Sorption of trace elements (Cd, Cu, Hg, Pb, and Zn) by macro- and microplastics within intertidal sediments; a laboratory, field and modeling approach

by

Tamara Kazmiruk

C Sc., Water Problems Institute, Russian Academy of Sciences, 1993
B.Sc. (Hons.), National University of Water and Environmental Engineering, 1987

Thesis Submitted in Partial Fulfillment of the
Requirements for the Degree of
Doctor of Philosophy

in the
Department of Biological Sciences
Faculty of Science

SIMON FRASER UNIVERSITY
Spring 2023

Declaration of Committee

Name:	**Tamara Kazmiruk**
Degree:	**Doctor of Philosophy**
Title:	**Sorption of trace elements (Cd, Cu, Hg, Pb, and Zn) by macro- and microplastics within intertidal sediments; a laboratory, field and modeling approach**
Committee:	**Chair:** **Gerhard Gries** Professor, Biological Sciences
	Leah Bendell Supervisor Professor, Biological Sciences
	Eirikur Palsson Committee Member Associate Professor, Biological Sciences
	Juan José Alava Committee Member Adjunct Professor, Resource and Environmental Management
	Curtis Eickhoff Examiner Adjunct Professor, Biological Sciences
	Maria T. Maldonado External Examiner Professor, Earth, Ocean & Atmospheric Sciences University of British Columbia

Abstract

Plastic are now the main fraction of marine and beach litter as a result of the increasing production and wide range of applications. Due to continuous degradation, long residence times, and behaviour, there is widespread concern and gaps in knowledge regarding the growing impacts of plastic macro- and microparticles on marine and freshwater ecosystems and human health. The potential threat that plastic particles impose on ecosystems varies from ingestion by a wide range of aquatic organisms to their ability to sorb a diversity of environmental pollutants including trace elements. Only a few studies have addressed trace elements-plastic particles interactions within marine intertidal sedimentary environments. To address these current knowledge gaps, *I applied laboratory, field, and modelling approaches* to examine the sorption of Cd, Cu, Hg, Pb, and Zn by macro- and microplastics of PETE and HDPE within marine intertidal sediments. *First, I used field experiments* in the intertidal area of Burrard Inlet (Canada) to compare long-term sorption of trace elements by 4 types of plastic macro- and microparticles within two contrasting intertidal sediment environments. *I found that* trace elements sorption by plastic macro- and microparticles are dependent of sediment geochemistry and polymer characteristics and degradation status. Sorption of trace elements by macro- and microplastics decreased with increasing organic matter concentration in sediments. Plastic particles play a minor role in trace elements sorption in the presence of organic matter at high concentrations as a result of competitive adsorption. *Second, I* used controlled laboratory experiments to test the dependence of temperature on trace element sorption by plastic macro- and microparticles within intertidal sediments. Temperature alters the sorption of metals by plastic by altering the rate of reaching equilibrium and equilibrium concentration. Constant temperature had only a minor influence on the partitioning of trace elements in presence of organic matter at high concentrations. *Lastly*, I show that PFOM and PSOM kinetic models do not perform well in testing data derived from sorption experiments and suggest a framework for the future development in modeling and predicting of trace elements sorption by plastic particles within intertidal sediments. *Overall,* this thesis enhances our understanding of trace elements-plastic particles interactions in intertidal sediments and provides a tool that can be used to assess the conditions under which macro- and microplastics pose the greatest threat by providing an additional vector of Cd, Cu, Hg, Pb, and Zn exposure into benthic food webs.

Keywords: intertidal sediments; plastic macro- and microparticles; organic matter; sorption of trace elements; partitioning of trace elements; kinetic studies

To my loving Mom, Maria Gorbach (1939 – 2022)

A proper dreams change reality.

Acknowledgements

I acknowledge the SFU Graduate Study for making it possible for me to join the Biological Sciences Department and for their financial support during my graduate program. Funding for this research was provided in part by Environment and Climate Change Canada (ECCC), the Cowichan Estuary Restoration and Conservation Association (CERCA), and the Nippon Foundation-Ocean Litter Project at UBC.

I would like to express my sincere gratitude to all who have assisted me in completing this thesis. I gratefully acknowledge my *senior supervisor, Dr. Leah I. Bendell,* for her valuable advice and suggestions as well as encouragement and unlimited support during my graduate program. Her ability to find the possible in the impossible was inspirational. Special thanks are due to my *supervisor Dr. Eirikur Palsson* for his knowledge and patient guidance. His advice and precise comments on my manuscript helped me to complete my work. I have been very lucky to have a supervisor like Dr. Eirikur Palsson who cared so much about my work. I wish to thank my *supervisor Dr. Juan José Alava* who was never too busy for academic discussions and who has provided me with the possibility to work with a group of scientists from the Pacific Wildlife Research Centre ECCC and CERCA. I greatly appreciate his unlimited support during my graduate program as well as his comments on the manuscript and helpful advice. Without the exceptional support of my supervisors throughout my research, this PhD thesis, presented here, would not have been possible.

I would like to thank Wen Zhou (Instrument Technician, Chemistry Department) for the support I have received for the FTIR analysis of my numerous samples. I would also like to express my appreciation to Eric Shen (Computer Technician), Alison Hadwin (Teaching Laboratory Technician), Melissa Stephens (Chair's Secretary), Laurie Sutterlin (Graduate Program Assistant), Debbie Sandher (Scholarship Secretary), Kathryn Coukell (Manager, Administrative Services), Catherine Louie and Peggy Fung (Assistant for Theses, SFU, WAC Bennett Library) for their expert guidance and assistance throughout my graduate program.

A huge thank you goes to *my family* for understanding and sharing good and bad times with me during the last years. I am very grateful to my son, Zakhar, for the love and motivation he has given me, which helped me to complete this project.

Table of Contents

List of Tables

List of Figures

List of Acronyms

ANOVA	Analysis of variance
Cd	Cadmium
Cu	Copper
dw	dry weight
FTIR	Fourier-transform infrared spectroscopy
GS	Grain size
HDPE	High-density polyethylene
HB	Horseshoe Bay
Hg	Mercury
HTM	High tide mark
LOI	Loss on ignition
LTM	Low tide mark
MWFCA	Maplewood Flats Conservation Area
OM	Organic matter
Pb	Lead
PETE	Polyethylene terephthalate /polyester
PFOM	Pseudo-first-order kinetic model
PS	Polystyrene
PSOM	Pseudo-second-order kinetic model
RSE	Residual Standard Error
T	Temperature
t	time
Zn	Zinc

Chapter 1.

Background on macro- and microplastics (occurrence, behaviour, and impact) and rationale for study

1.1. Source and occurrence of macro- and microplastics in the aquatic environment

The objectives of this chapter are to review the current state of knowledge on the source, distribution, occurrence, behaviour, and impact of the plastic macro- and microparticles in marine and freshwater, ecosystems. In addition, knowledge gaps are identified along with the problem statement and research/thesis objectives and hypotheses.

Marine and freshwater ecosystems associated with the input, transport, accumulation and export of materials (Gruiz et al., 2015; GESAMP, 2001; Sutherland et al., 2010) accumulates contaminants over time. These ecosystems can therefore act as a secondary source of pollution to the associated food webs resulting in the trophic transfer of contaminants to higher trophic levels including humans. Focus has been on contaminants of concern such as trace elements; now current/emerging contaminants of concern are plastic materials (Weber et al., 2022). The behaviour of these unique contaminants i.e., threats posed to the natural environment and human health, are not yet thoroughly understood despite their global importance.

The term “plastic” is used to define the class of materials called “polymers”. The first type of the modern synthetic plastic,”bakelite”, appeared in 1907 (Leo Baekeland invented “bakelite”) and marked the introduction of the “plastic age” (William, 2008). Plastics are synthetic materials of high molecular mass or macromolecules consisting of monomers and typically made from petroleum-based products (Andrady and Neal, 2009; GESAMP, 2001). The mass global production of plastic materials has increased from around 5 million tons per year during the 1950s to over 320 million tons per year in 2015, reaching 426 million worldwide in 2018, including 359 million tons of resins, according to Plastics Europe, and 67 million tons of synthetic fibres, according to The Fiber Year (Figure A1) (Lusher, 2015). Plastic materials production is expected to grow at a rate of

10% per year, as India, China, and the African continent begin to discover the benefits and advantages that plastics have to offer (Plastics Europe, 2019; Plastics Europe, 2015; Thompson et al., 2009; World Economic Forum, 2016).

At present, plastic materials have a wide range of applications in everyday life (clothing, packaging, ropes, basic household items, and personal care products), medicine, agriculture, and industry due to their versatile physical and unique chemical properties (lightweight, strong, durable, corrosion-resistant, chemically inert, and slow biodegradable), and inexpensive production costs (Table A1). “Plastic” is a generic term used for both natural and synthetic polymers. However, synthetic materials account for >90% of the plastic produced, such as polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polyethylene terephthalate (PET) and polystyrene (PS) (Andrady & Neal, 2009). A large amount of plastics are used as disposable items and only <5% of plastic materials have been recovered (Sutherland et al., 2010).

Increased production and wide use of the plastic materials and misuse and mismanagement of plastic waste has resulted in the growth in the amount of plastic debris accumulating in the surrounding environment (GESAMP, 2015; Klein et al., 2015; Rochman, 2013; Rochman et al., 2013(a); Thompson et al. 2009). Although most plastics come from land sources, the final receptors of plastic wastes are the oceans (Beaumont et al. 2019). Plastics enter the aquatic environment through a variety of means including wastewater and waste management systems, aerial deposition, and as litter from terrestrial and marine ecosystems. This eventually leads to plastics being reported as the main fraction of marine and beach litter (between 60 and 95% of the total amount of litter worldwide) (Derraik, 2002; Ryan et al., 2009; Andrady, 2011; Cole et al., 2011) found floating at the water surface as well as accumulating on the seafloor and in coastal sediments (Dekiff et al., 2014; Eriksen et al., 2014; Holmes et al., 2014). It has been estimated that between 4.8 million and 12.7 million metric tons of mismanaged plastic waste entered the ocean in 2010 (Ziccardi et al., 2016).

Over the last 10 years, plastic waste has received greater attention from scientists and an increasing number of studies have reported the occurrence and potential hazards of plastic particles in aquatic ecosystems. Besides the many technological benefits of living in the “plastic age”, plastic products, their unsustainable use and disposal combined with their high durability in the environment result in pollution risks with widespread environmental and public health concerns (Andrady, 2009; Barboza et al., 2019; Cowger et al., 2020; GESAMP, 2019; Koelmans, 2015; Rochman, 2015; Rochman et al., 2016; Thompson, 2009).

1.1.1. Characteristics of macro- and microplastics

Plastic litter present in the environment range in size from nano to micrometers to meters (Andrady 2011; Eerkes-Medrano et al. 2015). Environmental factors (e.g., water, sediments, temperature, bacterial community), polymer properties (composition, polymer chemistry, size, density), and physical, chemical, and microbial processes results in a continual breakdown (fragmentation) of large plastic materials into smaller plastic fragments and particles (macro-, >5 mm in size; micro-, <5 mm in size; nanopaticles, ≤0.0001 mm (0.1 µm) in size) commonly known as macroplastics, microplastics and nanoplastics (Figure A2.). Due to the large number of publications on microplastics (4500 papers in Web of Science in August 2021, keyword: microplastic), the size definition of macroplastic simplifies the distinction to microplastic as items with size ≤5mm but other definitions are also published (GESAMP, 2001; Lechthaler et al., 2020). However, both size classifications are not internationally standardised. But there has not been an all-inclusive definition until the ECHA Report (2019), where size ranges for plastic particles and fibers were given as well, and the need for polymer identification was strongly highlighted (ECHA, 2019).

The term "microplastic" was mentioned for the first time by Thompson et al. (2004). Since then, the definition has been broadened and the most widely used definition is that provided by the National Oceanic and Atmospheric Administration (NOAA), as "fragments smaller than 5 mm" (Arthur et al., 2009). Microplastics are tiny plastic fragments, fibers, granules, and micropellets. Based on their formation pathway, microplastics can be divided by origin into two groups such as primary and secondary microplastics (Arthur et al., 2009; Cole et al., 2011). Recently, Frias and Nash (2019) defined microplastics as "synthetic solid particle or polymeric matrix, with regular or irregular shape and with size ranging from 1 µm to 5 mm, of either of primary or secondary manufacturing origin, which are insoluble in water". Primary microplastics (virgin plastic granules, pellets, and fibres) originate from primary sources, are microscopic in size and are used to produce macroplastics (plastic materials, products) (Table A1). These microplastic particles are synthetically manufactured and widely used as feedstock for plastic production (e.g., resin pellets) or appliance manufacturing, textile fibers in clothing (e.g., acrylic fibres), industrial abrasives (e.g., air blasting), and exfoliates incorporated in personal care and cosmetic products (e.g., microbeads in hand and facial cleansers) (Atugoda et al., 2021; Cole et al., 2011; Duis and Coors, 2016; Li et al., 2019). For example, cosmetic formulations may contain 0.5%–5% primary microplastics, and in a single use may release approximately 4500–94,500 microbeads (Prata et al., 2021). Primary microplastics are produced and discharged to the environment in the micro- or milliscale size. Secondary microplastics originate from degradation and fragmentation of large plastic materials, primarily uncontrolled waste or litter (e.g., packaging, clothing, household items, and building materials) after being introduced into the environment (Andrady, 2011; Arthur et al., 2009; Holmes et al., 2014; Rochman et al., 2014).

Microplastics are made from a variety of organic plastic materials the most common being: polyamides/nylons (PA), polyester (PES), low-density polyethylene (LDPE), high-density polyethylene (HDPE), polyethylene terephthalate (PETE), polyvinyl chloride (PVC), polypropylene (PP), polystyrene (PS), polyurethanes (PU), and acrylic (AC). The density of plastic particles varies greatly with composition and structure, commonly ranging from 0.83 to 1.38 g/cm^{-3} (Andrady, 2011; Hidalgo-Ruz et al., 2012; Ziccardi et al., 2016) and therefore plastic materials can be either lighter (e.g., PE, PP, EPS) or heavier (e.g., PS, PETE, PVC) than water (Table A1). In addition, different types of additives are using for stability and longevity of the polymer materials. This is important for application of plastic materials, for example in construction, because degradation of plastic takes many years.

1.1.2. Macro- and microplastics in water

Since 2004, the number of studies on plastic macro- and microparticles has exponentially increased, with most studies having been conducted in marine environments. For example, in total, 2882 and 877 publications were distributed from1998 to 2020 from the Web of Science Core Collection (WOSCC) database for marine and terrestrial ecosystems, respectively (He et al., 2020). The presence of plastic macro- and microparticles within aquatic ecosystems was first reported in sea water in the early 1970s (Carpenter et al., 1972; Carpenter and Smith, 1972; Colton et al., 1974; Koelmans et al., 2017; Morris and Hamilton, 1974; Wong et al., 1974).

(A) Macroplastics

Sources. In general, macroplastics are released into the aquatic environment following land-based (e. g., littering, waste management, construction industry) and ocean-based (e. g., littering, fishing and shipping industries, waste management) sources. Lechthaler et al. (2020) noted that 71% of the detected environmental litter was plastic, and 59% was identified as consumer-related. Disposable plastic products (usually with short service life and the high production values) found in the environment, represent a large proportion of the plastics such as food wrappers (8.92% of all litter), bottles and lids (7.51% of all litter), bags (5.49% of all litter), cigarette butts (4.02% of all litter), sanitary items (3.72%), and smoking-related packaging (3.40%) (Winton et al., 2020). The COVID-19 pandemic also serves as an additional source of plastics litter which, as predicted, will increase plastic pollution by 2030 by dumped gloves and masks with expected consequences for marine biota and its biodiversity (Canning-Clode et al., 2020; Silva et al., 2020).

Abundance and distribution. Fresh water environments, such as rivers, are the main source of macroplastics in to the oceans with an annual input between 1.15-2.41 million tons of plastic waste, dependent on waste management, population density, and hydrological characteristics (Lebreton et al., 2017). Studies on macroplastic concentrations in the rivers indicate that averaged values are highest for South-East Asia (1000–10,000 macroplastic items/h) and significantly lower for Europe (100–1000 items/h), which are due to the heavy pollution of the rivers in Indonesia and Vietnam (van Calcar et al., 2019). The lowest quantity of macroplastic was measured in the Rhine (10–75 items/h) (Vriend et al., 2020). In marine aquatic environment macroplastics represent the largest proportion of floating marine waste that account for 75% of the total volume (Galgani et al., 2015). About half of the produced plastic materials are lighter than water and, as a result, currently, 230 thousand tons of macroplastic are floating in the oceans (Eriksen et al., 2013; Geyer et al., 2017). In addition, van Sebille et al. (2015) estimated that between 93 and 235 thousand tons of plastic are present at the ocean surface.

(B) Microplastics

Sources. Microplastics that find their way into the ocean environment enter the oceans via rivers, coastal or marine sources and can either be distributed from the input sites via ocean currents, tidal movements, wind and wave's action, or settle to the bottom sediment. In the marine environment, plastics are slowly broken into smaller particles and become microplastics (Andrady, 2011). In addition, primary and secondary plastic microparticles are directly released into the aquatic environment through industrial or domestic drainage systems. For example, in the United States, approximately 8 trillion microbeads enter aquatic habitats each day via wastewater treatment plants (Rochman, et al., 2015). These are considered to be the main sources of most microplastics found in marine ecosystems, although we have limited knowledge regarding the actual contributions of inputs from several sources including landfills, coastal littering, ports, fishing gear, and shipping (Law and Thompson, 2014; Waldschläger, et al., 2020). According to Ryan (2015) size-dependent sedimentation of plastic microparticles occurs in the oceans, which influences the size distribution and composition of the particles found at the water surface (Ryan, 2015). Another study assumes that 99% of the plastic entering the oceans ends up below 100 m or on the seabed (Koelmans et al., 2017).

Abundance and distribution. It was estimated that per year up to 0.9 million metric tons of microplastics are retained in the continental environments, while up to 0.11 million metric tons reach the oceans (Horton et al., 2017; Tourinho et al., 2019). The estimates on the total amount of microplastics present in oceans range from 15 to 51 trillion particles (van Sebille et al., 2015). Another study estimated that between 1.1 and 3.5 trillion pieces of plastic microparticles are floating in the GPGP (Greater Pacific Garbage Patch) (Lebreton et al., 2018). The reported microplastic concentrations within aquatic ecosystems vary from low background concentrations of 3 particles/m^3 in water and 8 particles per kg in sediment to very high hot-spot concentrations of 102 000 particles per m^3 in water and 621 000 particles per kg in sediments (Thompson et al., 2004). Recently studies indicated the concentrations of microplastics are up to 16,000 items/m^3 (particle size ranges 50 μm - 1000 μm) in marine water and from 3 to 390 items/kg (particle size ranges 38 μm - 1000 μm) in marine sediments (Claessens et al., 2013; Li et al., 2016; Zhang et al., 2021). In addition, research conducted in the Arctic Ocean has reported 38 to 234 particles/m^3 of microplastic in ice cores (Obbard, et al., 2014).

1.1.3. Macro- and microplastics in sediments

It was estimated that up to 99% of the plastic particles introduced into the aquatic environment since 1950, has settled to the ocean floor (Koelmans et al., 2017). This estimate highlights the uncertainties of the concentration and fate of plastic debris with in marine sedimentary environments. The macro- and microplastic pollution of marine sediments includes accumulation of the plastic particles on the sea floor (bottom sediments) as well as accumulation in the coastal areas (intertidal and beach sediments).

(A) Macroplastics

Abundance and distribution. In general, coastal zones include the splash zone, the high intertidal zone, and the low tide zone whereas intertidal areas are found between the high tide and low tide, experiencing fluctuating influences of land and sea. In coastal regions, macroplastics can be washed ashore, depending on water depth, windblown, waves, tides movement, coastline morphology, and hydrodynamic activities. In addition, 60- 90% of land-based macro- and microplastics are expected to be stranded on beaches and intertidal zones after being introduced into the oceans where it can be buried into sea floor sediments or transported into the backshore (Ho et al., 2019). Coastal sediments and especially sediments of the intertidal zones are the hot-spots for accumulation of plastic macro- and microparticles (Browne et al., 2011; Peng et al., 2019). Thus, coastal sediment can be seen as temporal sinks of plastic macro- and microparticles in the marine aquatic environment. The average density of global coastal debris was estimated at 1.0 items/m², with 75% of it being plastic (Galgani et al., 2015). The summarized available data on concentrations of macroplastics on shorelines study sites clearly show the predominated plastic pollution in the northern hemisphere compare to the southern hemisphere. The highest average plastic pollution was detected on Indian beaches (110 items/m²), while the lowest density was found on Israeli beaches (0.02–0.062 items/m² and 0.04–2.09 items/m²) (Lechthaler et al., 2020).

(B) Microplastics

Abundance and distribution. Only a few studies have examined the deep sea sediments for microplastics (Peng et al., 2018; van Cauwenberghe et al., 2013; Woodall et al., 2014). Woodall et al. (2014) examined a total of 12 sediment samples from different locations in the deep sea and estimated an average concentration of plastic microparticles of 268 ± 70 fibres /l. On the basis of this data it was estimated that there could be about 4 billion fibres/km^2 on the Indian Ocean seabed alone. Peng et al. (2018) examined seawater and sediment samples from the Mariana Trench, the deepest part of the earth's surface. They estimated that concentrations of microplastic in the water was 13.51 pieces/l (depth between 2673 m–10,908 m) and in the sediment was found up to 2200 pieces/l (depth between 5108 m and 10,908 m) (Peng et al., 2018). The comparison of microplastic concentrations in different environmental compartments show that the concentrations found in the deep sea are significantly higher (Waldschläger et al., 2020).

The early research of Gregory (1978) indicated that plastic macro- and microparticles enters the coastal sedimentary environment and could accumulate in large amounts from 20,000 to 100,000 pellets per meter of beach. The highest concentration of microplastic was detected on shorelines and beaches were 50,000 particles/kg dw on the East Frisian Islands (Liebezeit and Dubaish, 2012) and 285,673 particles/m3 on a beach in South Korea (Kim et al., 2015). Some studies have reported the concentration of microplastic debris to be up to 20% in the top 20 cm of sand (Moore, 2008). In marine sediments off of Irish continental shelf, microplastics have been detected to a depth of 3.5 ± 0.5 cm, with 97% of the particles found in the upper 2.5 cm and 66% in the upper 0.5 cm (Martin et al., 2017).

There are many studies have indicated that plastic materials of PE, PS, PP and PES in the form of microparticles are the more abundant in the marine sedimentary environments as compared to the overlying water column (GESAMP, 2015). As noted, all of these plastic materials are currently the most widely and extensively used in food-packaging, agricultural and textile industries (Park et al., 2004). Accordingly, maritime activities and land-based sources might be the main sources of microplastics in sediments of coastal areas (Zhu et al., 2020). Browne et al. (2011) investigated shorelines worldwide to identify sources and sinks of plastic microparticles and showed a correlation between microplastic abundance and the anthropogenic population density. In addition, other studies have indicated the close relationship between an increasing population density with the increase in the deposition of the plastic materials in coastal areas (Brandon et al., 2019; Browne et al., 2011; Eriksen et al., 2013). Moreover, Brandon et al., (2019) on the base of the sedimentary record concluded, that deposition of the plastic microparticles in the coastal sediments has a direct link with increasing in the worldwide plastic production. In summarizing, most plastic debris accumulates in the sediment, particularly in the coastal zones (Harris, 2020; Harrison et al., 2014; Peng et al., 2017; Wahyuningsih et al., 2018). Serving as the hydrographical link between anthropogenic activities in the land and the marine environments makes the coastal intertidal zone as a hot spot for plastic macro- and microparticles accumulation.

1.2. Behaviour of macro- and microplastics in aquatic ecosystems

The use of plastic materials is a reality nowadays and, therefore, a better understanding of their behaviour and interaction in the aquatic environments is necessary. The behaviours of plastic macro- and microparticles in the aquatic environment can be classified as physical (i.e. distribution /redistribution, sedimentation and accumulation), chemical (i.e. degradation, sorption/desorption) and biobehaviours (i.e. ingestion, translocation and biodegradation) (Elgarahy et al., 2021; Prata et al., 2021; Wang et al., 2016). The understanding of the behavioural mechanisms of microplastics will determine their impacts for the aquatic ecosystems (Auta et al., 2017).

1.2.1. Physical behaviour

Numerous studies on identification, quantification and characterization of plastic macro- and microparticles have been published, however the physical behaviour (hydrodynamics, transport pathways, and deposition) of plastic particles in aquatic environments remain poorly understood (Hidalgo-Ruz et al., 2012; Möhlenkamp et al., 2018). A large proportion of produced plastic remains floating and is dispersed by winds, currents, and tidal movement over long distances ultimately accumulates in depositional areas (Hammer et al., 2012; Eriksen et al., 2014). According to Wang et al. (2016), physical behaviours of the plastic macro- and microparticles include migration, sedimentation, and accumulation (temporal and spatial). In the frame of this study, physical behaviours of the plastic macro- and microparticles in the aquatic environment can be defined as a process of their distribution, accumulation, and redistribution by combination of vertical transport, which is mainly influenced by density, surface area, and plastic particle size, and horizontal transport which depends mainly on the dominating currents (ocean current, wind, tides, and tsunami).

The density of synthetic plastic materials varies greatly with composition and structure, commonly ranging from 0.83 g/cm^{-3} to 1.39 g/cm^{-3} (Table A1). If plastic particles have an initial density lower than that of water, they are transported by flow. If plastic particles with an initial density greater than water, they are deposited directly to the sediments, unless the water flow is strong enough to transport the particles before they will have hydrodynamic conditions to settle out. Besides the density difference between plastic particles and water, the settling behaviour depends also on the particles shape and surface area. Pellets behave significantly differently to fibres and fragments (Möhlenkamp et al., 2018; Waldschläger et al., 2020). Once the particle has settled out onto the bed sediments, they can either be superimposed by natural sediments and infiltrate into the sediment bed. Sedimentary microplastic could be either transported together with sediments, or re-suspended and transported by hydraulic forces in the case of stronger flow velocities, for example, during flood events, currents, and tides (Ballent et al., 2016). Such vertical and horizontal movements suggest that sediment particles can serve as carriers of microplastics (Horton and Dixon, 2017). This results in various distribution patterns of microplastics together with sediment particle transportation behaviour (Grant, 1981; He, 2020). As alterations of polymeric macro- and microparticle like biofouling, degradation and fragmentation change the particle properties over time and thus the transport behaviour (Fazey and Ryan, 2016). By biofouling, plastic particles would reach seawater density which may result in their settling (Wang et al., 2016). The vertical distribution of plastic macro- and microparticles drops exponentially with water depth and smaller particles tend to be less buoyant (Möhlenkamp et al., 2018; Reisser et al., 2014).

Coastal zones, including intertidal areas, experiencing fluctuating influences of land and sea and can be defined as an transition zone between fluvial/freshwater and marine environments and considered the main locations where a majority of macro- and microplastics are generated (Andrady, 2011). In addition, because plastic particles accumulate in the coastal/ intertidal areas as it has been proven for other pollutants such as trace elements it is particularly important to consider the behaviour of plastic particles in these areas (Browne et al., 2010). In coastal zones, macroplastic can be washed ashore, depending on water depth, wind, waves, tides, coastline morphology, and hydrodynamic activities. In addition, 60- 90% of land-based macroplastic are expected to stand on beaches and intertidal zones after being introduced into the oceans where it can be buried into sea floor sediments or transported into backshore (Ho et al., 2019). The intertidal zone as an accumulation zone is extremely affected by different types of contaminants including plastic macro- and microparticles and carries many pollutants to the open ocean.

1.2.2. Chemical behaviour

The chemical behaviour of the plastic macro- and microparticles includes two main processes: 1) degradation and 2) sorption/desorption or leaching (Wang et al., 2016). The degradation process of the plastic macro- and microparticles can be defined as a change in the properties of the plastic materials (e.g. tensile strength, color, shape) under the influence of environmental factors such as temperature, light, salinity, wave action, chemicals and residency time (Figure A2). Depending on different influencing factors, degradation can be classified as photo-oxidative degradation, thermal oxidative degradation, ozone-induced degradation, mechanical degradation, chemical degradation, catalytic degradation, microbial and biodegradation (Atugoda et al., 2021; Singh and Sharma, 2008; Wang et al., 2016). For most of the types of polymer materials, full degradation of the breakdown products into carbon dioxide, water and inorganic molecules is extremely slow. Importantly, though plastics own a long environmental life, with degradation especially slow in the marine environment (Andrady, 2011; Ryan et al., 2009).

The degradation rate of plastic debris into tiny particles is negligible. But, in some laboratory studies, the degradation of polystyrene and polyethylene by bacterial isolates (*Rhodococcus ruber*) resulted in a weight loss of 12.4% and 7.5% after 42 and 56 days, respectively (Sivan et al., 2006). Overall, larger plastic litter in the natural environment is usually disintegrated by ultraviolet (UV) radiation catalyzes, temperature, water turbulence, physical abrasion by waves and oxygenation availability. The presence of additives in the plastic materials would increase the tendency of photo-oxidative degradation (Andrady et al., 2003). The full decomposition of plastic materials “from macro to micro” will take from hundreds to thousands of years (GESAMP, 2001).

In the context of this study, the process of sorption and desorption is not only a kind of physical behaviour but also a kind of chemical behaviour that characterized the relationship between the chemical (pollutants) and the plastic materials (Brennecke et.al., 2016). While the physical sorption primarily depends on the great specific surface area and Van der Waals' force, the chemical sorption mainly due to greater affinity of pollutants for the hydrophobic surface of plastic materials compared to the surrounding environments. The physical and chemical properties of sorbent including surface area, diffusivity, and crystallinity influence the sorption of chemicals (Wang et al., 2016). It is reported that synthetic plastic materials of macro- and microparticles bind with wide range of pollutants such as, trace elements, polycyclic aromatic hydrocarbon (PAH), polychlorinated biphenyls (PCBs), and dichlorodiphenyltrichloroethane (DDT). For example, due to the small size of plastic microparticles and their high surface area-volume ratio, contaminants such as toxic trace elements were shown to readily sorb to their surfaces (Boucher et al., 2016; Cole et al., 2011; Holmes et al., 2014; Kazmiruk et al., 2018; Munier et al., 2018; Rochman et al., 2014). Plastic materials contain a wide range of chemical compounds and blend of substances such as plastic additives (catalyst remnants, polymerization solvents, and others) which have been shown to leach from the plastic materials and subsequently accumulate within food webs.

1.2.3. Biobehavior

In general, the biobehavior of plastic macro- and microparticles in the environment can be divided into ingestion, translocation and biodegradation that include microbial degradation (Figure A2). The first evidence of microscopic plastic particles in the environment came indirectly from the examination of the gut contents of seabirds in the 1960s (Derraik, 2002; Laist, 1997). Many studies indicated that species of marine organisms, such as seabirds, would mistake plastic microparticles for food (Derraik, 2002; Moore, 2008; Ryan et al., 2009). In the 1970s, small fragments were observed in the plankton samples from the North Sea (Buchanan, 1971). It is reported, that at least 267 species, including 86% of all sea turtle species, 44% of all seabird species, and 43% of all marine mammal species, have been affected by plastic macro- and microparticles and fragments (Table A2.). More than 180 species of organisms, including fish, turtles, marine birds and mammals, have been documented to ingest plastic particles (Laist, 1997). Plastic microparticles are reported in the gut content of fishes globally including from estuaries (Lusher et al., 2013). Due to their small size, plastic microparticles are known to be ingested a wide range of organisms, including amphipods (detritivores), lugworms (deposit feeders), barnacles (filter feeders), mussels (suspension feeders), wild seafood bivalves and sea cucumbers (Bendell et al., 2020; Browne et al., 2008; Thompson et al., 2004; Van Cauwenberghe and Janssen, 2014; Rochman et. al., 2013c).

Once ingested by marine organisms, microplastics may be retained in their digestive tract, egested in the form of feces, or translocated from the gut into the cells and to other tissues (Browne et al., 2007). Based on organs of the digestive system and such a dimensional difference of ingested microplastics in organisms, translocation of the plastic to other organs is possible (Avio et al., 2015; Brennecke et al., 2015). However, the precise mechanisms of translocation in organisms remain unknown. In addition to the transport in the different environments, biota takes a part in the distribution of plastic microparticles when they incorporate them at one location and excrete it at another (Waldschläger et al., 2020).

Biodegradation of macro- and microplastic occurs when “microorganisms break down the polymer chains by consuming the polymer as a food source” (Performance Evaluation, 2007). The process of biodegradation of the plastic materials may be characterized by formation of biofilm, weight loss of plastic particles, visual pits and change of the polymeric properties (Figure A2). Formation of biofilm on the plastic surface is the favourite mode of growth of plastic degrading bacteria (Wang et al., 2016). In addition, pits visualized on the surface of microplastics under the scanning electron microscope also show indications that oceanic bacterial populations may be contributing to degradation (Zettler et al., 2013).

1.2.4. Aging of plastic materials

In general, plastic macro- and microparticles are exposed to environmental factors such as temperature, light, air and water, microbial community which are the most significant in the degradation of plastic materials (Figure A2). These factors affect the physical properties of the plastic materials such as, strength, melt flow index, appearance and color. Time–related changes in properties are often termed "aging" (Pospisil et al., 1999). Aging behaviour of the plastic materials can be defined as a process of changing the polymer properties over a period of time. The plastic aging processes can be separated into physical aging, chemical aging, thermal aging, etc.

Measuring, evaluating or simulating aging of plastic materials is very important for a number of long-term plastic applications, however, research on the aging characteristics, mechanism, and behaviour of aged plastic macro- and microparticles in the natural environment is very limited. At present, the aging of microplastics has been studied under a series of different temperatures and conditions (Mao et al., 2020; Pospisil et al., 1999; Wu et al., 2020). Some studies indicated that during the process of aging the macro- and microplastic will change color and crack, even demonstrating embrittlement and collapse (Müller et al., 2018). Another experimental laboratory study on the aging mechanism of polystyrene (PS) with UV irradiation under different conditions (air, pure water and seawater) show that polystyrene displays different rates of aging under different exposure conditions with UV air > UV seawater > UV pure water (Mao et al., 2020). Thus, plastic macro- and microparticles entering the environment will continue to age under the influence of various factors, which will influence on the particle size, surface morphology and plastic microstructure.

1.2.5. Effects of macro- and microplastic on human health: classification of plastic macro- and microparticles as contaminants of emerging concern

Due to slow degradation and increasing production of plastic materials in the world there is a potential widespread concern regarding the growing impacts of plastic waste on environmental and human health (Prata et al., 2021; Wright et al., 2017). The presence, in terms of long residence times, behaviour, and effect of microplastic in the marine environment make them global pollutants of priority study. Plastic macro- and microparticles can endanger marine ecosystems and human health via three distinct physical, chemical, and biological mechanisms (Elgarahy et al., 2021).

Microplastic particles are ingested by a wide range of aquatic organisms (birds, fishes, invertebrates, etc.) (Alava, 2021, Bendell et al., 2020; Thompson et al., 2004) at various trophic levels and potentially transferred to higher-trophic-level organisms through the food chain that may induce a threat for the human health via bioaccumulation and biomagnification (Andrady, 2011; Bouwmeester et al., 2015; Davidson et al., 2016). Ecologically, major concerns are related to the plastic microparticles, because these plastic fragments with limited size, can also be very easily accidentally ingested, affecting various organisms along the trophic chain and human health (Frias and Nash, 2019; Hazimah et al., 2021; Rochman et al., 2019). Rochmann et al. (2019) have defined that “microplastic particles are not simply “microplastic” but a diverse suite of contaminants that we refer to as “microplastic.”

Plastic macro- and microparticles are currently one of the primary marine pollution problems around the world. There are many studies show that various anthropogenic environmental pollutants can be found sorbed on different types of marine plastic debris (Andrady 2011; Teuten et al., 2009). Most of these substances are considered to be harmful to humans and wildlife. Plastic are currently associated with at least 78% of the priority pollutants and 61% of priority substances listed as toxic by the United States Environmental Protection Agency and European Union (Rochman et al., 2013a). They can act as mutagens, carcinogens and endocrine disruptors. These include hydrophobic pollutants such as polycyclic aromatic hydrocarbons (PAHs), poly chlorinated biphenyls (PCBs) and other persistent organic pollutants (POPs), and metals (Rochman et al., 2013b; Teuten et al., 2009).

Recently published studies have determined that uptake of plastic by humans and animals can cause adverse health effects which can be classified into three possible: 1) particle toxicity (oxidative stress, cell damage, inflammation, and impairment of energy allocation functions); 2) chemical toxicity (macromolecular substances (plastic materials); micromolecular substances (chemical additives, residual monomers and ambient chemical substances that sorb to plastic); 3) pathogen and parasite vectors (human pathogenic bacteria such as *Escherichia coli, Bacillus cereus, Stenotrophomonas maltophilia*) (Vethaak et al., 2016). In addition, a recent study demonstrated that not only fish and shellfish (seafood), but other important source of food such as sea salt appear to be contaminated with microplastics (polyethylene, cellophane and polyethylene terephthalate) (Yang et al., 2015). This could affect not only the survival of higher organisms in the marine environment, but also the provision of seafood for human consumption.

Macro- and microplastic particles currently pose a potential threat to wildlife and human health because of their prevalence in the aquatic ecosystem (Tourinho et al., 2019; Wang et al., 2016). Small plastic particles are easily ingested, and can act as a Trojan horse making the consumption of food with microplastic and nanoplastic a risk to human health (Tourinho et al., 2019). The potential hazard associated with microplastic has been receiving increasing attention. According to the reports (UNEP Year Book 2014, and Valuing Plastic) the overall financial damage of plastic to marine ecosystems estimated around $13 billion each year (UNEP, 2014; Wang et al., 2016). Microplastics are considered to be vectors for the priority pollutants listed in the Stockholm Convention for their potential adverse human health effects (GESAMP, 2015). The Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP) advocates for all nations to lead urgent efforts on decreasing the amount of plastic entering the ocean by adopting the reduce-reuse-recycle circular economy (3-Rs) (GESAMP, 2015). On May 12, 2021, Canada amended their 1999 Canadian Environmental Protection Act to add “plastic manufactured items” (PMI) to Schedule 1, a list of noted toxic substances (Walker, 2021). Besides the many technological benefits of living in the “plastic age”, the plastic products, their unsustainable use and disposal combined with their high durability in the environment cause pollution risks with widespread environmental and public health concerns (Andrady et al., 2009; Hazimah et al., 2021; Koelmans, 2015; Rochman et al., 2019; Thompson, 2009).

1.3. Thesis objectives and hypothesis

1.3.1. Knowledge gaps and problem statement

Knowledge gaps

The presence, in terms of long residence times, behaviour, and effect of microplastics in the marine environment make them global pollutants of priority study. Microplastic particles are ingested by a wide range of aquatic organisms (birds, fishes, invertebrates, etc.) (Thompson et al., 2004) at various trophic levels and potentially transferred to higher-trophic-level organisms through the food chain that may induce a threat for the human health via bioaccumulation and biomagnification (Andrady, 2011; Bouwmeester et al., 2015; Davidson et al., 2016). Due to the small size of microplastic particles and their high surface area-volume ratio, contaminants such as toxic trace elements were shown to readily sorb to their surfaces (Cole et al., 2011; Holmes et al., 2014; Rochman et al., 2014; Kazmiruk, et al., 2018; Munier et al., 2018). In addition to the potential physical impacts of ingesting’s microplastic, threat to marine organisms could also arise from leaching constituent contaminants, such as monomers and plastic additives (e.g. catalysts, solvents, antimicrobial agents, pigments), or organic and inorganic pollutants absorbed to the microplastic (Holmes et al.,2014; Rochman et al., 2014). Due to the slow degradation and increasing production of plastic in the world over time there is a potential widespread concern and gaps in knowledge regarding the growing impacts of macro- and microplastics waste on marine environment, local organisms, and human health (Vethaak et al., 2016). The understanding of the behavioural mechanisms of microplastic will help to determine their impacts for the aquatic ecosystems. However, despite recent research, the knowledge gaps on this still remain.

Problem statement. Rationale for the proposed research

Pollution assessment programs have traditionally used sediments to determine the levels of different pollutants such as trace metals, as they accumulate at significantly higher concentrations in sediments than water and show a higher temporal stability (Caeiro et al., 2005; Chapman, 1996; Water Quality Assessments, 1996). Sediments are an essential, dynamic and integral part of marine ecosystems providing habitat for benthic dwelling organisms as well as providing key ecosystem services such as nutrient cycling (Cluzaud et al., 2015). Sediments can serve as a secondary source of pollution to the aquatic ecosystems and ultimately to higher trophic levels including humans (Rochman et al., 2014; Yang et al., 2015). Sediment-associated contaminants tend to accumulate in depositional areas on small, fine-grained particles which have a very high surface area and tendency for higher concentration of organic matter. In addition, “modern” sediments can contain the largest proportion of microplastics (up to 621000 particles/kg) as compared to the overlying water column (up to 102000 particles/m^3 in water) (Thompson et al., 2004; Liebezeit et al., 2012). Some studies have reported the concentration of microplastic debris to be up to 20% in the top 20 cm of surface sediments (Moore, 2008). Microplastics are ubiquitous and present in the sediments of intertidal/ coastal area and estuaries (Hidalgo-Ruz at al., 2012; Lusher, 2015; Van Cauwenberghe et al., 2015a; Van Cauwenberghe et al., 2015b; Wahyuningsih et al., 2018).

Only a few studies have addressed the ability of microplastics to interact with other contaminants, such as trace elements, and sorb them from aquatic and sedimentary environments. These studies have indicated that trace elements such as copper (Cu), zinc (Zn), lead (Pb), cadmium (Cd), and mercury (Hg) can sorb onto and accumulate on plastic macro- and microparticles to a high degree due to their hydrophobic potential, small size, and large surface area (Ashton et al., 2010; Barboza et al., 2018; Bouwmeester et al., 2015; Holmes et al., 2014; Rochman et al., 2014). Notably, some contaminants have a greater affinity for plastic matrix (up to one million times higher) than surrounding seawater and sediments (Bouwmeester et al 2015). Not yet known is the role of sediment composition (e.g., organic matter and grain size) in influencing the sorption of trace elements by microplastic within intertidal/coastal sedimentary environments. For example, through competition for sorption site sediments high in organic matter may reduce trace elements accumulation by microplastic as compared to sediments low in organic matter. Further it is unknown which polymer and microplastic particle type is most effective in the sorption and accumulation of trace elements within coastal intertidal sediments (Wahyuningsih et al., 2018). Finally, the role of temperature in modulating trace metal sorption characteristics by microplastics has not been determined. Modeling is clearly a fundamental and complementary tool for identifying behaviour, and effect of microplastics (Van Sebille, 2015). It is these significant knowledge gaps I aim to address in my thesis.

