, Colombus, Ohio, USA
Chemistry Software, drawing molecules	ChemDraw Professional 17.1	Waltham, Massachusetts, USA
Computer program for adding scale bar into picture	ImageJ 1.52a	LOCI, University of Wisconsin, Madison, USA
High Temperature Laboratory ovens	Carbolite cwf 1100, Carbolite LHT4/30/E301/OTC	Carbolite Gero, Hope Valley, UK
Extraction, cleaning equipment	Ultrasonic Cleaner USC - THD	VWR international, Radnor, Pennsylvania, USA
FTIR	Cary 630 FTIR	Agilent Technologies, Santa Clara, California, USA
Gas Chromatograph – Mass Spectrometer	TRACE 1310 – Q Exactive^{TM} GC Orbitrap^{TM}	Thermo Fisher Scientific, Waltham, Massachusetts, USA
GC column (15 m x 0.25 mm ID x 0.10 μm)	P/N 10296	Restek Corporation, Benner Cir, Bellefonte, USA
GC column (30 m x 0.25 mm ID x 0.25 μm)	P/N 26096-1425	Thermo Fisher Scientific, Waltham, Massachusetts, USA
GPC Columns	Envirogel GCP cleanup Columns: 19 x 300 mm 19 x 150 mm	Waters Corporation, Milford, Massachusetts, USA
GPC Fraction collecter	Fraction Collector II	Waters Corporation, Milford, Massachusetts, USA
GPC Pump	Waters 515 HPLC Pump	Waters Corporation, Milford, Massachusetts, USA
GPC UV-Detector	Waters 2487 Dual Absorbance Detector	Waters Corporation, Milford, Massachusetts, USA
Heating of florisil	Drying oven	
Plastic (Plastox specification)	PE-HD: PTX171 PE-LD: PTX102 PET: PTX401 PP: PTX200	Carat Gmbh, Harderhook, Bocholt, Germany
Scanning Electron Microscope	ZEISS Sigma	ZEISS, Oberkochen, Germany
SEM Carbon Conductive stickers	PELCO Tabs^{TM} (AGY5604)	Agar Scientific Ltd, Stansted, Essex, UK
SEM Coater	Polaron SC7640	Quorum Technologies, Ashford, Kent, UK

Silver paste	AGG3790	Agar Scientific Ltd, Stansted, Essex, UK
Software for quantification	TraceFinder v. 4.1 EFS	Thermo Fisher Scientific, Waltham, Massachusetts, USA
SPE Columns	SilactSPE™	AFFINISEP, Pôle d'innovation des couronnes, Boulevard, France
SPE Computer program	Biotage RapidTrace SPE Workstation Version 2.1.0.45	Biotage AB, Uppsala, Sweden
SPE Frits (3 ml)	Catalog # FRIT-100.3 lot: 180823	AFFINISEP, Pôle d'innovation des couronnes, Boulevard, France
SPE Robot	RapidTrace	Biotage AB, Uppsala, Sweden
Vials (300μl) with screw top	Chromacol 887119324130307	Thermo Fisher Scientific, Waltham, Massachusetts, USA
Volume reduction	MiVac QUATTRO	Genevac, Ipswich, UK
Volume reduction	RapidVap	LABCONCO, Kansas, Missouri, USA
Volume reduction	Reactic-Therm III #TS-18823 Heating/Stirring Module	Thermo Fisher Scientific, Waltham, Massachusetts, USA
Volume reduction	TurboVap 500	Zymark/Sotax AG, Aesch, Switzerland
Vortexer	Vortex	VWR international, Radnor, Pennsylvania, USA
Water purification system	ZLXS5003Y	Millipore S.A, Molsheim, France

Standards

Internal standards

PCB I

Component	Concentration (pg/(μl) (44.16)	Concentration (pg/(μl) (15.18)
13C PeCB	96.4	98.8
13C HCB	100	98.2
13C PCB- 28	243	237
13C PCB- 52	243	239
13C PCB- 101	245	236
13C PCB-105	243	240
13C PCB- 114	244	237
13C PCB- 118	244	236
13C PCB- 123	242	242
13C PCB- 138	245	238
13C PCB- 153	246	238
13C PCB- 156	242	236
13C PCB- 157	245	236
13C PCB- 167	243	238
13C PCB- 180	243	239
13C PCB- 189	244	237
13C PCB- 209	244	237

PEST I

Component	Concentration (pg/(µl) (39.17)
13C tr.Nonachlor	108
13C Cis-NonaChlor	49.3
13C tr.Chlordane	49.2
13C Cis-Chlordane	98.7
13C Oxychlordane	676
13C Heptachlor epoxid	815
13C HeptaChlor	1386
13C Dieldrin	1292
13C Mirex	765
13C Endosulfan I	108
13C Endosulfan II	128
13C Endosulfan Sulfate	69.5
13C Trifluralin (di-n-propyl)	70.5
13C Endrin	987
13C Aldrin	1250
13C Isodrin	2536

DDT I

Component	Concentration (pg/(µl) (01.17)
13C alpha-HCH	997
13C beta-HCH	197
13C gamma-HCH	998
13C delta-HCH	436
13C p.p.DDE	319
13C o.p.DDD	321
13C p.p.DDT	330

PBDE I

Component	Concentration (pg/(µl) (41.16)	Concentration (pg/(µl) (22.18)
13C PBDE- 28	260	254
13C PBDE- 47	263	269
13C PBDE- 99	263	244
13C PBDE- 153	265	255
13C PBDE- 183	265	257
13C PBDE- 197	261	255
13C PBDE- 206	262	257
13C PBDE- 209	589	1232

Internal standard mixtures

Name	Compound	Amount (µl)	Added to samples
ISTD MIX 10.04.18	PCB I (44.16)	250	S1(1), S2(1), S3(1),
	PEST I (39.17)	250	S4(1), S5(1), W1(1),
	DDT I (01.17)	250	W2(1), W3(1)
	PBDE I (41.16)	250	
	Isooctane	1500	
ISTD MIX 02.05.18	PCB I (44.16)	250	S1(2), S2(2), S3(2),
	PEST I (39.17)	250	S4(2), S5(2), W1(2),
	DDT I (01.17)	250	W2(2), W3(2)
	PBDE I (41.16)	250	
	Isooctane	1500	
ISTD MIX 3105.18	PCB I (15.18)	125	All garbage samples
	PEST I (39.17)	125	
	DDT I (01.17)	125	
	PBDE I (41.16)	125	
	Isooctane	750	
ISTD MIX 16.10.18	PCB I (15.18)	125	W4(1), W4(2),
	PEST I (39.17)	125	W5(1), W5(2)
	DDT I (01.17)	125	
	PBDE I (22.18)	125	
	Isooctane	750	
ISTD MIX 08.11.18	PCB I (15.18)	125	P(1), P(2)
	PEST I (39.17)	125	
	DDT I (01.17)	125	
	PBDE I (22.18)	125	
	Isooctane	750	

Recovery standard

Component	Concentration (pg/(µl)
13C PCB – 159	213

Quantification standards

PCB kv. Std

Component	Concentration (pg/(µl) (47.17)
13C PeCB	7.98
13C HCB	8.29
13C PCB- 28	20.1
13C PCB- 52	20.1
13C PCB- 101	20.3
13C PCB-105	20.1
13C PCB- 114	20.2
13C PCB- 118	20.2
13C PCB- 123	20.0
13C PCB- 138	20.3
13C PCB- 153	20.4
13C PCB- 156	20.0
13C PCB- 157	20.3
13C PCB- 167	20.1
13C PCB- 180	20.1
13C PCB- 189	20.2
13C PCB- 209	20.2
12C PCB- 18	7.62
12C PCB- 28	7.59
12C PCB- 31	7.59
12C PCB- 33	7.62
12C PCB- 37	7.62
12C PCB- 47	7.59
12C PCB- 52	7.59
12C PCB- 66	7.62
12C PCB- 74	7.59
12C PCB- 99	7.59
12C PCB- 101	7.59
12C PCB- 105	7.62
12C PCB- 114	7.62
12C PCB- 118	7.62
12C PCB- 122	7.62
12C PCB- 123	7.62
12C PCB- 128	7.62
12C PCB- 138	7.59
12C PCB- 141	7.62
12C PCB- 149	7.62
12C PCB- 153	7.59
12C PCB- 156	7.62
12C PCB- 157	7.62
12C PCB- 167	7.62
12C PCB- 170	7.62
12C PCB- 180	7.59
12C PCB- 183	7.62
12C PCB- 187	7.62
12C PCB- 189	7.59
12C PCB- 194	7.59

Component	Concentration (pg/(µl) (47.17)
12C PCB- 206	7.62
12C PCB- 209	7.59
12C HCB	8.69
12C PeCB	8.46
1, 2, 3, 4 TCN	72.0

PBDE kv. std

Component	Concentration (pg/(μl) (22.18)
13C PBDE- 28	49.9
13C PBDE- 47	52.9
13C PBDE- 99	48.0
13C PBDE- 153	50.2
13C PBDE- 183	50.5
13C PBDE- 197	50.2
13C PBDE- 206	50.6
13C PBDE- 209	135
PBDE- 3	49.2
PBDE- 7	49.2
PBDE- 15	49.2
PBDE- 17	49.2
PBDE- 28	49.2
PBDE- 47	49.2
PBDE- 49	49.2
PBDE- 66	49.2
PBDE- 71	49.2
PBDE- 77	49.2
PBDE- 85	49.2
PBDE- 99	49.2
PBDE- 100	49.2
PBDE- 119	49.2
PBDE- 126	49.2
PBDE- 138	98.3
PBDE- 153	98.3
PBDE- 154	98.3
PBDE- 156	98.3
PBDE- 183	98.3
PBDE- 184	98.3
PBDE- 191	98.3
PBDE- 196	98.3
PBDE- 197	98.3
PBDE- 206	246
PBDE- 207	246
PBDE- 209	246

Quantification standards mixtures for GC-MS

HCB and PCBs

Name	Compound	Amount (µl)
Kvstd mix nr. 1	PCB kv.std (47.17)	10
	13 C-PCB 159 REC.STD	20
	Isooctane	170

PBDEs

Name	Compound	Amount (µl)
Kvstd mix nr. 2	PBDE kv.std (22.18)	50
	Isooctane	180

Compound	Compound	Amount (µl)
Kvstd mix nr. 3	Kvstd mix nr. 2	20
	13 C-PCB 159 REC.STD	10
	Isooctane	180

Calibration solution for GPC

Compound	Amount (mg/L)
Corn oil	62.500
Bis(2-ethylhexyl)phthalate	2.500
Methoxychlor	500
Perylene	50
Sulfur	200
Methylene chloride	Add until total volume of solution is 1L

Solvents and amount needed to run 10 samples on SPE robot

Compound	Amount (ml)
20 % MeOH in DCM	60
DCM	60
10 % DCM in hexane	160
Hexane	40

Computer program for SPE robot

Name: FLOKORT.SPE

No	Step	Source	Output	Vol (ml)	ml/min	Liquid Sense
1	Purge-Cannula	MeOHdcm	Cannula	6	30	No
2	Purge-Cannula	dcm	Cannula	6	30	No
3	Condition	dcmhex	org	4	5	No
4	Condition	hex	org	2	3	No
5	Load	Sample	Fract1	0,6	0,6	No
6	Add to Sample	hex	Cannula	1	10	No
7	Load	Sample	Fract1	1,1	0,6	No
8	Collect	dcmhex	Fract1	6	0,6	No
9	Collect	dcmhex	Fract1	6	0,6	No
10	Collect	hex	org	1	10	No

Appendix 2: Sampling details: location, dates, type, mass and number of extracted pellets

Sampling location

Time trend sampling was done 3 meters under sea level in Kongsfjorden, hanging from a harbour in Ny-Ålesund. GPS location: 78°55'42.1"N 11°56'09.2"E. Garbage samples were collected along the shore in Longyearbyen.
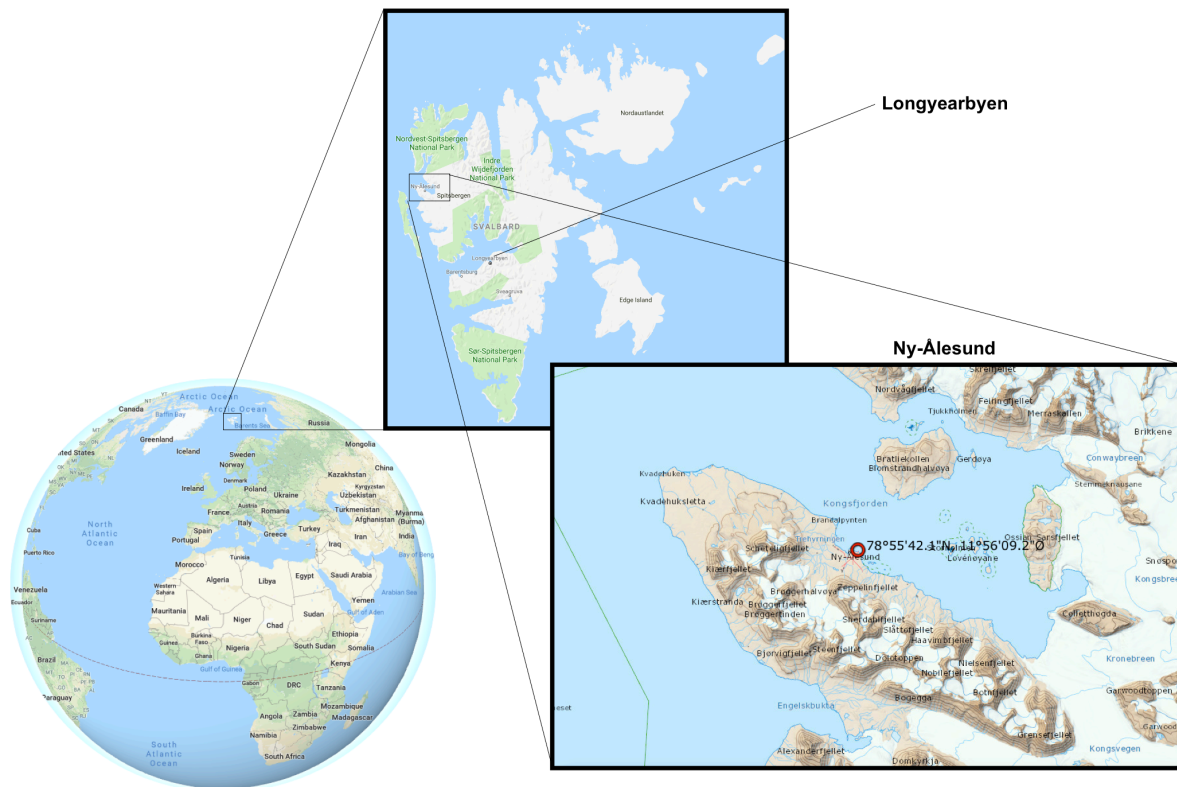
Figure 63: Sample location. Maps are taken from google maps (https://www.google.no/maps) and Topo Svalbard (©Nork Polarinstitutt https://toposvalbard.npolar.no).