1.3.2. Research objectives and hypotheses

The objectives of my research are therefore threefold:

(1) to contrast the sorption of trace elements by 2 types of plastic macroparticles and 2 types of plastic microparticles in relation to intertidal sediment geochemistry;

(2) through the use of controlled laboratory experiments determine the role of temperature in influencing trace elements sorption by plastic macro- and microparticles within intertidal sediments;

(3) through the integration of objectives (1)-(2) develop a set of guiding principles and kinetic modeling criteria on trace element sorption by plastic macro- and microparticles as influenced by sediment geochemistry and temperature.

Specific hypotheses are as follows:

H1: Sorption characteristics of plastic macro- and microparticles (PETE and HDEP) are dependent/ independent of the sediment geochemistry (e.g., grain size (GS), organic matter (OM)).

H2: Sorption characteristics of plastic macro- and microparticles (PETE and HDEP) are dependent/ independent of temperature.

Through the integration of H1-H2 I propose a modeling framework that represents the kinetics of traces elements (Cd, Cu, Hg, Pb, and Zn) sorption by plastic particles under condition of intertidal sedimentary environment. The modeling framework is based on two reversible reactions for exchange of trace elements with two elements bound at two different sites on the solid phase: sediment and plastic particles.

This framework can be as a template for future model development for predicting trace elements sorption by plastic particles within intertidal sediments. Such a model will provide an extremely useful tool to identify coastal intertidal marine environments at greatest risk to macro- and microplastic pollution and trace elements associated with the synthetic plastic materials in the form of macro- and microparticles.

To meet my proposed objectives and hypotheses, I applied a 3 tiered approach which combines laboratory, field, and modelling approaches.

1.4. Content and structure of the thesis

This thesis contains 5 general chapters and 3 appendixes.

Chapter 1 provides a general background and gives an overview of the content of this thesis. This chapter includes a comprehensive literature review, which highlights the most recent research and the current state of the knowledge on the source, distribution, occurrence, behaviour, and impact of the plastic macro- and microparticles in the aquatic environments with specific concentration on their fate and transport in the marine intertidal areas in order to track its evolution and trends. In addition, knowledge gaps are identified along with the state of the problem and research/thesis objectives and hypotheses.

Chapter 2 focuses on the field approach of the study. This chapter provides and discusses the results of the field experimental study on trace elements (Cd, Cu, Hg, Pb, and Zn) sorption by plastic macro- and microparticles of PETE and HDPE, determines the various factors that affect this process under condition of marine intertidal sedimentary environments, and provide data on macro- and microplastic characteristics (including composition, abundance, surface textures) acting as an indicator of degradation and interaction with trace metals.

Chapter 3 focuses on the laboratory approach of the study. This chapter provides and discusses the results of the laboratory study on simulation of sorption of trace elements (Cd, Cu, Hg, Pb, and Zn) by plastic macro- and microparticles of PETE and HDPE in the intertidal sediments under conditions of constant temperatures (T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C) with aim to determine the effect of temperature on trace elements-plastic macro- and microparticles interaction.

Chapter 4 focuses on the modeling approach of the study. This chapter was designed in response to the lack of modeling. Framework for modeling and predicting of the sorption of trace elements by plastic particles within intertidal sediments provide a theoretical basis for the environmental behavior of microplastics and their impact on trace elements migration.

Chapter 5 is a general discussion, conclusions and future perspectives of the study. This chapter is summarizing the key finding of this research and the linkage between the different chapters of the thesis and future research priorities.

It should be noted that as a result of the structure of the thesis, there is likely to be some repetition in the introduction among the chapters, as each had to stand alone as a full manuscript for publication as a scientific paper.

To avoid misleading interpretations, the main abbreviations used throughout this study are defined in the List of Acronyms section.

References

Alava, J. J. (2021). *Proposing a Bioaccumulation Metric Criteria Framework for Plastic Particles in Marine Biota and Foodweb. Bioaccumulation Beyond Lipid-based Processes: Microplastics, Nanoparticles, and Emerging Contaminants.* SETAC, North America 42nd Annual Meeting (SETAC SciCon4), 14-18 November, 2021 (Virtual Conference). https://www.researchgate.net/publication/35617.

Andrady, A.L. (2011). Microplastics in the marine environment. *Marine Pollution Bulletin*. *62* (8), 1596-1605.

Andrady, A.L., Hamid, H.S., & Torikai, A. (2003). Effects of climate change and UV-B on materials. *Photochemical & Photobiological Sciences. 2* (1), 68-72.

Andrady, A. L., & Neal, M. A. (2009). Applications and societal benefits of plastics. *Philosophical Transactions of the Royal Society. (Society B: Biological Sciences)* 364:1977-1984. DOI:10.1098/rstb.2008.0304

Arthur, C., J. Baker & H. Bamford (Eds). (2009). Proceedings of the International Research Workshop on the Occurrence, Effects and Fate of Microplastic Marine Debris. Sept 9-11, 2008. NOAA Technical Memorandum NOS-OR&R-30.

Ashton, K., Holmes, L., & Turner, A. (2010). Association of metals with plastic production pellets in the marine environment. *Marine Pollution Bulletin. 60* (11). 2050-2055.

Atugoda, T., Vithanage, M., Wijesekara, H., Bolan, N., Sarmah, A. K., Bank, M. S.,You, S., & Ok, Y. S. (2021). Interactions between microplastics, pharmaceuticals and personal care products: Implications for vector transport. *Environment International.*149, 106-137. https://doi.org/10.1016/j.envint.2020.106367

Auta, H.S., Emenike, C.U., & Fauziah, S.H. (2017). Distribution and importance of microplastics in the marine environment: a review of the sources, fate, effects, and potential solutions. *Environment International.*102, 165–176. https://doi.org/10.1016/j.envint.2017.02.013.

Avio, C.G., Gorbi, S., Milan, M., Benedetti, M., Fattorini, D., d'Errico, G., Pauletto, M., Bargelloni, L., & Regoli, F. (2015). Pollutants bioavailability and toxicological risk from microplastics to marine mussels. *Environmental Pollution. 198,* 211-222.

Ballent, A., Corcoran, P.L., Madden, O., Helm, P.A., & Longstaffe, F.J. (2016). Sources and sinks of microplastics in Canadian Lake Ontario nearshore, tributary and beach sediments. *Marine Pollution Bulletin. 110* (1), 383–395. https://doi.org/10.1016/j.marpolbul.2016.06.037.

Barboza, L.G.A., Vieira, L.R., Branco, V., Carvalho, C. & Guilhermino, L. (2018). Microplastics increase mercury bioconcentration in gills and bioaccumulation in the liver, and cause oxidative stress and damage in *Dicentrarchus labrax juveniles*. *Scientific Reports.* 8.15655. DOI:10.1038/s41598-018-34125-z

Barboza, L.G.A. , Co´zar, A., Gimenez, B.C.G., Barros, T.L., Kershaw, P.J., & Guilhermino, L. (2019). Macroplastics pollution in the marine environment. In: C. Sheppard (Ed.), *World Seas: An Environmental Evaluation.* (pp. 305–328). Amsterdam: Academic Press.

Beaumont, N.J., Aanesen, M., Austen, M.C., Börger, T., Clark,J.R., Cole, M., Hooper, T., Lindeque, P. K., Pascoe, C.,& Wyles, K. J. (2019). Global ecological, social and economic impacts of marine plastic. *Marine Pollution Bulletin.142*(2):189-195.

Bendell, L.I., LeCadre, E., & Zhou, W. (2020). Use of bivalves for monitoring microplastic pollution within intertidal sediments. *PLoS ONE 15*(5): e0232879.

Boucher, C., Morin, M., & Bendell, L.I. (2016). The influence of cosmetic microbeads on the sorptive behavior of cadmium and lead within intertidal sediments: a laboratory study. *Regional Studies in Marine Scienc,.* 3, 1–7.

Bouwmeester, H., Hollman ,P.C.H., & Peters, R.J.B. (2015) Potential health impact of environmentally released micro- and nanoplastics in the human food production chain: experiences from nanotoxicology. *Environmental Science and Technology. 49,* 8932−8947.

Brandon, J.A., Jones, W., & Ohman, M.D. (2019). Multidecadal increase in plastic particles in coastal ocean sediments. *Science Advances. 5*(9), DOI:10.1126/sciadv.aax0587

Brennecke, D., Ferreira, E.C., Costa, T.M., Appel, D., da Gama, B.A., & Lenz, M. (2015). Ingested microplastics (> 100mm) are translocated to organs of the tropical fiddler crab Ucarapax. *Marine Pollution Bulletin. 96*(1-2), 491-495.

Brennecke, D., Duarte, B., Paiva, F., Caçador, I., & Canning-Clode, J. (2016). Microplastics as vector for heavy metal contamination from the marine environment*. Estuarine, Coastal and Shelf Science. 178*, 189-195.

Browne, M.A., Galloway, T., & Thompson, R. (2007). Microplasticdan emerging contaminant of potential concern? *Integrated Environmental Assessment and Management. 3* (4), 559-561.

Browne, M.A., Dissanayake, A., Galloway, T.S., Lowe, M.D.,& Thompson, R.C. (2008). Ingested microscopic plastic translocates to the circulatory system of the mussel, Mytilus edulis (L.). *Environmental Science & Technology. 42* (13), 5026-5031.

Browne, M.A., Galloway, T.S., & Thompson, R.C. (2010). Spatial patterns of plastic debris along estuarine shorelines. *Environmental Science & Technology. 44* (9), 3404–3409. https://doi.org/10.1021/es903784e.

Browne, M.A., Crump, P., Niven, S.J., Teuten, E., Tonkin, A., Galloway, T., & Thompson, R. (2011). Accumulation of microplastic on shorelines worldwide: sources and sinks. *Environmental Science & Technology. 45* (21), 9175–9179.

Buchanan, J. B. (1971). Pollution by synthetic fibres. Marine Pollution Bulletin. (2), 23. DOI:10.1016/0025-326X(71)90136-6.

Caeiro S, Costa, M.H., Ramos, T.B., Fernandes, F., Silveira, N., Coimbra, A., Medeiros, G. & Painho., M. (2005). Assessing heavy metal contamination in Sado Estuary sediment: An index analysis approach. *Ecological Indicators. 5*. 151–169.

Canning-Clode, J., Sepúlveda, P., Almeida, S., & Monteiro, J. (2020). Will COVID-19 containment and treatment measures drive shifts in marine litter pollution? *Frontiers in Marine Sciences.* 25. https://doi.org/10.3389/fmars.2020.00691

Carpenter, E.J., Anderson, S.J., Harvey, G.R., Miklas, H.P., & Peck, B.B. (1972). Polystyrene spherules in coastal waters. *Science. 178*, 749–750.

Carpenter, E.J., & Smith, K.L. (1972). Plastics on the Sargasso Sea surface. *Science. 175*, 1240–1241.

Carson, H.S., Colbert, S.L., Kaylor, M.J., & McDermid, K.J. (2011). Small plastic debris changes water movement and heat transfer through beach sediments. *Marine Pollution Bulletin. 62* (8), 1708-1713.

Chapman, P.M. (1996). Presentation and interpretation of sediment Quality Triad data. *Ecotoxicology. 5,* 327–339.

Chisholm, C., Lindo, Z., & Gonzalez, A. (2011). Metacommunity diversity depends on connectivity and patch arrangement in heterogeneous habitat networks. *Ecography 34* (3), 415-424.

Claessens, M., van Cauwenberghe, L., Vandegehuchte, M.B., & Janssen, C.R. (2013). New techniques for the detection of microplastics in sediments and field collected organisms. *Marine Pollution Bulletin. 70* (1), 227-233. doi:10.1016/j.marpolbul.2013.03.009.

Cluzaud, M., Kazmiruk, T.N., Kazmiruk, V.D. & Bendell, L.I. (2015). Intertidal concentrations of microplastics and their influence on ammonium cycling as related to the shellfish industry. *Archives of Environmental Contamination and Toxicology. 68*(4). DOI:10.1007/s00244-015-0156-5.

Cole, M., Lindeque, P., Halsband, C. & Galloway, T.S. (2011). Microplastics as contaminants in the marine environment: a review. *Marine Pollution Bulletin, 62*(12), 2588–2597.

Colton, J.B., Burns, B.R., & Knapp, F.D. (1974). Plastic particles in surface waters of the northwestern Atlantic. *Science, 185*, 491–497.doi:10.1126/science.185.4150.491.

Cowger, W., Booth, M. A., Hamilton, B. M., Thaysen, C., Primpke, S., Munno, K., Lusher, L. A., Dehaut, A., Vaz, P. V., Liboiron, M., Devriese, I. L., Hermabessiere, L., Rochman, C., et al. (2020). Reporting quidelines to increase the reproducibility and comparability of research on microplastics. *Applied Spectroscopy, 74*(9). 1066–1077.

Davidson, K., & Dudas, S. E. (2016). Microplastic ingestion by wild and cultured Manila clams (Venerupis philippinarum) from Baynes Sound, British Columbia. *Archives of Environmental Contamination and Toxicology.71* (2), 147–156. https://doi.org/10.1007/s00244-016-0286-4.

Dekiff, J.H., Remy, D., Klasmeier, J. & Fries, E. (2014). Occurrence and spatial distribution of microplastics in sediments from Norderney. *Environmental Pollution. 186,* 248-256.

Derraik, J.G.B. (2002). The pollution of the marine environment by plastic debris: a review. *Marine Pollution Bulletin. 44*(9), 842-852.

Duis, K., & Coors, A. (2016). Microplastics in the aquatic and terrestrial environment: sources (with a specific focus on personal care products), fate and effects. *Environmental Sciences Europe. 28* (2), 1–25. https://doi.org/10.1186/s12302-15-0069-y.

ECHA (European Chemicals Agency). (2019). Annex XV Restriction Report Proposal for a Restriction. Report Version Number 1. (March 20th, 2019). 145 p. Helsinki. Available: https://echa.europa.eu/documents/10162/05bd96e3-b969-0a7c-c6d0-441182893720/[Accessed 18/01/2020].

Eerkes-Medrano, D., Thompson, R.C., & Aldridge, D.C. (2015). Microplastics in freshwater systems: a review of the emerging threats, identification of knowledge gaps and prioritization of research needs. *Water Research. 75*, 63–82. https://doi.org/10.1016/j.watres.2015.02.012.

Elgarahy, A. M., Akhdhar, A., & Elwakeel, K. Z. (2021). Microplastics prevalence, interactions, and remediation in the aquatic environment: A critical review. *Journal of Environmental Chemical Engineering*. 9. 106224.

Eriksen, M., Lebreton, L.C.M., Carson, H.S., Thiel, M., Moore, C.J., Borerro, J.C., Galgani, F., Ryan, P.G., & Reisser, J. (2014). Plastic pollution in the World's Oceans: More than 5 trillion plastic pieces weighing over 250,000 tons afloat at sea. *PLoS ONE. 9*, Article e111913. doi:10.1371/journal.pone.0111913.

Eriksen, M., Maximenko, N., Thiel, M., Cummins, A., Lattin, G., Wilson, S., Hafner, J., Zellers, A., & Rifman, S. (2013). Plastic pollution in the South Pacific subtropical gyre. *Marine Pollution Bulletin. 68,* 71–76, doi:10.1016/j.marpolbul.2012.12.021.

Fazey, F.M.C., & Ryan, P.G. (2016). Biofouling on buoyant marine plastics: An experimental study into the effect of size on surface longevity. *Environmental Pollution. 210*, 354–360. https://doi.org/10.1016/j.envpol.2016.01.026.

Frias, J.P., & Nash, R. (2019). Microplastics: finding a consensus on the definition. *Marine Pollution Bulletin. 138*, 145–147.

Galgani, F., Hanke, G., & Maes, T. (2015). Global Distribution, Composition and Abundance of Marine Litter. In Bergmann, M., Gutow, L., & Klages, M. (Eds.), *Marine Anthropogenic Litter* (pp. 29–56). Springer International Publishing: Cham, Switzerland. ISBN 978-3-319-16509-7.

Garnier, Y., Galgani, F., & Claro, F. (2021). Physical Impacts of Microplastics on Marine Species. In Rocha-Santos,T., Costa, M. F., & Mouneyrac, C. (Eds.), *Handbook of Microplastics in the Environment.* Springer, Cham. DOI:10.1007/978-3-030-10618-8_49-1.

GESAMP (Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection) and Advisory Committee on Protection of the Sea. (2001). Protecting the oceans from land-based activities - Land-based sources and activities affecting the quality and uses of the marine, coastal and associated freshwater environment. *GESAMP Report and Studies.* No. 71, 162 p. http://www.gesamp.org/site/assets/files/1251/protecting-the-oceans-from-land-based-activities-en.pdf

GESAMP (Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection). Bowmer, T. and Kershaw, P.J. (Eds.). (2010). Proceedings of the GESAMP International Workshop on microplastic particles as a vector in transporting persistent, bio-accumulating and toxic substances in the oceans. *GESAMP Report and Studies.* No. 82, 68 p. http://www.gesamp.org/site/assets/files/1264/proceedings-of-the-gesamp-workshop-on-microplastic-particles-en.pdf

GESAMP (Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection). Kershaw, P.J. (Ed.). (2015). Sources, fate and effects of microplastics in the marine environment: a global assessment. *GESAMP Report and Studies.* No. 90, 96 p. https://ec.europa.eu/environment/marine/goodnvironmental-status/descriptor-10/pdf/GESAMP_microplastics%20full%20study.pdf

GESAMP (Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection). Kershaw, P.J., & Rochman, C.M. (Eds). (2016). Sources, fate and effects of microplastics in the marine environment: part two of a global assessment. *GESAMP Report and Studies.* No. 93, 220 p. http://www.gesamp.org/site/assets/files/1275/sources-fate-and-effects-of-microplastics-in-the-marine-environment-part-2-of-a-global-assessment-en.pdf

GESAMP (Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection). P.J. Kershaw, B. Carney Almroth, P. Villarrubia-Gómez, A.A. Koelmans, & T. Gouin (Eds.). (2020). Proceedings of the GESAMP International Workshop on assessing the risks associated with plastics and microplastics in the marine environment. *GESAMP Report and Studies.* No.103, 68 p. http://www.gesamp.org/publications/gesamp-international-workshop-on assessing-the-risks-associated-with-plastics-and-microplastics-in-the-marine-environment

Geyer, R., Jambeck, J.R., & Law, K.L. (2017). Production, use, and fate of all plastics ever made. *Science Advances, 3*. Article e1700782. doi:10.1126/sciadv.1700782.

Grant, J. (1981). Sediment transport and disturbance on an intertidal sandflat: infaunal distribution and recolonization. *Marine Ecology - Progress Series. 6*. 249-255.

Gregory, M.R. (1978). Accumulation and distribution of virgin plastic granules on New Zealand beaches. *New Zealand Journal of Marine and Freshwater Research, 12*(4). 399-414. http://dx.doi.org/10.1080/ 00288330.1978.9515768.

Gruiz, K., Meggyes, T., & Fenyvesi. E. (Eds.). (2015). Environmental toxicology. Boca Raton, Florida; London; New York: CRC Press.

Hammer, J., Kraak, M.H.S., & Parsons, J.R. (2012). Plastics in the marine environment: The dark side of a modern gift. *Reviews of Environmental Contamination and Toxicology, 220*, 1–44. https://doi.org/10.1007/978-1-4614-3414-6_1

Harris, P. T. (2020). The fate of microplastic in marine sedimentary environments: A review and synthesis. *Marine Pollution Bulletin. 158.* Article 111398. 1-25.

Harrison, J.P., Schratzberger, M., Sapp, M. & Osborn, A.M. (2014). Rapid bacterial colonization of low-density polyethylene microplastics in coastal sediment microcosms. *BMC Microbiology, (14)*232. DOI:10.1186/s12866-014-0232-4

Hartmann, N.B., Rist, S., Bodin, J., Jensen, L.H., Schmidt, S.N., Mayer, P., Meibom, A., & Baun, A. (2017). Microplastics as vectors for environmental contaminants: exploring sorption, desorption, and transfer to biota. *Integrated Environmental Assessment and Management, (3)*13, 488-493.

Hazimah, N., Kooi, M., Diepens, N., & Koelmans, A.A. (2021). Lifetime Accumulation of Microplastic in Children and Adults. *Environmental Science and Technology, (55)*8, 5084–5096. https://doi.org/10.1021/acs.est.0c07384.

He, D.F., Bristow, K., Filipovi´c, V., Lv, J., & He, H. (2020). Microplastics in terrestrial ecosystems: A scientometric analysis. *Sustainability.* 12, Article 8739. doi:10.3390/su12208739 www.mdpi.com/journal/sustainability.

Hidalgo-Ruz, V., Gutow, L., Thompson, R. C. & Thiel, M. (2012). Microplastics in the Marine Environment: A Review of the Methods Used for Identification and Quantification. *Environmental Science & Technology, 46* (6), 3060-3075.

Ho, N.H.E., & Not, C. (2019). Selective accumulation of plastic debris at the breaking wave area of coastal waters. *Environmental Pollution, 245*, 702–710, doi:10.1016/j.envpol.2018.11.041.

Holmes, L.A., Turner, A., & Thompson, R.C. (2014). Interactions between trace metals and plastic production pellets under estuarine conditions. *Marine Chemistry,* 167, 25–32.

Horton, A.A., & Dixon, S.J. (2017). Microplastics: an introduction to environmental transport processes. *WIREs Water, 9* (12), Article e1268. https://doi.org/10.1002/wat2.1268.

Jiang, P., Zhao, S, Zhu, L., & Li, D. (2018). Microplastic-associated bacterial assemblages in the intertidal zone of the Yangtze Estuary. *Science of the Total Environment,* 624, 48–54.

Kazmiruk, T.N., Kazmiruk, V.D., Ashley, K.I., & Bendell, L.I. (2017). Trace metals in urban estuaries; Implications for remediation. In James, C.A., Lanksbury, J., Lester, D., O'Neill, S., Roberts, T., Sullivan, S., & West, J. (Eds.), *The 2016 Salish Sea Toxics Monitoring Review: A Selection of Research Puget Sound Ecosystem Monitoring Program* (pp.8-9). Tacoma, WA.

Kazmiruk, N. T., Kazmiruk, V.D., & Bendell, L.I. (2018). Abundance and distribution of microplastics within surface sediments of a key shellfish growing region of Canada, *PLoS ONE*, 13(5). https://doi.org/10.1371/journal.pone.0196005

Kim, I.-S., Chae,D.-H., Kim, S.-K., Choi, S., & Woo,S.-B. (2015). Factors influencing the spatial variation of microplastics on high-tidal coastal beaches in Korea. *Archives of Environmental Contamination and Toxicology, 69* (3), 299–309. https://doi.org/10.1007/s00244- 015-0155-6.

Klein, S., Worch, E., & Knepper, T.P. (2015). Occurrence and spatial distribution of microplastics in river shore sediments of the Rhine-Main area in Germany. *Environmental Science & Technology. 49*(10), 6070–6076. https://doi.org/10.1021/acs.est.5b00492.

Koelmans, A.A. (2015). Modeling the role of microplastics in Bioaccumulation of organic chemicals to marine aquatic organisms. A critical review. In: Bergmann, M., Gutow, L., & Klages, K. (Eds.), *Marine Anthropogenic Litter* (pp. 309-324). Springer. SpringerLink.com. DOI 10.1007/978-3-319-16510-3.

Koelmans, A.A., Bakir, A., Burton, G.A., & Janssen, C.R. (2016). Microplastic as a vector for chemicals in the aquatic environment: Critical review and model-supported reinterpretation of empirical studies. *Environmental Science & Technology, 50*(7), 3315-3326. https://doi.org/ 10.1021/acs.est.5b06069.

Koelmans, A.A., Kooi, M., Law, K.L., & van Sebille, E. (2017). All is not lost: deriving a top-down mass budget of plastic at sea. *Environmental Research Letters, 12*(11). Article 114028. DOI:10.1088/1748-9326/aa9500.

Laist, D.W. (1997). Impacts of marine debris: entanglement of marine life in marine debris including a comprehensive list of species with entanglement and ingestion records. In: Coe, J.M., Rogers, D.B. (Eds.), *Marine Debris: Sources, Impacts and Solutions.* (pp. 99-139). Springer: Verlag, New York.

Law, K. L., & Thompson, R. C. (2014). Oceans. Microplastics in the seas. *Science. 345*(6193), 144-1455. DOI:10.1126/science.1254065

Lebreton, L.C.M., van der Zwet, J., Damsteeg, J.-W., Slat, B., Andrady, A. & Reisser J. (2017). River plastic emissions to the world's oceans. *Nature Communications, 8.* Article 15611. DOI:10.1038/ncomms15611.

Lebreton, L., Slat, B., Ferrari, F., Sainte-Rose, B., Aitken, J., Marthouse, R., Hajbane, S., Cunsolo, S., Schwarz, A., Levivier, A., et al. (2018). Evidence that the Great Pacific garbage patch is rapidly accumulating plastic. *Scientific Reports, 8*. Article 4666. doi:10.1038/s41598-018-22939-w.

Lechthaler, S., Waldschläger, K., Stauch, G., & Schüttrump, H. (2020). The way of macroplastic through the environment: Review. *Environments, (7)*73. doi:10.3390/environments7100073.

Li, W., Tse, H., & Fok, L. (2016). Plastic waste in the marine environment: A review of sources, occurrence and effects. *Science of the Total Environment, 566,* 333–349.

Li, Y., Li, M., Li, Z., Yang, L., & Liu, X. (2019). Effects of particle size and solution chemistry on triclosan sorption on polystyrene microplastic. *Chemosphere, 231*, 308–314. https://doi.org/10.1016/j.chemosphere.2019.05.116.

Liebezeit, G., & Dubaish, F. (2012). Microplastics in beaches of the East Frisian Islands Spiekeroog and Kachelotplate. *Bulletin of Environmental Contamination and Toxicology, 89,* 213-217.

Lusher, A.L., McHugh, M., & Thompson, R.C. (2013). Occurrence of microplastics in the gastrointestinal tract of pelagic and demersal fish from the English Channel. *Marine Pollution Bulletin, 67*(1), 94-99. https://doi.org/10.1016/j.marpolbul.2012.11.028

Lusher, A. L. (2015). Microplastics in the marine environment: distribution, interactions and effects. In: Bergmann, M., Gutow, L., & Klages, K. (Eds.), *Marine Anthropogenic Litter* (pp. 245-307). Springer. DOI:10.1007/978-3-319-16510-3.

Ma, Y., Huang, A., Cao, S., Sun, F.,Wang, L., Guo, H., & Ji, R. (2016). Effects of nanoplastics and microplastics on toxicity, bioaccumulation, and environmental fate of phenanthrene in fresh water. *Environmental Pollution*. 219, 166–173.

Mao, R., Langa, M., Yua, X., Wub, R., Yanga, X., & Guoa, X. (2020). Aging mechanism of microplastics with UV irradiation and its effects on the adsorption of heavy metals. *Journal of Hazardous Materials.* 393. 1-10.

Martin, J., Lusher, A., Thompson, R.C., & Morley, A. (2017).The deposition and accumulation of microplastics in marine sediments and bottom water from the Irish continental shelf. *Scientific Reports, 7*(1), 1–9. https://doi.org/10.1038/s41598-017-11079-2.

Mato, Y., Isobe, T., Takada, H., Kanehiro, H., Ohtake, C., & Kaminuma, T. (2001). Plastic resin pellets as a transport medium for toxic chemicals in the marine environment. *Environmental Science & Technology*. 35, 318–324.

Möhlenkamp, P., Purser, A., & Thomsen, L. (2018). Plastic microbeads from cosmetic products: an experimental study of their hydrodynamic behavior, vertical transport and resuspension in phytoplankton and sediment aggregates. *Elementa: Science of the Anthropocene, 61*(6). https://doi.org/10.1525/elementa.317

Moore, C.J. (2008). Synthetic polymers in the marine environment: a rapidly increasing, long-term threat. *Environmental Pollution.*108, 131-139.

Morris, A.W., & Hamilton, E.I. (1974). Polystyrene spherules in the Bristol Channel. *Marine Pollution Bulletin, 5*(2), 26-27

Munier, B. & Bendell, L.I. (2018). Macro and micro plastics sorb and desorb metals and act as a point source of trace metals to coastal ecosystems*. PLoS ONE, 13*(2). Article e0191759. https://doi.org/10.1371/journal.pone.0191759

Müller, A., Becker, R., Dorgerloh, U., Simon, F.G., Braun, U. & (2018). The effect of polymer aging on the uptake of fuel aromatics and ethers by microplastics. *Environmental Pollution*. 240, 639–646.

Obbard, R.W., Sadri, S., Wong, Y.Q., Khitun, A.A., Baker, I., & Thompson, R.C. (2014). Global warming releases microplastic legacy frozen in Arctic Sea ice. *Earth's Future, 2*(6), 315–320. https://doi.org/10.1002/2014EF000240.

Park, C.H., Kang, Y.K., & Im, S.S. (2004). Biodegradability of cellulose fabrics. *Journal of Applied Polymer Science, (1)*94, 248–253. https://doi.org/10.1002/app.20879.

Peng, G., Zhu, B., Yang, D., Su, L., Shi, H., & Li, D. (2017). Microplastics in sediments of the Changjiang Estuary, China. *Environmental Pollution*. 225, 283–290. https://doi.org/10.1016/j.envpol.2016.12.064.

Peng, G., Xu, P., Zhu, B., Bai, M., & Li, D. (2018). Microplastics in freshwater river sediments in Shanghai, China: a case study of risk assessment in mega-cities. *Environmental Pollution*. 234, 448–456. https://doi.org/10.1016/j.envpol.2017.11.034.

Peng, L., Fu, D., Qi, H., Lan, C.Q., Yu, H., & Ge, C. (2019). Micro- and nano-plastics in marine environment: source, distribution and threats − a review. *Science of the Total Environment*. 698, Article 134254.

Peng, X., Chen, M., Chen, S., Dasgupta, S., Xu, H., Ta, K., Du, M., Li, J., Guo, Z., & Bai, S. (2018). Microplastics contaminate the deepest part of the world's ocean. *Geochemical Perspectives Letters*, 9, 1-5. doi:10.7185/geochemlet.1829.

Performance evaluation of environmentally degradable plastic packaging and disposable food service are. (2007). Final Report. (June 2007). California State University. Chico Research Foundation. 75 p.

Plastics Europe. (2015). Plastics - the Facts 2014. An Analysis of European Plastics Production, Demand and Waste Data for 2014*.* In: *Plastics Europe AISBL (Association of Plastic Manufacturers)*. Brussels. Belgium. https://plasticseurope.org/wp-content/uploads/2021/10/2015-Plastics-the-facts.pdf

Plastics Europe. (2019). Plastics - the Facts 2019. An Analysis of European Plastics Production, Demand and Waste Data. In: *Plastics Europe AISBL, Association of Plastics Manufacturers*, Brussels, Belgium. https://plasticseurope.org/wp-content/uploads/2021/10/2019-Plastics-the-facts.pdf

Pospisil, J., Horak, Z., Krulis, Z., Nesipuerek, S., & Kuroda, S. (1999). Degradation and aging of polymer blends. I. Thermomechanical and thermal degradation. *Polymer degradation and stability*. *65*(3). 405-414.

Prata, J. C., da Costa, J. P., Lopes, I., Andrady, A. L., Duarte, A. C., & Rocha-Santos, T. (2021). A one health perspective of the impacts of microplastics on animal, human and environmental health. *Science of the Total Environment*. 777. Article 146094.

Reisser, J., Slat, B., Noble, K., du Plessis, K., Epp, M., Proietti, M., de Sonneville, J., Becker, T., & Pattiaratchi, C. (2014). The vertical distribution of buoyant plastics at sea. *Biogeosciences, 11*(11), 1249–1256. DOI: https://doi.org/10.5194/bgd-11-16207-2014.

Rochman, C.M. (2013). Plastics and priority pollutants: a multiple stressor in aquatic habitats. *Environmental Science & Technology, 47*(6), 2439-2440.

Rochman, C.M., Browne, M.A., Halpern, B.S., Hentschel, B.T., Hoh, E., Karapanagioti, H.K., RiosMendoza, L.M., Takada, H., The, S., & Thompson, R.C. (2013a). Classify plastic waste as hazardous, *Nature* 494, 169-171.

Rochman, C.M., Hoh, E., Hentschel, B.T., & Kaye, S. (2013b). Long-term field measurement of sorption of organic contaminants to five types of plastic pellets: Implications for plastic marine debris. *Environmental Science & Technology. 47*(3), 1646-1654.

Rochman, C. M., Hoh, E., Kurobe, T., & Teh, S. J. (2013c). Ingested plastic transfers hazardous chemicals to fish and induces hepatic stress. *Scientific Reports,* 3, Article 3263. https://doi.org/10.1038/srep03263.

Rochman, C.M., Hentschel, B.T., & Teh, S.J. (2014). Long-term sorption of metals is similar among plastic types: implications for plastic debris in aquatic environments. *PLoS ONE, 9*(1). Article e85433. https://doi.org/10.1371/journal.pone.0085433

Rochman C. M. (2015).The complex mixture, fate and toxicity of chemicals associated with plastic debris in the marine environment. . In: Bergmann, M., Gutow, L., & Klages, K. (Eds.), *Marine Anthropogenic Litter* (pp. 117-142). Springer. Cham. Switzerland. DOI 10.1007/978-3-319-16510-3.

Rochman, C. M., Kross, S. M., Armstrong, J. B., Bogan, M. T., Darling, E. S., Green, S. J., Smyth, A. R., & Verissimo, D. (2015). Scientific evidence supports a ban on microbeads. *Environmental Science and Technology. 49*(18), 10759–10761.

Rochman, M. C., Browne, A. M., Underwood, J.A., & Van Franeker, J. A. (2016). The ecological impacts of marine debris: unraveling the demonstrated evidence from what is perceived. *Ecology. 97*(2): 302–312.

Rochman, C. M., Brookson, C., Bikker, J., Djuric, N., Earn, A., Bucci, K., Athey, S., Huntington, A., et al. (2019). Rethinking microplastics as a diverse contaminant suite. *Environmental Toxicology and Chemistry, 38*(4), 703–711.

Ryan, P.G., Moore, C.J., van Franeker, J.A., & Moloney, C.L. (2009). Monitoring the abundance of plastic debris in the marine environment. *Philosophical Transactions of the Royal Society B: Biological Sciences, 364*(1526), 1999-2012.

Sarkar, D. J., Sarkar, S.D., Das, B. K., & Samanta, S. (2021). Occurrence, fate and removal of microplastics as heavy metal vector in natural wastewater treatment wetland system. *Water Research.*192.116853 DOI:10.1016/j.watres.2021.116853.

Silva, A.P.L., Prata, J.C., Walker, T.R., Duarte, A.C., Ouyang, W., Barcelò, D., & Rocha-Santos, T. (2020). Increased plastic pollution due to Covid-19 pandemic: Challenges and recommendations. *Chemical Engineering Journal, 405*, Article 126683. doi:10.1016/j.cej.2020.126683.

Singh, B., & Sharma, N. (2008). Mechanistic implications of plastic degradation. *Polymer Degradation and Stability. 93*(3), 561-584.

Sivan, A., Szanto, M., & Pavlov, V. (2006). Biofilm development of the polyethylene-degrading bacterium *Rhodococcus ruber*. *Applied Microbiology and Biotechnology. 72*(2), 346-352. DOI:10.1007/s00253-005-0259-4

Sutherland, W.J., Clout, M., Isabelle, M., Daszak, C.P., Depledge, M.H., Fellman, L., Fleishman, E., Garthwaite, R., Gibbons, D.W., De Lurio, J., Impey, A.J., Lickorish, F., Lindenmayer, D., Madgwick, J., Margerison, C., Maynard, T., Peck, L.S., Pretty, J., Prior, S., Redford, K.H., Scharlemann, J.P.W., Spalding, M., & Watkinson, A.R. (2010). A horizon scan of global conservation issues for 2010. *Trends in Ecology & Evolution. 25* (1). 1–7.

Teuten, E.L., Saquing, J.M., Knappe, D.R.U., Barlaz, M.A., Jonsson, S., Bjorn, A., Rowland, S.J., Thompson, R.C., Galloway, T.S., Yamashita, R., Ochi, D., Watanuki, Y., Moore, C., Pham, H.V., Tana, T.S., Prudente, M., Boonyatumanond, R., Zakaria, M.P., Akkhavong, K., Ogata, Y., Hirai, H., Iwasa, S., Mizukawa, K., Hagino, Y., Imamura, A., Saha, M., &Takada, H. (2009). Transport and release of chemicals from plastics to the environment and to wildlife. *Philosophical Transactions of the Royal Society B: Biological Sciences*. *364*(1526), 2027-2045.

Thompson, R.C., Olsen, Y., Mitchell, R.P., Davis, A., Rowland, S.J., John, A.W.G., McGonigle, D., & Russel, A.E. 2004. Lost at sea: where is all the plastic? *Science*. 304, 838.

Thompson, R. C., Moore, C. J., Vom Saal, F. S. & Swan, S. H. (2009). Theme Issue. Plastics, the Environment, & Human Health. *Philosophical Transactions of the Royal Society B: Biological Sciences.* 364. 15-26.

Tourinho, P. S., Kocí, V., Loureiro, S., & van Gestel, C. A.M. (2019). Partitioning of chemical contaminants to microplastics: Sorption mechanisms, environmental distribution and effects on toxicity and bioaccumulation. *Environmental Pollution,* 252(Pt B), 1246-1256. doi:10.1016/j.envpol.2019.06.030.

UNEP (United Nations Environment Programme). Environment under review. (2014, June 23). Nairobi, 2014. PlasticWaste Causes Financial Damage of US$13 Billion to Marine Ecosystems Each Year as Concern Grows over Microplastics. https://www.unep.org/news-and-stories/press-release/plastic-waste-causes-financial-damage-us13-billion-marine-

van Calcar, C.J.; & van Emmerik, T.H.M. (2019). Abundance of plastic debris across European and Asian rivers. *Environmental Research Letters*, *14*, 124051. doi:10.1088/1748-9326/ab5468

van Cauwenberghe, L., Claessens, M., Vandegehuchte, M.B., & Janssen, C.R. (2015a). Microplastics are taken up by mussels *(Mytilus edulis)* and lugworms *(Arenicola marina)* living in natural habitats. *Environmental Pollution,*199, 10–17. https://doi.org/10.1016/j.envpol.2015.01.008.

van Cauwenberghe, L., Devriese, L., Galgani, F., Robbens, J., & Janssen, C.R. (2015b). Microplastics in sediments: A review of techniques, occurrence and effects. *Marine Environmental Research*. 111. 5-17. DOI:org/10.1016/j.marenvres.2015.06.007.

van Cauwenberghe, L., & Janssen, C.R. (2014). Microplastics in bivalves cultured for human consumption. *Environmental Pollution*.193, 65-70.

van Cauwenberghe, L., Vanreusel, A., Mees, J., & Janssen, C.R. (2013). Microplastic pollution in deep-sea sediments. *Environmental Pollution.* 182. 495-499. DOI:0.1016/j.envpol.2013.08.013.

van Sebille, E. (2015). The oceans' accumulating plastic garbage. *Physics Today. 68*(2), 60-61. DOI:10.1063/PT.3.2697

Vethaak, D. A. & Leslie, H.A. (2016). Plastic debris is a human health issue. *Environmental Science and Technology. 50*(13). 6825-6826. https://doi.org/10.1021/acs.est.6b02569

Vriend, P., van Calcar, C., Kooi, M., Landman, H., Pikaar, R., & van Emmerik, T. (2020). Rapid assessment of floating macroplastic transport in the Rhine. *Frontiers in Marine Science*, *7*(10). doi:10.3389/fmars.2020.00010.

Wahyuningsih, H., Bangun, A. P., & Muhtadi, A. (2018). The relation of sediment texture to macro- and microplastic abundance in intertidal zone. *IOP Conference Series: Earth and Environmental Science, 122*(1).012101. doi:10.1088/1755-1315/122/1/012101

Waldschläger, K., Lechthaler, S., Stauch, G.,& Schüttrump, H. (2020). The way of microplastic through the environment – Application of the source-pathway-receptor model: Review. *Science of the Total Environment.* 713. Article 136584.

Walker, R. T. (2021). Canada is right to classify single-use plastics as toxic. *Nature. 594*(7864):496. doi:10.1038/d41586-021-01701-9.

Wang, J., Tan, Z., Peng, J., Qiu, Q., & Li, M. (2016). The behaviors of microplastics in the marine environment: Review. *Marine Environmental Research.* 113. 7-17.

Ward J.E. & Shumway S.E. (2004). Separating the grain from the chaff: Particle selection in suspension- and deposit-feeding bivalves. *Journal of Experimental Marine Biology and Ecology,* 300. 83–130.

Water quality assessments: a guide to the use of biota, sediments and water in environmental monitoring. (1996). In Chapman, D. V. (Ed.). *World Health Organization, UNESCO & United Nations Environment Programme*. (2nd Ed.) E & FN Spon. https://apps.who.int/iris/handle/10665/41850

Weber, C.J., Hahn, J., & Opp, C. (2022). Spatial connections between microplastics and heavy metal pollution within floodplain soils. *Applied Sciences*, 12, 595. https://doi.org/10.3390/app12020595.

William B. J. (2008). Ask the historian: The origin of the polymer concept. *Journal of Chemical Education. University of California,* 85, 624–625. doi:10.1021/ed085p624

Winton, D.J., Anderson, L.G., Rocliffe, S., & Loiselle, S. (2019). Macroplastic pollution in freshwater environments: Focusing public and policy action. *Science of the Total Environment,* 704. Article 135242. doi:10.1016/j.scitotenv.2019.135242.

Wong, C.S., Green, D.R., & Cretney, W.J. (1974). Quantitative tar and plastic waste distributions in the Pacific Ocean. *Nature*, 247, 30-32.

Woodall, L.C., Sanchez-Vidal, A., Canals, M., Paterson, G.L.J., Coppock, R., Sleight, V., Calafat, A., Rogers, A.D., Narayanaswamy, B.E., & Thompson, R.C., 2014. The deep sea is a major sink for microplastic debris. R. Soc. Open Sci. 1 (4). https://doi.org/10.1098/ rsos.140317.

World Economic Forum. (2016). The new plastics economy: Rethinking the future of plastics. http://www3.weforum.org/docs/WEF_The_New_Plastics_Economy.pdf.

Wright, S.L., & Kelly, F.J. (2017). Plastic and human health: A micro issue? *Environmental Science & Technology*, 51, 6634–6647.

Wright, S.L., Thompson, R.C., & Galloway, T.S. (2013). The physical impacts of microplastics on marine organisms: a review. *Environmental Pollution.*178, 483–492.

Wu, J., Xua, P., Chen, Q., Ma, D., Ge, W., Jiang, T., & Chai, C. (2020). Effects of polymer aging on sorption of 2,20,4,40-tetrabromodiphenylether by polystyrene microplastics. *Chemosphere.* 253. Article 126706

Yang, D., Shi, H., Li, L., Li, J., Jabeen, K., & Kolandhasamy, P. (2015). Microplastic pollution intable salts from China. *Environmental Science and Technology, 49*(22),13622–13627. DOI:org/10.1021/acs.est.5b03163

Zhang, Y. T., Chen, M., Hea, S., Fang, C., Chen, M., Li, D., Wue, D., Chernick M, Hinton, D. E., Bo, J., Xie, L., & Mu, J. (2021). Microplastics decrease the toxicity of triphenyl phosphate (TPhP) in the marine medaka (Oryzias melastigma) larvae. *Science of the Total Environment.* 763. Article 143040. doi:10.1016/j.scitotenv.2020.143040.

Ziccardi, L. M., Edgington, A., Hentz, K., Kulacki, K.J., & Driscoll, S.K. (2016). Microplastics as vectors for bioaccumulation of hydrophobic organic contaminants in the marine environment: A state-of-the-science review. *Environmental Toxicology and Chemistry*. 35, 1667–1676.

Chapter 2.

Sorption of trace elements (Cd, Cu, Hg, Pb, and Zn) by plastic macro- and microparticles in the marine intertidal sedimentary environment; a field study

2.1. Introduction

An alarming amount of synthetic plastic macro- and microparticles are present in the marine environment with estimates ranging from 15 to 51 trillion particles (Bakir et al., 2020; van Sebille et al., 2015). Due to growing production and use of plastic materials, their continuing degradation and high persistence in the natural environment, plastic macro- and microparticles will accumulate and their quantities will increase with time.

Intertidal zones, the region that connects ocean and terrestrial ecosystems serves to integrate plastics originating from both upland and oceanic sources. These regions therefore are indicative of long-term interaction between waters and land surface providing information on the accumulation, transportation and fate of pollutants within marine and terrestrial ecosystems (Yu et al., 2016). Plastic debris will accumulate within the sediments of these coastal areas serving as hot spots for plastic particles accumulation as well as source of secondary pollution to the marine aquatic environment through re-suspension of intertidal sediments (Andrady, 2011; Harris, 2020; Harrison et al., 2014; Jiang et al., 2018).

Plastic or macro- and microparticles not only present as a yet unknown risk to coastal ecosystems, these compounds have the physicochemical ability to both sorb and desorb chemical contaminants (Wang et al., 2016; Wang et al., 2018a) (see Chapter 1). The first reported studies on the sorption of contaminants to plastic particles dated back to the 1970s and 1980s (Carpenter et al., 1972; Gregory et al., 1978). Only in the early 2000s the process of sorption/desorption was studied more intensively investigating high concentrations of chemical contaminants on macro- and microplastics collected from the marine environment (Endo et al., 2005; Mato et al., 2001).

The continued use of chemicals, such as trace elements that are past contaminants of concern and extensive production of plastic materials (modern and current contaminants of concern) has led to their ubiquitous presence, co-occurrence and interactions in the marine aquatic environments. While there are numerous studies which have demonstrated that within aqueous environments macro- and microplastics can indeed serve as sorption site for chemicals/contaminants such as trace elements (Holmes et al., 2012; Holmes et al., 2014; Rochman et al, 2014; Turner and Holmes, 2015), the number of studies conducted on sorption of contaminants such as trace elements by macro- and microplastics in the sedimentary environments are limited. In sediments, only a few studies have been conducted to assess the quantities and interactions of plastic macro- and microparticles by using passive samplers (Velzeboer et al., 2014), by performing microplastic filtration from sediment and subsequent analysis (Teuten et al., 2007), or by mass balance modeling (Kleinteich et al., 2018).

To date the partitioning of trace elements (Cd, Cu, Pb, Zn, and Hg) between plastic materials in the form of macro- and microparticles and parts of marine intertidal sedimentary environments (e.g., see water, sediments, pore water) and the sorption capacities of macro- and microplastic for different trace elements have not been investigated in the marine intertidal sedimentary conditions. Further, at this time, there are no long-term field studies on the sorption of trace elements such as copper (Cu), zinc (Zn), lead (Pb), cadmium (Cd), and mercury (Hg) by macro- and microplastic have been performed yet in the marine intertidal sedimentary environments.

Therefore the specific objective of this study/chapter is to compare the long-term sorption of trace elements to synthetic plastic materials within contrasting intertidal sediment environments. To meet this objective we compared the sorption of Cd, Cu, Pb, Zn and Hg, by 4 types of plastic macro- and microparticles within two contrasting sediment environments, one high in organic matter and silt and the other comprised of coarse sand and silt. Specific hypothesis being tested are that 1) trace element sorption by plastics is independent of plastic type and age and 2) trace element sorption by plastic polymers is independent of sediment type. Outcomes of this study will add to our knowledge base on the risks that plastic presents to intertidal environments and the role they play on the movement of these contaminants through intertidal food webs.

2.2. Materials

2.2.1. Study areas and sites selection and description

Study sites were located within Burrard Inlet, which itself is located within the Salish Sea on the Pacific West Coast (Figure 2.1a). Sites within Burrard Inlet included Horseshoe Bay (HB) and Maplewood Flats Conservation Area (MWFCA) (Figure 2.1a, b, c). Burrard Inlet is an estuarine ecosystem that encompasses the coastal waters and watersheds of the Strait of Georgia, the Strait of Juan de Fuca and Puget Sound in south-western of British Columbia and north-western Washington. Burrard Inlet is surrounded in part by mountains and by relatively flat lands, a fact that made it highly suitable for human settlement, including First Nations people, and development as a major harbour on the West Coast of Canada. Burrard Inlet is considered estuarine due to the heavy influence of freshwater inputs from the Fraser River (Davidson, 1979; Thompson, 1981).The catchment area for Burrard Inlet covers 98,000 ha (BIEAP, 2011).

Temperature and salinity is strongly influenced by the Fraser River (Thomson, 1981). At the surface salinities varying greatly and are more consistent at depth. In deep water, salinity is 29–30%. At the southwest of the Outer Harbour, surface salinity can be 10% and becomes approximately 20% at the North Shore (Levings et al., 2004). Within Burrard Inlet, tides are of the mixed diurnal type with daily tides range an average of 3.1m and maximum tide range is 4.9 m (BIEAP, 2011; Levings et al., 2004). The mean high tidal range is 4.4 m, mean low tidal range is 1.1 m, and mean tidal range is 3.3 m. In addition, large tides within the inlet system vary from a high-water level of 5.0 m near midnight in late December to a low-water level of 0.0 m (chart datum) near noon in late June. Extreme tides in Burrard Inlet have attained high-water marks of 5.6 m and low-water marks of -0.4 m. (Tompson, 1981). Sediments range from fine mud in depositional and intertidal areas to coarse cobble and gravel on estuary and river deltas. The undisturbed shorelines consist primarily of rock and cobble beaches, rocky shores, and mudflats.

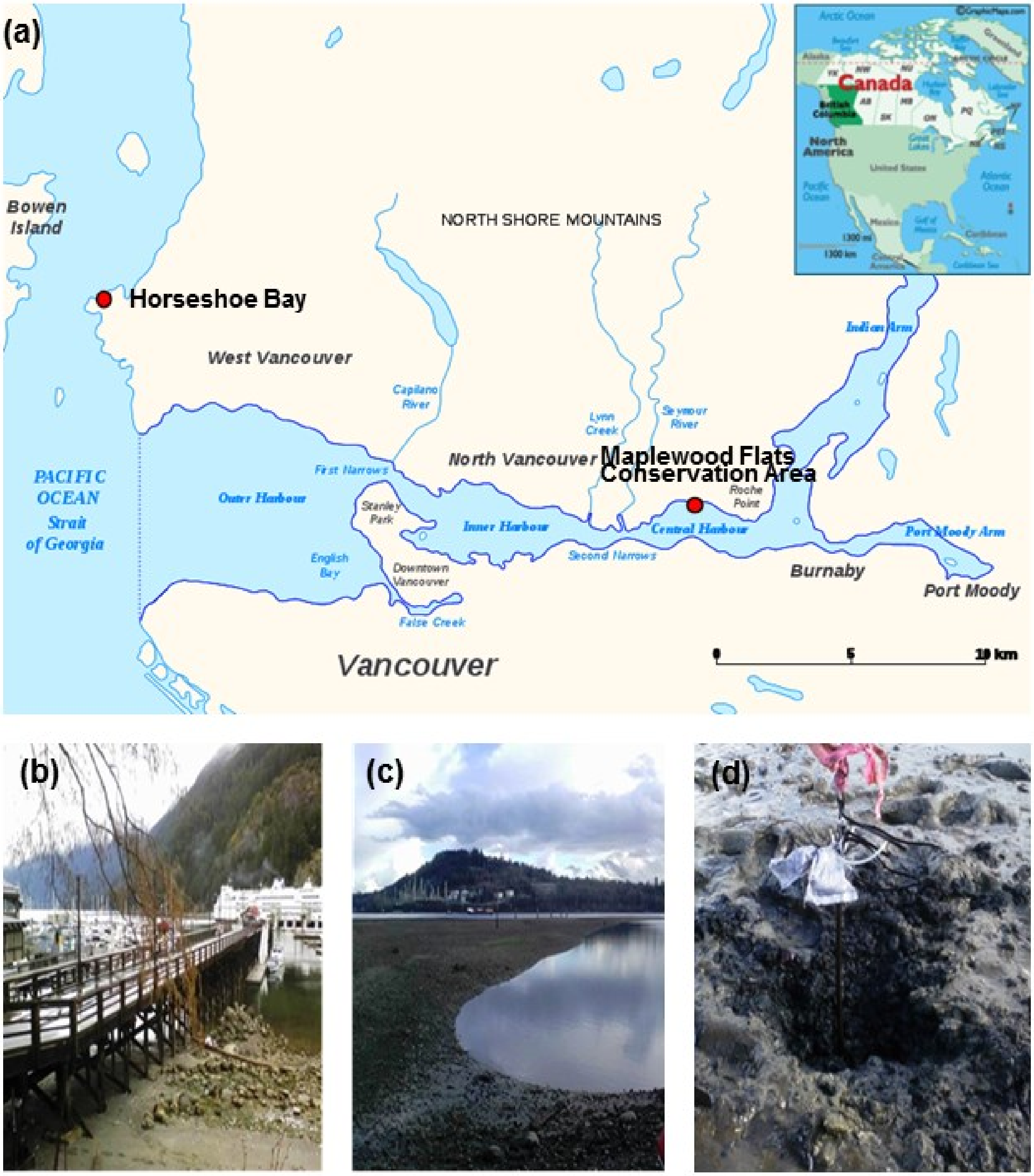


Figure 2.1. **Location of the study area within Burrard Inlet, British Columbia, Canada (a). Location of the study sites at Horseshoe Bay (b) and Maplewood Flats Conservation Area (c). Deployment of plastic macro- and microparticles for long-term field experiments (d)**

Source of map: File:Burrard-Inlet-map-en.svg; (Wikimedia Commons, the free media repository)
Photo credit (b-d): Taken by author.

Despite high levels of development and human activity, Burrard Inlet is still rich in biodiversity and functions as a significant component of Salish Sea ecosystem. Clean water and sediment are one of basic building blocks of a healthy marine ecosystem.

Contamination is of particular concern for human populations, especially First Nations people that rely on wild foods as a substantial component of their diet. Water and sediments quality and contaminant concerns within the marine environment have been previously identified as one of the most important stressors of the Burrard Inlet ecosystem (BIAP, 2016; Goyette and Boyd, 1989). While freshwater inputs, tidal flushing, and circulation patterns reduce the accumulation of contaminants to some extent, it has been known since the 1980s that the levels of some contaminants regularly or periodically exceed guidelines as the result of pollution discharged into Burrard Inlet from human activities (BIEAP, 2011). Sources of contaminants to Burrard Inlet include authorized industrial discharges, sewage treatment effluent, combined and sanitary sewer overflows, storm water runoff, illicit discharges, and spills. Water and sediment quality in Burrard Inlet varies widely by location depending on proximity to known discharges, circulation, stratification, sedimentation, assimilation, and breakdown rates within the marine environment. Because of water and sediment quality and contamination issues are complex, emerging issues such as contaminants of concern (e.g., trace elements), marine debris and microplastics, were underlined in the Burrard Inlet Action Plan: A Tsleil-Waututh Perspective (BIAP): A science-based, First Nations-led initiative to improve the health of the Burrard Inlet ecosystem by 2025 (BIAP, 2016).

Two sites were selected for the field studies on sorption of trace elements by macro- and microplastics; (A) Horseshoe Bay (gravel, sand, organic matter concentration: 5-15%); and (B) Maplewood Flats Conservation Area (sand, mud, organic matter concentration: 30- 50%) (Figure 2.1). Horseshoe Bay (HB) is a residential (community of about 1,000 permanent residents) and commercial district located on the western tip of West Vancouver (British Columbia, Canada) at the entrance to Burrard Inlet (Figure 2.1.a, b). Horseshoe Bay serves as one of three main ferry terminals within the Salish Sea. The intertidal region of Horseshoe Bay is heavily impacted by anthropogenic activities (BIAP, 2016). The Maplewood Flats Conservation Area (MWCA) is a 126 hectare (310 acre) conservation area located approximately 2 km east of the Second Narrows Bridge along Burrard Inlet in North Vancouver (British Columbia, Canada) (Figure 2.1.a, c). The area is composed of a 96 hectare (237 acre) intertidal zone of mudflats and salt marsh, and a 30 hectare (74 acre) upland area and was established as the Maplewood Flats Conservation Area in 1999. This is a unique area in the last waterfront wetland ecosystem on the North Shore (DFO, 2013; BIAP, 2016).

2.2.2. Plastic materials and macro- and microplastic particles selected for the study

Types of macro- and microplastics found on the beaches and in the marine intertidal areas tend to reflect common industry production trends. Since about a half of the produced plastic is used today in low-value products designed for disposable single-use, exactly these kinds of polymer materials are shown to be the major part (80%) of the coastal intertidal areas litter (PlasticsEurope, 2015; PlasticsEurope, 2017; UNEP, 2005). For instance, a study from Italy (Vianello et al., 2013) found the most predominant microplastic to be PE (48%) and PP (34%); Frias with co-authors (Frias et al., 2010) found PE, PP and polyacrylates (PA) dominating along the Portuguese coast; on the beaches of Hawaii, PE (85%) and PP (14%) are dominating (Carson et al., 2011); along the Belgian coast, the primary plastics were PP, PS, and PP (Claessens et al., 2011). The most commonly reported types of synthetic plastic materials are low-density polyethylene (LDPE), high-density polyethylene (HDPE), polyethylene terephthalate /polyester (PETE) and polyamides/nylons (PA) (Cole et al., 2011; Frias et al., 2018). The most commonly founded within surface layer of intertidal sediments and reported macro- and microplastics are fragments, pellets, and fibres (Andrady, 2011; Brandon et al., 2019; Cole et al., 2011; Frias et al., 2018; Hidalgo-Ruz et al., 2012; Vianello et al., 2013).

In relation to the areas of this study within Burrard Inlet, sources of macro- and microplastic include household and industrial waste, wastewater, as well as fishing, aquaculture and shipping (Bendell, 2019; Bendell et al., 2019; Cluzaud et al., 2015; Desforges et al., 2014; Munier et al., 2018). Based on the relevant literature review (Chapter 1) and analysis of macro- and microplastic contamination of Burrard Inlet study areas, 2 types of macroplastic in the form of polyethylene chips (high-density polyethylene (HDPE)) (Figure 2.2a) and textile fabric (polyethylene terephthalate /polyester (PETE)) (Figure 2.2b) and 2 types of microplastic (primary) in the form of microbeads (high-density polyethylene (HDPE)) (Figure 2.2c) and fibres (polyethylene terephthalate /polyester (PETE)) (Figure 2.2d) were selected for the study.

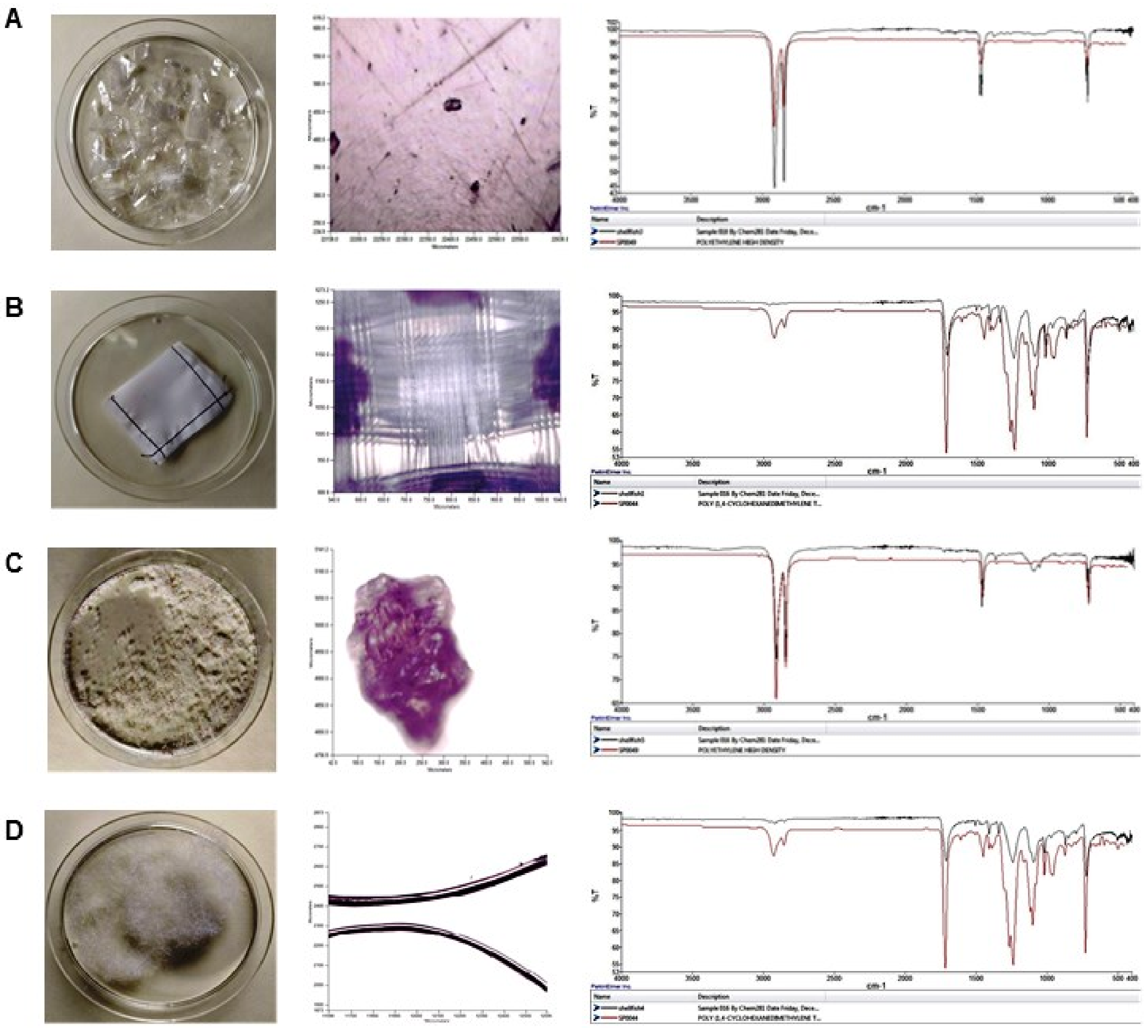


Figure 2.2. **Photo and microscopic images and FTIR spectrums of macroplastics (polyethylene chips, HDPE (a) and textile fabric PETE (b)) and microplastics (microbeads, HDPE (c) and fibers, PETE (d)) selected for the long-term field study.**

Note: The plastic macro- and microparticles used throughout this study were purchased from Science Stores (SFU) and Industry Co., Ltd., Canada.

2.2.3. Trace elements selected for the study

In the intertidal areas of Burrard Inlet (study area) trace elements such as cadmium (Cd), copper (Cu), lead (Pb), mercury (Hg), and (Zn) zinc are of concern because of the high levels and the wide variety of sources from which they are discharged to the inlet (BIAP, 2016). Monitoring of the water column indicated the most problematic trace elements to be Cu and Ni. Moreover, levels of Cu have not significantly improved since 1990s (Bull and Freyman, 2013). The concentrations of Cd, Cu, Pb, Hg, and Zn exceeded long-term objectives for sediments at most of sites in the

Burrard Inlet and could have negative effects on aquatic life (Alava et al., 2020; Boucher et al., 2016; Johannessen et al, 2005; Sutherland, 2004). Hotspots of trace element concentrations include estuaries where sediments are deposited, including the mouths of Mackay Creek, Mosquito Creek, Lynn Creek, and the Seymour River (Kazmiruk et al., 2016).

It is well known, that certain trace elements, when present in high enough amounts, can be toxic to aquatic life. For example, Cu is highly toxic to fish and other aquatic species in the water column. Mercury is very bioaccumulative, and can accumulate up the food chain (UNEP, 2013). In addition, six metals including Ni, Cd, Pb, Cu, and Zn are listed as priority pollutants by US Environmental Protection Agency (US EPA, 2012). Trace elements impact the condition of the benthic environment for organisms such as shellfish, bottom fish, and lower trophic invertebrates that live or feed in the upper layer of sediments (BIAP, 2016; Hecht et al., 2007). The adsorption of trace elements by macro- and microplastic is a further cause for concern as well (Chapter 1). Based on the analysis of the level of contamination in the water column and sediments, trace elements of primary concern, Cu, Zn, Pb, Cd and Hg were selected to study for the sorption/desorption of trace elements by macro- and microplastics in the intertidal sedimentary environment of Burrard Inlet.

2.3. Methods

2.3.1. Field experiments on sorption of trace elements (Cd, Cu, Hg, Pb, and Zn) by plastic macro- and microparticles

At each of the two sites when tides were at their lowest (summer solstice), triplicate mesh bags (0.063 µm), which contained microbeads (HDPE), fibres (PETE), and polyethylene chips (HDPE)) were buried into the upper 10-15 cm layer of sediments. Bags were secured to rebar by nylon zip ties to ensure they remain within the sediments (Figure 2.1d). Mesh bags were comprised of textile fabric (PETE). This resulted in 2 types of macroplastics, the HDPE chips, the PETE fabric enclosing 2 types of microplastics that are HDPE microbeads and PETE fibres (Figure 2.2). All long-term (38 months) field experiments on sorption of trace elements (Cd, Cu, Hg, Pb, and Zn) by plastic macro- and microparticles were conducted in triplicate.

2.3.2. Field measurements and sample collection

The Global Positioning System (GPS) was used to provide the location and time information for the sampling sites of study area. The date and time of the field sampling were determined based on the periods of tides at their lowest and optimal meteorological conditions during those periods. Samples of plastic macro- and microparticles and water and sediment samples were collected at time of residence t = 0, 1, 2, 3 , 8, 12, 21, 27, and 38 months respectively after deployment of plastic materials to observe the influence of sorption time on the sorption process.

Samples of plastic macro- and microparticles. During the long-term field experiments, mesh bags (textile fabric, PETE) with samples of plastic macroparticles (polyethylene chips, HDPE) and microparticles (microbeads, HDPE) and fibres, PETE) were collected in triplicated from each site at the time of residence t = 0, 1, 2, 3, 8, 12, 27 and 38 months respectively after deployment. The mesh bags were placed into plastic containers then into a cooler for transfer to the laboratory for further analysis.

Water samples. Water samples were also collected in triplicated at the same time of sampling (t = 0, 1, 2, 3, 8, 12, 27 and 38 months). The intertidal surface sea water samples were collected into a cleaned 500 mL glass bottle and closed with aluminum foil between lid and jar. To assess microplastic contamination by air, a second glass bottle was opened and closed simultaneously with the sample jar/bottle. Collected water samples were placed into cooler for transport back to the laboratory. Water samples were filtered immediately upon return to the laboratory through 0.45 μm Whatman cellulose nitrate filters using a vacuum filter unit. The water samples (filtrates) were frozen (−5 °C) and stored in the dark until further analysis.

Sediment samples. Sediment (intertidal) samples were also collected in triplicated at the same time of sampling (t = 0, 1, 2, 3, 8, 12, 27 and 38 months). At each point of sampling a corresponding sample was collected for grain size, organic matter content and macro- and microplastic analyses. As a general approach, usually three sediment samples where pooled for an integrated sample. For the sampling of sediments, two different methods were used: (1) sediments surface layer sampling and (2) sediments core sampling.

No standard protocol currently exists for sediment sampling for the macro- and microplastics due to difference in the positioning of sample locations (beach, intertidal zone), sampling techniques, and sample quantities (Lechthaler, et al., 2019; Stock, et al., 2019). The proposal for a standardized protocol for monitoring intertidal and subtidal sediments, based on the guidance document of the MSFD Technical Subgroup of Marine Litter was published within the Baseman Project (Frias et al., 2018; MSFD TSG, 2011). While most approaches from sampling to identification of microplastics in beach/intertidal sedimentary environments are lacking standardized methods (Frias et al., 2018; Hidalgo-Ruz et al., 2012; Stock et al., 2019), a modified existing protocol (Frias et al., 2018; Kazmiruk et al., 2018; MSFD TSG, 2011) for sampling and processing was applied for the collection of beach and intertidal sediments.

Triplicate samples were collected from the top 5 cm of the oxygenated layer of the sediments (Browne et al., 2010) from separated 0.50 m × 0.50 m quadrats, situated 3–5 m apart in undisturbed areas using a clean stainless-steel spatula (Claessens et al., 2011). The sediment samples were packed into prelabelled, previously unused, sealed bioplastic bags. Collected sediment samples were placed into plastic zip lock bags and then in cooler for transport back to the laboratory where they were frozen (−15 °C) and stored in the dark until further analysis. During the long-term field experiments each site had a paired background contamination control. At each sampling site, a prepared clean Petri Dish and three empty glass beakers were placed beside the sediment collection location and opened during sample collection and closed simultaneously with the sample plastic zip lock bags.

2.3.3. Laboratory analysis of samples

The laboratory analysis of water, sediments, and samples of plastic macro- and microparticles were conducted by using various analytical techniques.

2.3.3.1. Sediment quality parameters

Sediment samples were analyzed after methods of Batley et al. (2016), Kazmiruk et al. (2018), and Mudroch et al., (1997). The laboratory measurements for general sediment quality parameters include: (A) sediment samples preparation for analyses (pre-treatment), (B) grain (particle) size and (C) organic matter content.

(A) Sediment sample preparation for analyses (pre-treatment). Sample preparation includes separation of coarse material, homogenization and drying, and it is the first crucial step of sediment analysis (Batley, et al., 2016). In the laboratory, before analyses, all sediment samples were defrosted and air dried in laminar flow at room temperature. Each sediment sample was homogenized by thoroughly shaking sediments in their original bags, gently grounded using a mortar and pestle, dried to a constant weight (25°C - 30°C for 24–48 hours), and then stored at 4°C prior to analysis.

(B) Grain size analysis. A wet sieving technique was used to determine grain size (GS) distribution of sediment samples (Batley et al., 2016; Mudroch et al., 1997). Sediment particles were separated into four different size factions: gravel (GS >2 mm), coarse sand (2 mm > GS > 0.25 mm), fine sand (0.25 mm > GS > 0.063 mm), and mud or fines (silt, clay) (GS < 0.063 mm). Sediment particle size analysis by wet sieving was undertaken on the thoroughly homogenized wet sediment subsamples, using standard high quality nylon and stainless steel sieves. Wet sieving was achieved by using de-ionized water (dH_2O) to wash the wet sediment subsamples three times through 2000 µm (2 mm), 250 µm (0.25 mm) and 63 µm (0.063 mm) sieves. The sediment particles passing through the finest sieve and the sediment particles retained on each sieve were quantitatively collected and the relative amounts were determined by drying and weighing the respective sediment size fractions.

(C) Analysis for organic matter content. In the context of our research, sediment-associated contaminants tend to accumulate in depositional areas on small fine-grained particles having highest concentration of organic matter. Organic matter concentration in the sediment samples was determined by "loss-on-ignition" (LOI) method, the most appropriate method for the total organic carbon (TOC) content analysis that involves the heated destruction of all organic matter in the sediment (ASTM, 2000a; ASTM, 2000b; ASTM, 2000c; Mudroch et al., 1997). The dried sediment subsamples weighing approximately 1.0 g – 2.0 g were burned at the temperature of for 400°C – 440°C (to avoid the destruction of any inorganic carbonates in the sediments) for 5-10 hours. Organic matter content was determined as the difference between the initial and final (ashed) subsample weights.

2.3.3.2. Analysis of trace elements (Cd, Cu, Hg, Pb, and Zn)

Trace metal analysis was carried out by and Atomic Absorption Spectroscopy (AAS, PinAAcle 500, Perkin Elmer) and mercury (Hg) by Atomic Fluorescence Spectroscopy (AFS, PSA 10.025 Millennium Merlin Accessory Analyser) (ASTM, 2000a; ASTM, 2000b; ASTM, 2000c). The main controlling factors of quality samples analysis by Atomic Absorption Spectroscopy and Atomic Fluorescence Spectroscopy were statistical characteristics of measurements such as standard deviation (SD), relative standard deviation (RSD, <5.0%), and the standard error of replicate runs. Blanks and standards were run with the samples to ensure quality assurance and control.

Marine sediment reference materials (MESS-3) were used for cadmium (Cd), cooper (Cu), mercury (Hg), lead (Pb), and zinc (Zn) measurements (Cd = (0.24 ± 0.01) mg/kg; Cu = (33.9 ± 1.6) mg/kg; Hg = (0.091± 0.009) mg/kg; Pb = (21.1 ± 0.7) mg/kg; Zn = (159 ± 8) mg/kg).

Water samples. The method of directed measurements of trace elements was applied (ASTM, 2000a; PinAAcle 500 FlameAAS (Perkin Elmer) Brochure, 2010). Estuarine water samples containing more than 0.3% salt and sea water samples (more than about 1.0% salt in the sea water) were diluted five- or tenfold in Milli-Q Water (MQW) prior to analysis.

Sediments and macro- and microplastics samples. To determine the optimum amounts of samples for analytical procedure of sediments digestion, model experiments with various amounts of the sample were performed (Kazmiruk et al. 2018). Sediment for macro- and microplastics analysis were digested by Aqua Regia as hydrochloric acid (HCl) and nitric acid (HNO_3) mixture (3:1 volume to volume) and solutions analyzed for plastics after Kazmiruk et al. (2018) and for trace metals as described above.

Quality assurance/quality control (QA/QC) was maintained by the analysis of reference sediment MESS-3 (National Research Council of Canada) and reagent blanks, as well as sediment sample replicates were used as controls. Before instrumental analysis of subsample extracts, calibration standard was analyzed regularly to check the stability of the instrument response that is the quality control of measurements. Precision of analyses was determined by the absolute value of the coefficient of variation as relative standard deviation (RSD) of the repeated measures. Low variability RSD (not greater than 5.0 %) in repeated measures indicates a high precision of analysis. Accuracy as indicated by standards was always within 5% and precision as indicated by the residual standard deviations (RSD) of repeated measures was 3%.

2.3.4. Data analysis

Data analysis

Basic statistical analysis of the data were performed in Microsoft Excel 2010 (Microsoft; WA, USA), in Statistical Package software “IBM SPSS Statistics” (IBM SPSS Statistics 19.0, IBM, Amonk, NY) (means, t-test, ANOVA, correlation, regression), R (R Core Team, 2021), and RStudio (RStudio Inc.; MA, USA).

Sediment data (grain size, OM, Cd, Cu, Hg, Pb, and Zn) was first tested for normal distribution (Shapiro–Wilk) and equal variances prior to the application of a two-way ANOVA with site and time as the two factors. Plastic macro- and microparticles data (Cd, Cu, Hg, Pb, and Zn) was first tested for normal distribution (Shapiro–Wilk) and equal variances prior to the application of a two-way ANOVA for each of 2 plastic microparticles (HDPE and PETE) and 2 plastic macroparticles (HDPE and PETE) with site and time as the two factors. A further 2-way ANOVA was also applied to determine if within each site, sorption of trace elements by plastic macro- and microparticles were dependent on plastic type and time. Data were generally normally distributed with equal variances (Shapiro Wilk Test), so data were not transformed for statistical analysis. Statistical analysis was preformed through Sigma Plot 12 © and significance of all tests was set at p-value < 0.05.

Data visualization, tests for normal distribution (Shapiro–Wilk normality test), linear regression analyses, Spearman correlation analyses, and variance analyses (ANOVA) were conducted with the standard R-packages as well. Histograms and boxplots (represent the distribution of the data) were used to estimate the normality of the data distribution. Differences in sorption characteristics (concentration of trace elements, partitioning coefficients) among study sites versus plastic type and particle size and time were tested with linear regression models (lm) ($p < 0.05$) using R (R Core Team, 2021). We used linear models (lm) with site and plastic type as fixed factors to test for variations in concentration of trace elements (Cd, Cu, Hg, Pb, and Zn) with time in sediment samples and experimental samples of plastic macro- and microparticles. Significances were tested on the level of confidence interval 95%. We interpreted the results of statistical analysis to be significant when reaching a $p\text{-value} < 0.05$.

For the temporal and absolute comparison of trace elements content in water, sediments and plastic macro- and microparticles, the total concentration of trace elements was calculated as unit µg per g water and sediment/plastic particles dry weight (µg/g dw). Trace elements concentrations in water and sediments were also compared to the legal standards (Canadian Water Quality Guidelines (QG) and the Canadian Interim Sediment Quality Guideline (ISQG)) (CCME, 1999; CCME, 2007a; CCME, 2007b).

Data evaluation

It is important to note that the intertidal region is a highly dynamic exposed to storm and tide events. Sediments in the surface layer move both to the overlying water and deeper sediment during the disturbance process. Disturbance-induced re-suspension and vertical transport have significant effects on small-sized sediments (500-50 µm). Small-sized sediments can potentially migrate and redistribute via re-suspension at different temporal and spatial scales. Sediments are reworked each event such that each sampling event are independent events. In order to improve our ability to detect changes over time, data from time 0, 1 and 2 months, 3, 6, and 8 months and 21, 27 and 38 months were pooled to represented three time periods, “short -term”(0-2 months), “mid-term” (3-12 months) and “long-term” (21-38 months). We used linear regression model (lm) to test for variations in trace elements concentrations in sediment samples and experimental samples of plastic macro- and microparticles (PETE and HDPE) for three time periods of field sampling and measurements (“short -term”(0-2 months), “mid-term” (3-12 months), and “long-term” (21-38 months)) and at each of two study sites (HB and MWCA).

To provide an effective analysis of interaction between trace elements (Cd, Cu, Hg, Pb, and Zn) and plastic macro- and microparticles under conditions of marine coastal intertidal sediments, the relative concentration were applied and calculated as following:

$$C_{f(t+\Delta t)}/C_i \quad (2.1)$$

where $C_i = C_{f(T=0)}$ (µg/g) is the initial concentration of trace element at the beginning of the experiments at residence time t=0; $C_{f(t+\Delta t)}$ (µg/g) is concentration of trace element at residence time t = 0, 1, 2,… months. By using the relative concentration we can compare the concentration of trace elements at some residence time (time after deploying of plastic particles in sediments) and initial concentration (concentration at the beginning of the experiments and before deploying of plastic particles in sediments). The relative concentration is widely applied in sorption study such as sorption behavior of contaminants on plastic microparticles (Chen et al., 2022).

To assess the potential distribution and redistribution of trace elements concentration in the marine coastal intertidal sediments with macro- and microplastic content the partition (distribution) coefficient (K_d) were used. According to the definition, a partition coefficient is the ratio of the concentration of a substance in one medium or phase (C_1) to the concentration in a second phase (C_2) when the two concentrations are at equilibrium. In this study the equation for the partition (distribution) coefficient derived from the liner model (K_d) is as follows (Bakir et al., 2014; Wang et al., 2018a):

$$K_d = [q_e]/[C_e] \quad (2.2)$$

where q_e (µg/g) is the amount of contaminant sorbed onto solid phase at equilibrium; C_e (µg/mL) is the contaminant concentration in the aqueous phase at equilibrium. According to the equation (2.2), the sediments- sea water partitioning coefficient ($K_{sed\text{-}sw}$) is defined as:

$$K_{sed-sw} = [Me]_{sed}/[Me]_{sw} \quad (2.3)$$

where $[Me]_{sed}$ (µg/g) is the concentration of trace elements adsorbed to solid phase (sediments); $[Me]_{sw}$ (µg/mL) is the aqueous (sea water) trace elements concentration.

The sediments-pore water partitioning coefficient ($K_{sed\text{-}wp}$) is as follows:

$$K_{sed-wp} = [Me]_{sed}/[Me]_{wp} \quad (2.4)$$

where $[Me]_{sed}$ (µg/g) is the concentration of trace elements adsorbed to solid phase (sediments); $[Me]_{wp}$ (µg/mL) is the aqueous (pore water) trace elements concentration.

The plastic materials (macro- and microparticles)-pore water partitioning coefficient ($K_{pl\text{-}wp}$) is defined as follows:

$$K_{pl-wp} = [Me]_{pl}/[Me]_{wp} \tag{2.5}$$

where $[Me]_{pl}$ (µg/g) is the concentration of trace elements adsorbed to solid phase (plastic materials); $[Me]_{wp}$ (µg/mL) is the aqueous (pore water) trace elements concentration. By dividing sediments-pore water partitioning coefficient ($K_{sed\text{-}wp}$) (Equation 2.4) and plastic materials (macro- and microparticles)-pore water ($K_{pl\text{-}wp}$) partitioning coefficient (Eq.(2.5)) we will exclude the concentration of trace elements in pore water of sediments from the final equation:

$$K_{sed-wp}/K_{pl-wp} = \left([Me]_{sed}/[Me]_{wp}\right)/\left([Me]_{pl}/[Me]_{wp}\right) \tag{2.6}$$

The ratio of sediments-pore water partitioning coefficient ($K_{sed\text{-}wp}$) to the plastic materials-pore water partitioning coefficient ($K_{pl\text{-}wp}$) is as follows:

$$K_{sed-wp}/K_{pl-wp} = [Me]_{sed}/[Me]_{pl} \tag{2.7}$$

Linear model (lm) was used to test for variations in ratio between partition coefficients [log ($K_{sed\text{-}wp}$ / $K_{pl\text{-}wp}$)] of trace elements (Cu, Cd, Pb, Zn, and Hg) among the two study sites (HB and MWFCA). Significances were tested on the level of confidence interval 95%. We interpreted the results of statistical analysis to be significant when reaching a p-value < 0.05.

2.4. Results

2.4.1. Characteristics of intertidal sediments

Geochemical and physical characteristics of the two study sites are presented in (Table 2.1).

Grain size distribution is one of the most important characteristics of sediments because particle size is a dominant controlling factor in sediment geochemistry. Sediment grain size distribution varied among HB and MWFCA study sites and across the depth of tidal spectrum at each study sites. Specifically, sediment grain size at HB study site most commonly fell into 0.25 to 2.00 mm (average 44.2% of volume) and

>2.00 mm (average 35.0% of volume) size categories. In contrast, sediment grain size at MWFCA study site most commonly fell into 0.063 to 0.25 mm (average 41.4% of volume) and < 0.063 mm (average 36.5% of volume) size categories (Table 2.1). Sediment grain size distribution at MWFCA study site is right-skewed, which is consistent with recent reports (Lots et al., 2017; Vianello et al., 2013). Deposition thickness and grain size distribution of intertidal sediments is a reflection of the distance to source areas and the transport capacity of the hydrodynamic conditions in the intertidal area.

Table 2.1. Characteristics of sediments and GPS coordinates at study sites

Site description	Site location (coordinates)	Organic matter, %	Granulometric composition, %			
			>2 mm	2-0.25 mm	0.25-0.063 mm	<0.063 mm
Cates Park (intertidal sediments, LT)	N 049°18,077' W 122°57,285'	1.7	24.3	69.2	5.3	1.2
Horseshoe Bay (beach sediments, HT)	N 049°22,541' W 123°16,502'	1.1	28.5	60.5	9.3	1.7
Horseshoe Bay (intertidal sediments, MT)	N 049°22,541' W 123°16,502'	2.8	45.0	40.2	10.2	4.6
Horseshoe Bay (intertidal sediments, LT)	N 049°22,541' W 123°16,502'	4.8	35.0	44.2	12.2	8.6
Maplewood FCA (beach sediments, HT)	N 049°18,255' W 123°00,035'	10.3	10.3	16.8	48.2	24.7
Maplewood FCA (intertidal sediments, MT)	N 049°18,255' W 123°00,035'	15.8	7.3	18.8	39.4	34.5
Maplewood FCA (intertidal sediments, LT)	N 049°18,255' W 123°00,035'	20.3	5.1	16.0	41.4	36.5

Note: Surface layer (5-15 cm) of sediments was analyzed for organic matter and granulometric composition.

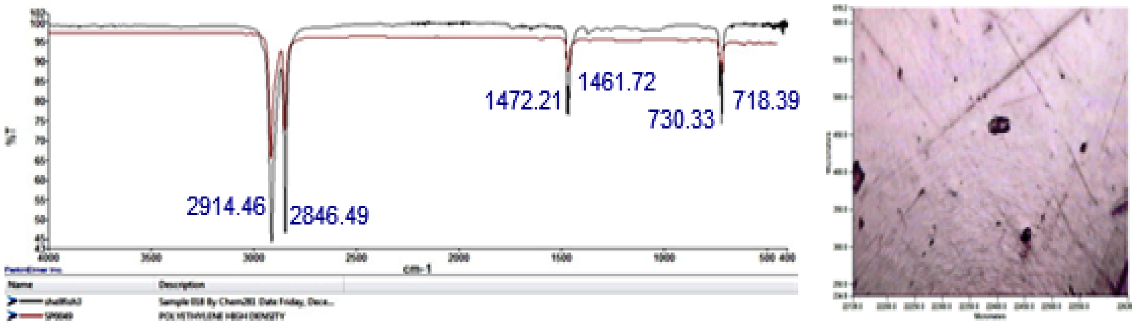
Organic matter concentrations were different between study sites and across the depth of tidal spectrum. The average total organic matter concentration of intertidal sediments at HB study site was 2.9% (range: 1.1- 4.8%) and 15.3% (range: 10.3-20.3%) at MWFCA study site (Table 2.1.).