Sampling dates for summer- and winter batch

Summer Batch (Placed in ocean 24.05.17)		Sample name (S = summer)
Sampling 1	26.06.17	S1
Sampling 2	19.07.17	S2
Sampling 3	22.08.17	S3
Sampling 4	19.09.17	S4
Sampling 5	20.10.17	S5

Winter Batch (Placed in ocean 20.10.17)		Sample name (W = winter)
Sampling 1	21.11.17	W1
Sampling 2	21.12.17	W2
Sampling 3	20.01.17	W3
Sampling 4	15.09.18	W4
Sampling 5	15.09.18	W5

Type of plastic, mass and number of extracted pellets

Sample name	Type of plastic extracted							
	PP		PE		PET		PE-HD	
	Mass (g)	Num. of pellets	Mass (g)	Num. of pellets	Mass (g)	Num. of pellets	Mass (g)	Num. of pellets
S1(1)	0.40	19	0.41	14	0.40	23	0.40	12
S2(1)	0.41	18	0.41	14	0.40	24	0.40	14
S3(1)	0.40	17	0.41	14	0.41	23	0.41	14
S4(1)	0.41	16	0.40	14	0.41	24	0.40	14
S5(1)	0.40	17	0.42	14	0.40	23	0.40	12
W1(1)	0.40	18	0.40	14	0.41	24	0.41	11
W2(1)	0.41	17	0.41	14	0.41	24	0.40	11
W3(1)	0.40	18	0.42	15	0.41	23	0.40	13
W4(1)	0.41	17	0.40	14	0.41	24	0.40	12
W5(1)	0.41	19	0.40	14	0.40	24	0.40	7

Type of plastic, mass and number of extracted pellets (parallel)

Sample name	Type of plastic extracted							
	PP		PE		PET		PE-HD	
	Mass (g)	Num. of pellets	Mass (g)	Num. of pellets	Mass (g)	Num. of pellets	Mass (g)	Num. of pellets
S1(2)	0.40	19	0.41	15	0.41	24	0.41	14
S2(2)	0.40	17	0.41	14	0.41	24	0.40	14
S3(2)	0.41	17	0.40	14	0.40	23	0.40	16
S4(2)	0.40	17	0.41	14	0.41	25	0.40	13
S5(2)	0.41	17	0.40	14	0.40	23	0.41	13
W1(2)	0.40	18	0.41	15	0.41	23	0.40	12
W2(2)	0.41	16	0.41	14	0.40	23	0.40	12
W3(2)	0.40	17	0.41	14	0.41	24	0.40	12
W4(2)	0.41	18	0.40	14	0.40	22	0.40	13
W5(2)	0.41	18	0.40	14	0.41	24	0.40	10

Type of plastic, mass and number of extracted pristine pellets (including parallel)

Sample name	Type of plastic extracted							
	PP		PE		PET		PE-HD	
	Mass (g)	Num. of pellets	Mass (g)	Num. of pellets	Mass (g)	Num. of pellets	Mass (g)	Num. of pellets
P(1)	0.40	16	0.41	14	0.40	24	0.40	11
P(2)	0.41	18	0.42	15	0.41	24	0.40	11

Mass and descriptiopn of extracted garbage samples

Sample id (randomly selected)	Type of plastic extracted		What it might be, soft/medium/hard
	Unknown (garbage samples)		
	Mass (g)	Num. of pellets	
B1	0.40	-	Rope, medium
B4	0.40	-	Unkown, hard
B6	0.41	-	Unkown, hard
B7	0.40	-	Rope, medium
B8	0.40	-	Rope, medium
G1	0.40	-	Rope, medium
G2	0.37	-	Rope, soft
G4	0.40	-	Plastic cup, soft
G9	0.40	-	Strips, hard
G10	0.40	-	Plastic net, soft
G11	0.20	-	Unkown, soft
G14	0.40	-	Unkown, hard
Y2	0.41	-	Unkown, hard
Y4	0.40	-	Philadelphia cover, soft
Y5	0.40	-	Plastic net, soft
Y6	0.40	-	Rope, medium
Y8	0.40	-	Plastic glove, soft
Y11	0.40	-	Plastic net, soft

Appendix 3: Detailed experimental section

General experimental considerations

The laboratory work during this study has been performed at the Norwegian Institute for Air Research (NILU), located at Framsenteret in Tromsø. Chemicals and solvents were used as received. Complete overview of chemicals, materials and instruments used are listed in Appendix 1. All glassware in the laboratory were first machine washed with washing powder (Neodisher®LaboClean A8) for 40 minutes, rinsed with acetone and cyclohexane respectively and burned at 450 °C for 8 hours. Depending on solvent involved during different parts in the procedure were parts of the glassware rinsed with corresponding solvent as well before use. The "preparation of samples before analysis"-step took place in a clean cabinet, while the rest of the work was carried out in a normal fume hood.

Preparation of time series samples before entering the ocean

Four different types of plastic pellets virgin PP, virgin PE-LD, virgin PET and pieces of PE-HD from a beached fisher box were positioned in four separated teabags, making each tea bag containing only one type of plastic. Each of these tea bags were gathered in a washing net which represented one interval in the experiment. A total of ten nets were made, divided in to two batches and sent to Svalbard.

Sampling of time series samples

Employees from Norwegian Polar Institute handled the batches at Svalbard and located them in the Arctic ocean for two different time periods, respectively summer and winter. The batches were placed 3 meters below sea level from a floating dock in Ny-Ålesund. Within each period, the five washing nets were collected at different time intervals, covered with aluminium foil, placed in a zip bag, labelled with date and stored in freezer until analysis at NILU in Tromsø. Sampling dates are listed in Appendix 2.

Preparation of time series samples before analysis

The alumina wrapped, weathered plastic samples were taken from the freezer and left on the bench to reach room temperature. To get rid of parts of the salty sea water, the tea bags were shortly dipped one by one in a beaker of Milli-Q water, opened and set out on aluminium foil in clean cabinet to dry overnight. This step was done in a clean cabinet to prevent dust from the laboratory, which possible can contain POPs, to contaminate the samples when they had to stay

around 24 hours in open air. Overpressure prevents dust to enter the cabinet, and the air in the clean cabinet goes through a HEPA filter and a filter with active coal which removes particles and impurities before entering the cabinet. The dried samples were transferred into cyclohexane rinsed and labelled glass vials and stored in freezer until analyses.

Preparation of garbage samples before analysis

A random selection of 28 plastic garbage items collected along the shore in Longyearbyen were cut into microplastic pieces and transferred to cyclohexane rinsed vials.

Internal standard

A mixture of PCB I, PEST I, DDT I and PBDE I was made in a 1:9 dilution with isooctane. The internal standard mixture was stored in refrigerator, but always left to reach room temperature before use. Weight at room temperature was always measured and noted before and after every use to control possible unwanted evaporation.

Extraction

Plastic samples were taken out from freezer and left for 1 hour to reach room temperature. In order to increase the quality of the work of the time series analysis, a parallel was made from this step. Garbage samples were analysed without parallel. Approximately 0.4 g of every plastic sample was weighed out and transferred to 4 ml vial. Complete overview of exact mass and number of pellets extracted for all samples are listed in Appendix 2. 50 µl of internal standard mix was added on top of the plastic pellets. Blank samples (vial without plastic pellets) was prepared for circa every fourth plastic sample and processed the same way as the plastic samples. The plastic pellets were extracted with 2 ml cyclohexane, vortexed for 30 seconds and placed in ultrasonic bath for 20 minutes. This was repeated three times, where the 3 x 2 ml extract from each step was combined in a 12 ml round bottom tube (with screw top). The temperature increased when the ultrasonic bath was intensively used. If the water temperature exceeded 40 °C ice was added. The extracted plastic pieces remaining in the 4 ml vials were left in fume hood overnight so eventual solvent residuals evaporated, then thrown away.

Concentration nr. 1: RapidVap

The extracts were concentrated from 6 ml to 0.5 ml by controlling heat, vortex motion and vacuum in RapidVap. Even though the samples were extracted the exact same way and contained the same amount of cyclohexane, they used unequal time to evaporate to 0.5 ml. RapidVap settings are listed in appendix 4.

Filtering

The concentrated extracts were vortexed some seconds before filtered from the round bottom tube over to a new 4 ml glass vial through a piece of Kimtech paper that was pressed to the bottom inside of a glass pipette. Each sample had a new filter pipette. A small amount of dichloromethane (DCM) was added to the empty round bottom tube, vortexed and transferred over the filter to wash possible sample materials left in the tube over to the sample.

Concentration nr. 2: Nitrogen gas and solvent shift

A solvent shift from cyclohexane to DCM was performed using nitrogen gas to steam down the filtered samples from ca. 1 ml to 0.1 ml, and then add 1.5 ml DCM. The nitrogen flowed through metal tips that were washed 10 minutes in DCM on ultrasonic bath. The tips were placed 0.5 to 1 cm above the sample vials, which were standing in a heat block at 35 °C. To avoid splash and loss of sample, the nitrogen flow was kept slow and soft, and the surface of the samples should nearly move during the evaporation. Cross contamination was prevented by washing the metal tips between every use.

GPC clean-up

The GPC clean up system was prepared from its standby modus where it was recycling DCM at flow rate 0.5 ml/min. The pump was set to stop, waste tube removed from the recycled DCM flask over to waste container, and the recycled DMC flask changed to a new DCM flask. The pump was then run again, and flow rate adjusted with 1 ml/min per minute from 0.5 ml/min to 5 ml/min. UV-detector was turned on, and the x-axis on the absorbance detector scale set to 30 minutes. On the beginning of every day the GPC system was used, 0.3 ml of calibration solution was run to check that things were OK, and that the pump worked as it should. A closer study of the calibration graph showed that fraction should be collected 14 minutes after sample injection for 11 minutes. Before sample injection, a turbovap fraction glass was placed under the fraction collector machine, and sample vortexed for minimum 1 minute. The injector was

set to its LOAD position (disconnected from the flow path) and sample injected to the sample loop with use of a syringe. Injector was then set back to inject position, and DCM (mobile phase) flow through the sample loop and lead sample contents to the column. Possible air inside of the syringe was removed before injection, preventing air to get inside the system. It took around 25-30 minutes to run one sample. Photo of the absorbance graph at 30 minutes after injection was taken for each sample. The syringe was taken apart, covered in DCM and placed in ultrasonic bath for 10 minutes between every injection. An eye was always kept on the amount of DCM in the flask to prevent the system to go dry, on the tubes to be aware of any leakages that could appear, and on the waste container volume. At the end of the day, the system was set back to standby modus where flow rate was down adjusted with 1 ml/min per minute from 5 ml/min to 0.5 ml/min, the waste tube and the inlet solvent tub returned to the recycled DCM flask, and the UV-detector turned off.

Concentration nr. 3: TurboVap

Before samples were concentrated with TurboVap, a two-step acetone cleaning routine of the system was performed. Sensor endpoint on the TurboVap machine was set to 0.5 ml, and fan speed to B. Around 10 ml acetone was added to an empty TurboVap glass and run until endpoint without cooling, then repeated once more with cooling. The collected fractions from GPC clean-up was concentrated from 55 ml to 0.5 ml by running them on TurboVap with cooling until endpoint. 3 pipettes of DCM were added along the glass wall to wash possible sample remaining back to the sample, then run again to endpoint. The sample was transferred to a 12 ml round bottom tube with screw top (fitting the robot module used in next clean-up step), and another washing along the TurboVap glass wall was done with 1-2 pipettes of hexane. This time without running it on the TurboVap machine, but just directly pipetting it over to the round bottom sample containing tube. Cross contamination was avoided with acetone cleaning with cooling between each sample run on TurboVap.