2.4.2. Polymer compositions and aging of plastic macro- and microparticles in the marine intertidal sedimentary environments

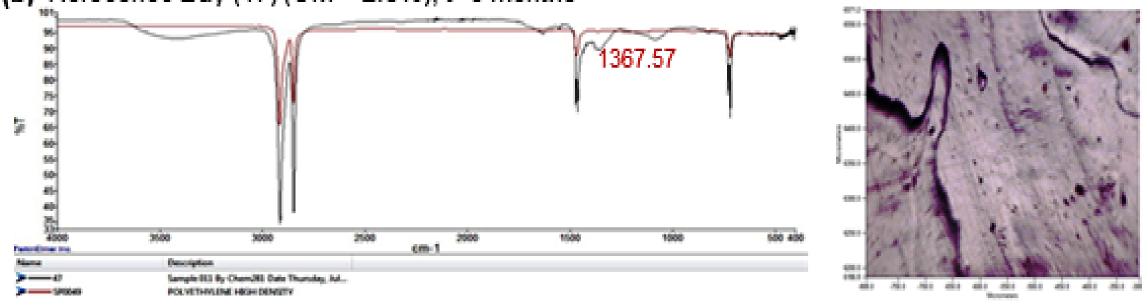
The FTIR analysis identified (search score range: 87–98.5%) of plastic macroparticles (polyethylene chips (HDPE) and textile fabric (PETE)) and microparticles (microbeads (HDPE) and fibres (PETE)) (Figure 2.2). Plastic macroparticles in the shape of polyethylene chips were identified as polyethylene high density (HDPE) (search score: composition: 98.5%) and macroparticles in the shape of textile fabric as polyethylene terephthalate (PETE, 1,4-cyclohexanedimethylene terephthalate) (search score: 87%) (Figure 2.2a; Figure 2.2b). Plastic microparticles in the shape of microbeads were identified as polyethylene high density (HDPE) (search score composition: 95.5%) and in the shape of fibre as polyethylene terephthalate (PETE, 1,4-cyclohexanedimethylene terephthalate) (search score compositions: 88.5%) (Figure 2.2c; Figure 2.2d).

In general, at the beginning of the field experiments, the FTIR spectra for plastic HDPE and PETE show standard characteristics bands at wave's numbers (Gulmine et al., 2002; Hummel, 2002). Importantly, after deploying in the intertidal sediments for 38 months, all of the samples of HDPE and PETE formed new functional groups. For instance, at the beginning of the field experiments the FTIR spectrums of initial HDPE macroparticles (polyethylene chips) and microparticles (microbeads) samples are shown characteristics bands at wave number 2914.46 cm^{-1} (CH2 asymmetric stretching) and 2846.49 cm^{-1} (CH2 symmetric stretching), 1472.21 and 1461.72 cm^{-1} (bending deformation), 1367.57 cm^{-1} (wagging deformation), 730.33 and 718.79 cm^{-1} (rocking deformation) that are seen for HDPE (Figure 2.2a; Figure 2.3a). For macroplastic (HDPE, polyethylene chips), the peak at 2914.46 cm^{-1} for HDPE is shifted to 2915.00 cm^{-1} and 2914.00 cm^{-1} after 12 months of deployment in the intertidal sediments at HB and MWFCA study site, respectively (Figure 2.3a, b, c; Figure 2.4a, b, c). The shifting of peak occurs due to degradation of HDPE in the presence of microbial culture (Ojha et al. 2017). In addition, for HDPE (polyethylene chips), formation of new functional groups is at 1619.75 cm^{-1} (HB) and 1628.75 cm^{-1} (MWFCA) after 12 months of deployment (Figure 2.3c, d; Figure 2.4c, d). The peak at wave number 1628.75 cm^{-1} corresponds to the carbonyl group which is due to oxidation of HDPE sample (Coates, 2006; Gulmine et al., 2002; Charles et al., 2009). Formation of another peak at 1619.75 cm^{-1} (HB) occurs and can be interpreting as the similar functional group as at 1628.75 cm^{-1} (MWFCA).

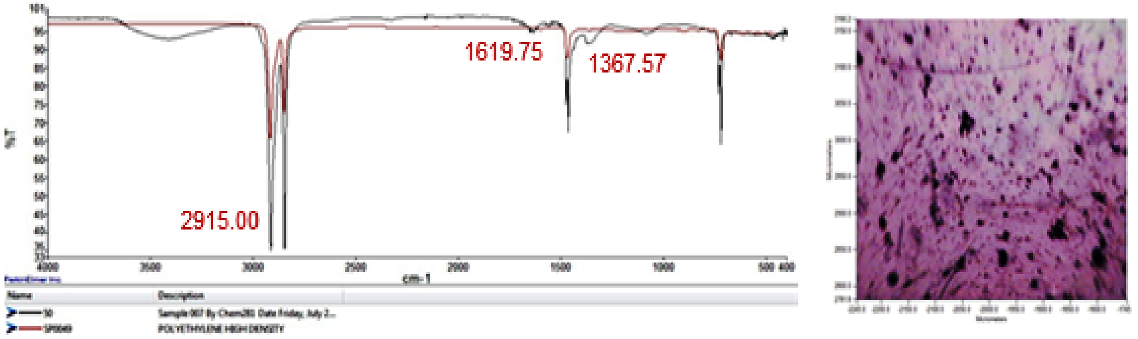
(a) Horseshoe Bay (3) (OM = 2.8%); t=0 months



(b) Horseshoe Bay (47) (OM = 2.8%); t=8 months



(c) Horseshoe Bay (50) (OM = 2.8%); t=12 months



(d) Horseshoe Bay (51) (OM = 2.8%); t=21 months

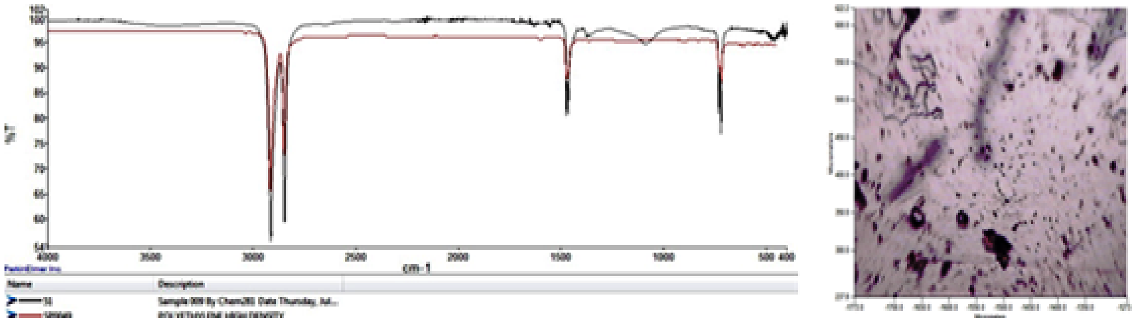
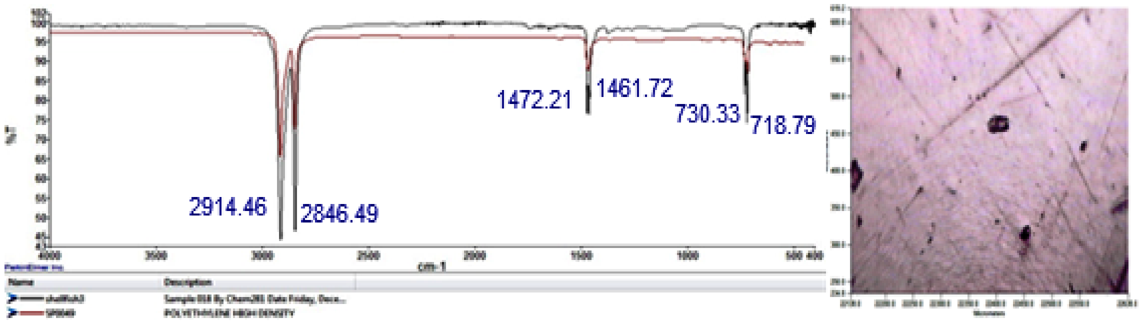


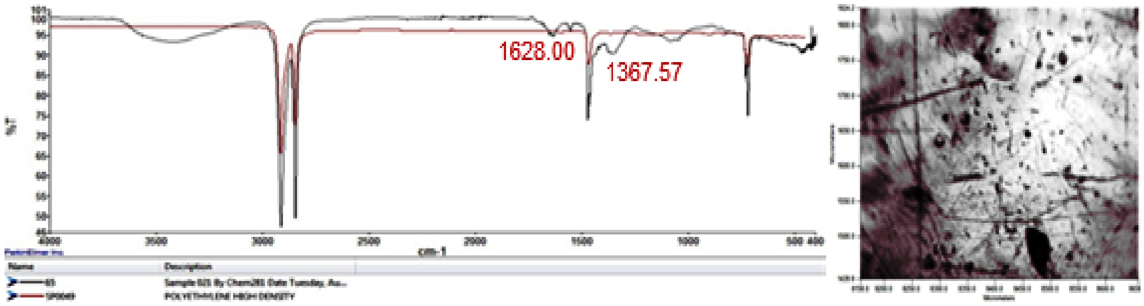
Figure 2.3. The FTIR spectra and microscopic images of plastic macroparticles (HDPE, polyethylene chips) via marine intertidal sediments (HB, OM= 2.8%) at residence time of t=0 months (a), t=8 months (b), t=12 months (c), and t=21 months (d).

Note: Red spectra are standard spectra of the polymer material (ATR Polymer Introductory Library); blue spectra are spectra of analyzed sample; numbers in red color are values of the spectra (wave number, cm^{-1}) of new functional group.

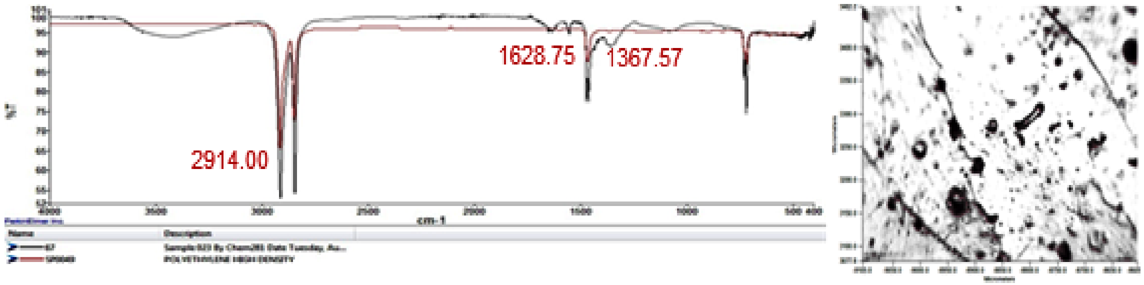
(a) Maplewood Flats Conservation Area (3) (OM = 15.8%); t= 0 months



(b) Maplewood Flats Conservation Area (65) (OM = 15.8%); t=8 months



(c) Maplewood Flats Conservation Area (67) (OM = 15.8%); t=12 months



(d) Maplewood Flats Conservation Area (70) (OM = 15.8%); t=21 months

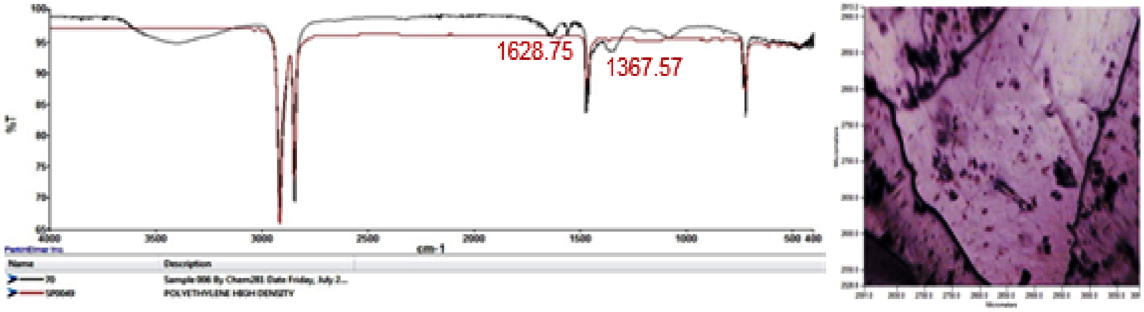


Figure 2.4. **The FTIR spectra and microscopic images of plastic macroparticles (HDPE, polyethylene chips) via marine intertidal sediments (MWFCA, OM = 15.8%) at residence time of t=0 months (a), t=8 months (b), t=12 months (c) and t=21 months (d).**

Note: Red spectra are standard spectra of the polymer material (ATR Polymer Introductory Library); blue spectra are spectra of analyzed sample; numbers in red color are values of the spectra (wave number, cm^{-1}) of new functional group.

The increment in the intensity of the band and the formation of new peaks supported the fact of continues degradation and aging of plastic macro- and microparticles (the same plastic materials) in the intertidal sediments, but very differently, depends on properties (type, size/shape) of the plastic materials and sediments (Figure 2.3; Figure 2.4). Microscopic images of plastic macro- and microparticles show the roughness, cracks, mechanical and oxidative weathering, indicating their continuous exposure in the sedimentary environment. The FTIR spectrums provide the presence of various elements on the macro- and microplastic surface (Figure 2.3; Figure 2.4). The results of scanning electron microscope (SEM) showed rough surfaces and obvious cracks on the microplastics isolated from sediments. Analyses of the FTIR spectrums and microscopic images confirmed the degradation and aging macro- and microparticles of both plastic materials HDPE and PETE after their deployment in the surface layer of the intertidal sediments.

2.4.3. Trace elements (Cd, Cu, Hg, Pb, and Zn)

2.4.3.1. Trace elements concentration in sediments

The concentration of Cd, Cu, Hg, Pb, and Zn extracted from sediment samples varied during the long-term (38 months) field experiments. The differences among study sites often varied according to sampling periods. Boxplots represent the distribution of trace elements (Cd, Cu, Hg, Pb, and Zn) observed concentration values and show accumulation patterns for each trace element at each period of time (sampling periods) and study site (Figure 2.5).

Temporal changes of cadmium (Cd) concentration in sediments at HB and MWCA have the opposite trends (desorption at HB and sorption at MWCA) at “short - term” (0-2 months) and “mid-term” (3-12 months) sampling periods and the same trend (desorption) at “long-term” (21-38 months) sampling period (Figure 2.5a). Concentrations of Cd in surface layer of the intertidal sediments and water were weakly negatively correlated at HB ((lm): r = - 0.43, df = 25, p = 0.035) and strongly positively correlated at MWFCA ((lm): r = 0.91, df = 25, p = 0.04) study sites.

Temporal changes of copper (Cu) concentration in sediments at HB and MWCA have the opposite trends (desorption at HB and sorption at MWCA) at “short -term” (0-2 months), “mid-term” (3-12 months), and “long-term” (21-38 months) sampling periods

(Figure 2.5b). Concentrations of Cu in surface layer of the intertidal sediments and water were very weakly correlated at both, HB ((lm): r = - 0.11, df = 25, p = 0.03) and MWFCA ((lm): r = 0.11, df = 25, p = 0.03) study sites.

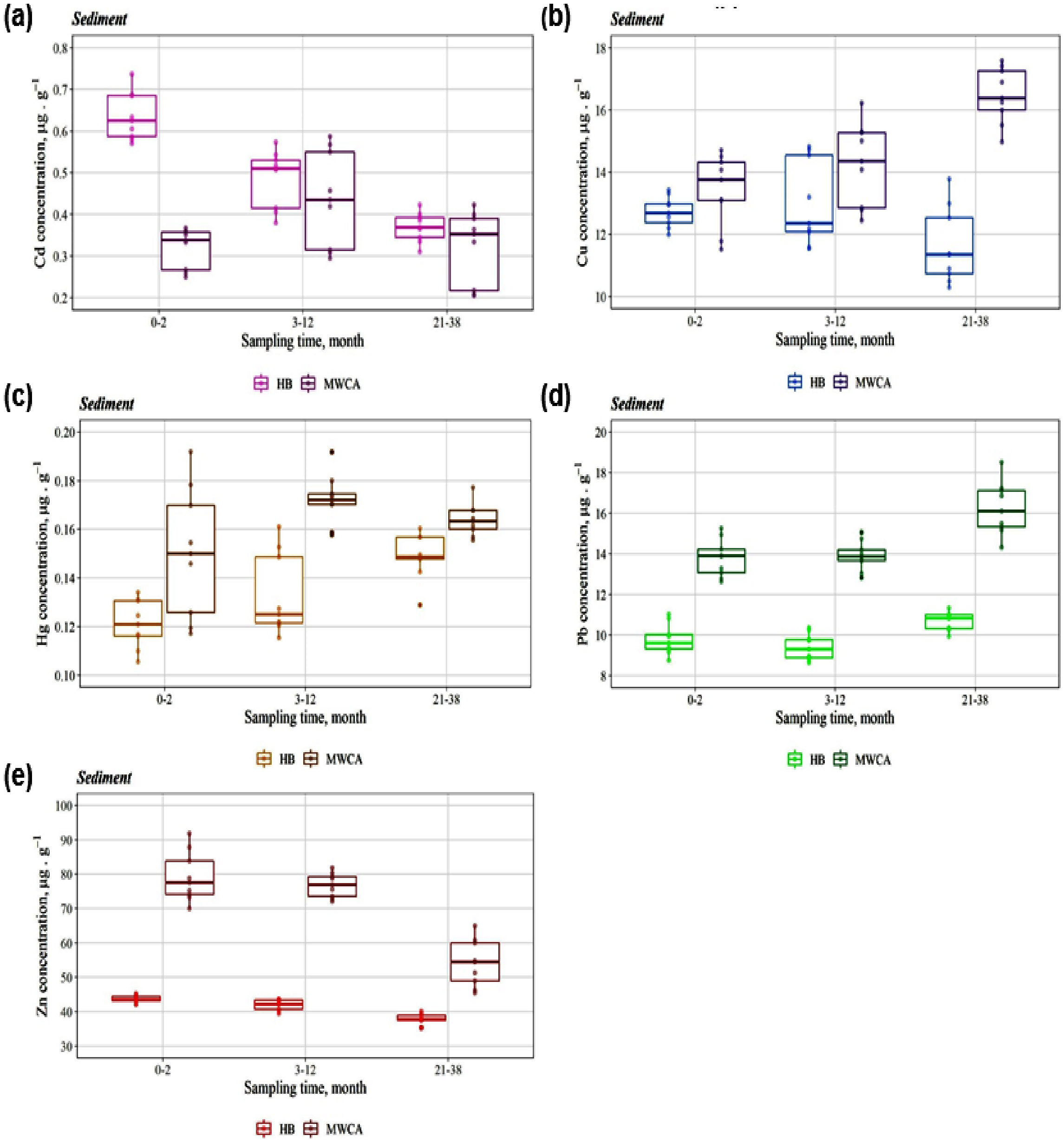


Figure 2.5. Concentration of Cd (a), Cu (b), Hg (c), Pb (d), and Zn (e) over time in the intertidal sediments at HB and MWFCA study sites.

Note: Boxplots represent the distribution of observed values, where midline is the median, with the upper and lower limits of the box being 75th and 25th percentiles. Whiskers extend up to the interquartile range and represent the ranges for the bottom 25% and the top 25% of the data values, excluding outliers. Measured values are depicted as points.

Temporal changes of mercury (Hg) concentration in sediments at HB and MWCA have the same trend (sorption) at “short -term” (0-2 months) and “mid-term” (3-12 months) and the opposite trend (sorption at HB and desorption at MWCA) at “long-term” (21-38 months) sampling periods (Figure 2.5c). The correlation coefficient between concentrations of Hg in surface layer of the intertidal sediments and water at both HB and MWFCA study sites were very close to zero that indicated there is no evidence of any relationship.

Temporal changes of lead (Pb) concentration in sediments at HB and MWCA have the same trend (sorption) at “short -term” (0-2 months), “mid-term” (3-12 months), and “long-term” (21-38 months) sampling periods (Figure 2.5d). Concentrations of Pb in surface layer of the intertidal sediments and water were strongly positively correlated at HB ((lm): $r = 0.75$, $df = 25$, $p = 0.015$) and weakly negatively correlated at MWFCA ((lm): $r = -0.48$, $df = 25$, $p = 0.03$) study sites.

Temporal changes of zinc (Zn) concentration in sediments at HB and MWCA have the same trend (desorption) at “short -term” (0-2 months), “mid-term” (3-12 months), and “long-term” (21-38 months) sampling periods (Figure 2.5e). Concentrations of Zn in surface layer of the intertidal sediments and water were very weakly positively correlated at HB ((lm): $r = 0.28$, $df = 25$, $p = 0.045$) and MWFCA ((lm): $r = 0.11$, $df = 25$, $p = 0.045$) study sites.

Overall, the concentrations of trace elements in the surface layer (35-40 cm) of the intertidal sediments was both site, and time dependent and in general (except of Cd at MWFCA and Pb at HB) independent on trace elements concentration in sea water the intertidal zone at both HB and MWCA study sites (Table B1). Concentrations of Cu, Pb, Zn, and Hg in the intertidal sediments show accumulation patterns and were always greater at the MWCA as compared to HB and independent of when sampled (Figure 2.5b-e). Only concentrations of Cd in sediments at HB were greater at “short -term” (0-2 months) as compared to MWCA with lower concentrations occurs at both, HB and MWFCA, sites at “mid-term” (3-12 months) and “long-term” (21-38 months) sampling periods (Figure 2.5a). Sediments at HB and MWCA that have different geochemistry characteristics have very different sorption ability towards all of the five trace elements and their sorption behaviour cannot to be grouped by the same trends at any period of study/sampling.

Trace elements concentrations were compared to legal standards for water and sediments (Canadian Water Quality Guidelines (QG) and Canadian Interim Sediment Quality Guideline (ISQG)) (CCME, 1999; CCME, 2007a; CCME, 2007b). In general, the total concentration of Cd, Cu, Pb, Zn, and Hg extracted from sediment and water samples were under absolute values in the Quality Guideline (ISQG) (Table B1).

2.4.3.2. Trace elements sorption by plastic macro- and microparticles

At the beginning of the field experiments the initial concentrations of trace elements (Cd, Cu, Hg, Pb, and Zn) in the experimental samples of plastic macro- and microparticles were greater than trace elements concentrations measured in seawater samples but significantly lower than that concentration measured in sediment samples taken at the HB (OM=2.8%) and MWFCA (OM=15.8%) study sites (Table B1). For all analyzed trace elements boxplots and summary output of the liner regression model (lm) showed that, in general, differences among plastic macro- and microparticles varied by type of polymeric materials, particle size, study site, and sampling period (Figure 2.6 – Figure 2.10, Table B2).

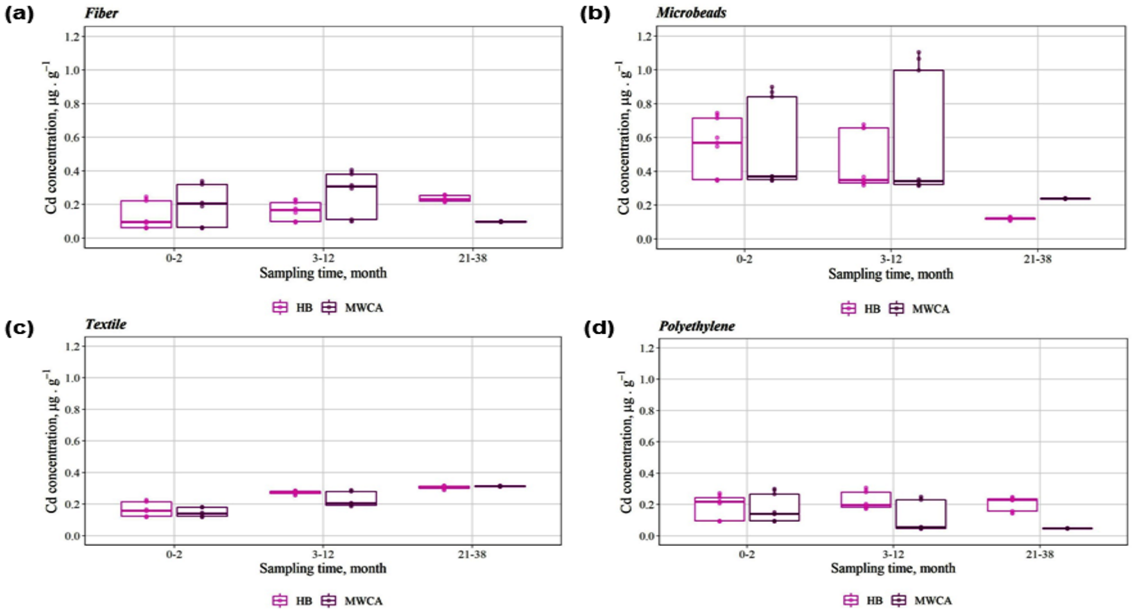


Figure 2.6. Concentration of Cd over time in micro-PETE (fibre) (a), micro-HDPE (microbeads) (b), macro-PETE (textile fabric) (c), and macro-HDPE (polyethylene chips) (d) deployed in the intertidal sediments at HB (OM=2.8%) and MWFCA (OM=15.8%) study sites.

Note: Boxplots represent the distribution of observed values, where midline is the median, with the upper and lower limits of the box being 75th and 25th percentiles. Whiskers extend up to the interquartile range and represent the ranges for the bottom 25% and the top 25% of the data values, excluding outliers. Measured values are depicted as points.

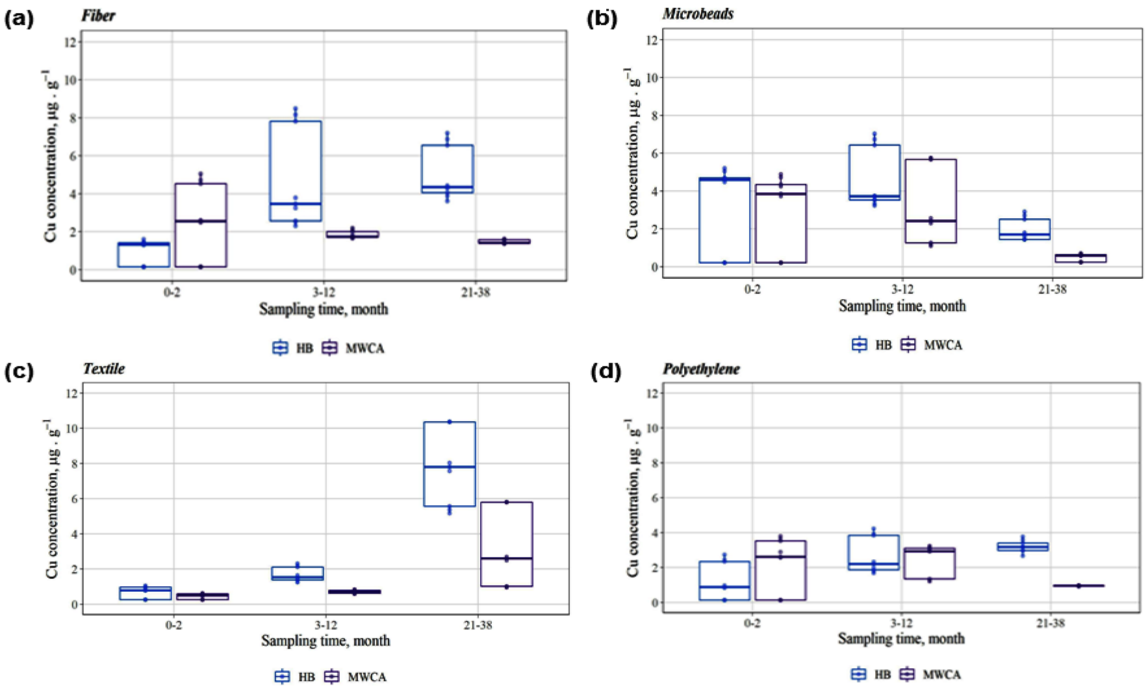


Figure 2.7. Concentration of Cu over time in micro-PETE (fibre) (a), micro-HDPE (microbeads) (b), macro-PETE (textile fabric) (c), and macro-HDPE (polyethylene chips) (d) deployed in the intertidal sediments at HB (OM=2.8%) and MWFCA (OM=15.8%)study sites.

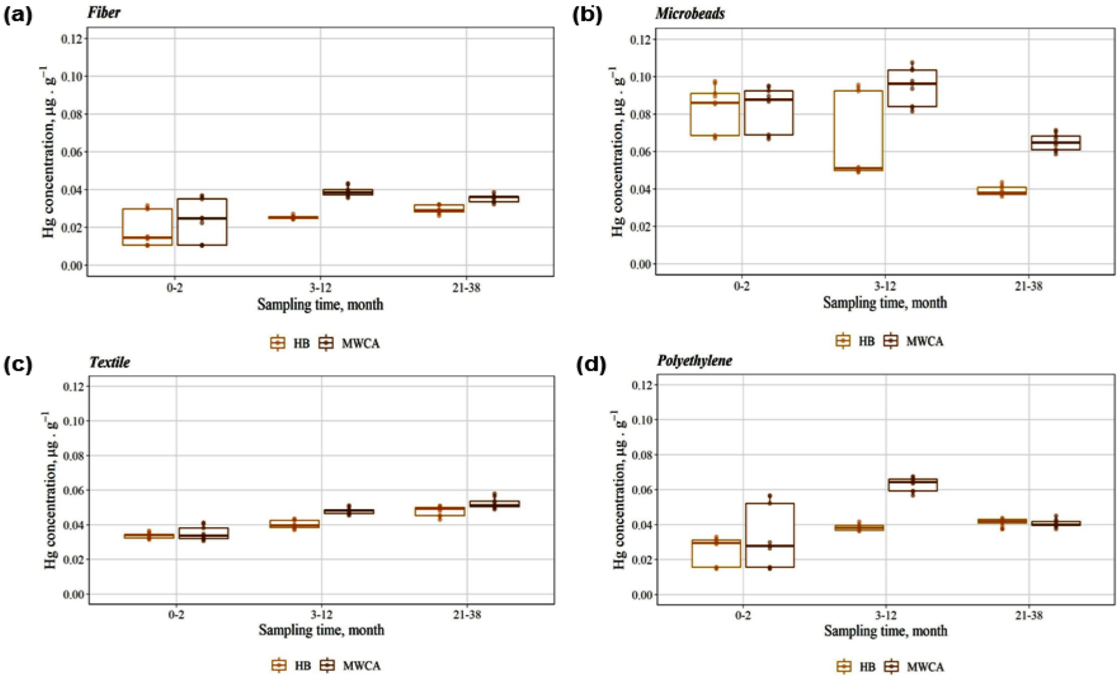


Figure 2.8. Concentration of Hg over time in micro-PETE (fibre) (a), micro-HDPE (microbeads) (b), macro-PETE (textile fabric) (c), and macro-HDPE (polyethylene chips) (d) deployed in the intertidal sediments at HB (OM=2.8%) and MWFCA (OM=15.8%) study sites.

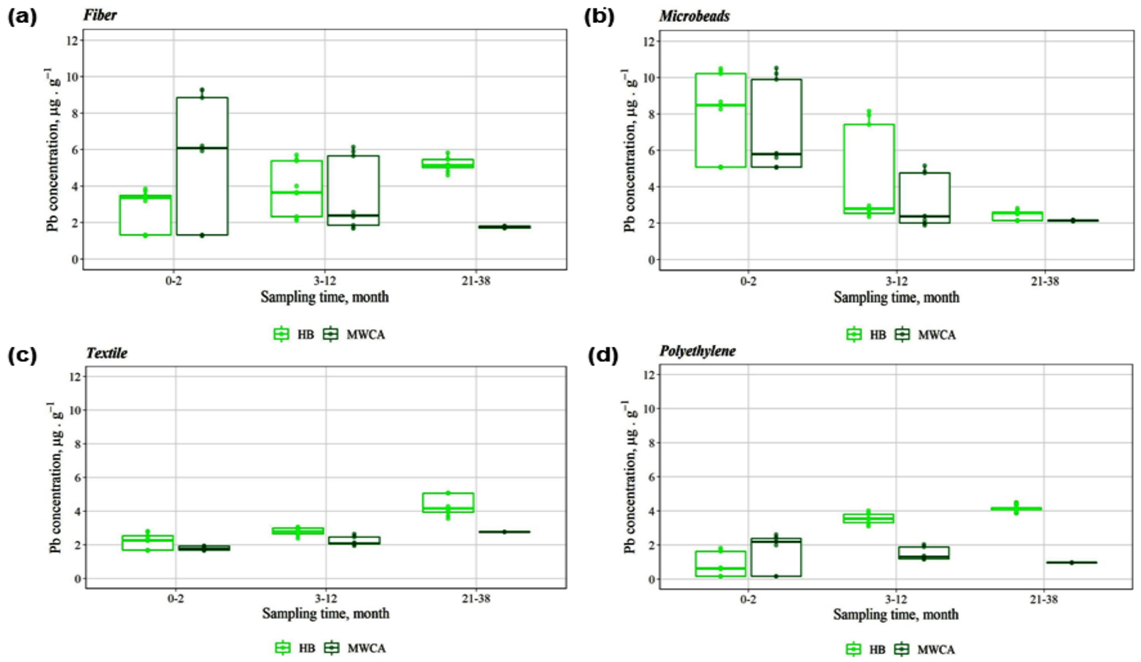


Figure 2.9. Concentration of Pb over time in micro-PETE (fibre) (a), micro-HDPE (microbeads) (b), macro-PETE (textile fabric) (c), and macro-HDPE (polyethylene chips) (d) deployed in the intertidal sediments at HB (OM=2.8%) and MWFCA (OM=15.8%) study sites.

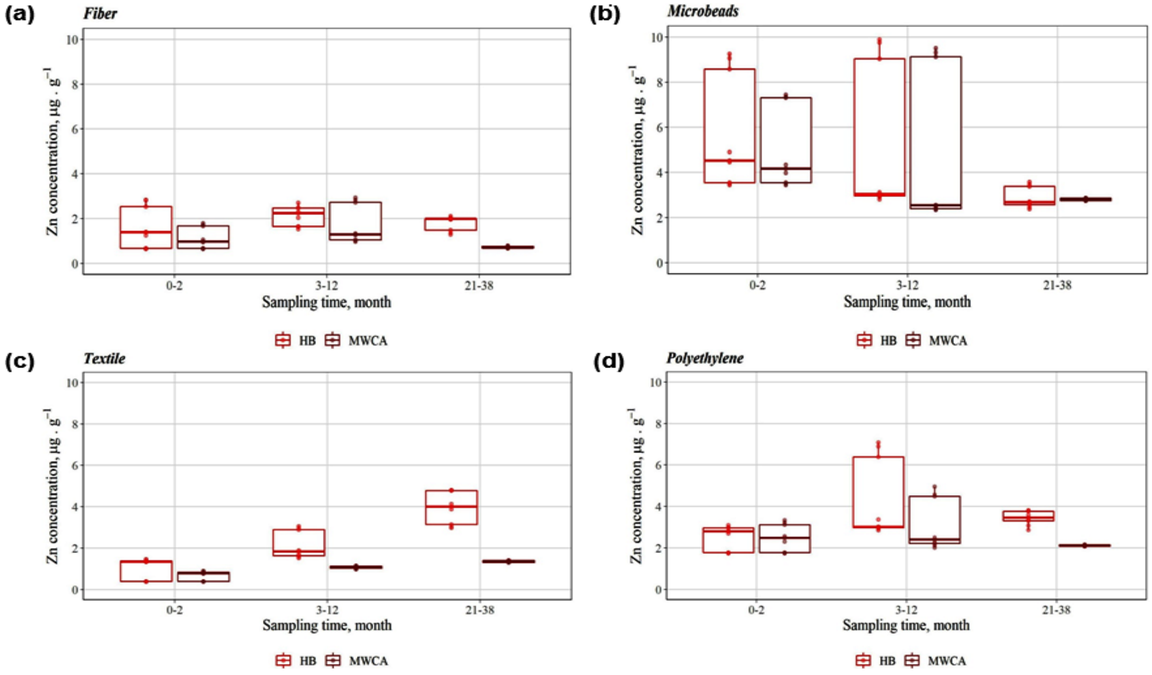


Figure 2.10. Concentration of Zn over time in micro-PETE (fibre) (a), micro-HDPE (microbeads) (b), macro-PETE (textile fabric) (c), and macro-HDPE (polyethylene chips) (d) deployed in the intertidal sediments at HB (OM=2.8%) and MWFCA (OM=15.8%) study sites.

The concentrations of Cd, Cu, Hg, Pb, and Zn accumulated over time, but with different intensities and trends at “short-term” (0-2 months), “mid-term” (3-12 months), and “long-term” (21-38 months) sampling periods. In general, trends in trace elements (except of Pb) sorption by macro-PETE (textile fabric) and macro-HDPE (polyethylene chips) are similar at both study sites. In contrast, sorption of trace elements (except of Zn) by micro-PETE (fibre) and micro-HDPE (microbeads) has opposite trends (sorption and desorption) at HB and MWCA study sites. Concentration of trace elements in plastic macro- and microparticles of PETE and HDPE has greater value in the intertidal sediments at HB (OM=2.8%) than that at MWCA (OM=15.8%). The differences in the trends and intensity of trace elements sorption by macro- and microplastics can be attributed to the features of plastic particles sorption behaviour within contrasting sedimentary environments.

2.5. Results and Discussion

2.5.1. The interaction between trace elements and plastic macro- and microparticles in the intertidal sedimentary environments

Following the specific objective of this study/chapter we compared the sorption of Cd, Cu, Hg, Pb and Zn by plastic macro- and microparticles of HDPE and PETE within two contrasting sedimentary environments, low (HB, OM = 2.8%) and high (MWFCA, OM = 15.8%) in organic matter content.

2.5.1.1. Defining the process of trace elements-plastic macro- and microparticles interaction

The co-occurrence of macro- and microplastics and trace elements in an aquatic ecosystem leads to their mutual interaction and the subsequent sorption of contaminants onto surfaces of the synthetic plastic macro- microparticles. In general, the interaction between trace elements and plastic macro- and microparticles can be described as process of sorption, desorption, and equilibrium state (Hartmann et al., 2017; Holmes, 2013; Kazmiruk and Bendell, 2020; Tourinho et al., 2019; Wang et al., 2016). Some field and laboratory studies on relationships between different types of plastic and trace elements in the marine aquatic environments (seawater) confirm that microplastics accumulate trace elements over time and process of accumulation include two different periods, such as, period of relatively rapid adsorption and period of reaching equilibrium state (Holmes, et al., 2012; Turner, et al., 2015; Rochman et al., 2014).

Results of our study highlight, that during the long-term field experiments (38 months) the experimental samples of plastic macroparticles (polyethylene chips, HDPE; textile fabric, PETE) and microparticles (microbeads, HDPE; fibers, PETE) deployed in intertidal sediments low (HB, OM = 2.8%) and high (MWFCA, OM = 15.8%) in organic matter content accumulate trace elements (Cd, Cu, Pb, Zn, and Hg) over time but very differently and varied significantly among study site, residence time, and polymer type ($p<0.05$) (Figure 2.6 –Figure 2.10; Figure B1, B2; Table B2). At the beginning of the field experiments, all type of plastic macro- and microparticles deployed in sediments at the HB and MWCA, study sites accumulated Cd, Cu, Pb, Zn, and Hg over “short -term” (0-2 months) period of sampling. This period can be estimated as period of rapid sorption. During the “mid-term” (3-12 months) and “long-term” (21-38 months) sampling periods interaction between trace elements and macro- and microparticles of PETE and HDPE may include period of sorption and period of desorption or only one of them. During the “long-term” (21-38 months) sampling periods interaction between trace elements and macro- and microparticles of PETE and HDPE usually have period of reaching equilibrium state (Figure 2.6 –Figure 2.10). For example, it was estimated, that temporal changes the concentration of cadmium (Cd) in micro-PETE (fibre) deployed in the intertidal sediments at MWFCA (OM=15.8%) have period of rapid sorption (0-2 months and 3-12 months)), period of desorption and reaching of equilibrium state (21-38 months). In contrast, temporal changes the concentration of Cd in micro-PETE (fiber) deployed in the intertidal sediments at HB (OM=2.8%) have only period of sorption (0-2 months and 3-12 months) and reaching equilibrium state (21-38 months) (Figure 2.6a). Changing the concentration of Cd in macro-PETE (textile fabric) has period of sorption (0-2 months and 3-12 months) and reaching equilibrium state (21-38 months) at both, HB and MWFCA study sites (Figure 2.6c). In contrast, changing the concentration of Cd in micro-HDPE (microbeads) and macro-HDPE (polyethylene chips) have the same periods, such as period of rapid sorption (0-2 months), period of desorption (3-12 months, 21-38 months) and reaching equilibrium state (21-38 months) at both, HB and MWFCA study sites (Figure 2.6b; Figure 2.6d). These finding assumes, that the interaction between trace elements (Cd, Cu, Hg, Pb, and Zn) and plastic macro- and microparticles of HDPE and PETE within contrasting intertidal sediment environments may include three periods, such as period of rapid adsorption, period of reaching equilibrium state, and period of desorption or two of them, depending on the rate of trace elements accumulation by plastic particles and characteristics of sedimentary environments. In addition, these findings showed that sorption of trace elements (Cd, Cu, Pb, Zn, and Hg) was related to the type of polymer and size/shape of the plastic particles.

The FTIR spectra and microscopic images demonstrated formation of new functional groups in plastic composition of macroparticles of HDPE (polyethylene chips) deployed in the intertidal sediments at both, HB (OM = 2.8%) and MWFCA (OM = 15.8%) study sites (Figure 2.3b; Figure 2.4b). It is important to note, that the formation of new peaks was possible to detect (FTIR spectra) only after 3 and 8 months of deploying at MWFCA and HB study sites respectively. The formation of new peaks supported the fact of continuing degradation and aging of plastic macro- and microparticles once they were deployed in the intertidal sediments (Figure 2.3; Figure 2.4). Moreover, the aging of macro- and microparticles may affects their sorption performance toward trace elements (Cu, Zn, Pb, Cd, and Hg) due to a series of changes in their specific surface area, shape, size, and oxygen-containing functional groups. For instance, changing the concentration of cadmium (Cd) in micro-HDPE (microbeads) and macro-HDPE (polyethylene chips), deployed at both, HB and MWFCA study sites, have the period of reaching equilibrium state (21-38 months) only after period of desorption (3-12 months) (Figure 2.6b; Figure 2.6d). This finding suggests that continues degradation and aging of plastic materials under conditions of the intertidal sediments influence the process of trace elements-macro- and microplastic interaction. However, how degradation and aging of plastic particles influence their sorption behaviour towards trace elements is very controversial because sorption could be to surface particles or into particles and depended on many factors especially on characteristics of surrounding environments and residence time of plastic particles in that environment (Endo et al., 2005; Wang et al., 2018). This question requires further study.

2.5.1.2. Intertidal sediment geochemistry

The results of the previous studies state that process of trace elements sorption by plastic macro- and microparticles depends mainly on the physical and chemical properties of the sorbent (surface area, diffusivity, crystallinity, polarity of polymers, etc.)

and characteristics of the surrounding environments (Li et al., 2019; Mato et al., 2001; Maršić-Lučić et al., 2018; Teuten et al., 2007; Wang et al., 2016). The intertidal sedimentary environmental matrices are heterogeneous and quite complicated in composition. Sediment-associated contaminants including trace elements (Cd, Cu, Pb, Zn, and Hg) tend to accumulate in depositional areas on small, fine-grained particles which have the highest surface area to volume ratio of any particle size class and tendency for higher concentration of organic matter (Murray et al., 1999; Zhang et al., 2021; Zhang et al., 2022; Wang et al., 2016).

During the field experiments (38 months), the value of Cu, Zn, Pb, Cd, and Hg concentration in sediments and water of intertidal area was higher at MWFCA compare to the HB study site (Figure 2.5; Table B1). However, the equilibrium concentration of trace elements Cd, Cu, Pb, Zn, and Hg sorbed by plastic macro- and microparticles of HDPE and PETE was greater in the intertidal sediments low in organic matter and percentages of fine-grained particles < 0.063 mm in size (HB: OM=2.8%; 4.6% of volume) than that in intertidal sediments high in organic matter and percentages of fine-grained particles < 0.063 mm (MWFCA: OM=15.8%; 36.5% of volume) (Table 2.1; Figure 2.6-Figure 2.10). These findings can be explained as that the sorption of trace elements Cu, Zn, Pb, Cd, and Hg was competitive between plastic particles and intertidal sediments at both study sites, low (HB, OM= 2.8%) and high (MWFCA, OM=15.8%) in organic matter concentration. Moreover, this finding indicates that plastic particles play a minor role in trace elements sorption within intertidal sedimentary environments in the presence of organic matter at high concentrations which is in accordance with Xu et al. (2018). Importantly, that through competition for sorption site, sediments high in organic matter content may reduce trace elements accumulation by macro- and microplastics as compared to sediments low in organic matter content.

To estimate the interactions between trace elements and 4 types of plastic macro- and microparticles under condition of two contrasting intertidal sedimentary environments, the relative equilibrium concentration as ratio of equilibrium concentration (C_e) to the initial concentration (C_i) of trace elements were calculated (Equation 2.1) for experimental samples of macroplastics (polyethylene chips, HDPE; textile fabric, PETE) and microplastics (primary) (microbeads, HDPE; and fibres, PETE) deployed in the intertidal sediments at HB (OM = 2.8%) and MWFCA (OM = 15.8%) study sites (Table

2.2). By estimating the value of the relative equilibrium concentration the trace elements-plastic particles interaction can be defined as following:

$(C_e/C_i) > 1 \; or \; \log(C_e/C_i) > 0 ===>$ sorption process (increase concentration) (2.8)

$(C_e/C_i) < 1 \; or \; \log(C_e/C_i) < 0 ===>$ desorption process (decrease concentration) (2.9)

Table 2.2. The values of the trace elements relative equilibrium concentration (C_e/C_i) for plastic macro- and microparticles deployed in the intertidal sediments at HB and MWFCA study sites

Study site	Organic mater, %	Microplastic		Macroplastic	
		PETE fiber	HDPE microbeads	PETE textile fabric	HDPE polyethylene chips
		Cd			
Horseshoe Bay	2.8	3.62 (21)	0.45 (27)	2.64 (27)	2.13 (27)
Maplewood FCA	15.8	1.63 (12)	0.86 (21)	2.50 (12)	0.55 (15)
		Cu			
Horseshoe Bay	2.8	**31.56** (27)	8.02 (27)	**35.56** (35)	**23.92** (21)
Maplewood FCA	15.8	10.03 (18)	**21.93** (12)	4.83 (27)	7.44 (12)
		Hg			
Horseshoe Bay	2.8	3.14 (27)	0.56 (27)	1.56 (27)	2.83 (27)
Maplewood FCA	15.8	3.36 (21)	0.96(21)	1.58 (21)	3.08 (21)
		Pb			
Horseshoe Bay	2.8	4.05 (27)	0.50 (27)	2.50 (27)	**25.10** (21)
Maplewood FCA	15.8	1.44 (12)	0.45 (21)	1.72 (21)	6.34 (12)
		Zn			
Horseshoe Bay	2.8%	3.13 (27)	0.93 (21)	10.05 (27)	1.95 (21)
Maplewood FCA	15.8%	1.31 (12)	0.74 (12)	3.24 (21)	1.23 (12)

Note: The value in the round brackets indicates the residence time (months) when the state of equilibrium and equilibrium concentration was reached. The maximum values in the bold text.

In our study, the relative equilibrium concentration of Cd, Hg, Pb and Zn in micro-HDPE (microbeads) deployed in sediments at HB and MWFCA study sites and Cd in macro-HDPE (polyethylene chips) deployed in sediments at MWFCA have value of $(C_e / C_i) < 1$ (Table 2.2). This suggests that plastic microparticles of HDPE may have the value of trace elements equilibrium concentration lower than their initial concentration as results of desorption process (Equation 2.9). In contrast, macro- and microparticles of PETE and macroparticles of HDPE in sediments at HB and MWFCA have an equilibrium concentration of trace elements (Cd, Cu, Hg, Pb and Zn) greater than their initial concentration (C_e / C_i) > 1 as results of sorption process (Equation 2.8).

Importantly, the value of the relative equilibrium concentration (C_e / C_i) of Cu for macro-PETE (textile fabric) deployed in sediments at HB (OM=2.8%) was observed as highest ((C_e / C_i) = 35.56) compare to that ((C_e / C_i) = 4.83) in sediments at MWFCA (OM=15.8%). This indicates that the relative equilibrium concentration of Cu for macro-PETE (textile fabric) can be in 35.56 and 4.83 fold greater in sediments low (HB) and high (MWFCA) in organic matter respectively compare to their initial concentration. The value of relative equilibrium concentration of Cd for micro-HDPE (microbeads) deployed in sediments at MWFCA (OM=15.8%) was observed as lowest ((C_e / C_i) = 0.33) compare to that ((C_e / C_i) = 0.45) in sediments at HB (OM=2.8%) (Table 2.2). These findings showed that interactions between trace elements (Cd, Cu, Pb, Zn, and Hg) and plastic particles under condition of two contrasting intertidal sedimentary environments can be reaching equilibrium through the process of sorption or desorption. In general, the relative equilibrium concentration (C_e / C_i) of five trace elements Cu, Zn, Pb, Cd, and Hg on plastic macro- and microparticles of HDPE and PETE was higher in intertidal sediments low in organic matter content (HB, OM = 2.8%) compare to that in sediments high in organic matter content (MWFCA, OM=15.8%) (Table 2.2). These results can be explained as a phenomenon of competitive adsorption between plastic materials and organic particles in sediments that is very similar with results of the sorption/desorption study in the terrestrial environments (Gomez et al., 1999).

Characteristics of the surrounding environment that influence interactions between trace elements and plastic particles and can affect the time of reaching equilibrium state and equilibrium concentration. Sorption capacity of plastic macro- and microparticles to the Cu, Zn, Pb, Cd, and Hg is significantly dependent on their size/shape and initial concentration of the trace elements in sediments (Table B1, Table B2). In relation to study sites, plastic particles of PETE and HDPE reached equilibrium concentration of Cd, Cu, Pb, Zn, and Hg faster in the intertidal sediments at MWFCA (OM = 15.8%; 12-21 months) compare to that at HB (OM = 2.8%; 21-35 months) (Table 2.2). This finding indicates that the initial concentration of trace elements in sediments influences sorption behaviour such as sorption rate of plastic particles which is in accordance with Wang et al. (2016).

In relation to plastic particle size, micro-PETE (fibre) reached an equilibrium concentration in sorption of Cd, Cu, Zn, and Pb faster (12-27 month) compare to the macro-PETE (textile fabric) (21-35 months), but micro-HDPE (microbeads) and macro-HDPE (polyethylene chips) reached an equilibrium concentration of Cd, Cu, Zn, and Pb approximately during the same period (12-27 months). It should be attributed to the fact, that rubbery plastics such as micro-PETE (fibre) had a higher affinity with chemicals than glassy plastics. In addition, some studies showed that chemicals usually had higher diffusion coefficient on low-density plastic particles than high-density. It can be attributed to the slow diffusion rate of chemicals on HDPE (Mato et al., 2001). In general, PETE has been reported to exhibit higher sorption capacity compare to the HDPE (Alimi et al., 2018; Wang et al., 2018a).

Sorption of Hg by plastic macro- and microparticles (PETE and HDPE) reached equilibrium concentration at both, HB and MWFCA, study sites approximately during the same period of their residence (21-27 months) in the intertidal sediments (Table 2.2). Such findings indicate that in the intertidal sedimentary environments plastic particle size/shape can affect sorption and desorption rate, rate of equilibrium establishment, and equilibration time (Wang et al., 2018a). In addition, sorption rate of trace elements (Cu, Zn, Pb, Cd, and Hg) by macro- and microparticles of PETE and HDPE increased with decreasing particle size (Table 2.2.). This phenomenon may be due to increasing the specific surface area, resulting in an increase in adsorption sites on the particle surface, and the amount of adsorption to trace elements is also increased (Ashton et al., 2010; Wang et al., 2016). Therefore, the low concentration of organic matter in sediments and high surface area-to-volume ratio of plastic macro- and microparticles facilitate the accumulation of the trace elements contaminants (Cd, Cu, Pb, Zn, and Hg) on their surface which is in accordance with previous study (Brennecke et al., 2016; Guo et al., 2018; Guo et al., 2020).

Dependence of trace elements sorption by plastic macro- and microparticles on organic matter concentration in the intertidal sediments can be expressed by gradient $\Delta(\log(C_e/C_i))/\Delta OM$ and are following the order (R^2= 0.7583-0.99) (Table 2.2):

(a) micro-PETE (fibre):
    Cu (-0.0388) > Pb (-0.0366) > Zn (-0.0311) > Cd (-0.0282) > Hg (-0.0049);
    micro-HDPE (microbeads):

Cu (-0.0271) > Cd (-0.0110) > Pb (-0.0094) > Zn (-0.0056) > Hg (-0.0037);

(b) macro-PETE (textile fabric):

Cu (-0.0660) > Zn (-0.0375) > Pb (-0.0145) > Cd (-0.0115) > Hg (-0.0027);

macro-HDPE (polyethylene chips):

Pb (-0.0461) > Cd (-0.0416) > Cu (-0.0383) > Zn (-0.0152) > Hg (-0.0049).

Sorption behaviour/capacity of macroparticles ($\Delta(\log(C_e / C_i))/\Delta OM = -0.0660$ (Cu)) and microparticles ($\Delta(\log(C_e / C_i))/\Delta OM = -0.0388$ (Cu)) of PETE towards Cd, Cu, Pb, Zn, and Hg) under conditions of intertidal sedimentary environments are more dependent on organic matter concentrations in the intertidal sediments as compared to the microparticles ($\Delta(\log(C_e / C_i))/\Delta OM = -0.0461$ (Pb)) and microparticles ($\Delta(\log(C_e / C_i))/\Delta OM = -0.0271$ (Cu)) of HDPE. Generally, plastic particles of PETE have been reported to exhibit greater adsorption capacity than other types of plastic, including HDPE which is in accordance with Alimi et al. (2018). In relation to the type of trace elements, sorption of Cu by plastic macro- and microparticles has higher dependence on sedimentary characteristics compare to sorption of Hg with strongly lower dependence. Sorption of Cd, Pb, and Zn by plastic macro- and microparticles of PETE and HDPE have moderated dependence on characteristics of intertidal sediments.

Partitioning of trace elements in the intertidal sediments with macro- and microplastic

Once being introduced into the environment, contaminants begin to interact between each other and with each component of those environments as well (Atkinson et al., 2007; Kleinteich et al., 2018). To date the co-occurrence, distribution and redistribution of trace elements such as Cu, Zn, Pb, Cd, and Hg (past contaminants of concern) in the marine intertidal sedimentary environment with components of plastic macro- and microparticles (currently emerging contaminants of concern) have not been investigated and number of studies in this field is very limited. Because of this, it was necessary to identify suitable parameters to describe the partitioning of trace elements (Cd, Cu, Pb, Zn, and Hg) between plastic particles and compartments of the marine intertidal sedimentary environments (e.g., see water, sediments, pore water). In this study we have used partition (distribution) coefficient (K_d) (Equation 2.2) to compare the affinities of trace elements to different particulates, or to assess sorption under varying conditions (Lindsay, 1979; US.EPA, 2012; Wang et al., 2018a).

Sorption of trace elements (Cd, Cu, Zn, Pb, and Hg) and their partitioning (distribution and redistribution) between compartments of marine intertidal sediments with macro- and microplastic component are determined by various physicochemical characteristics of sorbent (sea water, sediments, pore water, macro- and microparticles) and sorbate phases (trace elements) and environmental factors of specific matrices (Wang et al., 2018a). At the beginning of long-term field experiments the initial concentrations all five trace elements in the plastic macro- and microparticles were greater than in samples of intertidal seawater but significantly lower than in intertidal (surface layer 35-40 cm) at both, HB and MWFCA, study sites (Table B1). The concentration of Cd, Cu, Pb, Zn, and Hg in the intertidal sediments and water have time-dependent changes (variability/fluctuation) during the period of field experiments (38 months) and periods of sampling (0-2, "short term"; 3-12, "mid-term"; 21-38 "long term") at both, HB and MWFCA, study sites (Figure 2.5). There was no correlation between trace element concentration in the intertidal sediments and sea water, except concentration of Cd at MWFCA ((lm): $r(Cd) = 0.91$, $df = 25$, $p = 0.04$) and Pb at HB ((lm): $r(Pb) = 0.75$, $df = 25$, $p = 0.015$)). In general, the concentration of trace elements (Cd, Cu, Pb, Zn, and Hg) in the intertidal seawater does not depend on that concentration in the surface layer (25-30 cm) of intertidal sediments.

The values of the intertidal sediments-sea water partitioning coefficient (K_{sed-sw}) (Equation 2.3) of the 5 trace elements demonstrated that there are no significant time-dependent changes during all of three periods of sampling (0-2, "short term"; 3-12, "mid-term"; 21-38 "long term") at both, HB and MWFCA, study sites. The intertidal sediments-sea water partitioning coefficient (K_{sed-sw}) of Cu, Pb, and Zn was higher at MWFCA (OM=15.8%) compare to that at HB (OM=2.8%) study site. However, the (K_{sed-sw}) of Cd and Hg was lower at MWFCA than that at HB (Table 2.3). This suggests that trace elements Cu, Pb, and Zn, except of Cd and Hg, can partition to the intertidal sediments high in organic matter more readily than to sediments low in organic matter. Importantly, that the value of log (K_{sed-sw}) of Cd, Cu, Pb, Zn, and Hg follow the order: Hg (5.60-5.81) > Zn (4.63-4.98) > Cu (2.94-3.18) > Pb (1.97-2.12) > Cd (1.90-1.63) at HB and MWFCA respectively (Table 2.3). Such finding illustrates that order of the prevalence of Cd, Pb, Cu, Zn, and Hg distribution between sea water and intertidal sediments high (OM=15.8%) and low (OM=2.8%) in organic matter content is the same.

Table 2.3. The values of the ratio of intertidal sediments-pore water equilibrium partitioning coefficient (($K_{sed\text{-}wp})_e$) to the plastic particles-pore water equilibrium partitioning coefficient (($K_{pl\text{-}wp})_e$) as [$(K_{sed\text{-}wp})_e/(K_{pl\text{-}wp})_e$] of Cd, Cu, Hg, Pb, and Zn.

		$(K_{sed\text{-}wp})_e/(K_{pl\text{-}wp})_e$			
		Microplastic		Macroplastic	
Study site	$(K_{sed\text{-}ws})_e$	PETE fiber	HDPE microbeads	PETE textile fabric	HDPE polyethylene chips
		Cd			
HB (OM=2.8%)	79.4	1.62 (21)	1.59 (27)	1.23 (27)	1.48 (27)
MWFCA (OM=15.8%)	42.7	3.55 (12)	1.79 (21)	2.14 (12)	7.08 (15)
		Cu			
HB (OM=2.8%)	871.0	2.29 (27)	5.37 (27)	2.46 (35)	3.63 (21)
MWFCA (OM=15.8%)	1513.8	10.72(18)	**23.44** (12)	7.95 (27)	16.60 (12)
		Hg			
HB (OM=2.8%)	398107.2	4.90 (27)	2.51 (27)	2.85 (27)	3.55 (27)
MWFCA (OM=15.8%)	151356.2	5.25 (21)	2.63 (21)	3.39 (21)	4.37 (21)
		Pb			
HB (OM=2.8%)	93.4	2.24 (27)	4.17 (27)	2.13 (27)	2.52 (21)
MWFCA (OM=15.8%)	131.9	8.32 (12)	7.25 (21)	5.62 (21)	**12.60** (12)
		Zn			
HB (OM=2.8%)	43651.6	20.89 (27)	13.80 (21)	10.24 (27)	11.49 (21)
MWFCA (OM=15.8%)	95500.2	**72.44** (12)	**31.62** (12)	**50.12** (21)	**25.70** (12)

Note: The value in the round brackets indicates the residence time (months) when the state of equilibrium and equilibrium concentration was reached. The maximum values in the bold text.

To estimate and compare the distribution of trace elements (Cu, Cd, Hg, Pb, and Zn) in two contrasting intertidal sedimentary environment with components of plastic macro- and microparticles of PETE and HDPE, the ratio of intertidal sediments-pore water partitioning coefficient ($K_{sed\text{-}wp}$) to the plastic materials-pore water partitioning coefficient ($K_{pl\text{-}wp}$) of trace elements (Cd, Cu, Pb, Zn, and Hg) at HB (OM = 2.8%) and MWFCA (OM = 15.8%) study sites was calculated as [($K_{sed\text{-}wp}/K_{pl\text{-}wp}$)] (Equation 2.7). By estimating the logarithmic value of the ratio of intertidal sediments-pore water partitioning coefficient ($K_{sed\text{-}wp}$) to the plastic materials-pore water partitioning coefficient ($K_{pl\text{-}wp}$), the distribution of trace elements can be defined as following:

$$(K_{sed-wp}/K_{pl-wp}) = 1 \; or \; \log(K_{sed-wp}/K_{pl-wp}) = 0 \; ===> \; [Me]_{sed} = [Me]_{pl} \qquad (2.10)$$

$$(K_{sed-wp}/K_{pl-wp}) > 1 \; or \; \log(K_{sed-wp}/K_{pl-wp}) > 0 \; ===> \; [Me]_{sed} > [Me]_{pl} \qquad (2.11)$$

$$(K_{sed-wp}/K_{pl-wp}) < 1 \; or \; \log(K_{sed-wp}/K_{pl-wp}) < 0 \; ===> \; [Me]_{sed} < [Me]_{pl} \qquad (2.12)$$

Theoretically, the log($K_{sed\text{-}wp}$ / $K_{pl\text{-}wp}$) may have “positive”, “0”, or “negative” value which indicate that concentration of trace elements in the intertidal sediments is greater, the same, or lower than that in the plastic macro- and microparticles, respectively. In our study on sorption of trace elements by plastic particles under condition of intertidal sedimentary environments Cd and Cu have “positive”, “0”, and “negative” value and Hg, Pb, and Zn have only “positive” value of log($K_{sed\text{-}wp}$ / $K_{pl\text{-}wp}$) (Figure 2.11-2.15).

By estimating the trends in the temporary variation of the log ($K_{sed\text{-}wp}$/$K_{pl\text{-}wp}$), the distribution of Cd, Cu, Hg, Pb, and Zn between sediments and macro- and microparticles of PETE and HDPE deployed at HB (OM=2.8%) and MWFCA (15.8%) can be divided into three groups, such as: (a) Cd, Cu, and Pb; (b) Hg; and (c) Zn (Figure 2.11-2.15). The time dependent changes of the log ($K_{sed\text{-}wp}$/$K_{pl\text{-}wp}$) of trace elements in each group have the same or similar trends for each type of macro- and microparticles of PETE and HDPE. These indicate that trace elements of each group partition to plastic particles differently under condition of intertidal sediments.

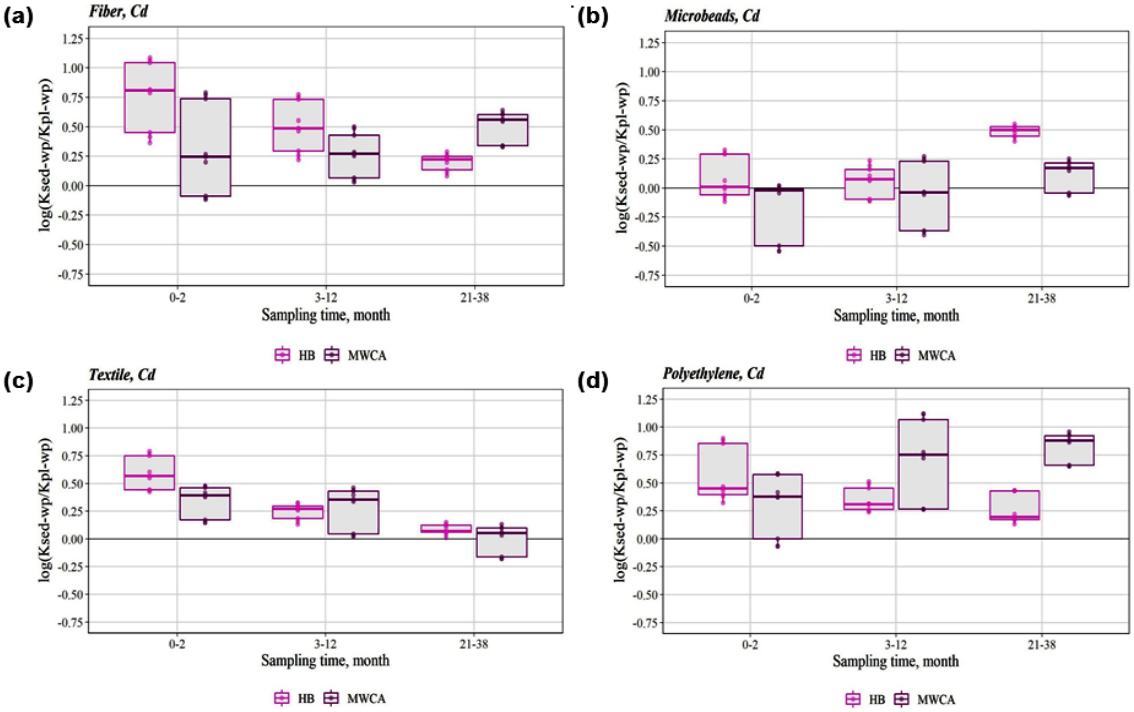


Figure 2.11. **The value of log($K_{sed\text{-}wp}$/$K_{pl\text{-}wp}$) of Cd over time in micro-PETE (fibre) (a); micro-HDPE (microbeads) (b), macro-PETE (textile fabric) (c), and macro-HDPE (polyethylene chips) (d) deployed at HB (OM = 2.8%) and MWFCA (OM = 15.8%) study sites.**

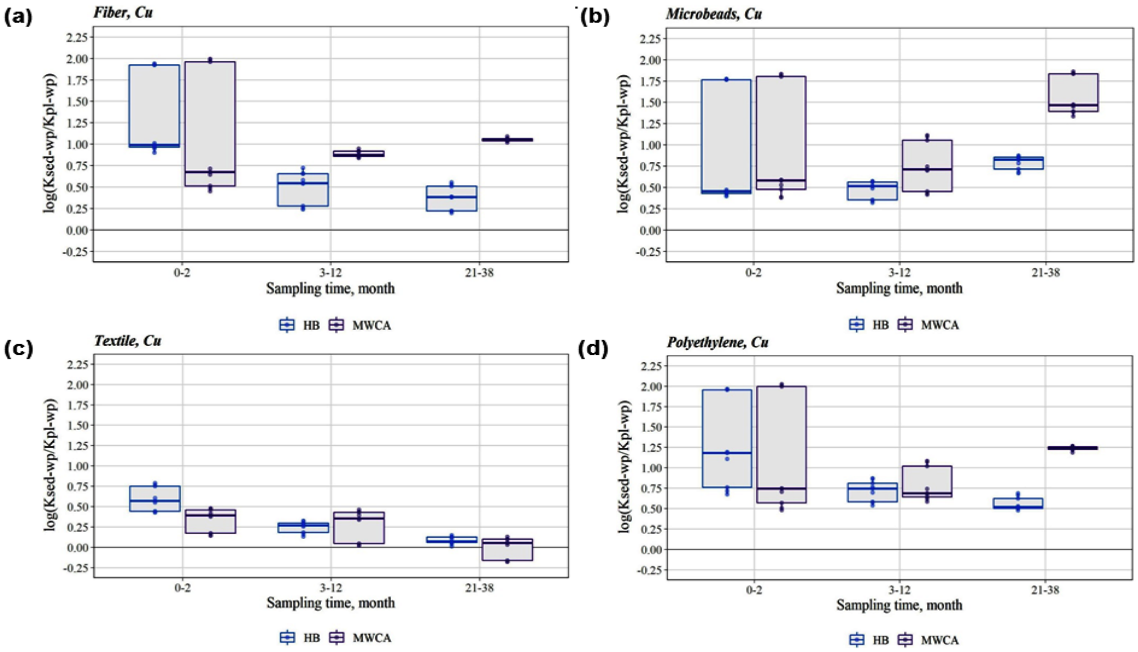


Figure 2.12. The value of log($K_{sed\text{-}wp}/K_{pl\text{-}wp}$) of Cu over time in micro-PETE (fibre) (a); micro-HDPE (microbeads) (b), macro-PETE (textile fabric) (c), and macro-HDPE (polyethylene chips) (d) deployed at HB (OM = 2.8%) and MWFCA (OM = 15.8%) study sites.

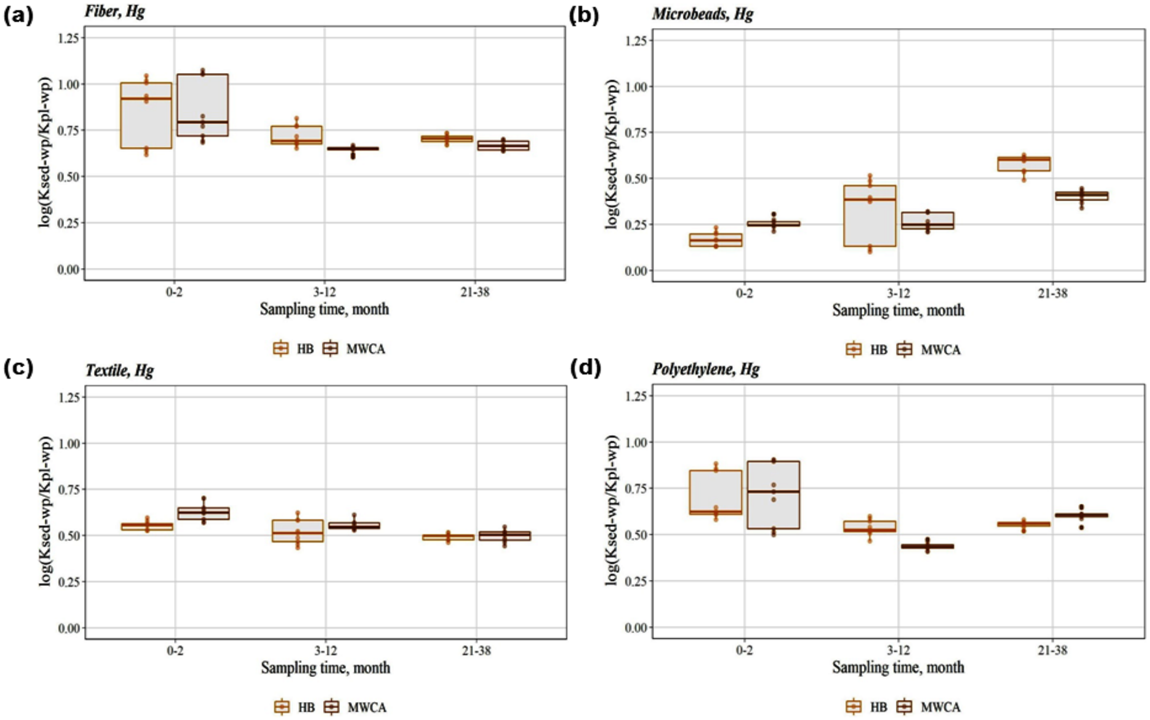


Figure 2.13. The value of log($K_{sed\text{-}wp}/K_{pl\text{-}wp}$) of Hg over time in micro-PETE (fibre) (a); micro-HDPE (microbeads) (b), macro-PETE (textile fabric) (c), and macro-HDPE (polyethylene chips) (d) deployed at HB (OM = 2.8%) and MWFCA (OM = 15.8%) study sites.

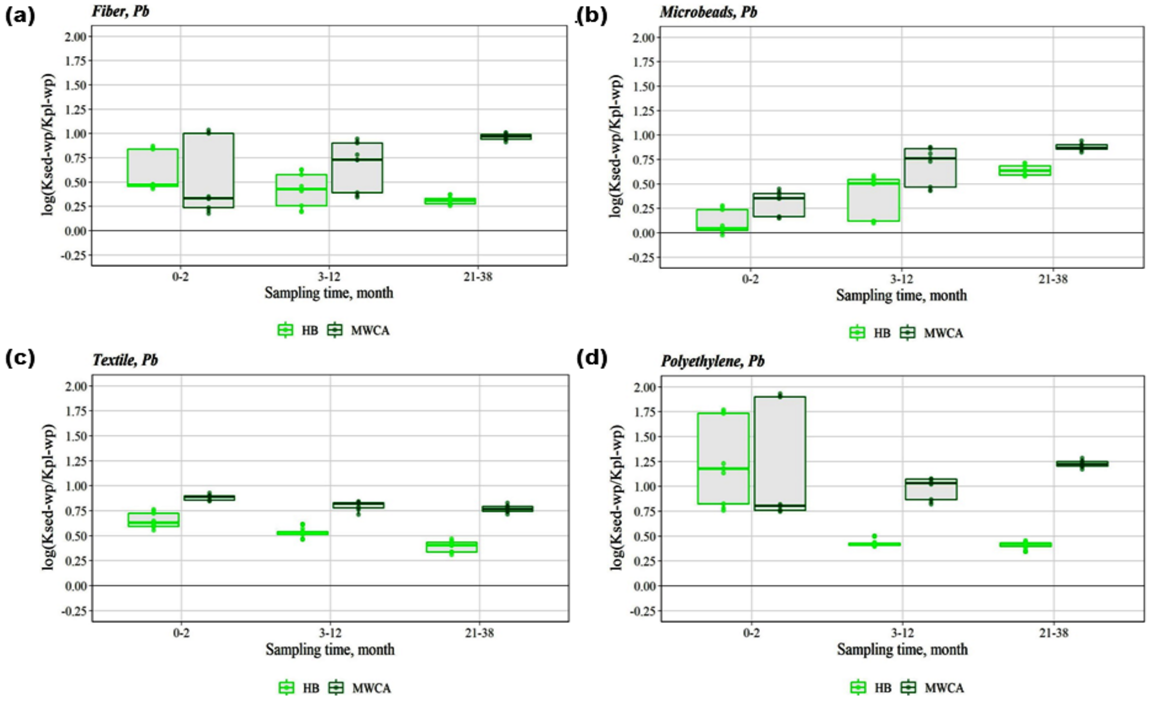


Figure 2.14. The value of log($K_{sed\text{-}wp}/K_{pl\text{-}wp}$) of Pb over time in micro-PETE (fibre) (a); micro-HDPE (microbeads) (b), macro-PETE (textile fabric) (c), and macro-HDPE (polyethylene chips) (d) deployed at HB (OM = 2.8%) and MWFCA (OM = 15.8%) study sites.

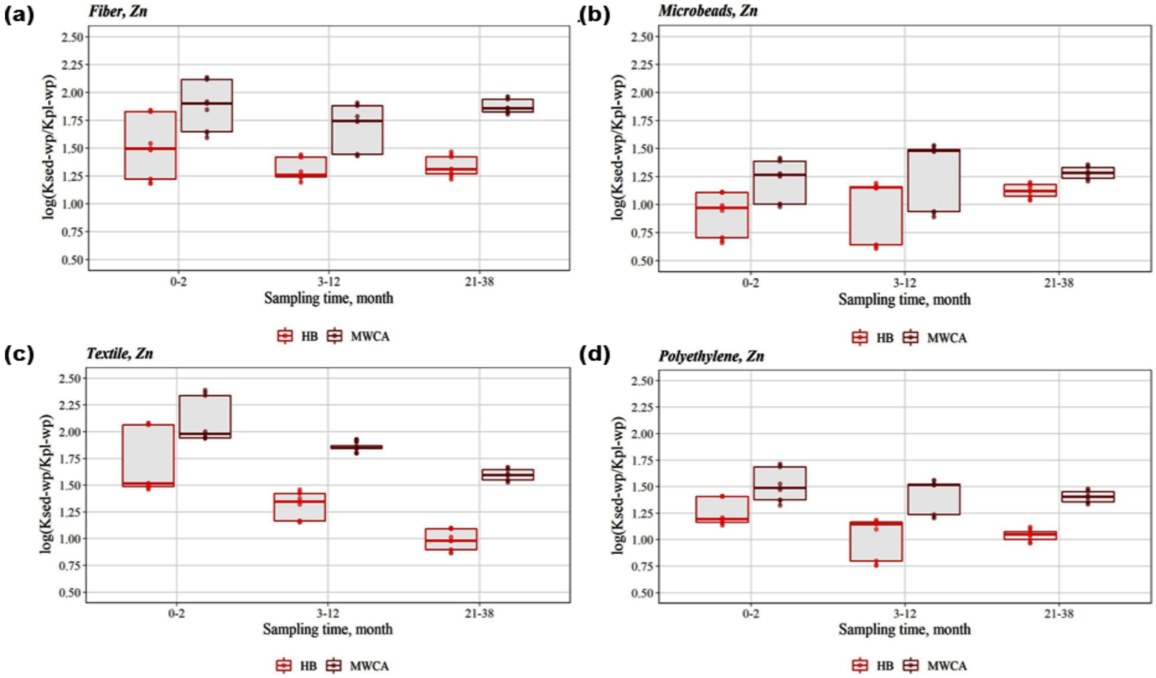


Figure 2.15. The value of log($K_{sed\text{-}wp}/K_{pl\text{-}wp}$) of Zn over time in micro-PETE (fibre) (a); micro-HDPE (microbeads) (b), macro-PETE (textile fabric) (c), and macro-HDPE (polyethylene chips) (d) deployed at HB (OM = 2.8%) and MWFCA (OM = 15.8%) study sites.

In relation to plastic particles, the value of log($K_{sed\text{-}wp}/K_{pl\text{-}wp}$) of Cd, Cu, Hg, Pb, and Zn increased over time for micro-HDPE (microbeads) in opposite to that for macro-PETE (textile fabric) when value of log ($K_{sed\text{-}wp}/K_{pl\text{-}wp}$) decreased over time (Figure 2.11b, c- 2.15b, c). Micro-PETE (fiber) and macro-HDPE (polyethylene chips) have the same trends in temporary variation of the log ($K_{sed\text{-}wp}/K_{pl\text{-}wp}$) of Cd, Cu, and Pb except of Hg and Zn (Figure 2.11a, d - 2.15a, d). These finding showed that the trace elements distribution was related to the polymer type and the size/shape of plastic particles which is also an important factor which is in accordance with (Wang et al., 2018a).

To estimate the degree of the influence of sediments properties (grain size distribution, organic matter content) on distribution of trace elements between intertidal sediments and plastic macro- and microparticles the logarithmical ratio of intertidal sediments-pore water equilibrium partitioning coefficient (($K_{sed\text{-}wp})_e$) to the polymer materials-pore water equilibrium partitioning coefficient (($K_{pl\text{-}wp})_e$) as log[$(K_{sed\text{-}wp})_e/(K_{pl\text{-}wp})_e$] of the trace elements for macro- and microparticles deployed at HB (OM = 2.8%) and MWFCA (OM = 15.8%) study sites were calculated (Equation 2.5-Equation 2.8) (Table 2.3). Additional data were derived from the test field experiments at Cates Park (Burrard Inlet) study site (OM = 1.7%) to estimate the large range of organic matter concentration in the intertidal sediments (Figure B3; Figure B4).

In general, at both study sites, low (HB, OM=2.8%) and high (MWFCA, OM=15.8%) in organic matter concentration, distribution of trace elements between intertidal sediments and macro- and microparticles were dependent on properties of sedimentary environments (Table 2.3.; Figure B3, B4). Importantly, that the value of log[$(K_{sed\text{-}wp})_e/(K_{pl\text{-}wp})_e$] of Cu, Zn, Pb, Cd, and Hg for macro-HDPE (polyethylene chips), macro-PETE (textile fabric), micro-HDPE (microbeads), and micro-PETE (fibres) increased with increasing of the organic matter content in sediments. The value of log[$(K_{sed\text{-}wp})_e/(K_{pl\text{-}wp})_e$] of Cu, Zn, Pb, Cd, and Hg for plastic macro- and microparticles of HDPE and PETE was grater in intertidal sediments high in organic matter content (MWFCA, OM=15.8%) compare to that in sediments low in organic matter content (Cates Park, OM = 1.7%) (Figure B3; B4). These finding can be explained as a phenomenon of competitive adsorption between plastic materials and organic particles in sediments which with accordance with results of the sorption/desorption study in the terrestrial environments performed by Gomez et al. (1999).

Dependence of trace elements distribution on percentages of organic matter in the intertidal sediments can be expressed by gradient $\Delta(\log[(K_{sed\text{-}wp})_e/(K_{pl\text{-}wp})_e])/\Delta OM$. The value of gradient $\Delta(\log[(K_{sed\text{-}wp})_e/(K_{pl\text{-}wp})_e])/\Delta OM$ of Cd, Cu, Hg, Pb, and Zn for macro- and microparticles of PETE and HDPE are following the order ($R^2 = 0.7860\text{-}0.98$):

(a) micro-PETE (fibre) (Figure B3a):
Cu (0.0498) > Pb (0.0439) > Zn (0.0425) > Cd (0.0287) > Hg (0.0151);
micro-HDPE (microbeads) (Figure B3b):
Cu (0.0442) > Zn (0.0281) > Pb (0.0222) > Hg (0.0090) > Cd (0.0037);
(b) macro-PETE (textile fabric) (Figure B4a):
Zn (0.0578) > Cu (0.0557) > Pb (0.0341) > Cd (0.0180) > Hg (0.0119);
macro-HDPE (polyethylene chips) (Figure B4b):
Pb (0.0535) > Cd (0.0512) > Cu (0.0486) > Zn (0.0302) > Hg (0.0090).

Hence in relation to the polymer type, partitioning of trace elements (Cu, Zn, Pb, Cd, and Hg) between sediments and plastic macro- and microparticles of PETE (Cu (0.0498); Zn (0.0578)) are more dependent on organic matter concentration in sediments compare to plastic particles of HDPE (Cu (0.0442); Pb (0.0535)). This suggest that PETE has a higher affinity and faster adsorption rate with most of trace elements (Cu, Zn, Pb, Cd, and Hg) which is in accordance with Alimi et al. (2018) and Wang et al. (2018a). In relation to the particle size, partitioning of trace elements (Cu, Zn, Pb, Cd, and Hg) between sediments and plastic microparticles of PETE (Cu (0.0557)) and HDPE (Cu (0.0486)) is more dependent on organic matter concentration in sediments compare to the microparticles (Cu (0.0498), PETE; Cu (0.0442), HDPE). In relation to the type of trace elements, partitioning of Cu, Zn, Pb between plastic macro- and microparticals and sediments have higher dependence on sedimentary characteristics compare to Cd, and Hg with lower dependence.

2.6. Conclusions

(1) Findings of the long-term field experiments indicated that sorption of trace elements (Cu, Zn, Pb, Cd, and Hg) by microplastics (fibre, PETE; microbeads, HDPE) and macroplastics (textile fabric, PETE; polyethylene chips, HDPE) is dependent on properties of intertidal sediments (grain size composition, organic matter content).

(2) The interaction between trace elements (Cd, Cu, Hg, Pb, and Zn) and plastic macro- and microparticles within contrasting intertidal sediment environments may include three periods, such as initial period of rapid adsorption, a period of reaching equilibrium state or slow adsorption, and a period of desorption or two of them, depending on the rate of trace elements accumulation by plastic particles and plastic materials degradation. The continuing degradation and aging of plastic materials under conditions of the intertidal sediments influences the process of trace elements-macro- and microplastic interactions.

(3) In the intertidal sedimentary environments plastic particle size can affect sorption rate, equilibrium concentration, and time of reaching equilibrium (Wang et al., 2018a). In addition, sorption rate of trace elements (Cu, Zn, Pb, Cd, and Hg) by macro- and microparticles of PETE and HDPE increased with decreasing particle size. This phenomenon may be due to increasing the specific surface area, resulting in an increase in adsorption sites on the particle surface and the amount of adsorbed trace elements is also increased (Ashton et al., 2010; Wang et al., 2016).

(4) In relation to the type of trace elements, sorption of Cu by plastic macro- and microparticles has higher dependence on sedimentary characteristics compare to sorption of Hg with strongly lower dependence. Sorption of Cd, Pb, and Zn by plastic macro- and microparticles of PETE and HDPE have moderated dependence on characteristics of intertidal sediments. The initial concentration of trace elements in sediments influences sorption rate and capacity of plastic particles (Wang et al., 2016)

(5) The distribution/partition of trace elements was related to the type of polymer and the size of plastic particles which is in accordance with (Wang et al., 2018a). The value of $\log[(K_{sed\text{-}wp})_e/(K_{pl\text{-}wp})_e]$ of Cu, Zn, Pb, Cd, and Hg for macro-HDPE (polyethylene chips), macro-PETE (textile fabric) and micro-HDPE (microbeads) and micro-PETE (fibres) increased with increasing of the organic matter concentration in sediments. These findings can be explained as a phenomenon of competitive adsorption between plastic materials and organic particles in sediments which with accordance with Gomez et al. (1999).

(6) We can conclude that in relation to plastic type, partitioning of Cu, Zn, Pb, Cd, and Hg between sediments and plastic macro- and microparticles of PETE are more

dependent on organic matter concentration in sediments compare to plastic particles of HDPE. This suggest that PETE has a higher affinity and faster adsorption rate with most of trace elements (Cu, Zn, Pb, Cd, and Hg) which is in accordance with Alimi et al. (2018) and Wang et al. (2018a). In relation to the plastic particle size, partitioning of Cu, Zn, Pb, Cd, and Hg between sediments and plastic macroparticles of PETE and HDPE is more dependent on organic matter concentration in sediments compare to the microparticles of PETE and HDPE.

(7) In relation to the type of trace elements, partitioning of Cu, Zn, Pb between plastic macro- and microparticles and sediments have higher dependence on sedimentary characteristics compare to Cd, and Hg with lower dependence on it.

References

Alava, J. J., Kazmiruk, N.T., Douglas, T., Schuerholz, G., Heath, B., Flemming, A. S., Bendell, L., & Drever, C. M. (2021). Occurrence and size distribution of microplastics in mudflat sediments of the Cowichan-Koksilah Estuary, Canada: A baseline for plastic particles contamination in an anthropogenic-influenced estuary*. Marine Pollution Bulletin.* 173. doi.org/10.1016/j.marpolbul.2021.113033

Alimi, O.S., Farner Budarz, J., Hernandez, L.M., & Tufenkji, N. (2018). Microplastics and nanoplastics in aquatic environments: aggregation, deposition, and enhanced contaminant transport. Environ. *Environmental Science & Technology. 52*(4), 1704-1724.