Concentration nr. 4: MiVac

Based on injection volume at the SPE clean-up robot (used in next step), volume had to be reduced from around 1 ml to 0.5 ml using MiVac. Samples were balanced inside of a concentrator, and adjustments in temperature, rotation and pressure evaporated first DCM, then hexane until wanted volume was achieved. Also here, the time needed to reach final volume varied for sample to sample. MiVac settings are listed in Appendix 4.

SPE clean-up

In SPE clean-up, each sample was injected by a robot and run through a florisil packed column. Preparations done prior to SPE: Florisil was burned at 450 °C for 8 hours (overnight), and columns and frits washed with DCM. Washing of columns was done by letting some pipettes of DCM run through the columns and then left to dry, while the frits were covered completely with DCM in an Erlenmeyer flask for 10 minutes, then set out on aluminium foil in fume hood to dry overnight. To run a sample, one column packed with 1 g florisil between two frits was needed. Dust mask was used to prevent inhalation of florisil. 12 ml round bottom tubes (with screw top) used for fraction collection by the robot (one per sample) were washed with hexane: 1-2 pipettes were added to the tubes, vortexed fast, then thrown to waste and tubes left to dry. Necessary solvents and mixtures were prepared with respect to the robot program "FLOKORT.SPE", see additional information in Appendix 1. The tubes were placed at the modules left side, samples on the right, and the packed columns above (gently pressed down a few times to check that the spring worked fine). The samples were run overnight by the automated system.

Concentration nr. 5: RapidVap nr. 2

Again heat, vortex motion and vacuum in the RapidVap was used to concentrate the samples from a volume around 10-12 ml (depending on how much solvent that had evaporated over night) to 1-2 ml. A half pipette of isooctane was added to wash possible sample remaining on the glass wall over to the sample. Concentration continued until volume was reduced to 0.2 ml, then the samples were transferred to labelled GC-MS vials. Drops of isooctane was added to the empty round bottom tube to wash possible sample remaining and transferred further over to the sample containing GC-MS vial until its maximum volume was reached. RapidVap settings are listed in Appendix 4.

Concentration nr. 6: Nitrogen gas

In the desire to achieve good signals on the GC-MS was sample volume yet reduced from 0.3 ml to ca. 0.15 ml by nitrogen gas. Metal tips were washed in DCM for 10 minutes in ultrasonic bath between every sample, and temperature on the heat block set to 35 °C. Final step before analysis was to add 10 µl recovery standard to each sample vial and vortex. The samples were stored in refrigerator until analysis.

GC-MS analysis

HCB, PCBs and PBDEs analysis were performed based on the journal article "Versatility of GC-Orbitrap mass spectrometry for the ultra-trace detection of persistent organic pollutants in penguin blood from Antarctica" (Warner and Cojocariu, 2018). T-SIM acquisition was used to detect HCB, 12 PCBs (CB#28/31, 52, 101, 99, 118, 153, 105, 138, 187, 183, 180, 170) and 25 PBDEs (BDE#17, 28, 49, 71, 47, 66, 77, 100, 119, 99, 85, 126, 154, 153, 138, 156, 184, 183, 191, 202, 197, 196, 207, 206, 209). The analysis was performed with two different CG columns and setups: one for HCB and PCBs analysis and another for the PBDEs analysis. Additional details about type of column, injection volume, liner, inlet temperature and oven temperature program surrounding both analyses are described in Appendix 6. Internal standard calibration with isotopic dilution was used for quantification, and data processing carried out using Tracefinder software v. 4.1 EFS. The results were transferred to Microsoft Excel and grouped by day of extraction.

Time series samples: Blank correction was done by subtracting the average of blanks within each group from corresponding samples. LOD for each compound in each group was found by taking 3 times the standard deviation of its corresponding blank samples. If results had value < LOD they were replaced with ½ LOD. Mean and standard deviations were calculated with formulas (=GJENNOMSNITT(Tall1:Tall2)) and (=STDAV.P(Tall1:Tall2)).

Garbage samples: The garbage samples had only one blank sample following their extraction, therefore was LOD set to 2 times the blank values. If results were < LOD (without doing blank correction first), they were replaced whit 2 x LOD.

Significant differences was investigated in Excel with a two-sided "Paired Two Sample for Means" t.test (=t.test(matrise1; matrise2; sider; type)). Significance level was set to 95 % ($\alpha = 0{,}05$). If $p < \alpha$ it is a significant difference .

FTIR

Minimum three unextracted plastic pieces from: each of the four plastic types from every time interval in the experiment, the 28 garbage samples and a selection of known, pristine plastic pellets were wrapped in aluminium foil sheets and labelled. To avoid contamination, a tweezer was used to handle the plastic particles. The samples were brought to the Chemistry Department at UiT, where the FTIR instrument with Diamond (ATR) sampling accessory is located. Step by step instructions about how to use it was simply given by the instrument's computer program. Step one was to clean the crystal, and here acetone was used. After about 1-3 minutes when the crystal was dry again, the next-button on the computer program was hit, and the system performed crystal check and collection of background FTIR-spectra. A plastic particle was placed on the crystal using a tweezer, and easily squeezed towards the crystal by twisting the upper part of the instrument until it clicked. The FTIR spectra could then be observed live on the screen. If the spectral quality was bad with weak or weird signals, the contact between sample and crystal may be bad, and adjustments of the pellet was done. By pressing "next" the sample collection was done and the FTIR spectra (not live anymore) came up on the screen. A right-click and "pick peaks" allowed wavenumbers to selected peaks to appear in the spectra. The document was saved as PDF-file, and the procedure finished. This went on repetitively, always starting with cleaning the crystal and collecting background spectra. The results were acquired in triplicate using three different pellets from the same sample.

Scanning Electron Microscope

This step was performed at the Scanning Electron Microscopy Lab located at The Faculty of Health Sciences at UiT, with good help from senior engineer Augusta H. A. Sundbø.

Preparation of samples

A piece of Kimtech paper with ethanol was used to wipe away possible dust and contamination on 16 aluminium mounting pins, and a permanent marker to label them on their underside. The cleaned, labelled pins were placed on a mounting pin holder. It was very important to always wear gloves when working with equipment and samples going to be positioned inside the scanning electron microscope, since oil from hands could contaminate and make the inside of the chamber dirty in vacuum. Double-sided carbon stickers were mounted on top of each pin, and unextracted plastic pellets from 16 selected samples were mounted on top of that again using a tweezer. More than one pellet could be placed on one pin, as long as they did not touch

each other. Only pellets from the same sample were placed on each pin. The pins were then removed from the laboratory bench to a fume hood, were a small amount of conductive silver paste was attached to a little part of the plastic, over to the carbon sticker and down to the pin. The mounting pin holder was placed in an incubator over night to let the paste dry properly.

Coating

Since the samples are made of plastic, and therefore non-conducting, they need surface coating by a conducting material. In that way electrons can be reflected when they hit the sample surface inside the microscope, so that a picture can be made. The sample containing pins were placed inside a vacuum chamber in a Polaron Sputter Coater instrument, and a thin layer of gold/palladium automatically imposed by pressing "start sequence". The instrument was capable to fit six pins. When the process (which only took a few minutes) was finish, the red "wait/stop" button was pressed for 30 seconds before the pins were taken out from the vacuum chamber. A silver/gray color was observed on the sample surfaces.

SEM

A specimen stub inside the microscope was taken out and the newly coated sample pins placed on it. The stub could hold nine pins, and they were properly attached. It was set back in the microscope chamber, and vacuum turned on. It took around five minutes until vacuum was achieved and the scanning electron microscopy could start. The stub holding the samples was placed close to the electron beam (1 mm) with help from a camera installed inside the chamber. The stub could be moved up, down, tilted and rotated. Adjustments on the computer connected to the microscope made it possible to zoom in, out and around on the different samples. Electrons from the beam, that were reflected when entering the sample surface, was translated into a picture by the detector. The picture was live-observed on the computer screen. Overview and close up pictures of the different samples were saved. Changes in resolution affected time needed for the microscope to scan over the sample surface. The higher resolution, the more time-consuming. When moving around on the samples trying to find interesting spots, resolution setting was set to number 4. When an interesting spot was found, the resolution was changed to number 9 before picture was saved. The coated sample pins were stored in a box at the laboratory afterwards, available for SEM if wanted in the future.

Adding scale bar in to SEM pictures

ImageJ is a computer software program that simply allows you to add scale bar into pictures. The SEM picture of interest was uploaded to the program, and the function "Straight" used to drag a line horizontally over the whole picture. In "Analyze" menu the option "Set Scale" was selected. The distance in pixels of the dragged line was then shown, and the only thing that needed to be filled out was the "known distance". This distance was found by converting the distance in pixels over to distance in µm with use of an online converter (https://www.translatorscafe.com/unit-converter/en/length/110-14/pixel-micron/) and dividing this number by the magnitude each picture was taken at. In "Tools" menu "Scale bar" was selected and satisfying length of the scale bar to show in the picture written.

Appendix 4: Settings for up concentrations

NB! Time needed to reach final volume varies from sample to sample. It is therefore very important to keep an eye on the samples and check their volume continually during the up concentrations. The times listed here are total time until every sample was done.

Up concentration nr. 1: Rapidvap

Cyclohexane 6 ml → 0.5 ml

Speed(%)	Heat (ºC)	Time (min)	Vac (mbar)
50	35	20	400 --> 230
50	35	25	230 --> 210
50	35	40	210 --> 200
50	35	30	200 --> 190
50	35	66	190

Up concentration nr. 4: MiVac

DCM/hexane ca. 1.5-2 ml → 0.5 ml

Heat (ºC)	Time (min)	Vac (mbar)
35	10	450
35	10	350
35	10	300
35	50	265

Up concentration nr. 5: Rapidvap nr. 2

DCM/hexane 12 ml → 0.2 ml

Speed(%)	Heat (ºC)	Time (min)	Vac (mbar)
40	35	5	500
40	35	5	450
45	35	30	350
60	35	43	280
Adding iscooctane			
60	35	145	280

Appendix 5: Example GPC graphs.

Test/calibration solution, PE-HD, PE-LD (named PE in picture below), PP, PET and blank
sample:
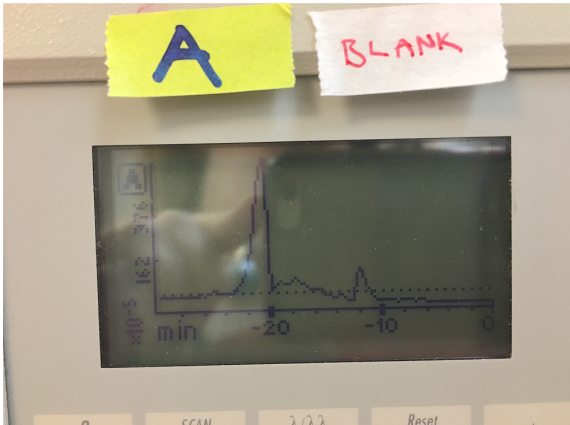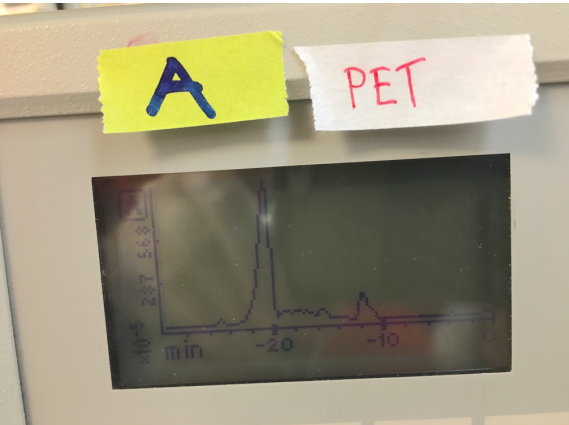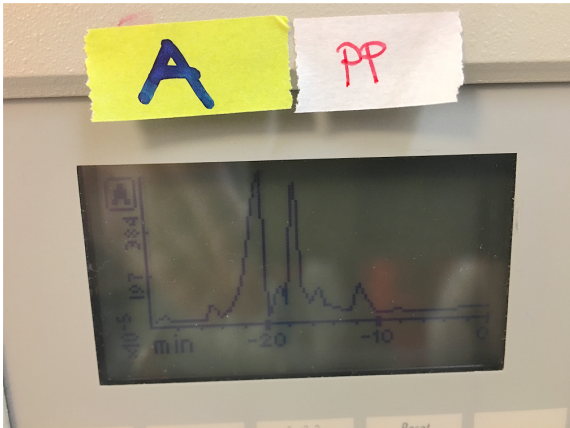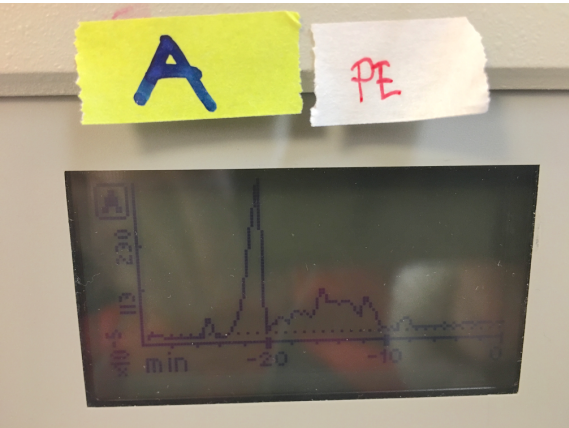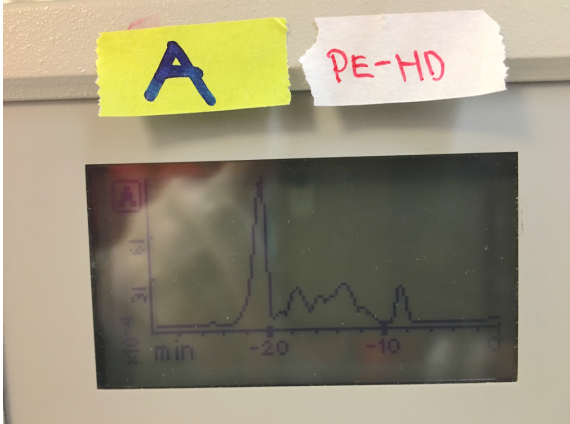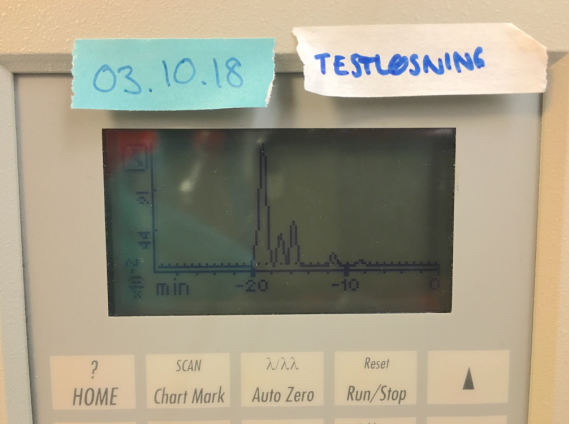
Appendix 6: GC-MS details