Andrady, A.L. (2011). Microplastics in the marine environment. *Marine Pollution Bulletin*. 62, 1596–1605.

Ashton, K., Holmes, L., & Turner, A. (2010). Association of metals with plastic production pellets in the marine environment. *Marine Pollution Bulletin*. 60. 2050-2055.

ASTM. (2000a). Standard guide for collection, storage, characterization, and manipulation of sediments for toxicological testing, E 1391-94. American Society for Testing and Materials, West Conshohocken, PA, USA.

ASTM. (2000b). Guide for core-sampling submerged unconsolidated sediments, D 4823 -95. American Society for Testing and Materials, West Conshohocken, PA, USA.

ASTM. (2000c). Standard test methods for moisture, ash, and organic matter of peat and other organic soils. Method D 2974-00. American Society for Testing and Materials. West Conshohocken, PA, USA.

Archived copy. (2020). Maplewood Flats Conservation Area. https://en.wikipedia.org/wiki/Maplewood_Flats_Conservation_Area

Atkinson., C. A, Jolley, D.F, & Simpson, S.L. (2007). Effect of overlying water pH, dissolved oxygen, salinity and sediment disturbances on metal release and sequestration from metal contaminated marine sediments. *Chemosphere*. *69*(9): 1428–1437.

Bakir, A., Rowland, S.J.,& Thompson, R.C. (2014). Enhanced desorption of persistent organic pollutants from microplastics under simulated physiological conditions. *Environmental Pollution.* 185, 16–23. doi.org/10.1016/j.envpol.2013.10.007.

Bakir, A., Desender, M., Wilkinson, T., Van Hoytema, N., Amos, R., Airahui, S., Graham, J., & Maes, T. (2020). Occurrence and abundance of meso and microplastics in sediment, surface waters, and marine biota from the South Pacific region. *Marine Pollution Bulletin,* 160. Article 111572. doi.org/10.1016/j.marpolbul.2020.111572

Batley, G. E., & Simpson, S. L. (2016). Sediment sampling, sample preparation and general analysis. In: S. L. Simpson & G. E. Batley (Eds.), *Sediment quality assessment: A practical guide* (2nd ed., 15-45). Clayton South, Vic.: CSIRO Publishing. http://hdl.handle.net/102.100.100/91038?index=1

Bendell, L. I. (2019). Baynes Sound, an ecologically and biologically sensitive area. In L.I. Bendell, P. Gallaugher, S. McKeachie & L. Wood (Eds.), *Stewarding the Sound; The challenge of managing sensitive ecosystems* (pp.25-40). CRC Press, Taylor and Francis Group, New York.

Bendell, L.I., Gallaugher, P., McKeachie S., & Wood, L. (2019). Solutions to the challenge of managing sensitive ecosystems. In L.I. Bendell, P. Gallaugher, S. McKeachie & L. Wood (Eds.), *Stewarding the Sound; The challenge of managing sensitive ecosystems* (pp.41-67). CRC Press, New York.

Burrard Inlet Environmental Action Program (BIEAP). (2011). Consolidated Environmental Management Plan for Burrard Inlet Update (CEMP). Burrard Inlet Environmental Action Program.(November 2011). Retrieved October 10, 2021, from https://waves-vagues.dfo-mpo.gc.ca/library-bibliotheque/218464_2012.pdf

Burrard Inlet Action Plan: A Tsleil-Waututh Perspective (BIAP). (2016). A science-based, First Nations-led initiative to improve the health of the Burrard Inlet ecosystem by 2025. Public Review Draft. (January 2016). The Burrard Inlet Action Plan: A Tsleil-Waututh Perspective. Kerr Wood Leidal Associates Ltd. (KWL). 128p. Retrieved October 15, 2020, from https://msbernabei.weebly.com/uploads/8/7/7/6/8776151/twn-burrard-inlet-action-plan-summary_1.pdf

Boucher, C., Morin, M., & Bendell, L.I. (2016). The influence of cosmetic microbeads on the sorptive behavior of cadmium and lead within intertidal sediments: a laboratory study. *Regional Studies in Marine Science.* 3, 1–7.

Brandon, J.A., Jones, W., & Ohman, M.D. (2019). Multidecadal increase in plastic particles in coastal ocean sediments. *Science Advances. 5*(9). DOI:10.1126/sciadv.aax0587.

Brennecke, D., Duarte, B., Paiva, F., Caçador, I., & Canning-Clode, J. (2016). Microplastics as vector for heavy metal contamination from the marine environment. *Estuarine, Coastal and Shelf Science.* 178, 189–195. https://doi.org/10.1016/j.ecss.2015.12.003

Browne, M.A., Galloway, T.S., & Thompson, R.C. (2010). Spatial patterns of plastic debris along estuarine shorelines. *Environmental Science & Technology. 44*(9), 3404–3409. https://doi.org/10.1021/es903784e.

Bull, J., & Freyman L. (2013). Status of Water Quality Objectives Attainment in Burrard Inlet and Tributaries 1990-2010. Report prepared for Burrard Inlet Environmental Action Program. July 2013. 56 p.

Carpenter, E.J., Anderson, S.J., Harvey, G.R., Miklas, H.P., & Peck, B.B. (1972). Polystyrene spherules in coastal waters. *Science*, 178, 749–750.

Carson, H.S., Colbert, S.L., Kaylor, M.J.,& McDermid, K.J. (2011). Small plastic debris changes water movement and heat transfer through beach sediments. *Marine Pollution Bulletin. 62*(8), 1708-1713.

CCME (Canadian Council of Ministers of the Environment). (1999). Canadian sediment quality guidelines for the protection of aquatic life: Mercury. In *Canadian Environmental Quality Guidelines*. Winnipeg.

CCME (Canadian Council of Ministers of the Environment). (2007a). Canadian water quality guidelines for the protection of aquatic life: Summary table. Updated September, 2007. In: *Canadian Environmental Quality Guidelines.* Winnipeg.

CCME (Canadian Council of Ministers of the Environment). (2007b). Canadian sediment quality guidelines for the protection of aquatic life: Summary table. Updated September, 2007. In: *Canadian environmental quality guidelines*. Winnipeg

Charles, J. & Ramkumaar, G.R. (2009). Qualitative analysis of high density polyethylene using FTIR spectroscopy. Asian Journal of Chemistry. 21(5). 4477- 4484.

Chen, X., Liang, J., Bao, L., Gu, X., Zha, S., & Chen, X. (2022).Competitive and cooperative sorption between triclosan and methyltriclosan on microplastics and soil. *Environmental Research*, 212. https://doi.org/10.1016/j.envres.2022.113548

Chubarenko, I., Esiukova, E., Bagaev, A., Isachenko, I., Demchenko, N., Zobkov, M., Efimova, I., Bagaeva, M., & Khatmullina, L. (2018). Behavior of microplastics in coastal zones. In: Zeng, E.Y. (Ed.). *Microplastic Contamination in Aquatic Environments* (pp. 175–223). Elsevier: Amsterdam, Netherlands. https://doi.org/10.1016/B978-0-12- 813747-5.00006-0. 2018.

Claessens, M., De Meester, S., Van Landuyt, L., De Clerck, K., & Janssen, C. R. (2011). Occurrence and distribution of microplastics in marine sediments along the Belgian coast. *Marine Pollution Bulletin, 62* (10), 2199–2204. DOI:10.1016/j.marpolbul.2011.06.030.

Cluzaud, M., Kazmiruk, T.N., Kazmiruk, V.D.& Bendell, L.I. (2015). Intertidal concentrations of microplastics and their influence on ammonium cycling as related to the shellfish industry. *Archives of Environmental Contamination and Toxicology. 68*(4). DOI: 10.1007/s00244-015-0156-5

Coates, J. (2006). Interpretation of infrared spectra, a practical approach. In R.A. Meyers (Ed.), *Encyclopedia of Analytical Chemistry* (pp. 10815–10837). John Wiley & Sons Ltd, Chichester. https://doi.org/10.1002/9780470027318.a5606.

Cole, M., Lindeque, P., Halsband, C. & Galloway, T.S. (2011). Microplastics as contaminants in the marine environment: a review. *Marine Pollution Bulletin*, 62(12), 2588–2597.

Davidson, L. W. (1979).On the physical oceanography of Burrard Inlet and Indian Arm, British Columbia. (MSc thesis, University of British Columbia, Canada). 156 p.

Desforges, J.P.W., Galbraith M., Dangerfield, N. & Ross, P.S. (2014). Widespread distribution of microplastics in subsurface seawater in the NE Pacific Ocean. *Marine Pollution Bulletin,* 79, 94–99.

DFO. (2013). Evaluation of proposed ecologically and biologically significant areas in marine waters of British Columbia. DFO. Canadian Science Advisory Secretariat Science Advisory. Report 2012/075. Pacific Region. 21p. Retrieved October 10, 2021, from https://psf.ca/wp-content/uploads/2021/10/Download-PDF841-1.pdf

Endo, S., Takizawa, R., Okuda, K., Takada, H., Chiba, K., Kanehiro, H., Ogi, H., Yamashita, R., & Date, T. (2005). Concentration of polychlorinated biphenyls (PCBs) in beached resin pellets: variability among individual particles and regional differences. *Marine Pollution Bulletin*. 50, 1103-1114.

Frias, J.P.G.L., Sobral, P., & Ferreira, A.M. (2010). Organic pollutants in microplastics from two beaches of the Portuguese coast. Marine Pollution Bulletin, 60, 1988–1992. doi.org/ 10.1016/j.marpolbul.2010.07.030

Frias, J., Pagter, E., Nash, R., O'Connor, I., Carretero, O., & Filgueiras, G. (2018). Standardised protocol for monitoring microplastics in sediments. In *JPI-Oceans BASEMAN project. Technical Report: May 2018.* DOI:10.13140/RG.2.2.36256.89601/1. http://www.jpi-oceans.eu/baseman/main-page.

Frias, J.P., & Nash, R. (2019). Microplastics: finding a consensus on the definition. *Marine Pollution Bulletin.* 138, 145–147.

GESAMP (Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection). Kershaw, P.J. (Ed.). (2015). Sources, fate and effects of microplastics in the marine environment: a global assessment. *GESAMP Report and Studies.* No. 90, 96 p. https://ec.europa.eu/environment/marine/goodnvironmental-status/descriptor-10/pdf/GESAMP_microplastics%20full%20study.pdf

GESAMP (Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection). Kershaw, P.J., & Rochman, C.M. (Eds). (2016). Sources, fate and effects of microplastics in the marine environment: part two of a global assessment. *GESAMP Report and Studies.* No. 93, 220 p. http://www.gesamp.org/site/assets/files/1275/sources-fate-and-effects-of-microplastics-in-the-marine-environment-part-2-of-a-global-assessment-en.pdf

GESAMP (Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection). P.J. Kershaw, B. Carney Almroth, P. Villarrubia-Gómez, A.A. Koelmans, & T. Gouin (Eds.). (2020). Proceedings of the GESAMP International Workshop on assessing the risks associated with plastics and microplastics in the marine environment. *GESAMP Report and Studies.* No.103, 68 p. http://www.gesamp.org/publications/gesamp-international-workshop-on assessing-the-risks-associated-with-plastics-and-microplastics-in-the-marine-environment

Gomez, C. & Bosecker, K. (1999). Leaching heavy metals from contaminated soil using Thiobacillus ferrooxidans or Thiobacillus thiooxidans, *Geomicrobiology Journal*. 16. 233–244. https://doi.org/10.1080/014904599270613

Goyette, D., & J. Boyd. (1989). Distribution and environmental impact of selected benthic contaminants in Vancouver Harbour, British Columbia, 1985–1987. Regional Program Report 89-02.Environment Canada, Conservation and Protection, Environmental Protection, Pacific and Yukon Region. (October 1989). https://publications.gc.ca/site/eng/9.880338/publication.html

Gregory, M.R. (1978). Accumulation and distribution of virgin plastic granules on New Zealand beaches. *New Zealand Journal of Marine and Freshwater Research, 12*(4). 399-414. http://dx.doi.org/10.1080/ 00288330.1978.9515768.

Gulmine, J. V., Janissek, P. R., Heise, H. M., & Akcelrud, L. (2002). Polyethylene characterization by FTIR. *Polymer Testing*, 21(5), 557–563. https://doi.org/10.1016/S0142-9418(01)00124-6.

Guo, X.T., Pang, J.W., Chen, S.Y., & Jia, H.Z. (2018). Sorption properties of tylosin on four different microplastics. *Chemosphere,* 209, 240–245.

Guo, X., Hu, G., Fan, X., & Jia, H. (2020). Sorption properties of cadmium on microplastics: The common practice experiment and A two-dimensional correlation spectroscopic study. *Ecotoxicology and Environmental Safety*. 190, 110-118. https://doi.org/10.1016/j.ecoenv.2019.110118.

Hartmann, N.B., Rist, S., Bodin, J., Jensen, L.H., Schmidt, S.N., Mayer, P., Meibom, A., & Baun, A. (2017). Microplastics as vectors for environmental contaminants: exploring sorption, desorption, and transfer to biota. *Integrated Environmental Assessment and Management. 13*(3), 488-493.

Harris, P. T. (2020). The fate of microplastic in marine sedimentary environments: A review and Synthesis. *Marine Pollution Bulletin*.158. 1-25. Article 111398. https://doi.org/10.1016/j.marpolbul.2020.111398.

Harrison, J.P., Schratzberger, M., Sapp, M. & Osborn, A.M. (2014). Rapid bacterial colonization of low-density polyethylene microplastics in coastal sediment microcosms. *BMC Microbiology*. 14, 232. DOI:10.1186/s12866-014-0232-4.

Hecht, S.A., Baldwin, D.H., Mebane, C.A., Hawkes, T., Gross, S.J., & Scholz. N.L. (2007). An overview of sensory effects on juvenile salmonids exposed to dissolved copper: Applying a benchmark concentration approach to evaluate sublethal neurobehavioral toxicity. U.S. Department of Commerce, NOAA Technical Memorandum. NMFS-NWFSC-83, 39 p. http://www.nwfsc.noaa.gov.

Hermsen E., Mintenig S.M., Besseling E., & Koelmans A.A. (2018). Quality criteria for the analysis of microplastic in biota samples: a critical review. *Environmental Science & Technology*. *52*(18), 10230–10240.

Hidalgo-Ruz, V., Gutow, L., Thompson, R.C., & Thiel, M. 2012. Microplastics in the Marine Environment: A Review of the Methods Used for Identification and Quantification. *Environmental Science & Technology*, 46, 3060-3075. DOI:dx.doi.org/10.1021/es2031505

Holmes, L.A., Turner, A., & Thompson, R.C. (2012). Adsorption of trace metals to plastic resin pellets in the marine environment. *Environmental Pollution*.160, 42–48.

Holmes, L.A. (2013). Interactions of Trace Metals with Plastic Production Pellets in the Marine Environment. (PhD Thesis, University of Plymouth, UK). 199 p.

Holmes, L.A., Turner, A., & Thompson, R.C. (2014). Interactions between trace metals and plastic production pellets under estuarine conditions. *Marine Chemistry*. 167, 25-32.

Hummel, D.O. (2002). Atlas of plastics additives: analysis by spectrometric methods. Springer: Verlag, Berlin, Heidelberg. 566 p.

Jiang, P., Zhao, S, Zhu, L., & Li, D. (2018). Microplastic-associated bacterial assemblages in the intertidal zone of the Yangtze Estuary. *Science of the Total Environment*. 624. 48–54.

Johannessen, S.C., Macdonald, R.W. & Magnus Eek, K. (2005). Historical trends in mercury sedimentation and mixing in the Strait of Georgia, Canada. *Environmental Science and Technology*, 39, 4361–4368.

Kazmiruk, T.N., Kazmiruk, V.D., & Bendell, L.I. (2016). Trace metals in urban estuaries; implication for remediation. 39th Annual Meeting Pacific Estuarine Research Society, Cheakamus Centre, Brackendale, Canada, March 2016.

Kazmiruk, T.N., Kazmiruk, V.D., & Bendell, L.I. (2017). Abundance and distribution of microplastics within surface sediments of a key shellfish growing region of Canada, The 2017 CGU-CSAFM Joint Meeting, University of British Columbia, Vancouver, Canada, May 28-31, 2017.

Kazmiruk, T.N. & Bendell, L.I. (2018). Occurrence of microplastics in an intertidal ecosystem; Baynes Sound a key shellfish growing region of Canada. The Sixth International Marine Debris Conference (6IMDC) 12-16 March 2018, San Diego, United States of America. 2018.

Kazmiruk, N. T., Kazmiruk, V.D. & Bendell, L.I. (2018). Abundance and distribution of microplastics within surface sediments of a key shellfish growing region of Canada . *PLoS ONE, 13* (5). https://doi.org/10.1371/journal.pone.0196005.

Kazmiruk, T.N. & Bendell, L.I. (2020). Sorption of trace elements (Cu, Zn, Pb, Cd and Hg) by microplastics within marine intertidal sediments; a laboratory and field approach. 2020 Salish Sea Ecosystem Virtual Conference. 21-22 April 2020, Vancouver, Canada.

Kleinteich, J., Seidensticker, S., Marggrander, N., & Zarfl, C. (2018). Microplastics reduce short-term effects of environmental contaminants. Part II: polyethylene particles decrease the effect of polycyclic aromatic hydrocarbons on microorganisms. *International Journal of Environmental Research and Public Health, 15*(2), 287. doi:10.3390/ijerph15020287.

Koelmans, A.A., Nor, N.H.M., Hermsen, E., Kooi, M., Mintenig, S.M., & De France, J. (2019). Microplastics in freshwaters and drinking water: critical review and assessment of data quality. *Water Research. 15*(155), 410–422. https://doi.org/10.1016/j.watres.2019.02.054

Lechthaler, S., Waldschläger, K., Stauch, G., & Schüttrump, H. (2020). The way of macroplastic through the environment: Review. *Environments, 7*(73). doi:10.3390/environments7100073

Levings, C.D., Stein, J.E., Stehr, C.M., & Samis, S.C. (2004). Introduction to the PICES practical workshop: objectives, overview of the study area, and projects conducted by the participants. *Marine Environmental Research*. 57. 3-18.

Li, Y., Li, M., Li, Z., Yang, L., & Liu, X. (2019). Effects of particle size and solution chemistry on triclosan sorption on polystyrene microplastic. *Chemosphere*. 231, 308–314. https://doi.org/10.1016/j.chemosphere.2019.05.116

Lindsay, W.L. (1979).Chemical Equilibrium in Soils. John Wiley & Sons, New York.

Lots, F.A.E., Behrens, P., Vijver, M.G., Horton, A.A., & Bosker, T. (2017). A large-scale investigation of microplastic contamination: abundance and characteristics of microplastics in European beach sediment. *Marine Pollution Bulletin.123*(1-2), 219-226. doi:10.1016/j.marpolbul.2017.08.057.

Mato, Y., Isobe, T., Takada, H., Kanehiro, H., Ohtake, C., & Kaminuma, T. (2001). Plastic resin pellets as a transport medium for toxic chemicals in the marine environment. *Environmental Science & Technology*. 35, 318-324.

Maršić-Lučić, J., Lušić, J., Tutman, P., Bojanić, V. D., Šiljić, J., & Pribudić, J. (2018). Levels of trace metals on microplastic particles in beach sediments of the island of Vis, Adriatic Sea, Croatia. *Marine Pollution Bulletin,* 137, 231-236. doi:10.1016/j.marpolbul.2018.10.027.

MSFD GES Technical Subgroup on Marine Litter. (2011). MSFD TSG Marine Litter Report EUR 25009 EN. European Union. Luxembourg. 93p.

Munier, B. & Bendell, L.I. (2018). Macro and micro plastics sorb and desorb metals and act as a point source of trace metals to coastal ecosystems. PLoS ONE. 13(2), Article e0191759. https://doi.org/10.1371/journal.pone.0191759

Murray, H. H. (1999). Applied clay mineralogy today and tomorrow. *Clay Minerals*. 34, 39-49.

Mudroch, A., Azcue, J.M., & Mudroch, P. (1997). Manual of Physico-Chemical Analysis of Aquatic Sediments. Lewis Publishers, New York, NY.

Ojha, N., Pradhan, N., Singh, S., Barla, A., Shrivastava, A., & Khatua, P., et al. (2017). Evaluation of HDPE and LDPE degradation by fungus, implemented by statistical optimization. *Scientific Reports, (*January 7), https://doi.org/10.1038/srep39515.

Pagès, P. (2008). Characterization of polymer materials using FT-IR and DSC techniques. https://ruc.udc.es/dspace/bitstream/handle/2183/11499/CC-80%20art%208.pdf

Plastics Europe. (2015). Plastics - the Facts 2014. An Analysis of European Plastics Production, Demand and Waste Data for 2014. In: *Plastics Europe AISBL (Association of Plastic Manufacturers)*. Brussels. Belgium. https://plasticseurope.org/wp-content/uploads/2021/10/2015-Plastics-the-facts.pdf

Plastic Europe (2017). Plastics -the Facts 2017. An Analysis of European Latest Plastics Production, Demand and Waste Data for 2017. In *Plastics Europe AISBL (Association of Plastics Manufacturers)*. Brussels, Belgium. https://www.plasticseurope.org/application/files/5715/1717/4180/Plastics_the_facts_2017_FINAL_for_website_one_page.pdf.

R Core Team (2021). R: A language and environment for statistical computing. R Foundation 771 for Statistical Computing, Vienna, Austria. https://www.R-project.org/.

Report of Working Group on Emerging Topics in Marine Pollution. (2020). In J.J, Alava, O.N. Lukyanova, P.S. Ross,W.J. Shim (Eds.) *PICES Scientific Reports*. No. 56, 161 pg. Retrieved January 10, 2021, from https://meetings.pices.int/publications/scientific-reports/Report56/Rpt56.pdf

Robin, R.S., Karthik, R., Mugilarasan, M., & Ramesh, R. (2020). Holistic assessment of microplastics in various coastal environmental matrices, southwest coast of India. *Science of the Total Environment*. 703. https://doi.org/10.1016/j.scitotenv.2019.134947

Rochman, C.M., Hentschel, B.T., & Teh, S.J. (2014). Long-term sorption of metals is similar among plastic types: implications for plastic debris in aquatic environments. *PLoS One,* 9, Article e85433. doi:10.1371/journal.pone.0085433.

Stock, F., Kochleus, C., Baensch-Baltruscha, B., Brennholt, N., & Reifferscheid, G. (2019). Sampling techniques and preparation methods for microplastic analyses in the aquatic environment – A review *Trends in Analytical Chemistry.113* (2), 84-92. DOI: 10.1016/j.trac.2019.01.014

Sutherland D. (2004). Water Quality Objectives Attainment Monitoring in Burrard Inlet in 2002. Environmental Quality Section, Ministry of Water, Land and Air Protection. (July 2004). Retrieved April 10, 2019, from https://www2.gov.bc.ca/assets/gov/environment/air-land-water/water/waterquality/wqgs-wqos/wq-attainment-report-archive/sechelt_inletattainment2002.pdf.

Teuten, E.L., Rowland, S.J., Galloway, T.S., & Thompson, R.C. (2007). Potential for plastics to transport hydrophobic contaminants. *Environmental Science & Technology,* 41, 7759–7764. https://doi.org/10.1021/es071737s.

Thomson, R. E. (1981). Oceanography of the British Columbia Coast. *Canadian Special Publication of Fisheries and Aquatic Sciences*, 156.

Thompson, R. C., Olsen, Y., Mitchell, R.P., Davis A, Rowland, S. J., John, A. W. G., McGonigle, D., & Russell, A. E. (2004). Lost at sea: where is all the plastic? *Science*, 304, 838‑844.

Tourinho, P. S., Kocí, V., Loureiro, S., & van Gestel, C. A. M. (2019). Partitioning of chemical contaminants to microplastics: Sorption mechanisms, environmental distribution and effects on toxicity and bioaccumulation. *Environmental Pollution,* 252(Pt B), 1246-1256. doi:10.1016/j.envpol.2019.06.030.

Turner, A., & Holmes, L.A. (2015). Adsorption of trace metals by microplastic pellets in fresh water. *Environmental Chemistry*, 12 (5), 600-610.

Tylkowski, B., Marturano, V., Cerruti, P., & Ambrogi, V. (2017). Polymer additives. *Physical Sciences Reviews, 2*(6). DOI:10.1515/psr-2016-0130

US EPA. (2012). Understanding variation in partition coefficient, Kd, values. United States Environmental Protection Agency. Available online: http://www.epa.gov/radiation/cleanup/402-r-99-004.html.

UNEP (United Nations Environment Programme). (2005). Toolkit for identification and quantification of mercury releases. Pilot draft (November, 2005). UNEP Chemicals Branch, Geneva, Switzerland. Available online: http://www.chem.unep.ch/mercury/Guidance-trainingmaterials.htm.

UNEP (United Nations Environment Programme). (2013). Global mercury assessment 2013: Sources, emissions, releases and environmental transport. UNEP Chemicals Branch, Geneva, Switzerland.

van Sebille, E. (2015). The oceans' accumulating plastic garbage. *Physics Today. 68*(2), 60-61. DOI: 10.1063/PT.3.2697

Veerasingam, S., Al-Khayat, J., Aboobacker V. M, & Vethamony, P. (2020). Sources, spatial distribution and characteristics of marine litter along the west coast of Qatar. *Marine Pollution Bulletin*, 159. DOI:10.1016/j.marpolbul.2020.111478

Veerasingam, S., Ranjani, M., Venkatachalapathy, R., Bagaev, A., Mukhanov, V., Litvinyuk, D., Mugilarasan, M., Gurumoorthi, K., Guganathan, L., Aboobacker, V.M., & Vethamony, P. (2021). Contributions of Fourier transform infrared spectroscopy in microplastic pollution research: A review. *Critical Reviews in Environmental Science and Technology*, 51, 2681–2743. https://doi.org/10.1080/10643389.2020.1807450

Velzeboer, I., Kwadijk, C., & Koelmans, A. (2014). Strong sorption of PCBs to nanoplastics, microplastics, carbon nanotubes, and fullerenes. *Environmental Science and Technology, 48*(9). DOI: 10.1021/es405721v

Vethaak, D. A. & Leslie, H.A. (2016). Plastic debris is a human health issue. *Environmental Science and Technology*. 50(13). 6825-6826. https://doi.org/10.1021/acs.est.6b02569 PMID: 27331860

Vianello, A., Boldrin, A., Guerriero, P., Moschino, V., Rella, R., Sturaro, A., & Da Ros, L. (2013). Microplastic particles in sediments of Lagoon of Venice, Italy: first observations on occurrence, spatial patterns and identification. *Estuarine, Coastal and Shelf Science,* 130, 54–61. https://doi.org/10.1016/j.ecss.2013.03.022.

Wang, Y., Li, X., & Zhang, D. (2016) Study of methods for extracting microplastics in sediments. *World Sci-Tech R & D*, 1,105–109.

Wang, J., Tan, Z., Peng, J., Qiu, Q.,& Li, M. (2016). The behaviors of microplastics in the marine environment: Review. *Marine Environmental Research*, 113, 7-17.

Wang, F., Wong, C.S., Chen, D., Lu, X., & Zeng, E. Y. (2018a). Interaction of toxic chemicals with microplastics: A critical review. *Water Research,*139, 208-219.

Wang, W., & Wang, J. (2018b). Investigation of microplastics in aquatic environments: an overview of the methods used, from field sampling to laboratory analysis. TrAC Trends in Analytical Chemistry, 108,195–202.

Xu, B., Liu, F., Brookes, P.C., & Xu, J. (2018b). Microplastics play a minor role in tetracycline sorption in the presence of dissolved organic matter. *Environmental Pollution*. 240, 87–94. https://doi.org/10.1016/j.envpol.2018.04.113.

Yu, X., Peng, J., Wang, J., Wang, K., & Bao, S. (2016). Occurrence of microplastics in the beach sand of the Chinese inner sea: the Bohai Sea. *Environmental Pollution*. 214, 722-730.

Zhang,T., Jiang, B., Xing, Y., Ya, H., Lv, M., & Wang, X. (2022). Current status of microplastics pollution in the aquatic environment, interaction with other pollutants, and effects on aquatic organisms. *Environmental Science and Pollution Research,*29,16830-16859.https://doi.org/10.1007/s11356-022-18504-8

Zhang, Y. T., Chen, M., Hea, S., Fang, C., Chen, M., Li, D., Wue, D., Chernick M, Hinton, D. E., Bo, J., Xie, L., Mua, J. (2021). Microplastics decrease the toxicity of triphenyl phosphate (TPhP) in the marine medaka (Oryzias melastigma) larvae. *Science of the Total Environment, 1*(763), 143040. doi:10.1016/j.scitotenv.2020.143040.

Chapter 3.

The influence of temperature on the sorption of trace elements (Cd, Cu, Pb, and Zn) by plastic macro- and microparticles within intertidal sediments; a laboratory study

3.1. Introduction

Several physicochemical factors that are associated with properties of plastic macro- and microparticles (e. g., type, shape, size, plastic materials) and characteristics of the marine environmental compartments (e. g., pH, salinity, temperature, hydrodynamic conditions, presence of organic matter, sediment quality parameters) have been shown to affect the sorption/desorption of different contaminants, including trace elements (Holms et al., 2012; Holms, 2013; Holms et al., 2014; Performance Evaluation, 2007; Rochman et al., 2013; Rochman et al., 2014; Wang et al., 2018). However, our understanding on how these factors influence the process of sorption/desorption of different contaminants by plastic macro- and microparticles within marine environmental compartments is still largely limited.

To date macro- and microplastics study on the sorption of trace elements have been conducted as field experiments in the aquatic environments, with little attention given to the temperature as a factor influencing the sorption behaviour of the plastic particles (Holms et al., 2012; Holms et al., 2014; Rochman et al., 2013; Rochman et al., 2014; Wang et al., 2018). Only a few studies have addressed how temperature may affect the sorption characteristics of trace metals by plastic particles and the results of these studies are contradictory. For example, in the study conducted by Li et al. (2019) the process of sorption on polystyrene (PS) microparticles was investigated as a function of temperature, pH, and ionic strength of trace elements (Cu(II) and Zn(II)) concentrations through batch (aqua) incubation experiments (Li et al., 2019). Results show that sorption on polystyrene microparticles was pH-dependent, while temperature and ionic strength are having no significant influence on trace elements sorption. In contrast, temperature-dependent behaviour of plastic nanoparticles has been reported for a typical range of groundwater temperatures (4.0–20.0°C) (Alimi et al., 2020).

Given this lack of research on the role of temperature on influencing the sorption characteristics of metals onto micro- and macroplastic the objectives of this study were two-fold: 1) under controlled laboratory conditions determine the role of environmentally realistic temperature conditions on the sorption of trace elements onto plastic macro- and microparticles (PETE and HDEP) and 2) through such experiments, extrapolate our findings to intertidal sedimentary environments under field conditions. Such extrapolations will provide some insight as to how temperature may affect trace elements-plastic particles interactions under conditions of marine intertidal sedimentary environments. This is to our knowledge the first study to assess the interactions between trace elements and plastic macro- and microparticles in the intertidal sediments under conditions of different constant temperature regime. In addition, these results will help our understanding the impact of environmental factors on sorption/desorption of contaminants to different plastic materials serving as a useful baseline for further studies especially of their reversible (physical) mechanisms.

3.2. Materials and methods

3.2.1. Sedimentary environments selected for the study

Sediments were sampled at the same two sites where the long-term (up to 38 months) field experiments were performed and were used for the controlled laboratory-based experiments: A) Horseshoe Bay (gravel, sand, organic matter: 5-15%); and B) Maplewood Flats Conservation Area (sand, mud, organic matter: 15-50%) (Figure 2.1; Table 2.1). An overview of the sampling stations and characteristics of intertidal sediments is given in the Chapter 2.

3.2.2. Plastic materials and macro- and microparticles selected for the study

The types of polymeric materials and shapes of polymeric particles are the same that were used in the long-term (38 months) field experiments (Chapter 2) in order to receive comparable data obtained from the field and laboratory experiments. An overview of the plastic materials and macro- and microparticles selected for the laboratory-based study is given in section 2.2.2., Chapter 2 (Figure 2.5).

3.2.3. Trace elements selected for the study

The types of trace elements (Cd, Cu, Pb, and Zn) selected for the controlled laboratory-based study are the same that were used in the long-term (38 months) field experiments (Chapter 2) in order to receive comparable data obtained from the field and laboratory experiments. An overview of trace elements selected for the laboratory-based study is given in section 2.2.3, Chapter 2.

3.2.4. Laboratory experiments setup

To increase environmental relevance, the temperature conditions were chosen on the base of the analysis of temperature amplitude and annual temperature range relevant to the intertidal area of Burrard Inlet (British Columbia, Canada) where our field study was performed (Figure 2.1). To simulate different scenarios for sorption of trace elements (Cd, Cu, Pb, and Zn) by a particular type of plastic macro- and microparticles under conditions of different temperature, long-term (up to 28 months) controlled laboratory-based experiments with constant temperature of T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C were performed.

In the laboratory-based experiments 6 (3 constant temperatures x 2 sediment types) containers (plastic boxes 45cm x 25 cm x 25 cm) with glass-covered sides were used (Figure 3.1). Containers were filled with sea water and sediments (16-18 cm layer) taken from the surface layer (15 cm) of the intertidal sediments at the same study sites (Horseshoe Bay (HB) and Maplewood Flats Conservation Area (MWFCA)) where the long-term field experiments were implemented (Figure 2.1a-c). At each container, triplicate mesh bags (0.063 µm), which contained macroplastic in the shape of polyethylene chips (high-density polyethylene (HDPE)) and textile fabric (polyethylene terephthalate /polyester (PETE)) and microplastic in the form of microbeads (high-density polyethylene (HDPE)) and fibers (polyethylene terephthalate /polyester (PETE)) were buried into the upper 10 cm layer of sediment at each experimental unit (Figure 3.1). All sorption experiments were undertaken in three replicates, and the average values are reported here.

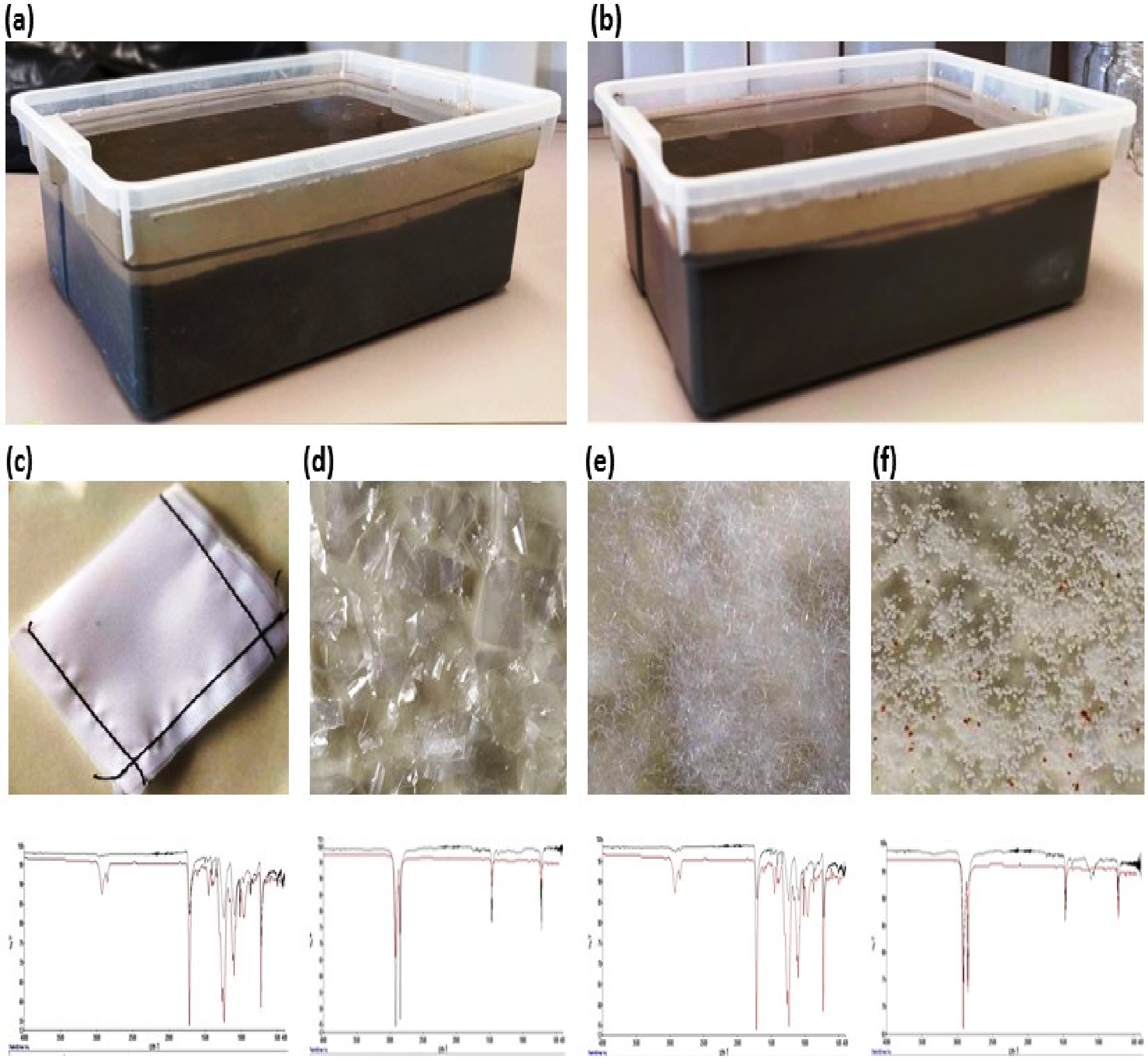


Figure 3.1. **Photo images of experimental units (a, b) and plastic macroparticles (textile fabric, PETE (c) and polyethylene chips, HDPE (d)) and microparticles (fiber, PETE (e) and microbeads, HDPE (f)) used in the laboratory-based study.**

Note: Experimental units (plastic boxes (45cm x 25 cm x 25 cm) with glass-covered sides) were filled with sea water and sediments (l6-18 cm layer) taken from the surface layer (15-25 cm) of the intertidal sediments at HB (a) and MWFCA (b) study sites where the long-term field experiments were implemented. The FTIR spectrums of the plastic macro- and microparticles are provided at the bottom of their photo images.

3.2.5. Sampling methodology and quality control criteria (QA/QC)

The date and time of the sampling during controlled laboratory-based experiments were determined as the same with the date and time of sampling at the sites of field experiments. The samples of water, sediments and experimental macro- and microplastic were collected on the 1 day of experiments and then at the time of residence t = 1, 2, 3 , 8, 12, and 21 months respectively after deployment of plastic materials into sediments to observe sorption of trace elements by plastic macro- and microparticles under condition of different constant temperatures. Water, sediments, and plastic macro- and microparticles were sampled at the same time as in the field experiments in order to receive comparable data (field and laboratory experiments).

Water samples. Water samples were collected in triplicated from each experimental unit (container). Water was sampled from the surface layer using syringe cores (diameter: 2.6 cm). Water samples were filtered immediately after sampling through 0.45 µm Whatman cellulose nitrate filters using a vacuum filter unit. The water samples (filtrates) were frozen (T= -5.0°C) and stored in the dark until further analysis.

Sediment samples. During the laboratory experiments sediments were collected in triplicated from each container. Sediments were sampled from surface layer using syringe cores (diameter: 2.6 cm). Collected sediment samples were placed into plastic zip lock bags and then were frozen (T= -15.0°C) and stored in the dark until further analysis.

Samples of plastic macro- and microparticles. At each experimental container triplicate mesh bags (textile fabric, PETE) with samples of plastic macroparticles (polyethylene chips, HDPE) and microparticles (microbeads, HDPE; fibres PETE) were collected. Samples were taken according to the general methodology of laboratory sampling with some our modifications to the existing protocols (Chapter 2).

Quality control criteria (QA/QC). During the long-term (21 months) laboratory experiments at each time of sampling we had a paired background contamination control. At each sampling time, prepared clean Petri Dish and three empty glass beakers was placed beside the experimental unit and opened during sample collection (plastic macro- and microparticles, water, and sediments) and closed simultaneously with the sample plastic zip lock bags.

3.2.6. Laboratory measurements and quality control criteria (QA/QC)

The laboratory analysis of water, sediments, and samples of plastic macro- and microparticles were conducted as outlined in sections 2.3.3 and 2.3.4 Chapter 2.

3.2.7. Data analysis

Data analysis

After laboratory sampling and measurements 120 variables ((4 plastic particles + sediments) x 4 trace elements x 3 temperature x 2 sediment types = 120) were created and analyzed. For the temporal and absolute comparison of trace elements contents in water, sediments and plastic macro- and microparticles, the concentration of trace elements was calculated as unit µg per g water, sediment, and plastic particles dry weight (µg/g). Basic statistical analysis of the data were performed in Microsoft Excel 2010 (Microsoft; WA, USA), Statistical Package software "IBM SPSS Statistics" (IBM SPSS Statistics 19.0, IBM, Amonk, NY) (means, t-test, ANOVA, correlation, regression), R (R Core Team, 2021), and RStudio (RStudio Inc.; MA, USA).

Sediment data (grain size, OM, Cd, Cu, Pb, and Zn) was first tested for normal distribution (Shapiro–Wilk) and equal variances prior to the application of a two-way ANOVA with sediments/temperature and time as the two factors. Plastic macro- and microplastic data (Cd, Cu, Pb, and Zn) was first tested for normal distribution (Shapiro–Wilk) and equal variances prior to the application of a two-way ANOVA for each of 2 plastic microparticles (HDPE and PETE) and 2 plastic macroparticles (HDPE and PETE) with sediments/temperature and time as the two factors. A further 2-way ANOVA was also applied to determine if within each sediments, sorption of trace elements by plastic macro- and microparticles were dependent on plastic type, temperature, and time. Data were generally normally distributed with equal variances (Shapiro Wilk Test), so data were not transformed for statistical analysis. Statistical analysis was performed using Sigma Plot 12 © and significance of all tests was set at p-value <0.05.

Data visualization, tests for normal distribution (Shapiro–Wilk normality test), linear regression analyses, Spearman correlation analyses, and variance analyses (ANOVA) were conducted with the standard R-packages as well. Histograms and boxplots (represent the distribution of the data) were used to estimate the normality of the data distribution. Differences in sorption characteristics (trace elements concentrations, partitioning coefficients) among type of sediments and temperatures versus plastic macro and microparticles and time were tested with linear models (lm) ($p < 0.05$) using R (R Core Team, 2021). We used linear regression models (lm) with sediments, temperature, and polymeric type as fixed factors to test for temporal variations in concentration of trace elements (Cd, Cu, Pb, and Zn) in sediment samples and experimental samples of plastic macro- and microparticles (HDPE and PETE). Significances were tested on the level of confidence interval 95%. We interpreted the results of statistical analysis to be significant when reaching a p-value < 0.05.

Data evaluation

To improve our ability to detect changes over time, and as done for the field studies, data from time 0, 1, and 2 months, 3 and 8 months, and 12 and 21 months were pooled to represented three time periods, “short-term”(0-2 months), “mid-term” (3-8 months) and “long-term” (12-21months). This approach of data analysis is the same as we applied in the field experiments in order to receive comparable data of field and laboratory study. We used linear regression model (lm) (R Core Team, 2021), to test for variations in trace elements concentrations in sediment samples and experimental samples of plastic macro- and microparticles (PETE and HDPE) for three time periods of sampling and measurements (“short -term”(0-2 months), “mid-term” (3-8 months), and “long-term” (12-21 months)) in each of two types of sediments (OM=2.8% and OM=15.8%) and under conditions of three temperatures (T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C).

To provide an effective analysis of interaction between trace elements (Cd, Cu, Pb, and Zn) and plastic macro- and microparticles in intertidal sediments under temperature conditions of T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C the relative concentration ($C_{f(t+\Delta t)} / C_i$) were applied and calculated (Equation 2.1, Chapter 2).

To assess the potential distribution of trace elements concentration between the intertidal sediments and macro- and microplastics under temperature conditions of T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C the partition (distribution) coefficient (K_d) were used and the ratio of sediments-pore water partitioning coefficient ($K_{sed\text{-}wp}$) to the plastic materials-pore water partitioning coefficient ($K_{pl\text{-}wp}$) as $K_{sed\text{-}wp} / K_{pl\text{-}wp} = [Me]_{sed} / [Me]_{pl}$ were applied and calculated (Equations 2.2-2.7, Chapter 2). Linear regression model (lm) was used to test for variations in [log ($K_{sed\text{-}wp} / K_{pl\text{-}wp}$)] of trace elements (Cu, Cd, Pb, and Zn) among two type of sediments (OM=2.8% and OM=15.8%) and three temperature conditions (T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C). Significances were tested on the level of confidence interval 95%. We interpreted the results of statistical analysis to be significant when reaching a p-value < 0.05.

3.3. Results

3.3.1. Characteristics of intertidal sediments

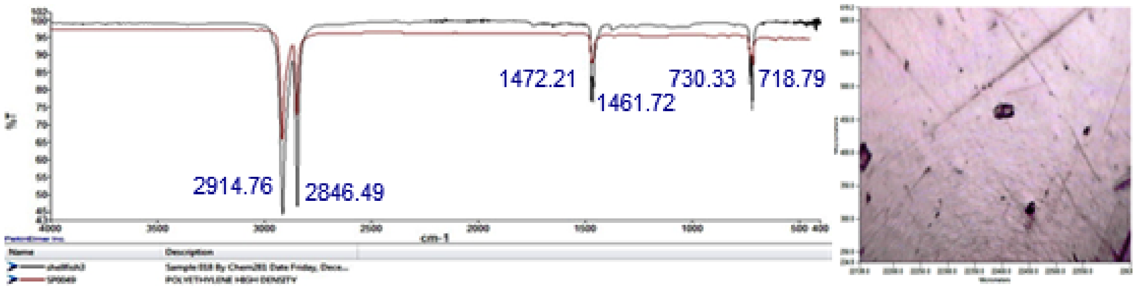
Sediments from HB were more coarse, 0.25 to 2.00 mm (average 44.2% of volume) and >2.00 mm (average 35.0% of volume) as compared to sediments collected from MWFCA study site which were finer, 0.063 to 0.25 mm (average 41.4% of volume) and < 0.063 mm (average 36.5% of volume). The average total organic matter concentration of intertidal sediments taken at HB study site was 2.8% and 15.8% at MWFCA. The detailed description of grain size distribution, organic matter concentrations is provided in the Chapter 2 (Table 2.1, Table B1).

3.3.2. Plastic composition and aging of plastic macro- and microparticles in sediments under conditions of constant temperatures (T=- 4.0°C, T=+4.0°C, and T=+18.0°C)

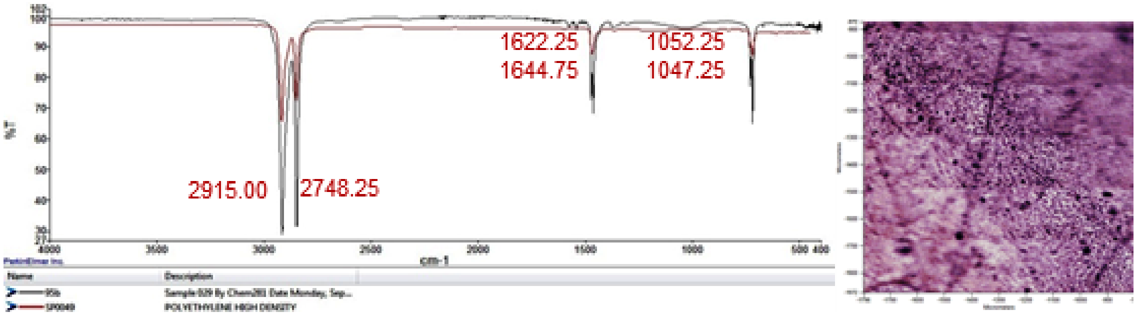
The FTIR spectra for initial plastic macro- and microparticles of HDPE and PETE are shown standard characteristics bands at wave's numbers for those plastic material types (Gulmine et al. 2002; Hummel, 2002). For example, as seen in Figure 3.2 (a) at the beginning of the laboratory experiments (t=0) the FTIR spectrums of initial macro-HDPE (polyethylene chips) samples are shown characteristics bands at wave number 2914.46 cm^{-1} (CH2 asymmetric stretching) and 2846.49 cm^{-1} (CH2 symmetric stretching), 1472.21 cm^{-1} and 1461.72 cm^{-1} (bending deformation), 1367.57 cm^{-1} (wagging deformation), 730.33 and 718.79 cm^{-1} (rocking deformation) that are seen for HDPE (Charles et al., 2009; Gulmine et al., 2002; Hummel, 2002; Pagès, 2008).

For macro-HDPE (polyethylene chips) after 21 months of deploying in sediments with organic matter content of OM = 15.8% and at constant temperatures of T=-4.0°C, the FTIR spectrums have occurrence changes as following: (1) the peak at 2914.46 cm−1 (CH2 asymmetric stretching) is intensified and shifted to 2915.00 cm−1; (2) the peak at 2846.49 cm−1 (CH2 symmetric stretching) is shifted to 2748.25 cm−1; (3) the peak at 1615.25 cm−1 is intensified and shifted to 1622.25 cm−1; (4) the peak at 1646.00 cm−1 is intensified and shifted to 1644.75 cm−1; (5) formation of new functional groups is at 1052.25 cm−1 and 1047.25 cm−1(Figure 3.2b).

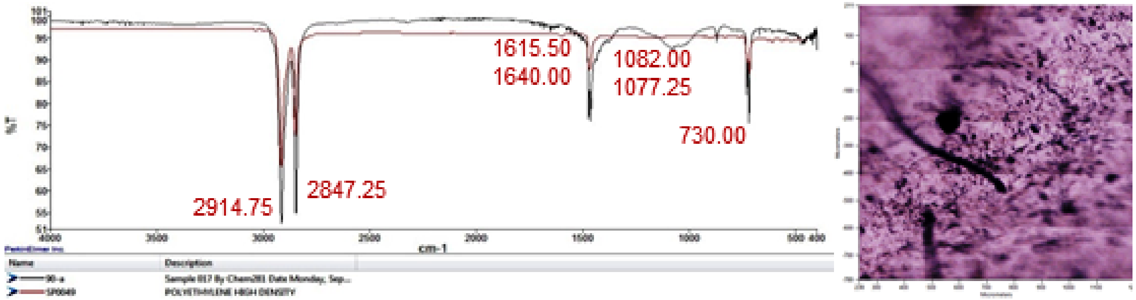
(a) Marine intertidal sediments (MWFCA): OM = 15.8%; t= 0 months



(b) Marine intertidal sediments (MWFCA): OM = 15.8%; T= -4.0°C; t= 21 months



(c) Marine intertidal sediments (MWFCA): OM = 15.8%; T=+4.0°C; t= 21 months



(d) Marine intertidal sediments (MWFCA): OM = 15.8%; T=+18.0°C; t= 21 months

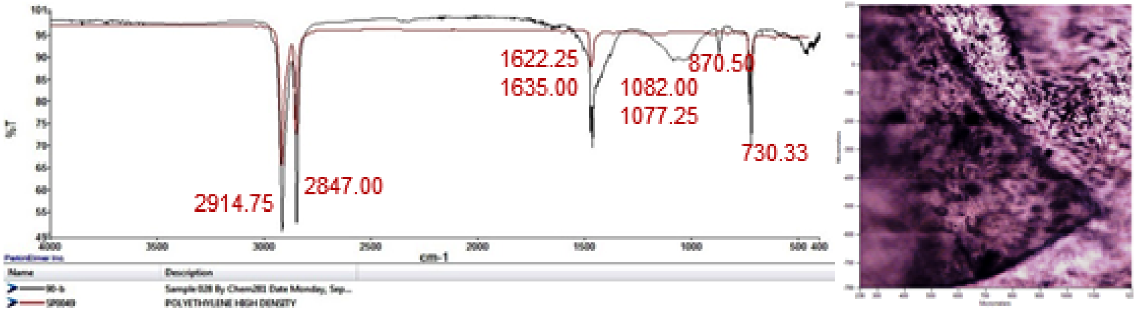


Figure 3.2. The FTIR spectra and microscopic images of the surface morphology of macroplastic (HDPE, polyethylene chips) in marine intertidal sediments (OM = 15.8%) under conditions of constant temperature of T=- 4.0°C (b), T= +4.0°C (c), and T= +18.0°C (d) at residence time of t=0 months (a) and t=21 months (b), (c), (d).

Note: Red spectra are standard spectra of the polymer material (ATR Polymer Introductory Library); blue spectra are spectra of analyzed sample; numbers in red color are values of the spectra (wave number, cm^{-1}) of new functional group.

For macro-HDPE (polyethylene chips) after 21 months of deploying in sediments (OM = 15.8%) at constant temperature of T=+4.0°C, the FTIR spectrums have occurrence changes as following: (1) the peak at 2914.46 cm^{-1}(CH2 asymmetric stretching) is intensified and shifted to 2914.75 cm^{-1}; (2) the peak at 2846.49 cm^{-1} (CH2 symmetric stretching) is shifted to 2847.25 cm^{-1}; (3) the peak at 1615.25 cm^{-1} is shifted to 1615.50cm^{-1}; (4) the peak at 1646.00 cm^{-1} is shifted to 1640.00cm^{-1}; (5) formation of new functional groups is at 1082.50 cm^{-1} and 1077.25 and 864.25 (Figure 3.2c).

For macro-HDPE (polyethylene chips) after 21 months of deploying in the sediments (MWFCA, OM = 15.8%) at constant temperature T=+18.0°C, the FTIR spectrums have occurrence changes as following: (1) the peak at 2914.46 cm^{-1} (CH2 asymmetric stretching) is shifted to 2914.75 cm^{-1}; (2) the peak at 2846.49 cm^{-1} (CH2 symmetric stretching) is shifted to 2847.00 cm^{-1}; (3) the peak at 1615.25 $cm^{-1}$is shifted to 1622.25 cm^{-1}; (4) the peak at 1646.00 $cm^{-1}$is shifted to 1635.50cm^{-1}; (5) formation of new functional groups is at 1082.50 cm^{-1} and 1077.25 and 870.50 cm^{-1} (this peaks are intensified and shifted) (Figure 3.2d).

In general the FTIR spectrums of HDPE and PETE samples after deploying in the intertidal sediments with low and high in organic matter concentration and under the 3 temperature regimes has shown shifted and intensified peak spectrums and formation of new functional groups in their plastic composition. The shifting of peaks 2914.46 cm^{-1} and 2846.49 cm^{-1} occurs due to degradation of HDPE in the presence of microbial culture (Ojha et al. 2017). The peak at wave number 1628.75 cm^{-1} corresponds to the carbonyl group (Rajandas et al. 2012) which is due to oxidation of HDPE sample (Coates, 2006; Gulmine et al., 2002). Formation and shifting of another peak at 1646.00 cm^{-1} (Figure 3b, c, d) occurs and can be interpreting as the formation of the similar functional group as at 1628.75 cm^{-1}. Formation of new functional groups at 1082.50 cm−1 and 1077.25 cm−1 occurs due to C-C stretching (Charles et al., 2009).

Formation of two new functional groups at 1052.25 cm^{-1} and 1047.25 cm^{-1} are seen for macroplastic (HDPE, polyethylene chips) deploying at temperature T=-4.0°C (Figure 3.2b). Formation of three new functional groups is seen at 1082.50 cm^{-1} and 1077.25 and 864.25 (T=+4.0°C) and at 1082.50 cm^{-1} and 1077.25 and 870.50 cm^{-1} (T=+18.0°C) (Figure 3.2c, d). Formation of new functional groups at 1052.25 cm^{-1} and 1047.25 cm−1 can be interpreting as the formation of the similar functional group as at

1082.50 cm^{-1} and 1077.25 cm^{-1} which occurs due to C-C stretching (Charles et al., 2009; Pagès, 2008). Formation of the peaks at 864.25 cm^{-1} (T=+ 4.0°C) and 870.50 cm^{-1} (T=+18.0°C) occurs and Sheik et al. (2015) had observed the formation of the similar functional group at 864 cm^{-1} when pre-treated HDPE subjected to microbial treatment (Figure 3.2c, d).

Importantly, the FTIR spectra for plastic macro- and microparticles samples of HDPE and PETE deployed in sediments under condition of low temperature (T=-4.0°C) are shown less changes of standard characteristics bands at wave's numbers compare to those plastic particles deployed in sediments under condition of higher temperature (T= +18.0°C) (Figure 3.2b, d). Microscopic images of the surface morphology of plastic macro- and microparticles show the roughness, cracks, mechanical and oxidative weathering, indicating their continuous exposure in the sedimentary environment. The FTIR spectrums of macro-HDPE (polyethylene chips) deployed in marine intertidal sediments (OM = 15.8%) under condition of constant temperature provide the presence of various elements on the macroparticles surface (Figure 3.2). Analyses of the FTIR spectra and microscopic images confirmed the degradation and aging macro- and microparticles of both, HDPE and PETE plastic materials after their deployment in the intertidal sediments with temperature of T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C.

3.3.3. Trace element concentrations

3.3.3.1. Trace element concentrations in sediments

In general, concentration of Cu, Pb, and Zn were greater in sediments high in organic matter as compared to that in sediments low in organic matter content and only concentration of Cd was greater in sediments low in organic matter (OM=2.8%) as compare to that in sediments high in organic matter content (OM=15.8%) (Table B1).

3.3.3.2. Trace element sorption by plastic macro- and microparticles

The initial concentrations of trace elements (Cd, Cu, Pb, and Zn) in the experimental samples of plastic macro- and microparticles (prepared for deployment in sediments) were greater than trace elements concentrations measured in seawater samples but significantly lower than that concentration measured in sediment samples taken within intertidal area of Burrard Inlet at the HB (OM=2.8%) and MWFCA

(OM=15.8%) study sites and used in the laboratory experiments (Table B1.). This comparison indicates that plastic macro- and microparticles primarily sorb trace elements from the sedimentary environment.

In the controlled laboratory-based experiments the concentrations of Cd, Cu, Pb, and Zn increased over time, but with different intensity. The total (initial and adsorbed/loaded) measured concentrations of Cd, Cu, Pb, and Zn recovered from the plastic particles varied from (A) time of residence in sedimentary environment, (B) type of plastic material (HDPE, PETE) and plastic particles (macro-HDPE, polyethylene chips; macro-PETE, textile fabric; micro-HDPE, microbeads; micro-PETE, fibers), (C) characteristics of intertidal sediments (grain size, organic matter), and (E) temperature conditions (Figure 3.3- Figure 3.6).

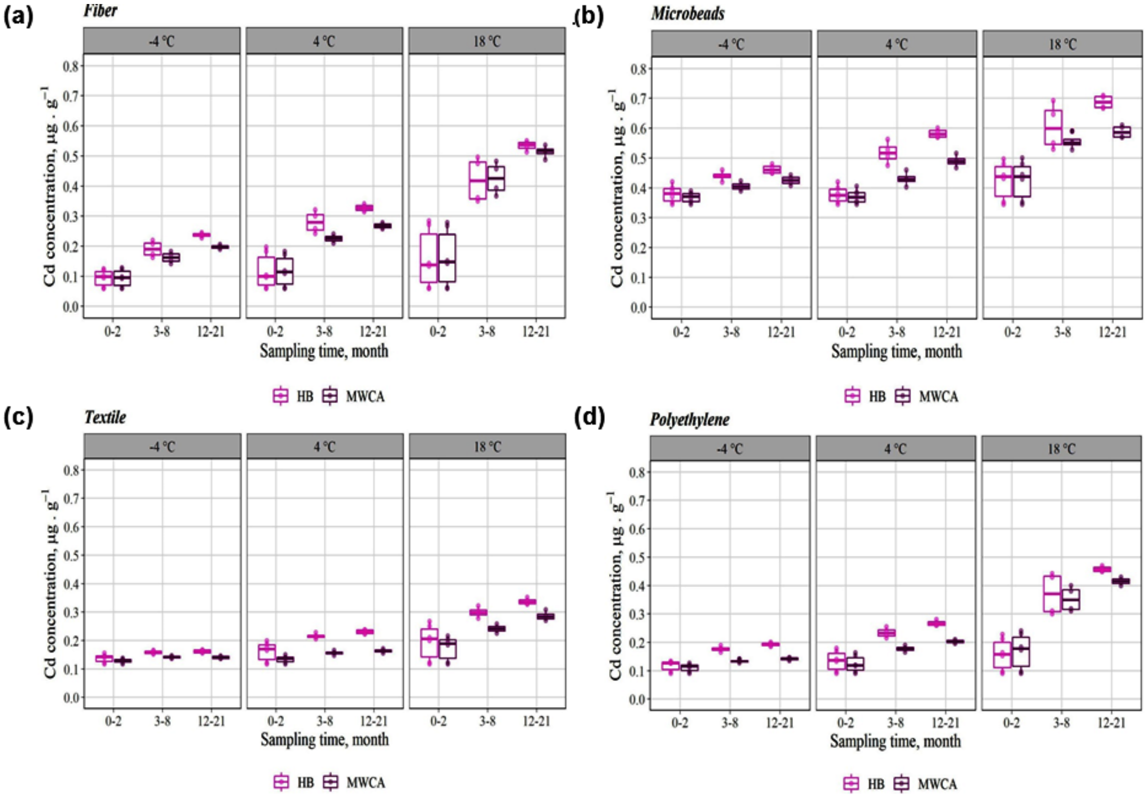


Figure 3.3. **Concentration of Cd over time in micro-PETE (fiber) (a); micro-HDPE (microbeads) (b), macro-PETE (textile fabric) (c), and macro-HDPE, (polyethylene chips) (d) deployed in sediments.**

Note: Laboratory experiments were performed with sediments low (OM=2.8%) and high (OM=15.8%) in organic matter content and constant temperature of T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C. Boxplots represent the distribution of observed values, where midline is the median, with the upper and lower limits of the box being 75th and 25th percentiles. Whiskers extend up to the interquartile range and represent the ranges for the bottom 25% and the top 25% of the data values, excluding outliers. Measured values are depicted as points.

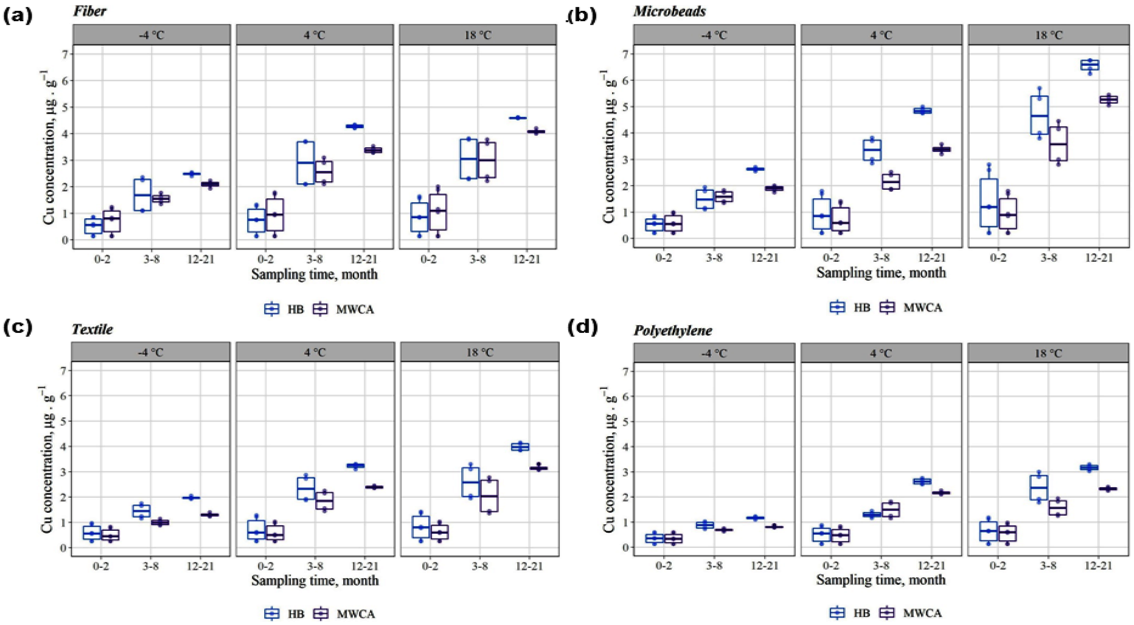


Figure 3.4. Concentration of Cu over time in micro-PETE (fiber) (a); micro-HDPE (microbeads) (b), macro-PETE (textile fabric) (c), and macro-HDPE, (polyethylene chips) (d) deployed in sediments.

Note: Laboratory experiments were performed with sediments low (OM=2.8%) and high (OM=15.8%) in organic matter content and constant temperature of T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C.

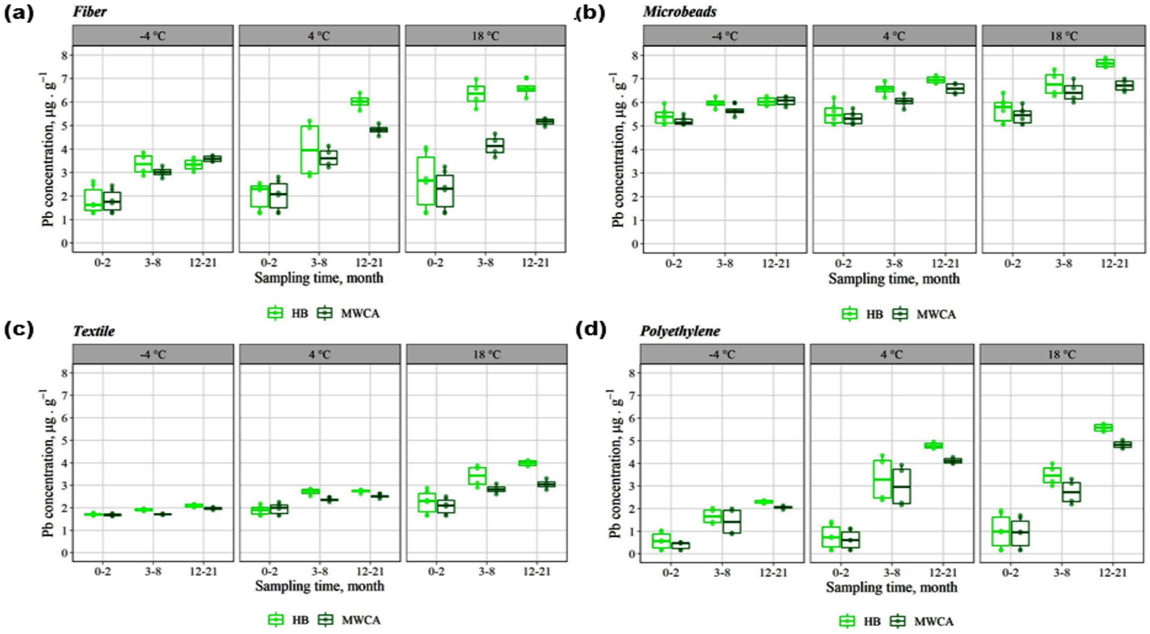


Figure 3.5. Concentration of Pb over time in micro-PETE (fiber) (a); micro-HDPE (microbeads) (b), macro-PETE (textile fabric) (c), and macro-HDPE, (polyethylene chips) (d) deployed in sediments.

Note: Laboratory experiments were performed with sediments low (OM=2.8%) and high (OM=15.8%) in organic matter content and constant temperature of T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C.

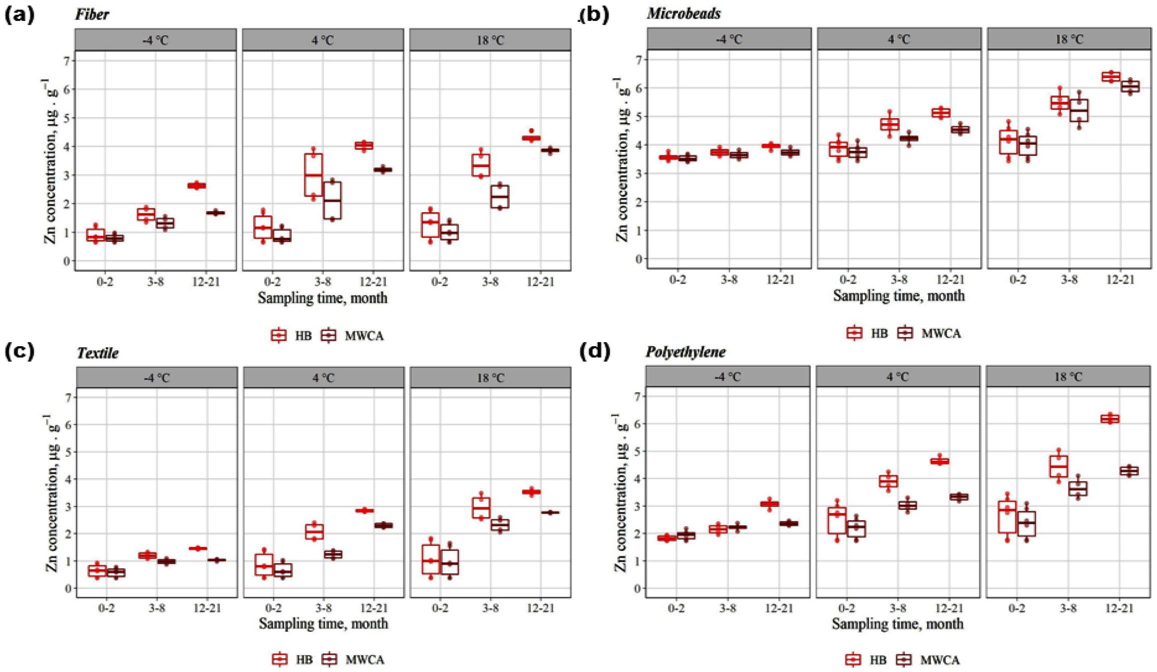


Figure 3.6. **Concentration of Zn over time in micro-PETE (fiber) (a); micro-HDPE (microbeads) (b), macro-PETE (textile fabric) (c), and macro-HDPE, (polyethylene chips) (d) deployed in sediments.**

Note: Laboratory experiments were performed with sediments low (OM=2.8%) and high (OM=15.8%) in organic matter content and constant temperature of T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C.

3.4. Discussion

3.4.1. The interaction between trace elements and plastic macro- and microparticles in the intertidal sediments under the three constant temperature conditions

3.4.1.1. Defining the process of trace elements-plastic macro- and microparticles interaction

Temperature is a crucial parameter in the sorption/desorption process of trace elements by plastic macro- and microparticles in many very important applications (Bakir et al., 2014; Engler, 2012; Holms et al., 2014; Rochman et al., 2014; Turner et al., 2015; Wang et al., 2018). In general, according to the adsorption theory, adsorption decreases with increase in temperature and molecules adsorbed earlier on a surface tend to desorb from the surface at elevated temperatures (Aksu and Kutsal, 1991). Some published studies on dependence of trace elements sorption on temperature in the terrestrial environments (soil) have reported an increase in loading capacities of trace elements with increasing temperature (Gomez et al., 1999). Importantly, that temperature of surrounding environments has impact on aging and degradation of plastic materials (Figure 3.2). The temperature significantly influences all of the physical and chemical characteristics of plastic materials and trough this has impact on their sorption/desorption behavior which can be defined as temperature-dependent (Alimi et al., 2020; Lohman et al., 2012; Reis et al, 2013). To date, the influence of temperature on interaction between trace elements and plastic macro- and microparticles in the intertidal sedimentary environments has not been comprehensively characterized.

The results of our experimental study highlight, that the interaction between trace elements Cd, Cu, Pb, and Zn and plastic macro- and microparticles of PETE and HDPE in the intertidal sediments under laboratory-controlled conditions can be described as a process of time-dependent sorbance. In general, at the beginning of the sorption experiments, during the “short -term” (0-2 months) and “mid-term” (3-8 months) of sampling periods, the concentration of all four trace elements (Cd, Cu, Pb, and Zn) in plastic macro- and microparticles rapidly increased, almost to 1/3-2/3 the value of the total adsorbed/loaded concentration at the end of the experiments (21 months). After the initial period, during the “long-term” (12-21 months) sampling period, the concentration of trace elements (Cd, Cu, Pb, and Zn) increased reaching equilibrium concentrations (observed stable concentration) after 21 months (Figure 3.3- Figure 3.6). These finding assumes that interaction between trace elements and plastic macro- and microparticles in the intertidal sediments under laboratory-controlled conditions of constant temperatures can be described as process of trace elements accumulation over time which include two periods such as, period of rapid adsorption and period of reaching equilibrium state which is in accordance with results of the study on trace elements-plastic particles interaction in the aquatic environments (Gao et al., 2019; Holmes et al., 2012; Rochman et al., 2014).

3.4.1.2. The influence of temperature

The laboratory-based experimental study demonstrated that plastic macro- and microparticles of HDPE and PETE accumulate Cd, Cu, Pb, and Zn over time but very differently in relation to the type of sediments, temperature conditions, and plastic type and particles shape/size ($p<0.05$) (Figure 3.3-3.6; Figure C1-C4; Table C1). To estimate the influence of temperature on trace elements-plastic particles interaction under conditions of three constant temperatures the relative equilibrium concentration (C_e / C_i)

as ratio of equilibrium concentration (C_e) to the initial concentration (C_i) was used (Equation 2.1). The value of the relative equilibrium concentration was calculated for concentration of Cd, Cu, Pb, and Zn sorbed by macro-HDPE (polyethylene chips), macro-PETE (textile fabric), micro-HDPE (microbeads), and micro-PETE (fibres) deployed in intertidal sediments low (OM=2.8%) and high (OM=15.8%) in organic matter and under temperature conditions of T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C (Table 3.1).

The value of the equilibrium concentration of Cu, Zn, Pb, and Cd in macro- and microparticles of HDPE and PETE were significantly dependent on temperature (Table C1). By comparing the sorption of trace elements under conditions of three temperatures (T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C) it was found that the concentration of Cd, Cu, Pb, and Zn in plastic macro- and microparticles of HDPE and PETE was higher and reached the state of equilibrium and equilibrium concentration faster under condition of higher temperature T=+18.0°C (8-12 months) compare to that at lower temperature T=-4.0°C (12-21 months) (Figure 3.3 – Figure 3.6; Table 3.1). Importantly, that the value of relative equilibrium concentration (C_e / C_i) of all four trace elements (Cu, Zn, Pb, and Cd) in plastic macro- and microparticles of HDPE and PETE is greater under condition of high temperature (T=+18.0°C) compare to that at low temperature T=-4.0°C. Copper (Cu) exhibited the high relative equilibrium concentration in microplastic of both types of plastic materials, PETE (fiber) and HDPE (microbeads), and Cu and Pb in macroplastic of HDPE (polyethylene chips). The highest value of relative equilibrium concentration were observed for microplastic of PETE to Cu (C_e / C_i = 35.5) and HDPE to Cu (C_e / C_i =30.2) and macroplastic of HDPE to Pb (C_e / C_i =33.89) (Table 3.1). It means, for example, that at temperature of T= +18.0°C the equilibrium concentration of Cu can be in 35.5 and 30.2 fold greater in microparticles of PETE and HDPE respectively, compare to their initial concentration which is in accordance with Liu et al. (2019).

The value of the relative equilibrium concentration (C_e /C_i) indicated that the sorption behaviour of Cd, Cu, Pb, and Zn varied significantly depending on the type of plastic materials and their size/shape (Table 3.1, Fig. 3.3 - 3.6; Table C1). By comparing the difference in sorption between two different types of plastic materials it was found that under conditions of all three constant temperatures (T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C) the sorbance of micro-PETE (fibre) to Cd, Cu, Pb, and Zn was higher than micro-HDPE (microbeads). In contrast, the sorbance of macro-PETE (textile fabric) to Cu, Pb, and Cd was lower than macro-HDPE (polyethylene chips), but the sorbance of macro-PETE (textile fabric) to Zn was higher than sorbance of macro-HDPE (polyethylene chips) (Table 3.1). Such findings may suggest that the same temperature regime influence differently on sorption of trace elements by plastic macro- and microparticles of the same plastic materials (HDPE and PETE).

Table 3.1. The value of the relative equilibrium concentration (C_e/C_i) of trace elements in plastic macro- and microparticles deployed in the intertidal sediments

Temperature, °C	Organic mater, %	Microplastic		Macroplastic	
		PETE fiber	HDPE microbeads	PETE textile fabric	HDPE polyethylene chips
Cd					
T= 18.0	2.8%	8.71 (8)	2.00 (8)	2.82 (8)	4.90 (8)
T= 4.0	2.8%	5.37 (8)	1.66 (12)	1.87 (8)	2.82 (8)
T= -4.0	2.8%	3.98 (12)	1.32 (12)	1.35 (8)	2.09 (12)
T= 18.0	15.8%	8.51 (12)	1.70 (8)	2.24 (12)	4.57 (12)
T= 4.0	15.8%	4.47 (12)	1.42 (12)	1.38 (12)	2.19 (12)
T= -4.0	15.8%	3.31 (12)	1.21 (12)	1.18 (12)	1.51 (12)
Cu					
T= 18.0	2.8%	**35.5** (12)	**30.2** (8)	15.2 (12)	22.9 (8)
T= 4.0	2.8%	29.6 (12)	23.5 (12)	12.6 (12)	19.5 (12)
T= -4.0	2.8%	17.4 (21)	12.6 (21)	7.6 (12)	8.1 (12)
T= 18.0	15.8%	28.1 (8)	25.7 (12)	12.1 (12)	17.8 (12)
T= 4.0	15.8%	23.5 (12)	16.2 (12)	9.2 (12)	16.2 (12)
T= -4.0	15.8%	14.8 (21)	9.4 (21)	5.1 (21)	6.2 (12)
Pb					
T= 18.0	2.8%	5.12 (8)	1.52 (12)	2.40 (8)	**33.89** (12)
T= 4.0	2.8%	4.57 (12)	1.38 (12)	1.62 (8)	29.52 (12)
T= -4.0	2.8%	2.76 (21)	1.21 (21)	1.26 (12)	14.13 (12)
T= 18.0	15.8%	4.08 (12)	1.35 (8)	1.78 (8)	29.51 (12)
T= 4.0	15.8%	3.72 (12)	1.29 (12)	1.52 (12)	25.12 (12)
T= -4.0	15.8%	2.76 (12)	1.20 (12)	1.21 (21)	12.59 (12)
Zn					
T= 18.0	2.8%	6.33 (8)	1.93 (8)	9.33 (8)	3.55 (12)
T= 4.0	2.8%	6.14 (8)	1.51 (8)	7.59 (12)	2.70 (12)
T= -4.0	2.8%	4.01 (12)	1.12 (12)	3.90 (12)	1.74 (12)
T= 18.0	15.8%	5.93 (8)	1.74 (8)	7.25 (12)	2.45 (8)
T= 4.0	15.8%	4.95 (12)	1.32 (12)	6.03 (12)	1.91 (12)
T= -4.0	15.8%	2.63 (12)	1.08 (12)	2.70 (12)	1.35 (12)

Note: The value in the round brackets indicates the residence time (months) when the state of equilibrium and equilibrium concentration was reached. The maximum values of the equilibrium concentration is in the bold text.

At the same time, the relative equilibrium concentration of all trace elements (Cd, Cu, Pb, and Zn) in macro- and microparticles of HDPE and PETE deployed under temperature conditions of T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C was higher in sediments with low (OM= 2.8%) organic matter content compare to that in sediments high (OM=15.8%) in organic matter (Table 3.1). These findings can be explained that sorption of Cu, Zn, Pb, and Cd by macro- and microplastics were highly competitive between plastic materials and sediments. It is likely that the characteristics of intertidal sediments (OM=2.8% and OM=15.8%, grain size distribution) have greater influence on sorption of trace elements compare to the influence of constant temperature applied in our simulation experiments (T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C).

The influence of temperature on trace elements sorption by plastic macro- and microparticles in the intertidal sediments can be expressed by gradient $\Delta(\log(C_e/C_i))/\Delta T)$ (relative equilibrium concentration as function of temperature) (Figure 3.3-3.6). In general, in the range of the constant temperatures of T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C adsorption of Cu, Zn, Pb, and Cd by macro-HDPE (polyethylene chips), macro-PETE (textile fabric), micro-HDPE (microbeads), and micro-PETE (fibres) increased with increasing of temperature, and gradients $(\Delta(\log(C_e/C_i))/\Delta T)$ have positive values. According to the gradient $(\Delta(\log(C_e/C_i))/\Delta T)$, dependence of trace elements sorption by plastic particles on constant temperature are following the order (R^2=0.7788-0.99):

(a) OM=2.8% (Table 3.1):
  micro-PETE (fiber): Cd (0.0158) > Cu (0.0131) > Pb (0.0125) > Zn (0.0078)
  micro-HDPE (microbeads): Cu (0.0162) > Zn (0.0097) > Cd (0.0079) > Pb (0.0044)
(b) OM=15.8% (Table 3.1):
  micro-PETE (fiber): Cd (0.0189) > Zn (0.0147) > Cu (0.0119) > Pb (0.0072)
  micro-HDPE (microbeads): Cu (0.0194) > Zn (0.0095) > Cd (0.0067) > Pb (0.0022)

By estimating the value of the $(\Delta(\log(C_e/C_i))/\Delta T)$ we can conclude that in relation to polymer type, sorption behaviour of micro-PETE towards Cd $(\Delta(\log (C_e/C_i))/\Delta T = 0.0189$ (Cd)) is more dependent on temperature compare to the micro-HDPE $(\Delta(\log(C_e/C_i))/\Delta T = 0.0067$ (Cd)). In contrast, sorption behaviour of macro-PETE towards Pb $(\Delta(\log(C_e/C_i))/\Delta T = 0.0079$ (Pb)) is less dependent on temperature compare to the macro-HDPE $(\Delta(\log (C_e/C_i))/\Delta T = 0.0150$ (Pb)). In relation to the particle size, sorption behaviour of plastic macroparticles towards trace elements (Cd, Cu, Pb, and Zn) is more dependent on temperature compare to the microparticles (Figure 3.3 - Figure 3.6).

In relation to the type of trace elements, sorption of copper (Cu) by plastic microparticles have higher dependence on temperature compare to cadmium (Cd), lead (Pb) and zinc (Zn). Sorption of trace elements by macroparticles has very similar dependent on temperature, except of Zn sorption by macro-HDPE ((Δ(log (C_e /C_i))/ΔT = 0.0084 (Zn)) and Pb by macro-PETE ((Δ(log(C_e /C_i))/ΔT = 0.0079 (Zn)) with lower dependence on temperature in sediments high in organic matter. In general, dependence of trace elements sorption by plastic macro- and microparticles on temperature slightly different in sediments low (OM=2.8%) and high (OM=15.8%) in organic matter content.

3.4.2. Partitioning of trace elements in the intertidal sediments with macro- and microplastics content under conditions of three constant temperatures

To compare the distribution of trace elements in two contrasting sedimentary environments with components of plastic particles (PETE and HDPE) and under the three temperature conditions the ratio of intertidal sediments-pore water partitioning coefficients ($K_{sed\text{-}wp}$) to the polymer materials-pore water partitioning coefficients ($K_{pl\text{-}wp}$) of trace elements (Cd, Cu, Pb, and Zn) in sediments low (OM = 2.8%) and high (OM = 15.8%) in organic matter was calculated as [($K_{sed\text{-}wp}$ / $K_{pl\text{-}wp}$)] (Equation (2.4)-(2.7); Figure 3.7-3.10).

In general, the values of log[($K_{sed\text{-}wp}$)/($K_{pl\text{-}wp}$)] of Cd, Cu, Pb, and Zn for macro-HDPE (polyethylene chips), macro-PETE (textile fabric), micro-HDPE (microbeads), and micro-PETE (fibres) are significantly time-dependent and strongly decreased over time during all of three periods of sampling (0-2, "short term"; 3-8, "mid-term"; 12-21 "long term") before reaching equilibrium at both sedimentary environments, high and low in organic matter, and under conditions of all three constant temperature applied in the laboratory experiments: T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C. The intensity of decreasing the value log [($K_{sed\text{-}wp}$)/($K_{pl\text{-}wp}$)] of Cd, Cu, Pb, and Zn for plastic macro- and microparticles is higher under conditions of high temperature (T=+18°C) compare to that at low temperature (T=- 4.0°C) (Figure 3.7-3.10). These findings can be interpreted that the partitioning of trace elements between sediments and plastic macro- and microparticles is greater at high temperature of T=+18.0°C compare to that at low temperature (T=- 4.0°C).

The value of log[($K_{sed\text{-}wp}$)/($K_{pl\text{-}wp}$)] of Cu, Pb, and Zn, except of Cd, was greater for macro- and microparticles of HDPE and PETE deployed in sediments high in organic matter (OM = 15.8%) compare to that in sediments low in organic matter (OM = 2.8%) and under conditions of each temperature (T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C) (Figure 3.7-3.10). These finding can be explained as a phenomenon of competitive adsorption between plastic particles and organic particles in sediments which is in accordance with Gomez et al. (1999). Such findings suggest that temperature has minor influence on the partitioning of Cu, Pb, and Zn, except of Cd, between plastic particles and intertidal sediments compare to the influence of organic matter content of OM=15.8%.