Analysis of HCB and PCBs

Table 6: GC and injection conditions for HCB and PCBs analysis.

TRACE 1310 GC System Parameters	
Column:	TG-5SILMS (30 m x 0.25 mm ID x 0.25 μm) (P/N 26096-1425)
Injection volume:	1 μL
Liner:	Thermo Scientific™ LinerGOLD™ GC Liner (P/N 453A1345-UI)
Inlet:	250 °C (SSL)
Carrier gas:	He, 1.2 mL/min (constant flow)
Oven temperature program	
Temperature 1:	40 °C
Hold time:	1.5 min
Temperature 2:	180 °C
Rate:	25 °C/min
Hold time:	0 min
Temperature 3:	280 °C
Rate:	5 °C/min
Hold time:	0 min
Temperature 3:	320 °C
Rate:	40 °C/min
Hold time:	5 min

Table 7: Mass spectrometer conditions for data acquisition for HCB and PCBs analysis using targeted single ion monitoring (t-SIM) mode.

Q Exactive GC Mass Spectrometer Parameters	
Transfer line:	280 °C
Ionization type:	Electron Ion (EI)
Ion source:	250 °C
Electron energy:	70 eV
Acquisition mode:	t-SIM
Isolation window:	8 Da
Mass range:	50–600 Da
Resolving power:	30 000 (FWHM at *m/z* 200)
Lock mass, column bleed:	207.03235 *m/z*

Analysis of PBDEs

Table 8: GC and injection conditions for PBDEs analysis.

TRACE 1310 GC System Parameters	
Column:	RESTEK Rtx - 1614 (15 m x 0.25 mm ID x 0.10 μm) (P/N 10296)
Injection volume:	1 μL
Liner:	RESTEK Topaz Liner (P/N 23438)
Inlet:	40-330 °C (PTV)
Carrier gas:	He, 1.5 mL/min (constant flow)
Oven temperature program	
Temperature 1:	80 °C
Hold time:	2 min
Temperature 2:	340°C
Rate:	30 °C/min
Hold time:	3 min

Table 9: Mass spectrometer conditions for data acquisition for PBDEs analysis using targeted single ion monitoring (t-SIM) mode.

Q Exactive GC Mass Spectrometer Parameters	
Transfer line 1:	300 °C
Transfer line 2:	300 °C
MS Transfer line:	280 °C
Ionization type:	Electron Ion (EI)
Ion source:	300 °C
Electron energy:	35 eV
Acquisition mode:	t-SIM
Isolation window:	10 Da
Mass range:	320 – 820 Da
Resolving power:	30 000 (FWHM at *m/z* 200)
Lock mass, column bleed:	207.03235 *m/z*

Appendix 7: Raw data

Numbers are in concentration (pg/g).

PBDEs

Season:	Summer 1 month					Summer 2 months					Summer 3 months					Summer 4 months					Summer 5 months				
Plastic:	PP	PE-LD	PET	PE-HD	Blank	PP	PE-LD	PET	PE-HD	Blank	PP	PE-LD	PET	PE-HD	Blank	PP	PE-LD	PET	PE-HD	Blank	PP	PE-LD	PET	PE-HD	Blank
PBDE 17	0	0	0	0	-	-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 28	0	0	0	7,71	-	-	0	0	6,65	0	0	0	0	8,26	0	0	0	0	6,72	0	0	0	0	7,97	0
PBDE 49	0	0	0	6,52	-	-	0	0	7,66	0	0	0	0	6,83	0	0	0	0	5,20	0	0	0	0	11,1	0
PBDE 71	0	0	0	0	-	-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 47	18,3	4,64	4,62	114	-	-	4,80	5,07	109	4,30	4,66	6,25	6,12	110	4,53	8,30	3,46	3,42	102	2,82	10,43	7,96	8,16	141	5,53
PBDE 66	5,82	2,78	6,13	3,57	-	-	4,52	6,37	4,46	5,79	5,20	5,10	4,57	6,05	5,43	4,16	3,73	5,54	3,37	5,57	0	4,55	0	8,32	6,82
PBDE 77	0	0	0	0	-	-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 100	0	0	0	5,73	-	-	0	0	5,57	0	0	0	0	8,33	0	0	0	0	6,20	0	0	0	0	10,2	0
PBDE 119	0	0	0	0	-	-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 99	8,67	0	4,15	62,68	-	-	3,53	4,51	59,62	3,22	0	0	0	87,69	0	14,9	0	0	53,1	0	9,31	0	0	81,9	3,15
PBDE 85	0	0	0	0	-	-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 126	0	0	0	0	-	-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 154	0	0	0	7,04	-	-	0	0	6,87	0	0	0	0	10,3	0	0	0	0	5,65	0	0	0	0	8,33	0
PBDE 153	0	0	0	7,96	-	-	0	0	5,85	0	0	0	0	9,44	0	0	0	0	6,93	0	0	0	0	9,19	0
PBDE 138	0	0	0	0	-	-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 156	0	0	0	0	-	-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 184	0	0	0	0	-	-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 183	0	0	0	4,68	-	-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 191	0	0	0	0	-	-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 202	0	0	0	0	-	-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 197	0	0	0	0	-	-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 196	0	0	0	0	-	-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 207	0	0	0	0	-	-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 206	0	0	0	0	-	-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 209	0	0	0	0	-	-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Season:	Winter 1					Winter 2					Winter 3					Winter 4					Winter 5				
Plastic:	PP	PE-LD	PET	PE-HD	Blank	PP	PE-LD	PET	PE-HD	Blank	PP	PE-LD	PET	PE-HD	Blank	PP	PE-LD	PET	PE-HD	Blank	PP	PE-LD	PET	PE-HD	Blank
PBDE 17	0		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 28	0	0	0	6,25	0	0	0	0	7,26	0	0	0	0	3,34	0	0	0	0	4,04	0	0	0	0	4,33	0
PBDE 49	0	0	0	7,32	0	0	0	0	6,00	0	0	0	0	5,00	0	0	0	0	5,28	0	0	0	0	5,20	0
PBDE 71	0		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 47	7,18	7,90	8,13	119	5,07	5,24	2,64	5,02	92,6	2,23	4,72	9,19	7,56	83,4	41,5	0	9,56	9,44	83,0	4,87	12,0	6,73	9,94	83,5	5,75
PBDE 66	4,85	4,95	5,60	5,73	5,77	0	4,57	5,37	4,50	6,55	4,92	4,06	4,94	3,80	5	0	5,31	6,03	4,90	6,55	0	4,28	4,81	3,11	5,41
PBDE 77	0		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0,00	0,00	0	0	0	0	0	0	0
PBDE 100	0	0	0	7,93	0	0	0	0	7,55	0	0	0	0	4,03	2	0	0	0	5,71	0	0	0	0	5,33	0
PBDE 119	0		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 99	0	0	6,15	69,0	3	0	0	0	69,9	0	0	11,3	0	65,5	25,8	0	0	0	47,1	0	0	0	5,37	39,4	0
PBDE 85	0		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 126	0		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 154	0	0	0	6,52	0	0	0	0	6,08	0	0	0	0	6,08	0	0	0	0	6,33	0	0	0	0	5,35	0
PBDE 153	0	0	0	7,62	0	0	0	0	7,76	0	0	1,74	0	8,72	0	0	0	0	5,31	0	0	0	0	4,64	0
PBDE 138	0		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 156	0		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 184	0		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 183	0		0	0	0	0	0	0	5,38	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 191	0		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 202	0		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 197	0		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 196	0		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 207	0		0	0	0	0	0	0	5679	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 206	0		0	0	0	0	0	0	653	0	0	0	197	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 209	0		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Winter seasons

Season:	Winter 1 (2)					Winter 2 (2)					Winter 3 (2)					Winter 4 (2)					Winter 5 (2)				
Plastic:	PP	PE-LD	PET	PE-HD	Blank	PP	PE-LD	PET	PE-HD	Blank	PP	PE-LD	PET	PE-HD	Blank	PP	PE-LD	PET	PE-HD	Blank	PP	PE-LD	PET	PE-HD	Blank
PBDE 17	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 28	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	4,64	0	0	0	0	4,56	0
PBDE 49	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	4,62	0	0	0	0	4,14	0
PBDE 71	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 47	0	0	0	117	0	0	0	0	48,3	0	0	0	8,83	72,0	15,0	6,96	0	6,05	68,6	7,73	5,31	10,6	4,98	98,7	8,87
PBDE 66	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	5,21	0	7,02	3,10	9,93	5,26	5,51	6,63	2,68	6,74
PBDE 77	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 100	0	0	0	18,2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	6,89	0	0	0	0	7,60	0
PBDE 119	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 99	0	0	0	107	0	0	0	0	30,3	0	0	0	0	34,1	0	3,23	0	1,81	49,34	3,55	0	4,09	0	56,4	2,79
PBDE 85	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1,59	0	0	0	0	0	0
PBDE 126	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 154	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3,67	0	0	0	0	5,61	0
PBDE 153	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	5,26	0	0	0	0	6,67	0
PBDE 138	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 156	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 184	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 183	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	5,17	0	0	0	0	0	0
PBDE 191	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 202	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 197	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 196	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 207	0	0	0	0	0	0	0	0	28,5	0	0	0	0	77,1	0	0	0	0	0	0	0	0	0	0	0
PBDE 206	0	0	0	0	0	0	0	0	0	0	0	0	0	33,2	0	0	0	0	0	0	0	0	0	0	0
PBDE 209	8,43	6,16	2,03	3,91	174	2,68	9,96	2,16	13,6	138	4,17	7,51	3,47	43,4	160	0	0	0	0	0	0	0	0	0	0

Pristine

Season:	Pristine					Pristine (2)				
Plastic:	PP	PE-LD	PET	PE-HD	Blank	PP	PE-LD	PET	PE-HD	Blank
PBDE 17	0	0	0	0	0	0	0	0	0	0
PBDE 28	0	0	0	3,06	0	0	0	0	0	0
PBDE 49	0	0	0	3,55	0	0	0	0	0	0
PBDE 71	0	0	0	0	0	0	0	0	0	0
PBDE 47	9,93	5,55	11,4	60,4	7,73	6,83	9,51	11,1	65,5	4
PBDE 66	5,64	5,43	7,47	5,61	5,82	7,40	0	0	6,39	9
PBDE 77	0	0	0	0	0	0	0	0	0	0
PBDE 100	0	0	0	4,61	0	0	0	0	4,31	0
PBDE 119	0	0	0	0	0	0	0	0	0	0
PBDE 99	5,12	0	5,81	36,1	2,47	0	0	0	27,6	0
PBDE 85	0	0	0	0	0	0	0	0	0	0
PBDE 126	0	0	0	0	0	0	0	0	0	0
PBDE 154	0	0	0	5,25	0	0	0	0	3,80	0
PBDE 153	0	0	0	5,61	0	0	0	0	3,74	0
PBDE 138	0	0	0	0	0	0	0	0	0	0
PBDE 156	0	0	0	0	0	0	0	0	0	0
PBDE 184	0	0	0	0	0	0	0	0	0	0
PBDE 183	0	0	0	5,37	0	0	0	0	0	0
PBDE 191	0	0	0	0	0	0	0	0	0	0
PBDE 202	0	0	0	0	0	0	0	0	0	0
PBDE 197	0	0	0	0	0	0	0	0	0	0
PBDE 196	0	0	0	0	0	0	0	0	0	0
PBDE 207	0	0	0	47,2	0	0	0	0	0	0
PBDE 206	0	0	0	0	0	0	0	0	0	0
PBDE 209	0	0	0	0	0	0	0	0	0	0

Garbage samples

Season:	Garbage samples																		
Plastic:	B1	B4	B6	B7	B8	Y2	Y4	Y5	Y6	Y8	Y11	G1	G2	G4	G9	G10	G11	G14	Blank
PBDE 17	0	0	0	0	0	0	0	56,6	0	0	0	0	0	0	0	0	0	0	0
PBDE 28	0	0	0	0	0	0	0	107	6,41	7,59	0	0	30,7	7,10	0	25,2	22,6	0	0
PBDE 49	0	0	0	0	0	0	0	179	5,40	0	0	0	0	0	0	136	13,6	0	0
PBDE 71	0	0	0	0	0	0	0	0	0	20,9	0	0	27,8	9,82	0	0	0	0	0
PBDE 47	14,9	14,7	0	22,7	0	19,0	32,7	675	65,1	0	67,0	57,2	611	69,7	16,0	0	181	0	12,3
PBDE 66	0	5,77	0	5,56	0	0	5,50	167	2,86	159	480	89,3	35,9	8,69	6,63	2757	11,2	0	8,99
PBDE 77	0	0	0	0	0	0	0	0	0	18,8	33,0	0	0	0	0	303	0	0	0
PBDE 100	0	1,10	0	1,18	0	0	0	110	7,16	0	41,6	0	31,6	3,43	0,66	0	15,9	0	0
PBDE 119	0	0	0	0	0	0	0	11,9	0	0	0	20,0	0	0	0	1612	0	0	0
PBDE 99	12,0	9,61	0	17,3	0	9,79	15,9	159	61,2	18,7	621	44,9	199	21,6	13,1	75,4	133	0	6,98
PBDE 85	0	0	0	0	0	0	0	0	1,40	0	64,9	0	0	0	0	0	0	0	0
PBDE 126	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 154	0	0	0	0	0	0	0	41,5	5,59	0	41,4	13,3	0	3,60	0	49,3	0	0	0
PBDE 153	0	0	0	0	0	0	0	19,0	5,96	0	174	35,7	0	2,20	1,52	0	7,63	0	0
PBDE 138	0	0	0	0	0	0	0	0	0	0	161	0	0	0	0	0	0	0	0
PBDE 156	0	0	0	0	0	0	0	0	0	0	165	0	0	0	0	0	0	0	0
PBDE 184	0	0	0	0	0	0	0	0	0	0	21,2	0	0	0	0	0	0	0	0
PBDE 183	0	0	0	0	0	0	0	28,1	9,58	0	766	74,4	0	0	0	0	0	0	0
PBDE 191	0	0	0	0	0	0	0	0	0	0	224	0	0	0	0	0	0	0	0
PBDE 202	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 197	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 196	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 207	0	0	0	0	0	0	0	0	0	0	0	146823	0	0	0	0	0	0	0
PBDE 206	0	0	0	0	0	0	0	555	0	0	0	15290	0	0	0	0	0	0	0
PBDE 209	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

HCB/PCBs

Summer 1–5 months

Season:	Summer 1 month					Summer 2 months					Summer 3 months					Summer 4 months					Summer 5 months				
Plastic:	PP	PE-HD	PET	PE-HD	Blank	PP	PE-HD	PET	PE-HD	Blank	PP	PE-HD	PET	PE-HD	Blank	PP	PE-HD	PET	PE-HD	Blank	PP	PE-HD	PET	PE-HD	Blank
HCB	505	3672	321	3340	-	-	1537	356	3675	253	473	1338	266	3517	264	423	1383	242	3434	270	2033	4846	1187	7914	947
PCB 28/31	253	741	129	855	-	-	332	109	1039	140	277	309	133	858	104	272	421	114	858	157	803	1051	521	1741	262
PCB 52	301	594	230	951	-	-	291	228	1196	336	402	322	221	865	228	306	510	172	765	293	1940	1452	1395	2370	1003
PCB 101	99	236	120	1127	-	-	107	0	1269	137	118	123	39	1138	57	119	157		1036	70	188	340	680	2722	716
PCB 99	48	0	0	411	-	-	0	0	477	0	0	0	0	387	0	0	0	0	379	0	157	285	104	1159	212
PCB 118	0	0	0	0	-	-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	107	1210	78
PCB 153	607	129	11	2404	-	-	51	0	2341	13	20	0	111	2443	121	537	59	12	2154	80	225	215	881	4913	131
PCB 105	0	0	0	0	-	-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	255	0
PCB 138	317	24	0	1812	-	-	0	0	1861	0	10	0	10	1670	49	327	7	13	1627	16	95	0	169	4050	47
PCB 187	0	0	0	0	-	-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	729	0
PCB 183	21	0	0	368	-	-	0	0	503	0	0	0	0	48	0	0	0	0	723	0	47	0	0	87	0
PCB 180	231	0		608	-	-	16	0	644	0	0	0	0	625	0	33	0	0	1091	0	0	0	0	1173	0
PCB 170	0	0	0	0	-	-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	258	0

Winter 1–5

Season:	Winter 1					Winter 2					Winter 3					Winter 4					Winter 5				
Plastic:	PP	PE-HD	PET	PE-HD	Blank	PP	PE-HD	PET	PE-HD	Blank	PP	PE-HD	PET	PE-HD	Blank	PP	PE-HD	PET	PE-HD	Blank	PP	PE-HD	PET	PE-HD	Blank
HCB	1924	10877	862	7820	848	3267	21367	739	8371	784	3038	19410	918	12147	979	889	6440	690	6289	524	772	5990	390	5396	-
PCB 28/31	609	2398	260	1680	251	1684	4103	274	2057	285	1455	3339	390	2138	335	544	1461	219	1861	300	492	1225	215	1440	-
PCB 52	689	2592	871	1732	663	2190	3521	741	2183	758	1803	3426	822	1920	1005	702	1325	674	1736	631	835	1388	645	1105	-
PCB 101	260	874	463	2566	463	473	838	372	2538	294	855	1201	516	2108	715	385	584	353	1563	482	536	774	495	1023	-
PCB 99	217	174	47	1112	387	395	127	244	765	246	231	328	432	790	556	101	178		489	62	154	244	149	411	-
PCB 118	154	181	139	1150	78	0	152	112	1093	48	175	306	165	836	841	0	0	0	0	0	0	0	0	0	-
PCB 153	320	262	61	5051	256	186	234	493	4425	137	241	616	736	3949	1767	468	98	11	2163	39	136	333	153	1374	-
PCB 105	0	0	0	374	0	0	0	46	356	0	0	53	0	147	302	0	0	0	0	0	0	0	0	0	-
PCB 138	0	90	25	3319	24	0	79	188	3056	86	165	92	264	2878	1258	191	11		1680	0	73	235	82	0	-
PCB 187	0	0	0	776	0	0	0	0	475	0	0	28	0	486	28	0	0	0	0	0	0	0	0	0	-
PCB 183	21	0	0	145	18	0	0	0	46	0	0	0	0	36	41	0	0	0	19	0	0	0	0	11	-
PCB 180	0	0	0	1079	0	0	0	0	867	0	52	40	123	1028	533	0	0	0	717	0	0	43	0	392	-
PCB 170	0	0	0	231	0	0	0	0	112	0	0	0	0	120	22	0	0	0	0	0	0	0	0	0	-

Summer 1–5 months (2)

Season:	Summer 1 month (2)					Summer 2 months (2)					Summer 3 months (2)					Summer 4 months (2)					Summer 5 months (2)				
Plastic:	PP	PE-HD	PET	PE-HD	Blank	PP	PE-HD	PET	PE-HD	Blank	PP	PE-HD	PET	PE-HD	Blank	PP	PE-HD	PET	PE-HD	Blank	PP	PE-HD	PET	PE-HD	Blank
HCB	2487	8032	2103	6375	1690	-	3424	1815	8009	1713	5456	3319	1536	6571	1457	1534	3710	1514	6831	1673	3130	4455	1294	8357	989
PCB 28/31	577	1410	441	1270	322	-	602	381	1486	311	1889	518	415	1391	386	437	812	416	1269	375	172	656	228	1636	125
PCB 52	890	2322	1471	1902	620	-	892	1201	1694	736	5786	1302	1261	2424	1155	787	1827	1434	1750	910	706	763	464	1953	69
PCB 101	495	1078	1115	2127	436	-	432	765	2677	446	2803	1041	739	2570	881	322	819	1060	2514	514	433	0	310	2910	67
PCB 99	80	273	384	730	48	-	174	513	1142	288	625	326	388	873	243	210	421	384	1015	178	362	0	161	1275	56
PCB 118	287	378	201	804	176	-	366	1744	1139	527	1508	280	624	1105	506	242	795	337	1286	233	0	0	474	1208	143
PCB 153	530	344	660	3016	393	-	682	3581	4282	1392	5150	517	1425	3673	826	255	1336	572	4170	40	574	160	874	6187	397
PCB 105	0	135	0	230	0	-	0	582	276	147	254	0	156	314	0	37	53	83	386	42	0	110	193	96	0
PCB 138	55	189	176	1903	159	-	316	2291	2857	834	1227	395	743	2545	521	87	847	67	3199	277	0	0	580	3310	0
PCB 187	0	0	0	279	0	-	0	157	470	68	0	0	34	398	0	0	0	28	602	0	171	0	17	896	0
PCB 183	0	0	0	25	0	-	0	53	69	17	0	0	0	0	21	0	0	0	190	0	0	0	0	0	24
PCB 180	0	0	0	583	0	-	81	1042	733	196	0	57	368	455	50	0	292	24	944	0	277	0	212	1481	0
PCB 170	0	0	0	28	0	-	0	309	146	0	0	0	0	30	0	0	21	0	320	0	0	0	12	46	0

Winter 1–5 (2)

Season:	Winter 1 (2)					Winter 2 (2)					Winter 3 (2)					Winter 4 (2)					Winter 5 (2)				
Plastic:	PP	PE-HD	PET	PE-HD	Blank	PP	PE-HD	PET	PE-HD	Blank	PP	PE-HD	PET	PE-HD	Blank	PP	PE-HD	PET	PE-HD	Blank	PP	PE-HD	PET	PE-HD	Blank
HCB	1869	10439	809	7577	943	3463	15374	1031	5385	827	3601	13250	1176	10200	1097	1201	5198	354	3170	349	706	4961	361	4332	347
PCB 28/31	725	1966	170	1642	233	1671	2706	270	1200	136	1197	1904	147	1809	128	702	878	283	775	184	432	838	226	938	262
PCB 52	1166	1579	329	2157	378	1304	2465	630	1312	387	1179	1395	335	1283	695	1898	1253	762	1175	557	762	1116	684	1177	720
PCB 101	387	608	83	2641	302	400	655	244	1200	143	536	482	293	1652	555	1186	748	675	1154	368	421	577	341	1132	413
PCB 99	133	251	69	1120	80	82	295	232	579	78	74	88	75	629	722	211	162	132	426	0	81	171	99	437	173
PCB 118	291	244	91	1537	336	301	290	135	685	275	409	388	338	1093	517	0	0	0	0	0	0	0	0	0	0
PCB 153	680	918	530	6162	1744	280	652	613	2417	452	368	802	1067	3351	3012	69	118	75	1945	45	69	143	19	1801	248
PCB 105	0	64	0	391	0	0	141	60	110	0	91	73	72	155	58	0	0	0	0	0	0	0	0	0	0
PCB 138	270	372	151	3731	929	252	55	40	1600	212	251	156	656	2353	2338	18	6	20	1432	9	0	57	10	1610	125
PCB 187	0	38	66	795	36	0	0	0	166	39	0	0	32	425	365	0	0	0	602	0	0	0	0	0	0
PCB 183	23	0	21	194	25	0	0	0	0	0	0	0	26	34	26	0	0	0	367	0	0	0	0	23	0
PCB 180	33	62	0	1543	330	0	0	0	384	0	0	133	46	716	469	0	0	0	497	0	0	0	0	595	0
PCB 170	0	0	0	267	0	0	0	0	0	51	0	0	0	38	85	0	0	0	0	0	0	0	0	0	0

Season:	Pristine					Pristine (2)				
Plastic:	PP	PE-LD	PET	PE-HD	Blank	PP	PE-LD	PET	PE-HD	Blank
HCB	409	450	355	1934	381	563	792	806	-	380
PCB 28/31	347	313	312	679	250	404	406	508	-	317
PCB 52	650	617	716	874	701	901	1380	1749	-	895
PCB 101	493	377	408	899	502	641	1015	1127	-	660
PCB 99	129	87		336	113	51	232	206	-	159
PCB 118	0	0	0	0	0	0	0	0	-	0
PCB 153	122	36	77	1174	106	12	97	18	-	72
PCB 105	0	0	0	0	0	0	0	0	-	0
PCB 138	49	8	17	937	14		13	28	-	14
PCB 187	0	0	0	0	0	0	0	0	-	0
PCB 183	0	0	0	22	0	0	0	0	-	0
PCB 180	0	0	0	321	0	0	0	0	-	0
PCB 170	0	0	0	0	0	0	0	0	-	0

Season:	Garbage samples																		
Plastic:	B1	B4	B6	B7	B8	Y2	Y4	Y5	Y6	Y8	Y11	G1	G2	G4	G9	G10	G11	G14	Blank
HCB	9874	2110	26946	2003	6077	2926	11162	21327	53625	6747	24634	3590	3795	15205	536	21117	10320	9639	569
PCB 28/31	674	347	565	554	403	806	1185	926	1926	1141	0	558	6047	1354	183	1762	711	826	210
PCB 52	1487	454	1626	775	1113	1093	1247	1802	2207	1691	2133	605	3159	2528	510	3245	1590	1049	557
PCB 101	1042	372	13414	593	871	870	526	5870	1407	1401	17919	380	1928	4973	374	6472	2729	1531	238
PCB 99	352	117	4021	172	0	213	0	1871	379	506	4991	0	666	1557	0	1930	737	826	0
PCB 118	0,0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PCB 153	276	231	26365	318	1663	454	180	15092	2023	1115	73581	473	1852	6379	95	17576	8063	3934	49
PCB 105	0,0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PCB 138	23	135		114	89	256	40	13268	1729	861	72795	216	1763	5645	24	14108	6380	3451	30
PCB 187	0,0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PCB 183	0	0	114	0	25	0	0	8638	34	101	31697	47	56	133	0	10610	652	37	0
PCB 180	32	14	0	60	0	156	0	18173	904	74	143245	96	197	2278	0	23217	8093	1433	0
PCB 170	0,0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Appendix 8: Average and standard deviation (Time series samples)

Numbers are in concentration (pg/g).

PBDEs

Plastic:	PE-HD (summer)											
Time(mos)	T = 0		T = 1		T=2		T = 3		T = 4		T = 5	
	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev
PBDE-47	57	3	85	25	93	12	102	4	91	7	114	23
PBDE-99	31	4	52	9	49	9	72	14	51	0	73	8

Plastic:	PE-LD (summer)											
Time(mos)	T = 0		T = 1		T=2		T = 3		T = 4		T = 5	
	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev
PBDE-47	3	0	6	4	6	4	6	4	6	4	7	3
PBDE-99	2	0	1	1	1	1	1	1	1	1	1	1

Plastic:	PP (summer)											
Time(mos)	T = 0		T = 1		T=2		T = 3		T = 4		T = 5	
	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev
PBDE-47	3	0	12	2	10	0	42	40	7	3	6	4
PBDE-99	2	0	4	4	0	0	21	19	7	7	1	1

Plastic:	PET (summer)											
Time(mos)	T = 0		T = 1		T=2		T = 3		T = 4		T = 5	
	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev
PBDE-47	3	0	6	4	36	34	24	22	6	4	7	3
PBDE-99	3	1	1	1	22	20	12	10	1	1	1	1

Plastic:	PE-HD (winter)									
Time(mos)	T = 0		T = 1		T=2		T = 3		T = 11	
	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev
PBDE-47	57	3	114	1	66	22	74	7	77	12
PBDE-99	31	4	87	20	49	19	49	1	46	6

Plastic:	PE-LD (winter)									
Time(mos)	T = 0		T = 1		T=2		T = 3		T = 11	
	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev
PBDE-47	3	0	7	3	6	4	8	3	2	0
PBDE-99	2	0	1	1	1	1	5	5	2	0

Plastic:	PP (winter)									
Time(mos)	T = 0		T = 1		T=2		T = 3		T = 11	
	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev
PBDE-47	3	0	6	4	6	4	6	4	2	0
PBDE-99	2	0	1	1	1	1	1	1	2	0

Plastic:	PET (winter)									
Time(mos)	T = 0		T = 1		T=2		T = 3		T = 11	
	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev
PBDE-47	3	0	7	3	6	4	6	4	2	0
PBDE-99	3	1	1	1	1	1	1	1	2	0

PCBs

Plastic:	PE-HD (summer)											
Time(mos)	T = 0		T = 1		T=2		T = 3		T = 4		T = 5	
	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev
HCB	1554	-	3910	1177	4894	2095	4096	1190	4184	1433	7231	292
PCB 28/31	396	-	822	141	1022	164	884	225	823	139	1465	10
PCB 52	145	-	856	270	874	51	1074	699	687	294	1594	115
PCB 101	318	-	1298	367	1644	655	1525	672	1446	705	2457	399
PCB 99	200	-	476	92	715	336	535	210	602	316	1006	279
PCB 118	0	-	118	167	389	551	372	527	463	654	730	322
PCB 153	1085	-	2343	15	2944	955	2691	451	2795	1007	4831	695
PCB 105	0	-	91	129	114	162	133	189	170	240	146	71
PCB 138	923	-	1623	237	2124	403	1873	318	2178	810	3313	542
PCB 187	0	-	131	186	227	321	190	269	292	414	796	105
PCB 183	22	-	191	250	281	314	31	24	452	384	43	41
PCB 180	321	-	564	61	658	19	509	164	987	148	1205	234
PCB 170	0	-	14	19	73	103	15	21	160	226	144	153
TOTAL	4963	-	12437	2014	15959	5399	13929	4583	15239	5705	24961	1644

Plastic:	PE-LD (summer)											
Time(mos)	T = 0		T = 1		T=2		T = 3		T = 4		T = 5	
	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev
HCB	241	241	4904	755	1532	365	1381	431	1598	676	3746	297
PCB 28/31	87	51	834	316	226	38	172	4	375	124	629	196
PCB 52	363	308	887	609	185	167	185	167	598	528	540	78
PCB 101	276	222	211	85	163	157	163	157	163	157	208	85
PCB 99	65	44	68	61	68	96	68	96	68	96	110	132
PCB 118	0	0	118	270	118	167	118	167	118	167	311	270
PCB 153	26	0	412	73	412	488	412	488	412	488	985	73
PCB 105	0	0	45	139	45	64	45	64	45	64	98	139
PCB 138	1	0	209	132	209	253	209	253	209	253	690	132
PCB 187	0	0	22	90	22	31	22	31	22	31	22	6
PCB 183	0	0	7	6	7	10	7	10	7	10	21	6
PCB 180	0	0	60	80	68	73	60	85	60	85	290	80
PCB 170	0	0	0	16	0	0	0	0	11	15	25	16
TOTAL	1058	867	7778	4536	3056	1908	2842	1944	3687	2694	7675	1466

Plastic:	PP (summer)											
Time(mos)	T = 0		T = 1		T=2		T = 3		T = 4		T = 5	
	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev
HCB	106	109	548	432	-	-	2017	2554	157	4	1677	755
PCB 28/31	85	50	174	77	-	-	842	988	94	63	297	316
PCB 52	145	0	185	167	-	-	2499	3440	185	167	652	609
PCB 101	119	0	163	157	-	-	1132	1558	163	157	208	85
PCB 99	34	0	68	96	-	-	218	308	68	96	247	61
PCB 118	0	0	118	167	-	-	574	812	118	167	311	270
PCB 153	26	0	646	157	-	-	2277	3126	612	206	985	73
PCB 105	0	0	45	64	-	-	103	146	45	64	98	139
PCB 138	18	24	342	66	-	-	405	529	347	58	690	132
PCB 187	0	0	22	31	-	-	22	31	22	31	82	90
PCB 183	0	0	17	4	-	-	7	10	7	10	21	6
PCB 180	0	0	176	78	-	-	60	85	77	61	290	80
PCB 170	0	0	0	0	-	-	0	0	0	0	25	16
TOTAL	533	135	2504	1330	-	-	10156	13587	1894	949	5583	788

Plastic:	PET (summer)											
Time(mos)	T = 0		T = 1		T=2		T = 3		T = 4		T = 5	
	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev
HCB	213	300	264	290	124	43	82	102	82	102	336	55
PCB 28/31	138	124	41	11	41	11	41	11	41	11	156	117
PCB 52	548	569	341	388	185	167	185	167	185	167	380	224
PCB 101	332	302	163	157	163	157	163	157	163	157	208	85
PCB 99	52	25	68	96	162	229	68	96	68	96	147	80
PCB 118	0	0	118	167	692	978	118	167	118	167	311	270
PCB 153	26	0	412	488	1492	2016	412	488	412	488	985	73
PCB 105	0	0	45	64	267	378	45	64	45	64	194	3
PCB 138	9	8	209	253	937	1281	209	253	209	253	690	132
PCB 187	0	0	22	31	70	99	22	31	22	31	22	6
PCB 183	0	0	7	10	22	31	7	10	7	10	21	6
PCB 180	0	0	60	85	490	693	153	216	60	85	290	80
PCB 170	0	0	0	0	154	218	0	0	0	0	25	16
TOTAL	1318	1328	1751	2040	4799	6300	1506	1761	1413	1630	3765	993

Plastic:	PE-HD (winter)									
Time(mos)	T = 0		T = 1		T=2		T = 3		T = 11	
	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev
HCB	1554	-	6794	193	5973	2132	10269	1398	4390	1479
PCB 28/31	396	-	1437	57	1404	522	1749	149	1005	561
PCB 52	145	-	1377	710	1180	206	1033	41	662	173
PCB 101	318	-	2244	319	1510	680	1521	56	797	106
PCB 99	200	-	905	203	461	66	499	84	323	13
PCB 118	0	-	894	554	468	48	672	240	0	0
PCB 153	1085	-	4888	580	2393	2064	2931	629	1710	74
PCB 105	0	-	294	138	153	61	175	30	0	0
PCB 138	923	-	3158	272	1961	1048	2249	390	1389	92
PCB 187	0	-	769	1	304	231	440	56	0	0
PCB 183	22	-	154	33	21	6	21	5	105	127
PCB 180	321	-	1190	345	484	354	750	204	550	6
PCB 170	0	-	238	18	72	50	75	55	0	0
TOTAL	4963	-	24341	3036	16383	7337	22385	2689	10932	2045

Plastic:	PE-LD (winter)									
Time(mos)	T = 0		T = 1		T=2		T = 3		T = 11	
	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev
HCB	241	241	9753	331	16449	2821	15425	4377	5241	803
PCB 28/31	87	51	1958	221	2779	336	2397	931	852	343
PCB 52	363	308	1518	307	1455	1035	1843	1027	634	122
PCB 101	276	222	382	78	376	153	483	242	250	11
PCB 99	65	44	192	17	214	14	110	132	83	0
PCB 118	0	0	311	270	311	270	311	270	0	0
PCB 153	26	0	985	73	985	73	985	73	146	0
PCB 105	0	0	98	139	169	39	134	88	0	0
PCB 138	1	0	690	132	690	132	690	132	87	0
PCB 187	0	0	22	6	22	6	22	6	0	0
PCB 183	0	0	21	6	21	6	21	6	0	0
PCB 180	0	0	290	80	290	80	290	80	0	0
PCB 170	0	0	25	16	25	16	25	16	0	0
TOTAL	1058	867	16245	1476	23786	2533	22737	7336	7292	1279

Plastic:	PP (winter)									
Time(mos)	T = 0		T = 1		T=2		T = 3		T = 11	
	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev
HCB	106	109	992	60	2460	118	2415	378	485	87
PCB 28/31	85	50	443	166	1454	74	1102	98	294	35
PCB 52	145	0	557	468	1179	217	923	31	415	376
PCB 101	119	0	208	85	208	85	316	69	226	270
PCB 99	34	0	132	101	110	132	110	132	83	0
PCB 118	0	0	311	270	311	270	311	270	0	0
PCB 153	26	0	985	73	985	73	985	73	198	75
PCB 105	0	0	98	139	98	139	144	74	0	0
PCB 138	18	24	690	132	690	132	690	132	87	0
PCB 187	0	0	22	6	22	6	22	6	0	0
PCB 183	0	0	21	6	21	6	21	6	0	0
PCB 180	0	0	290	80	290	80	290	80	0	0
PCB 170	0	0	25	16	25	16	25	16	0	0
TOTAL	533	135	4774	291	7853	920	7355	429	1789	693

Plastic:	PET (winter)									
Time(mos)	T = 0		T = 1		T=2		T = 3		T = 11	
	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev	Average	St.dev
HCB	213	300	109	10	109	10	186	99	164	56
PCB 28/31	138	124	61	18	61	18	90	24	72	0
PCB 52	548	569	224	3	224	3	224	3	100	0
PCB 101	332	302	208	85	208	85	208	85	116	65
PCB 99	52	25	110	132	182	31	110	132	83	0
PCB 118	0	0	311	270	311	270	311	270	0	0
PCB 153	26	0	985	73	985	73	985	73	146	0
PCB 105	0	0	98	139	128	96	134	88	0	0
PCB 138	9	8	690	132	690	132	690	132	87	0
PCB 187	0	0	22	6	22	6	22	6	0	0
PCB 183	0	0	21	6	21	6	21	6	0	0
PCB 180	0	0	290	80	290	80	290	80	0	0
PCB 170	0	0	25	16	25	16	25	16	0	0
TOTAL	1318	1328	3155	891	3256	748	3297	773	768	9

Appendix 9: LOD

Samples are grouped by day of extraction. Numbers are in concentration (pg/g).

PBDEs

PBDE	S1-S4		S5-W3		W4-W5		S1(2)-S4(2)		S5(2)-W3(2)		W4(2)-W5(2)		P + P(2)		Garbage samples	
	LOD	1/2 LOD	LOD	1/2 LOD	LOD	1/2 LOD	LOD	1/2 LOD	LOD	1/2 LOD	LOD	1/2 LOD	LOD	1/2 LOD	LOD	2* LOD
PBDE 17	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 28	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 49	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 71	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 47	3,54	1,77	3,54	1,77	4,75	2,37	20,7	10,3	20,7	10,3	4,75	2,37	5,90	2,95	24,5	49,1
PBDE 66	1,75	0,87	1,75	0,87	5,04	2,52	0	0	0	0	5,04	2,52	4,06	2,03	18,0	36,0
PBDE 77	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 100	2,33	1,16	2,33	1,16	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 119	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 99	4,76	2,38	4,76	2,38	4,82	2,41	0	0	0	0	4,82	2,41	3,70	1,85	14,0	27,9
PBDE 85	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 126	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 154	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 153	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 138	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 156	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 184	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 183	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 191	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 202	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 197	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 196	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 207	0	0	0	0	0	0	57,3	28,6	57,3	28,6	0	0	0	0	0	0
PBDE 206	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PBDE 209	0	0	0	0	0	0	496	248	496	248	0	0	0	0	0	0

PCBs

PCB	S1-S4		S5-W3		W4-W5		S1(2)-S4(2)		S5(2)-W3(2)		W4(2)-W5(2)		P + P(2)		Garbage samples	
	LOD	1/2 LOD	LOD	1/2 LOD	LOD	1/2 LOD	LOD	1/2 LOD	LOD	1/2 LOD	LOD	1/2 LOD	LOD	1/2 LOD	LOD	2* LOD
HCB	20,7	10,4	233	117	249	125	309	154	204	102	249	125	2,6	1,3	1139	2277
PCB 28/	66,8	33,4	96,7	48,3	144	72,0	97,7	49	147	73,3	144	72,0	100	50,2	420	841
PCB 52	133	66,6	453	226	200	99,8	605	303	443	222	200	99,8	290	145	1114	2228
PCB 101	105	52,3	536	268	140	70,2	548	274	294	147	140	70,2	237	119	477	953
PCB 99	0,0	0,0	407	204	166	83,1	271	136	33	16,7	166	83,1	68,8	34,4	0,0	0,0
PCB 118	0,0	0,0	1004	502	0,0	0,0	471	236	241	120	0,0	0,0	0,0	0,0	0,0	0,0
PCB 153	134	67,0	2073	1037	291	146	1515	757	1867	933	291	146	51,8	25,9	97,4	195
PCB 105	0,0	0,0	393	196	0,0	0,0	181	90,3	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
PCB 138	61,3	30,6	1567	783	173	86,7	776	388	1193	596	173	86,7	1,1	0,6	59,6	119
PCB 187	0,0	0,0	36,8	18,4	0,0	0,0	87,9	43,9	53,0	26,5	0,0	0,0	0,0	0,0	0,0	0,0
PCB 183	0,0	0,0	50,0	25,0	0,0	0,0	28,5	14,3	34,5	17,2	0,0	0,0	0,0	0,0	0,0	0,0
PCB 180	0,0	0,0	692	346	0,0	0,0	241	120	466	233	0,0	0,0	0,0	0,0	0,0	0,0
PCB 170	0,0	0,0	28,3	14,2	0,0	0,0	0,0	0,0	72,3	36,2	0,0	0,0	-	-	-	-

Appendix 10: Recovery

Recovery						
Samples	**13C PBDE**	**Average**	**St.dev**	**Min**	**Max**	**% RSD**
S1-S5	PBDE 47	105	25	44	144	24
W1-W3	PBDE 99	97	22	42	132	23
S1(2)-S5(2)	PBDE 47	87	55	14	360	63
W1(2)-W3(2)	PBDE 99	85	50	13	360	59
W4-W5	PBDE 47	108	29	40	144	27
W4(2)-W5(2	PBDE 99	95	26	35	121	27
P	PBDE 47	92	37	43	141	41
P(2)	PBDE 99	80	32	37	123	40
Garbage samples	PBDE 47	128	130	34	504	101
	PBDE 99	181	189	39	504	104
In total	PBDE 47	97	41	14	360	42
	PBDE 99	91	37	13	331	41

| Recovery						
Samples	**13C Comp.**	**Average**	**St.dev**	**Min**	**Max**	**% RSD**
S2 S5 W1-W3 S1(2)-S5(2) W1(2)-W3(2)	HCB	54	29	8	225	54
	PCB 28	64	35	10	257	55
	PCB 52	62	34	10	247	56
	PCB 101	69	39	10	258	56
	PCB 118	76	43	11	281	56
	PCB 153	77	44	11	284	57
	PCB 105	82	45	12	302	55
	PCB 138	79	45	11	290	57
	PCB 167	83	46	13	301	56
	PCB 180	84	47	12	304	56
	PCB 189	95	53	14	347	56
	PCB 209	89	50	13	327	57
S1 S3-S4 W4-W5 W4(2)-W5(2) P P(2)	HCB	130	195	38	1182	150
	PCB 28	112	137	36	881	122
	PCB 52	148	129	47	843	87
	PCB 101	203	56	79	329	28
	PCB 118	181	57	69	374	31
	PCB 153	155	44	63	239	28
	PCB 138	187	47	76	262	25
	PCB 180	142	38	57	198	27
Garbage samples	HCB	99	48	27	207	48
	PCB 28	79	33	27	149	41
	PCB 52	120	58	30	236	48
	PCB 101	168	73	39	304	44
	PCB 118	147	64	34	265	44
	PCB 153	120	52	20	196	43
	PCB 138	142	56	36	227	40
	PCB 180	97	45	19	176	47

Appendix 11: Achieved FTIR Library
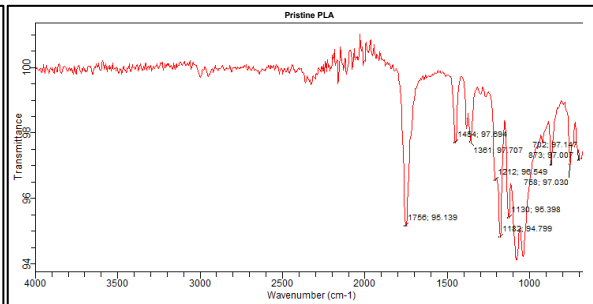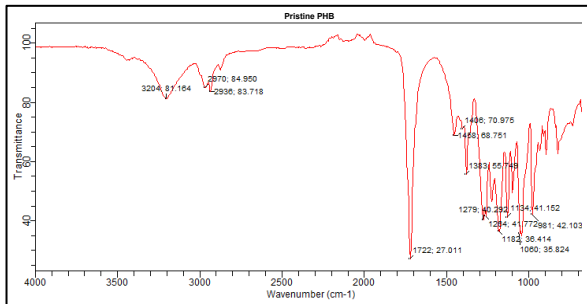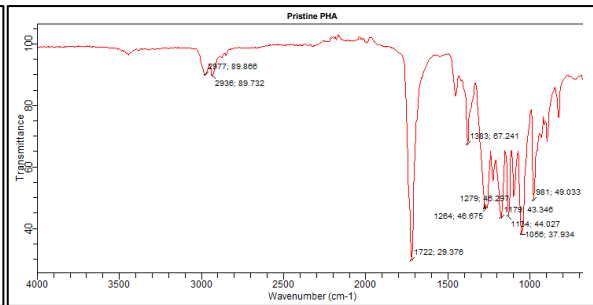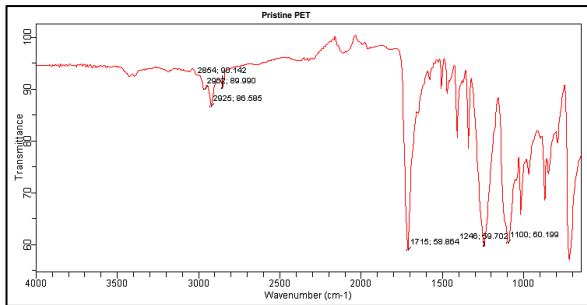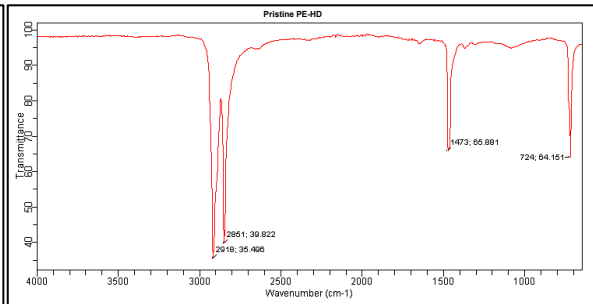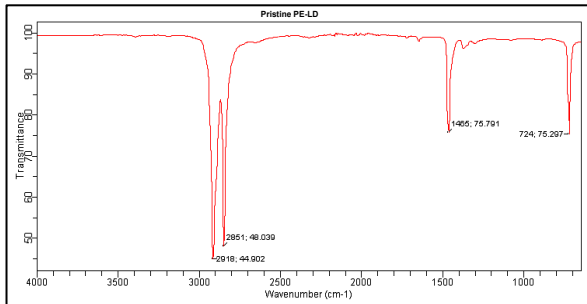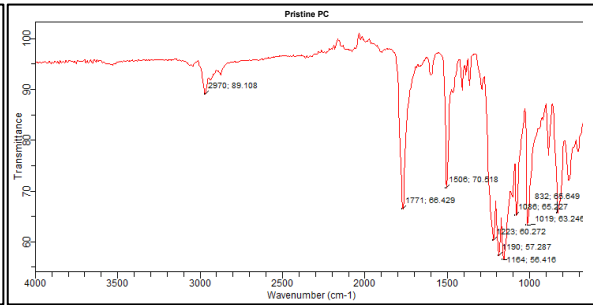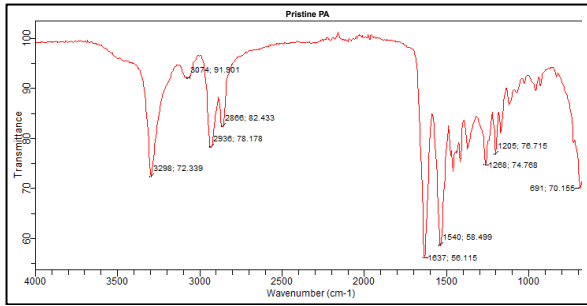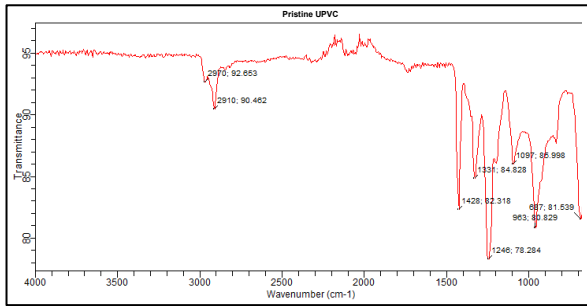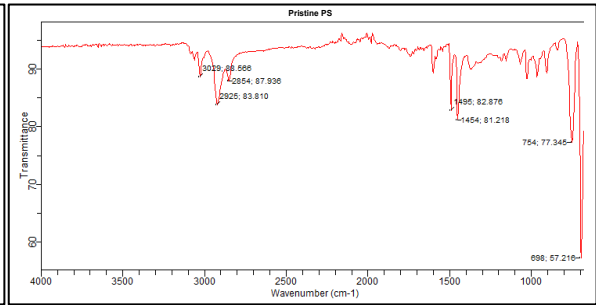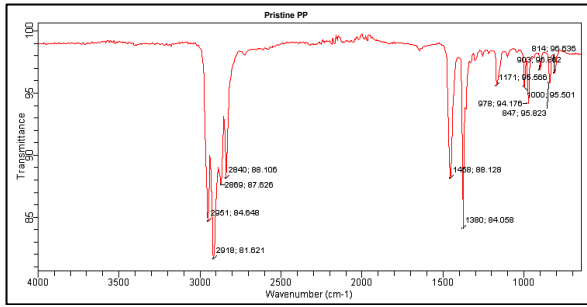
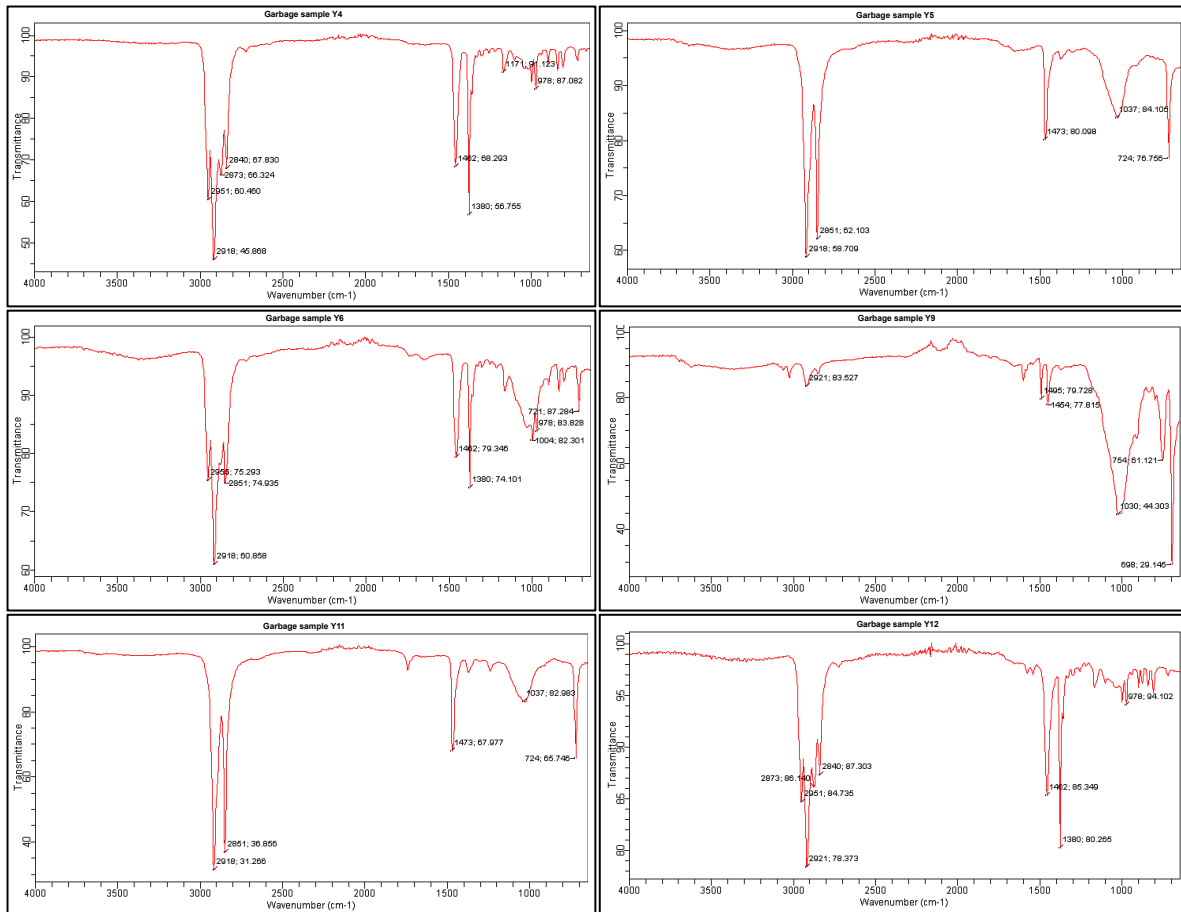# Appendix 12: IR-spectra and identification of garbage samples
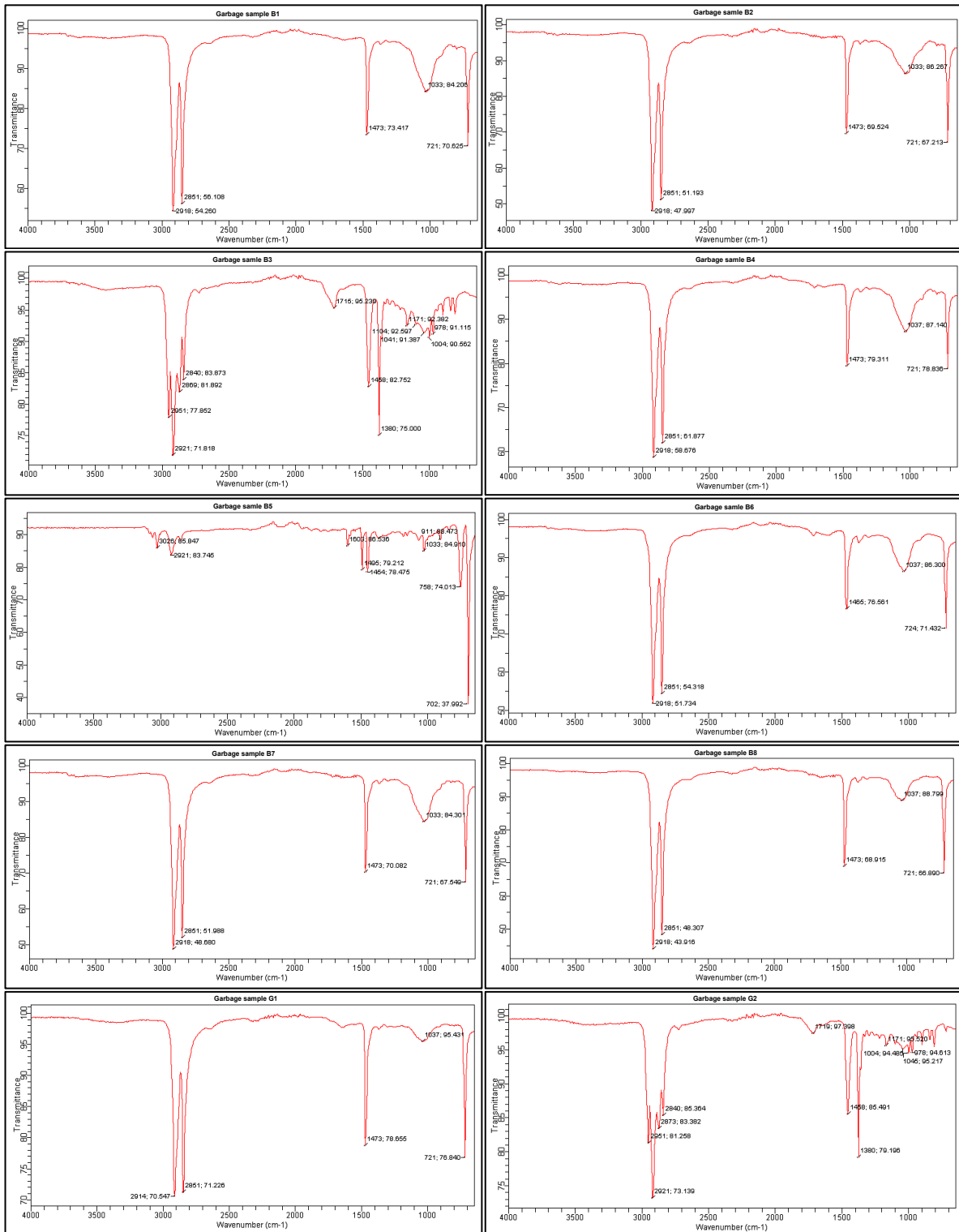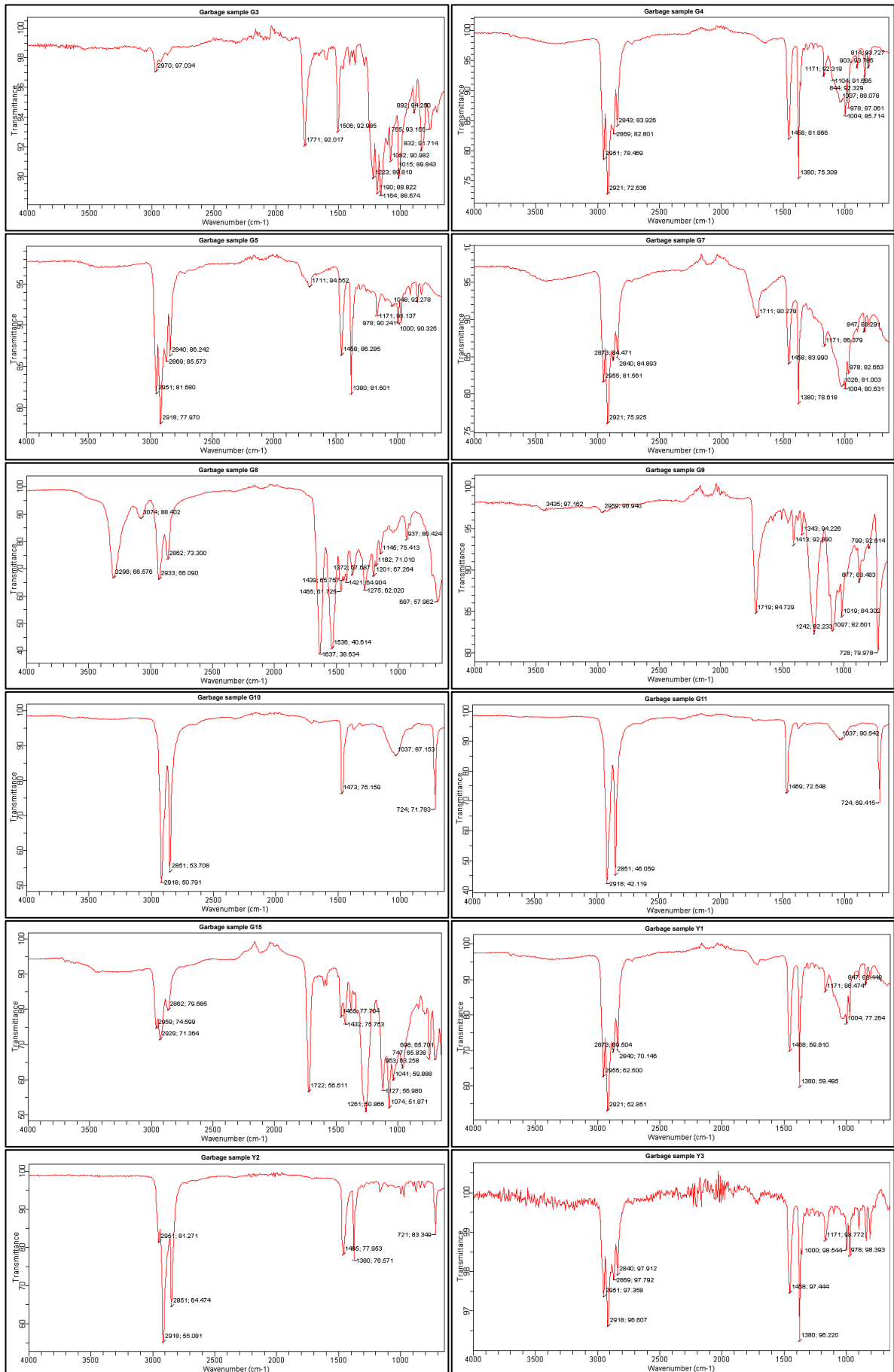
Table 10: Garbage samples and their suggested type of plastic.

Garbage sample	Plastic type suggestion	Garbage sample	Plastic type suggestion	Garbage sample	Plastic type suggestion
B1	PE(HD/LD)	G1	PE(HD/LD)	Y1	PP
B2	PE(HD/LD)	G2	PP	Y2	PP
B3	PP	G3	PC	Y3	PP
B4	PE(HD/LD)	G4	PP	Y4	PP
B5	PS	G5	PP	Y5	PE(HD/LD)
B6	PE(HD/LD)	G7	PP	Y6	PP
B7	PE(HD/LD)	G8	PA	Y9	PS
B8	PE(HD/LD)	G9	PET	Y11	PE(HD/LD)
		G10	PE(HD/LD)	Y12	PP
		G11	PE(HD/LD)		
		G15	PC		

Appendix 13: Log K_{ow} values

Compound	Num. of Cl/Br	Log K_{ow}
HCB		5.5
PCB 28/31	Tri	5.7
PCB 52	Tetra	6.1
PCB 99	Penta	6.4
PCB 101	Penta	6.4
PCB 105	Penta	6.7
PCB 118	Penta	6.7
PCB 138	Hexa	6.8
PCB 153	Hexa	6.9
PCB 180	Hepta	6.9
PCB 187	Hepta	7.2
PCB 183	Hepta	7.2
PCB 170	Hepta	7.3
PBDE 17	Tri	5.7
PBDE 28	Tri	5.9
PBDE 49	Tetra	-
PBDE 71	Tetra	-
PBDE 47	Tetra	6.8
PBDE 66	Tetra	-
PBDE 77	Tetra	-
PBDE 100	Penta	7.2
PBDE 119	Penta	-
PBDE 99	Penta	7.3
PBDE 85	Penta	-
PBDE 126	Penta	-
PBDE 154	Hexa	7.8
PBDE 153	Hexa	7.9
PBDE 138	Hexa	-
PBDE 156	Hexa	-
PBDE 184	Hepta	-
PBDE 183	Hepta	8.3
PBDE 191	Hepta	-
PBDE 202	Octa	-
PBDE 197	Octa	-
PBDE 196	Octa	-
PBDE 207	Nona	-
PBDE 206	Nona	-
PBDE 209	Deca	-

- = No data reported

Sources:
https://brage.bibsys.no/xmlui/bitstream/handle/11250/174176/BorgaDiGuardoSciTotEnv2005.pdf?sequence=1
https://monographs.iarc.fr/wp-content/uploads/2018/06/mono107-001.pdf
https://www.atsdr.cdc.gov/toxprofiles/tp207-c4.pdf