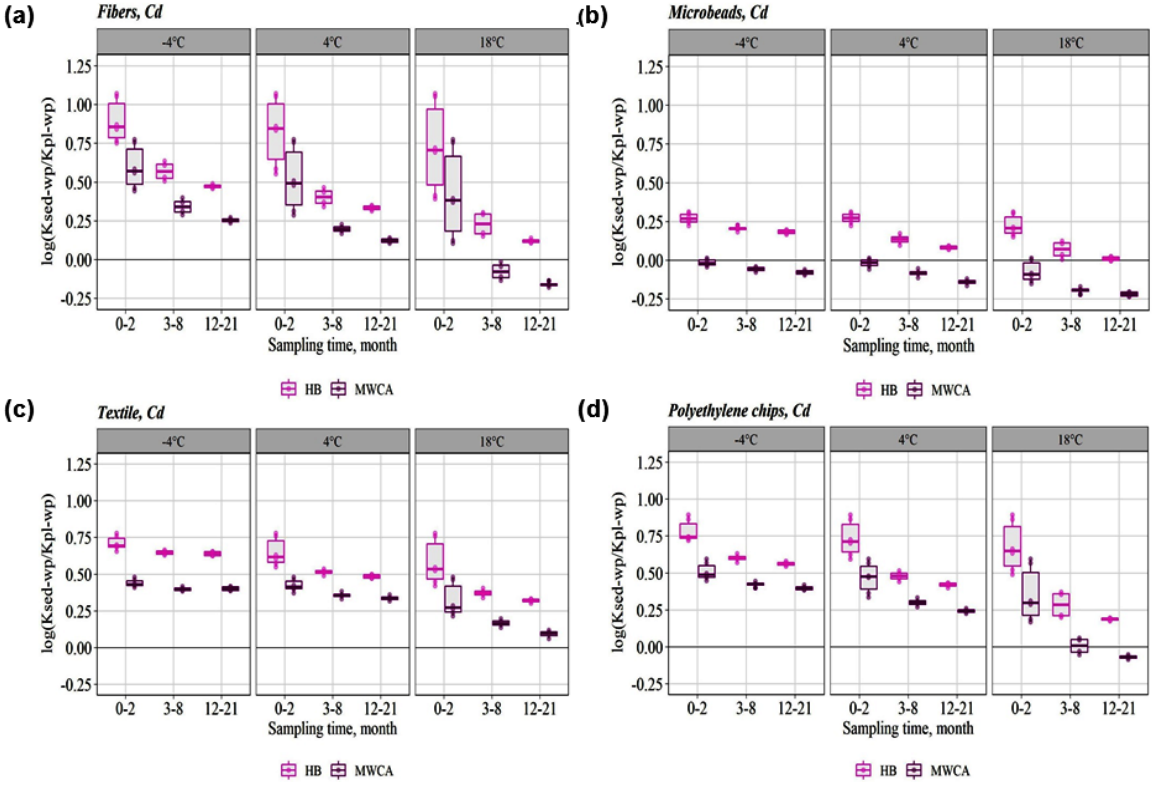


Figure 3.7. The value of log($K_{sed\text{-}wp}$/$K_{pl\text{-}wp}$) of Cd over time in micro-PETE (fiber) (a); micro-HDPE (microbeads) (b), macro-PETE (textile fabric) (c), and macro-HDPE (polyethylene chips) (d) deployed in sediments.

Note: Laboratory experiments were performed with sediments low (HB, OM=2.8%) and high (MWFCA, OM=15.8%) in organic matter and constant temperature of T=- 4.0°C, T=+4.0°C, and T=+18.0°C

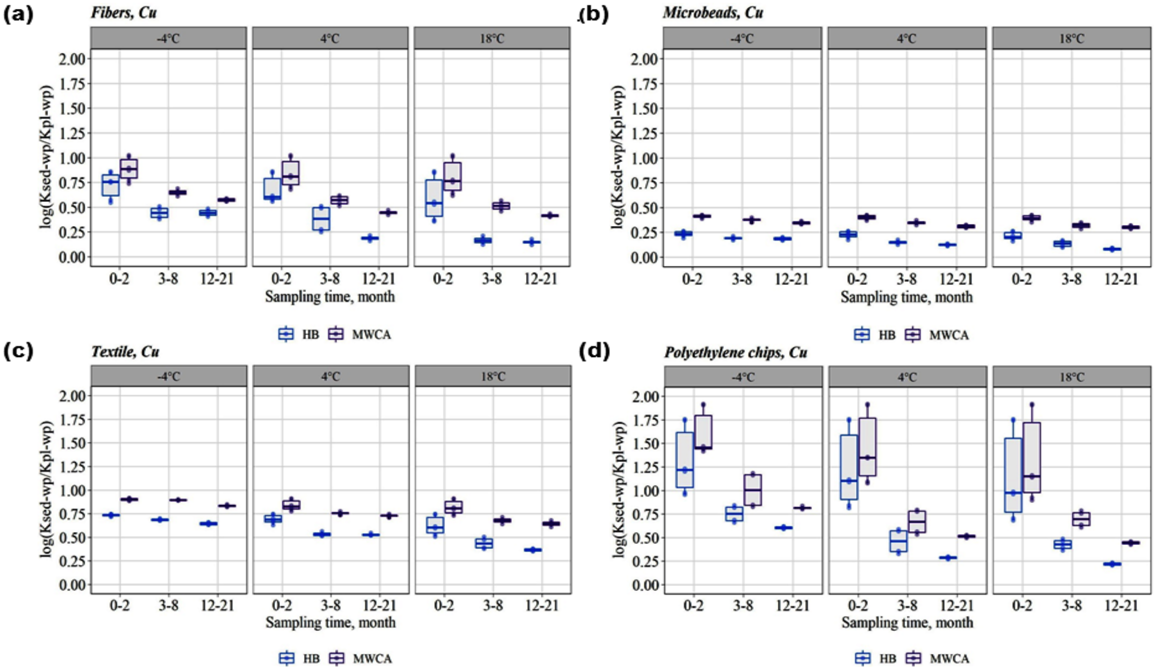


Figure 3.8. The value of log($K_{sed\text{-}wp}$/$K_{pl\text{-}wp}$) of Cu over time in micro-PETE (fiber) (a); micro-HDPE (microbeads) (b), macro-PETE (textile fabric) (c), and macro-HDPE (polyethylene chips) (d) deployed in sediments.

Laboratory experiments were performed with sediments low (HB, OM=2.8%) and high (MWFCA, OM=15.8%) in organic matter and constant temperature of T=- 4.0°C, T=+4.0°C, and T=+18.0°C

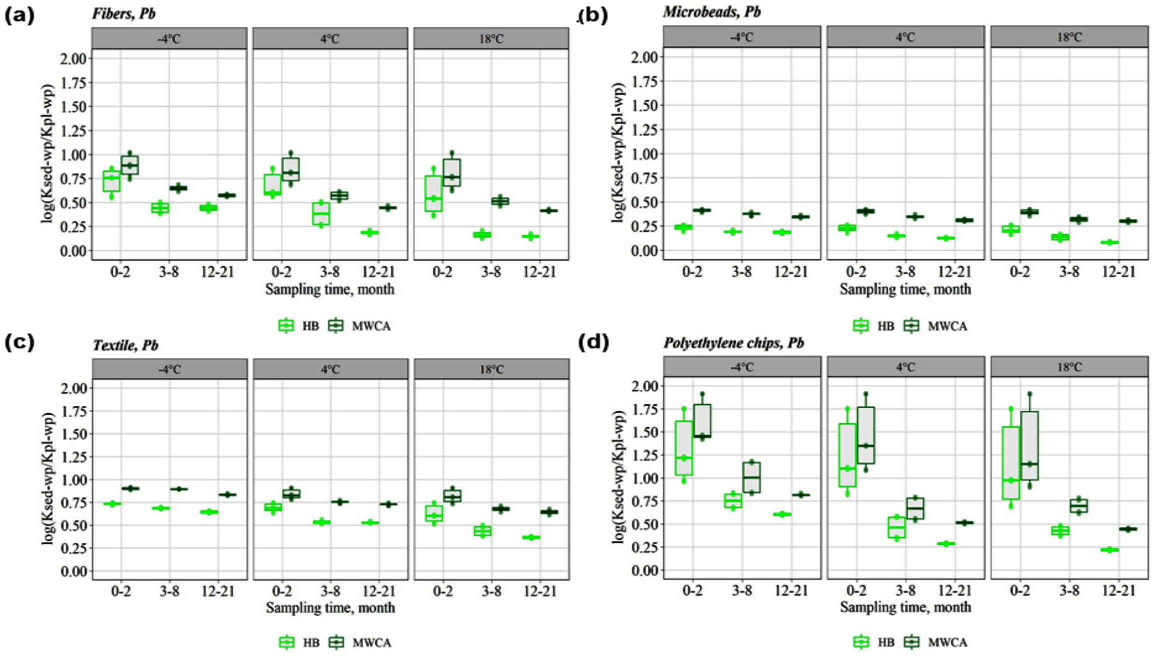


Figure 3.9. The value of log($K_{sed\text{-}wp}$/$K_{pl\text{-}wp}$) of Pb over time in micro-PETE (fiber) (a); micro-HDPE (microbeads) (b), macro-PETE (textile fabric) (c), and macro-HDPE (polyethylene chips) (d) deployed in sediments.

Laboratory experiments were performed with sediments low (HB, OM=2.8%) and high (MWFCA, OM=15.8%) in organic matter and constant temperature of T=- 4.0°C, T=+4.0°C, and T=+18.0°C

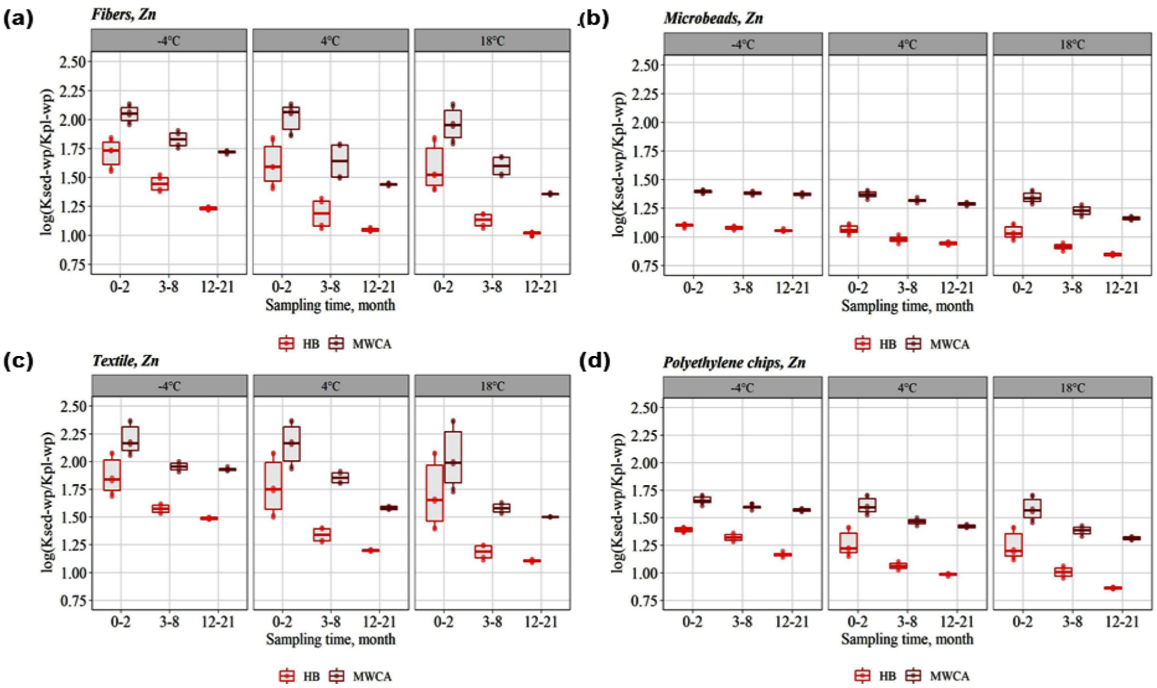


Figure 3.10. The value of log($K_{sed\text{-}wp}$/$K_{pl\text{-}wp}$) of Zn over time in micro-PETE (fiber) (a); micro-HDPE (microbeads) (b), macro-PETE (textile fabric) (c), and macro-HDPE (polyethylene chips) (d) deployed in sediments.
Laboratory experiments were performed with sediments low (HB, OM=2.8%) and high (MWFCA, OM=15.8%) in organic matter and constant temperature of T=- 4.0°C, T=+4.0°C, and T=+18.0°C

By estimating the logarithmic value of the ratio of intertidal sediments-pore water partitioning coefficient ($K_{sed\text{-}wp}$) to the polymer particles-pore water partitioning coefficient ($K_{pl\text{-}wp}$) of trace elements, the distribution of Cd, Cu, Pb, and Zn can be defined as following (Equation 2.5-2.8):

$$(K_{sed-wp}/K_{pl-wp}) = 1 \; or \; \log(K_{sed-wp}/K_{pl-wp}) = 0 \;\; ===> \;\; [Me]_{sed} = [Me]_{pl} \qquad (3.1)$$

$$(K_{sed-wp}/K_{pl-wp}) > 1 \; or \; \log(K_{sed-wp}/K_{pl-wp}) > 0 \;\; ===> \;\; [Me]_{sed} > [Me]_{pl} \qquad (3.2)$$

$$(K_{sed-wp}/K_{pl-wp}) < 1 \; or \; \log(K_{sed-wp}/K_{pl-wp}) < 0 \;\; ===> \;\; [Me]_{sed} < [Me]_{pl} \qquad (3.3)$$

The log[($K_{sed\text{-}wp}$)/($K_{pl\text{-}wp}$)] may have “positive”, “0”, or “negative” value which indicate that concentration of trace elements in the intertidal sediments is greater, the same, or lower respectively than that in the plastic macro- and microparticles. In our laboratory study on the trace elements-plastic macro- and microparticles interaction in the intertidal sediments with temperature conditions of T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C the log($K_{sed\text{-}wp}$/$K_{pl\text{-}wp}$) have “positive” value for Cu, Zn, and Pb and “0” and “negative” value for Cd only in sediments high in organic matter (micro-HDPE (microbeads) at T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C; micro-PETE (fibres) and macro-HDPE (polyethylene chips) at T=+18.0°C (Figure 3.7-3.10). These results illustrate the phenomenon of competitive adsorption between plastic materials and organic particles in sediments. This can be interpreted that under temperature condition of T=+18.0°C only Cd, compare to Cu, Zn, and Pb, can partition to plastic particles more readily than to sediments high in organic matter (OM=15.8%) (Figure 3.7a, 3.7b, and 3.7d).

To estimate the degree to which temperature influences the distribution of trace elements between intertidal sediments and plastic macro- and microparticles the ratio of intertidal sediments-pore water equilibrium partitioning coefficient $(K_{sed\text{-}wp})_e$ to the polymer materials-pore water equilibrium partitioning coefficient $(K_{pl\text{-}wp})_e$ of Cd, Cu, Pb, and Zn in sediments low (OM = 2.8%) and high (OM = 15.8%) in organic matter concentrations were calculated as $[(K_{sed\text{-}wp})_e/(K_{pl\text{-}wp})_e]$ (Equation 2.7; Table 3.2). In general, the value of $\log[(K_{sed\text{-}wp})_e/(K_{pl\text{-}wp})_e]$ of Cd, Cu, Pb, and Zn for macro- and microparticles of HDPE and PETE decreased with increasing of temperature (T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C) in both, intertidal sediments low (OM=2.8%) and high (OM=15.8%) in organic matter concentration.

The value of $\log[(K_{sed\text{-}wp})_e/(K_{pl\text{-}wp})_e]$ of Cd, Cu, Pb, and Zn was greater for plastic macro- and microparticles of HDPE and PETE deployed in intertidal sediments high in organic matter content (OM=15.8%) compare to that in sediments low in organic matter content (OM = 2.8%) at each constant temperature (T=- 4.0°C, T=+4.0°C, and T=+18.0°C) (Table 3.2). These finding can be explained that under laboratory controlled temperature conditions of T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C have minor influence on the partitioning of Cu, Pb, and Zn, except of Cd, between plastic particles and intertidal sediments compare to the influence of organic matter of OM=15.8%.

Dependence of trace elements distribution in sediments on temperature can be expressed by gradient $(\Delta(\log[(K_{sed\text{-}wp})_e/(K_{pl\text{-}wp})_e])/\Delta T)$. The value of the gradient $\Delta(\log[(K_{sed\text{-}wp})_e/(K_{pl\text{-}wp})_e])/\Delta T$ of Cd, Cu, Pb, and Zn has very small variation for macro-PETE and HDPE (-0.0165 (Zn, R^2=0.83); -0.0163 (Pb, R^2=0.77)) and micro-PETE and HDPE (-0.0077 (Zn, R^2=0.66); -0.0075 (Cd, R^2=0.97)) deployed in sediments low in organic matter (OM=2.8%) (Figure C6). In addition, macroparticles of HDPE and PETE deployed in sediments low and high in organic matter, showed greater dependence on temperature. Hence, a sediment geochemical characteristic such as organic matter content has a greater influence on the sorption of trace elements by plastics as compared to temperature.

Table 3.2. The values of the ratio of intertidal sediments-pore water equilibrium partitioning coefficient ($(K_{sed-wp})_e$) to the plastic particles-pore water equilibrium partitioning coefficient ($(K_{pl-wp})_e$) as $[(K_{sed-wp})_e/(K_{pl-wp})_e]$ of Cd, Cu, Pb and Zn.

Organic matter, %	Temperature, °C	$(K_{sed-ws})_e$	$(K_{sed-wp})_e/(K_{pl-wp})_e$			
			Microplastic		Macroplastic	
			PETE fiber	HDPE microbeads	PETE textile fabric	HDPE polyethylene chips
			Cd			
2.8	**18.0**	75.9	1.31 (8)	1.02 (8)	2.10 (8)	1.54 (8)
	4.0	79.9	2.17 (8)	1.21 (12)	3.10 (8)	2.65 (8)
	- 4.0	85.9	3.01 (12)	1.53 (12)	4.37 (8)	3.70 (12)
15.8	**18.0**	38.3	0.70 (12)	0.61 (8)	1.32 (12)	0.86 (12)
	4.0	41.5	1.34 (12)	0.72 (12)	2.15 (12)	1.77 (12)
	- 4.0	44.3	1.82 (12)	0.84 (12)	2.53 (12)	2.51 (12)
			Cu			
2.8	**18.0**	512.9	2.66 (12)	1.88 (8)	3.05 (12)	3.90 (8)
	4.0	542.6	2.82 (12)	2.52 (12)	3.81 (12)	4.62 (12)
	- 4.0	577.2	4.98 **(21)**	4.62 **(21)**	6.10 (12)	10.24 (12)
15.8	**18.0**	1202.5	3.38 (8)	2.59 (12)	4.40 (12)	5.81 (12)
	4.0	1227.6	4.05 (12)	4.05 (12)	5.69 (12)	6.31 (12)
	- 4.0	1245.5	6.45 **(21)**	7.05 **(21)**	10.56 **(21)**	16.65 (12)
			Pb			
2.8	**18.0**	92.5	1.37 (8)	1.21 (12)	2.33 (8)	1.66 (12)
	4.0	96.7	1.54 (12)	1.34 (12)	3.40 (8)	2.45(12)
	- 4.0	102.5	2.76 **(21)**	1.52 **(21)**	4.41 (12)	4.04 (12)
15.8	**18.0**	117.5	2.58 (12)	1.98 (8)	4.37 (8)	2.78 (12)
	4.0	125.7	2.82 (12)	2.05 (12)	5.37 (12)	3.29 (12)
	- 4.0	136.4	3.73 (12)	2.24 (12)	6.75 **(21)**	6.72 (12)
			Zn			
2.8	**18.0**	42658.5	10.95 (8)	7.03 (8)	12.69 (8)	7.28 (12)
	4.0	42837.6	11.12 (8)	8.80 (8)	15.81 (12)	9.56 (12)
	- 4.0	42988.5	17.01 (12)	11.49 (12)	30.76 (12)	14.45 (12)
15.8	**18.0**	81282.3	23.00 (8)	14.64 (8)	31.83 (12)	20.67 (8)
	4.0	81537.5	27.62 (12)	19.57 (12)	38.19 (12)	26.30 (12)
	- 4.0	81824.3	52.92 (12)	23.80 (12)	85.11 (12)	36.91 (12)

Note: The value in the round brackets indicates the residence time (months) when the state of equilibrium and equilibrium concentration was reached. The maximum values in the bold text.

3.5. Conclusions

(1) Temperature influences the sorption and partitioning of Cu, Zn, Pb, and Cd. Concentrations of Cd, Cu, Pb, and Zn in plastic macro- and microparticles of HDPE and PETE was higher and reached the state of equilibrium and equilibrium concentration faster under condition of higher temperature T=+18.0°C (8-12 months) compare to that at lower temperature T=- 4.0°C (12-21 months).

(2) The interaction between trace elements (Cd, Cu, Pb, and Zn) and plastic macro- and microparticles in the intertidal sediments under laboratory-controlled temperatures conditions of T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C can be described as the process of accumulation over time which includes two periods such as, period of rapid adsorption and period of reaching equilibrium.

(3) The adsorbed concentration of Cd, Cu, Pb, and Zn in plastic macro- and microparticles of HDPE and PETE deployed under the three temperature conditions was higher in sediments low in organic matter (OM = 2.8%) compare to that in sediments high in organic matter content.

(4) In relation to polymer type, sorption behaviour of micro-PETE towards Cd, Cu, Pb, and Zn are more dependent on temperature compare to the micro-HDPE. In contrast, sorption behaviour of macro-PETE towards Cd, Cu, Pb, and Zn are less dependent on temperature compare to the macro-HDPE. In relation to the particle size, sorption behaviour of plastic macroparticles towards trace elements (Cu, Zn, Pb, Cd, and Hg) is more dependent on temperature compare to the microparticles.

(5) In relation to the type of trace elements, sorption of Cu by plastic microparticles has higher dependence on temperature as compared to Cd, Pb, and Zn.

(6) The partitioning of trace elements (Cd, Cu, Pb, and Zn) between sediments and plastic macro- and microparticles is higher under condition of high temperature (T=+18.0°C) as compared to that at low temperature (T=-4.0°C). In general, the value of $\log[(K_{sed\text{-}wp})_e/(K_{pl\text{-}wp})_e]$ of Cd, Cu, Pb, and Zn for macro- and microparticles of HDPE and PETE decreased with increasing of temperature (T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C) in both, intertidal sediments low (OM=2.8%) and high (OM=15.8%) in organic matter concentration.

(7) Under laboratory controlled conditions temperature had a minor influence on the partitioning of Cu, Pb, and Zn, except of Cd, between plastic particles and intertidal sediments compared to the influence of organic matter of OM=15.8%. It was found that at high temperature (T=+18.0°C) only Cd can partition to plastic particles more readily than to sediments high in organic matter (OM=15.8%).

References

Aksu, Z., & Kutsal, T. A. (1991). A bioseparation process for removing Pb (II) Ions from wastewater by using *C. Vulgaris*. *Journal of Chemical Technology & Biotechnology,* 52, 108-118.

Alimi, O. S., Farner, J. M., & Tufenkji N. (2020). Exposure of nanoplastics to freeze-thaw leads to aggregation and reduced transport in model groundwater environments. *Water Research.* 189. 116533.

ASTM. (2000a). Standard guide for collection, storage, characterization, and manipulation of sediments for toxicological testing, E 1391-94. American Society for Testing and Materials, West Conshohocken, PA, USA.

ASTM. (2000b). Guide for core-sampling submerged unconsolidated sediments, D 4823 -95. American Society for Testing and Materials, West Conshohocken, PA, USA.

ASTM. (2000c). Standard test methods for moisture, ash, and organic matter of peat and other organic soils. Method D 2974-00. American Society for Testing and Materials. West Conshohocken, PA, USA.

Archived copy. (2020). Maplewood Flats Conservation Area. https://en.wikipedia.org/wiki/Maplewood_Flats_Conservation_Area

Bakir, A., Rowland, S.J.,& Thompson, R.C. (2014). Enhanced desorption of persistent organic pollutants from microplastics under simulated physiological conditions. *Environmental Pollution.* 185, 16–23. doi.org/10.1016/j.envpol.2013.10.007.

Batley, G. E., & Simpson, S. L. (2016) Sediment sampling, sample preparation and general analysis. In: S. L. Simpson & G. E. Batley (Eds.), *Sediment quality assessment: A practical guide* (2nd ed., 15-45). Clayton South, Vic.: CSIRO Publishing. http://hdl.handle.net/102.100.100/91038?index=1

Brennecke, D., Duarte, B., Paiva, F., Caçador, I., & Canning-Clode, J. (2016). Microplastics as vector for heavy metal contamination from the marine environment. *Estuarine, Coastal and Shelf Science.* 178, 189–195. https://doi.org/10.1016/j.ecss.2015.12.003

Charles, J. & Ramkumaar, G.R. (2009). Qualitative analysis of high density polyethylene using FTIR spectroscopy. Asian Journal of Chemistry. 21(5). 4477- 4484.

Coates, J. (2006). Interpretation of infrared spectra, a practical approach. In R.A. Meyers (Ed.), *Encyclopedia of analytical chemistry* (pp. 10815–10837). John Wiley & Sons Ltd, Chichester. https://doi.org/10.1002/9780470027318.a5606.

Engler, R.E. (2012). The complex interaction between marine debris and toxic chemicals in the ocean. *Environmental Science & Technology*. 46, 12302-12315.

Gao, F., Li, J., Sun, C., Zhang, L., Jiang, F., Cao, W., & Zheng, L. (2019). Study on the capability and characteristics of heavy metals enriched on microplastics in marine environment. *Marine Pollution Bulletin,* 144, 61–67.

Gomez, C. & Bosecker, K. (1999). Leaching heavy metals from contaminated soil using Thiobacillus ferrooxidans or Thiobacillus thiooxidans, *Geomicrobiology Journal*. 16. 233–244. https://doi.org/10.1080/014904599270613

Gulmine, J. V., Janissek, P. R., Heise, H. M., & Akcelrud, L. (2002). Polyethylene characterization by FTIR. *Polymer Testing*, 21(5), 557–563. https://doi.org/10.1016/S0142-9418(01)00124-6.

Guo, X., & Wang, J.L., (2019). The chemical behaviours of microplastics in marine environment: a review. *Marine Pollution Bulletin*, 142, 1–14.

Guo, X., & Wang, J.L. (2021).Projecting the sorption capacity of heavy metal ions onto microplastics in global aquatic environments using artificial neural networks. *Journal of Hazardous Materials,* 402. Article 123709. https://doi.org/10.1016/j.jhazmat.2020.123709

Holmes, L.A. (2013). Interactions of Trace Metals with Plastic Production Pellets in the Marine Environment. (PhD Thesis, University of Plymouth, UK) 199 pp.

Holmes, L.A., Turner, A., & Thompson, R.C. (2012). Adsorption of trace metals to plastic resin pellets in the marine environment. *Environmental Pollution*. 160, 42–48.

Holmes, L.A., Turner, A., & Thompson, R.C. (2014). Interactions between trace metals and plastic production pellets under estuarine conditions. *Marine Chemistry*, 167, 25–32.

Hummel, D.O. (2002). Atlas of Plastics Additives: Analysis by Spectrometric Methods. Springer-Verlag, Berlin Heidelberg.

Lindsay, W.L. (1979). Chemical Equilibrium in Soils. John Wiley & Sons, New York.

Liu, J., Zhang, T., Tian, L.L., Liu, X.L., Qi, Z.C., Ma, Y.N., Ji, R., & Chen, W. (2019). Aging significantly affects mobility and contaminant-mobilizing ability of nanoplastics in saturated loamy sand. *Environmental Science & Technology*. 53, 5805–5815.

Li, Y., Li, M., Li, Z., Yang, L., & Liu, X. (2019). Effects of particle size and solution chemistry on Triclosan sorption on polystyrene microplastic. *Chemosphere.* 231, 308–314. https://doi.org/10.1016/j.chemosphere.2019.05.116.

Li, W., Lo, H.S., Wong, H.M., Zhou, M., Wong, C.Y., Tem, N.F.Y., & Cheung, S.G., (2020). Heavy metals contamination of sedimentary microplastics in Hong Kong. *Marine Pollution Bulletin*, 153, 110977.

Lohmann, R. (2017). Microplastics are not important for the cycling and bioaccumulation of organic pollutants in the oceans-but should microplastics be considered POPs themselves? *Integrated Environmental Assessment and Management (IEAM). 13*(3), 460-465.

Mato, Y., Isobe, T., Takada, H., Kanehiro, H., Ohtake, C., & Kaminuma, T. (2001). Plastic resin pellets as a transport medium for toxic chemicals in the marine environment. *Environmental Science and Technology*. 35, 318–324. https://doi.org/10.1021/es0010498

Maršić-Lučić, J., Lušić, J., Tutman, P., Bojanić, V. D., Šiljić, J., & Pribudić, J. (2018). Levels of trace metals on microplastic particles in beach sediments of the island of Vis, Adriatic Sea, Croatia. *Marine Pollution Bulletin 137 (2018) 231–236.*

Mudroch, A., Azcue, J.M., Mudroch, P. (1997). Manual of Physico-Chemical Analysis of Aquatic Sediments. Lewis Publishers, New York, NY

Ojha, N., Pradhan, N., Singh, S., Barla, A., Shrivastava, A., Khatua, P., et al. (2017). Evaluation of HDPE and LDPE degradation by fungus, implemented by statistical optimization. *Scientific Reports, (*January 7th). https://doi.org/10.1038/srep39515.

Pagès, P. (2008). Characterization of polymer materials using FT-IR and DSC techniques. https://ruc.udc.es/dspace/bitstream/handle/2183/11499/CC-80%20art%208.pdf

Performance Evaluation of Environmentally Degradable Plastic Packaging and Disposable Food Service Ware. (432-2008-0001). Final Report June 2007. Produced under contract by: California State University Chico Research Foundation. Integrated Waste Management Board Public Affairs Office, Publications Clearinghouse (MS 6) 75 p.

Rajandas, H., Parimannan, S., Sathasivam, K., Ravichandran, M., & Yin, L. S. (2012). Analysis method A novel FTIR–ATR spectroscopy based technique for the estimation of low-density polyethylene biodegradation. *Polymer Testing, 31*(8), 1094–1099. https://doi.org/10.1016/j.polymertesting.2012.07.015.

R Core Team (2021). R: A language and environment for statistical computing. R Foundation 771 for Statistical Computing, Vienna, Austria. https://www.R-project.org/.

Reis, J.M.L., Pacheco, L.J., & da Costa Mattos, H.S. (2013). Influence of the temperature and strain rate on the tensile behaviour of post-consumer recycled high-density polyethylene. *Polymer Testing*. 32. 1576–1581.

Rochman, C.M., Hentschel, B.T., & Teh, S.J. (2014). Long-term sorption of metals is similar among plastic types: implications for plastic debris in aquatic environments. *PLoS One,* 9, Article e85433. doi:10.1371/journal.pone.0085433

Rochman, C.M., Hoh, E., Hentschel, B.T., & Kaye, S. (2013). Long-term field measurement of sorption of organic contaminants to five types of plastic pellets: implications for plastic marine debris. *Environmental Science and Technology. 47*(3), 1646–1654. https://doi.org/10.1021/es303700s.

Sheik, S., Chandrashekar, K. R. R., Swaroop, K., & Somashekarappa, H. M. M. (2015). Biodegradation of gamma irradiated low density polyethylene and polypropylene by endophytic fungi. International Biodeterioration and Biodegradation, 105, 21–29. https://doi.org/10.1016/j.ibiod.2015.08.006.

Turner, A., & Holmes, L.A. (2015). Adsorption of trace metals by microplastic pellets in fresh water. *Environmental Chemistry, 12*(5), 600-610.

Wang J., Tan Z., Peng J., Qiu Q., & Li M. (2016). The behaviours of microplastics in the marine environment: Review. *Marine Environmental Research.* 113. 7-17.

Wang, F., Wong, C.S., Chen, D., Lu, X., Wang, F., & Zeng, E. Y. (2018). Interaction of toxic chemicals with microplastics: A critical review. *Water Research.* 139. 208-219.

Chapter 4.

Kinetic studies on trace elements (Cd, Cu, Hg, Pb, and Zn) sorption by plastic macro- and microparticles within intertidal sediments; guiding principles for the development and application

4.1. Introduction

To date there are several studies on trace elements-plastic particles interaction which have focused on partitioning and sorption kinetics of trace elements under conditions of marine aquatic environments (Brennecke et al., 2016; Rochman et al., 2013; Rochman et al., 2014; Turner and Holmes, 2015; Wang et al., 2019). Few studies have addressed the sorption of metals by plastics within intertidal sediments. Brennecke et al. (2016) examined the adsorption of two trace elements, copper (Cu) and zinc (Zn), leached from an antifouling paint to virgin polystyrene (PS) beads and aged polyvinyl chloride (PVC) fragments in seawater and described adsorption kinetics (14 days of experimental manipulation) using partition coefficients and mathematical models. Turner and Holms (2015) studied adsorption of trace metals (Ag, Cd, Co, Cr, Cu, Hg, Ni, Pb, Zn) to new (virgin) and aged (beached) plastic production pellets suspended in river water (pH, 6.5) and found, that sorption kinetics (7-day period of laboratory conditions) largely conformed to a pseudo-first-order reversible mechanism with forward rate constants. Another batch experiments was performed in aqueous solution to investigate the adsorption characteristics of Cd onto high-density polyethylene (HDPE) microplastic with different particle sizes that is 1-2 mm, 0.6-1 mm, and 100-154 μm (Wang et al., 2019). The authors confirmed that adsorption of Cd was quite rapid initially and equilibrium time was approximately 90 min. Microplastic with particle size of 100-154 μm had the highest adsorption capacity and adsorption kinetics fitted the pseudo-second-order model (Wang et al., 2019). Rochman et al. (2014) studied sorption of Mn, Co, Ni, Zn and Cd by microparticles of different plastic types (PET, HDPE, PVC, LDPE and PP) in the marine aquatic environments under field conditions. The adsorption data only for several trace elements were successfully fit to the pseudo-first-order kinetic model with an exponential rise to the predicted equilibrium concentration (Rochman et al., 2014). As we can see from the literature review, the process/mechanism of trace elements sorption by macro- and microplastic is not well understood. Moreover, the specific characteristics (e.g., partitioning coefficients, sorption kinetics and rate constants) of interactions between trace elements and plastic macro- and microparticles under influence of marine intertidal sedimentary environmental conditions (e. g., sediments grain size distribution, organic matter content, temperature) are very limited and still unclear despite of it importance.

The common approach of many studies to understand the kinetics and mechanisms of trace elements adsorption/desorption processes in sedimentary and terrestrial/soil environments, is based on conducting equilibrium batch laboratory experiments (solutions) with samples of sediments or soil taken in the field and analyzing the data using Langmuir and Freundlich isotherms and more frequently applied kinetic models (e.g., pseudo-first-order, pseudo-second-order, Weber–Morris diffusion models). However, the results/data of the previous studies have not been tested under environmental realistic and laboratory controlled conditions (e.g., temperature ranges). Our field study on trace elements sorption by plastic particles deployed in the surface layer (10-15 cm) of bed sediments was carried out in the intertidal environments. It is important to note that sediments of the surface layer (3-5 cm) may suspend and re-suspend (exchange of materials between bed load sediments and the overlying water column) under influence of hydrodynamic activities (e.g., waves, tides movement) (Andrady, 2011; Browne et al., 2010; Grant, 1981). The suspension of bed load sediments will have influence on sorption/desorption processes.

By acknowledging the complexity of many factors influencing the behaviour of trace elements in the marine environments, adsorption kinetics can be a good approach for predicting their sorption to plastic macro- and microparticles under conditions of the intertidal sediments. Kinetic models are useful for identifying sorption and partition mechanisms, understanding rate-limiting steps, and evaluating the sorption efficiency (Febrianto et al., 2009; Kajjumba et al., 2018). The objective of this study/chapter is to develop a set of guiding principles and kinetic modeling criteria through the integration of recent studies on sorption of trace elements by plastic particles and the results of long-term field study (Chapter 2) and controlled laboratory experiments under conditions of different constant temperatures (T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C) (Chapter 3). The emphasis will be on the equilibrium and kinetic aspects of Cd, Cu, Hg, Pb, and Zn sorption by plastic macro- and microparticles as influenced by sediment geochemistry and temperature.

4.2. Materials and methods. Kinetic modelling criteria and guiding principles

4.2.1. Predictive modelling on trace elements sorption by macro- and microparticles

The development of a kinetic model on trace elements-plastic particles interactions within marine intertidal/coastal sedimentary environment is very important for predicting the environmental behaviour of these contaminants. The data used for sorption kinetic studies was derived from the following studies: a) long-term (up to 38 months) field experiments on trace elements sorption by plastic macro- and microparticles within intertidal sediments at two sites, low (HB, OM =2.8%) and high (MWFCA, OM = 15.8%) in organic matter content (Chapter 2) and b) long-term (up to 21 months) controlled laboratory experiments on simulation of trace elements sorption by plastic macro- and microparticles in the intertidal sediments (OM=2.8% and OM=15.8%) under conditions of constant temperature of T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C (Chapter 3). The detailed characterization of trace elements (Cu, Zn, Pb, Cd, and Hg) and plastic particles (macro-HDPE (polyethylene chips), macro-PETE (textile fabric), micro-HDPE (microbeads), and micro-PETE (fibres)), description of the experimental setup, sampling procedures, laboratory measurements and quality assurance and quality control (QA/QC) of measurements is provided in the Chapter 2 and Chapter 3.

4.2.2. Sorption kinetic models for estimating sorption coefficient

To investigate the mechanism of trace elements (Cd, Cu, Pb, Zn and Hg) sorption by plastic macro- and microparticles within two contrasting sedimentary environments, kinetic models have been used to test the experimental data generated from long-term field experiments (Chapters 2) and controlled laboratory experiments (Chapters 3). The adsorption kinetics provides insight into the reaction rate and the sorption mechanism (Alberti et al., 2012; Febrianto et al., 2009; Kajjumba et al., 2018; Moussout et al., 2018). Various adsorption kinetic models have been used to understand the adsorption kinetics. Several of these models including pseudo-first-order rate model (PFOM), pseudo-second-order rate model (PSOM), intra-particle diffusion (IP) model (Weber and Morris sorption kinetic model), first-order reversible reaction model and Elovich's model are widely applied in describing adsorption kinetics in soil and sediments (Pen et al., 2010; Pen and Xing, 2010). From the literature review, the simple empirical expressions are frequently applied and pseudo-first-order and pseudo-second-order kinetic models which are based on the sorption at vacant biosorbent surface sites, are the most commonly used models to study the sorption kinetics. These two models have been applied to a wide variety of adsorption systems, from aqueous solution to soil/sediments, from biomass to nanoplastic as adsorbent, and from trace elements to pharmaceuticals as adsorbate or contaminants (Febrianto et al., 2009; Ho, 2006; Ho and McKay, 1998; Hu et al., 2021; Kajjumba et al., 2018; Moussout et al., 2018; Rochman et al., 2014; Tourinho et al., 2019). We used pseudo-first-order and pseudo-second-order kinetic models to test the data on sorption of trace elements by plastic particles within marine intertidal sediments and showed that these models are not well suited for our data. Therefore, at the end of this chapter, we suggest a different kinetic modeling framework that is better suited for our data.

4.2.2.1. Pseudo-first-order kinetic model

The pseudo-first-order kinetic model (PFOM) also known as Lagergren model describes the adsorption of solute onto adsorbent following a first order mechanism. The pseudo-first-order rate equation based on solid phase capacity is generally expressed as follows (Alberti et al., 2012; Febrianto et al., 2009; Fred-Ahmadu et al., 2020; Kajjumba et al., 2018; Lagergren, 1898; Moussout et al., 2018):

$$dq_t/dt = k_1\,(q_e - q_t) \qquad (4.1)$$

where q_t (mg/g) is the amount of solute sorbed on the surface of the sorbent at time t; q_e (mg/g) is the amount of solute sorbed at equilibrium, and k_1 (min^{-1}) is the pseudo-first-order rate constant of sorption. The integration of Equation (4.1) with the boundary condition q = 0 at t =0 gives a linear expression of the PFOM:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \qquad (4.2)$$

Equation (4.2) can be re-written in the non-linear form:

$$q_t = q_e(1 - \exp(-k_1 t)) \qquad (4.3)$$

The value of k_1 (min^{-1}) is determined by plotting $\ln(q_e - q_t)$ versus t and finding the slope of the curve. The q_e value needed by this method is determined from the experimental values. Nonlinear procedure fitting of Equation (4.3) gives a predicted value of $q_{e,calc}$ and k_1.

4.2.2.2. Pseudo-second-order kinetic model

The pseudo-second-order kinetic model (PSOM) assumes that the rate of adsorption of solute is proportional to the available sorption sites on the adsorbent. The pseudo-second-order kinetic model is derived on the basis of the sorption capacity of the solid phase, expressed as following (Febrianto et al., 2009; Kajjumba et al., 2018; Moussout et al., 2018):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{4.4}$$

where q_t is adsorbate adsorbed onto adsorbent at time t (mg/g), q_e is equilibrium adsorption capacity (mg/g), and k_2 is rate constant. Integration of Equation (4.4) with the boundary conditions as follow: t =0, q = 0, and at t = t, q=q, gives an expression of the pseudo-second-order kinetic model:

$$1/(q_e - q_t) = 1/q_e + k_2 t \tag{4.5}$$

Equation (4.5) can be rewritten in the linear form as:

$$t/q_t = t/q_e + 1/k_2\, q_e^2 \tag{4.6}$$

where k_2 (g/(mg min)) is the pseudo-second-order rate constant of sorption.

Therefore, the value of the PSOM kinetic constants k_2 can be determined by plotting (t/q_t) against t. The q_e value needed is determined from the experimental value ($q_{e,exp}$). Even though the PFOM and PSOM kinetic models are affected by many factors, including initial trace elements concentration, temperature, sorbent particle size (plastic macro- and microparticles), and types of trace elements, the kinetic models can simulate the impact of observable rate parameters. It is clear from the literature review that many sorption studies applied PFOM and PSOM kinetic models, but most experimental data fit best to pseudo-second-order kinetic model (Alberti et al., 2012; Febrianto et al., 2009; Ho, 2006; Ho et al., 2006; Ho et al., 2000; Kajjumba et al., 2018).

4.2.2.3. Statistical analysis. Goodness of fit.

To determine the sorption kinetic model that best describes the interaction between the solid and solute phases, the goodness of fit is used. According to the definition, the goodness of fit of a statistical model describes how well it fits a set of observations. Measures of goodness of fit evaluates the discrepancy between observed values and the values expected under the model in question (Alberti et al., 2012; Febrianto et al., 2009; Kajjumba et al., 2018).

To estimate the fit of a model, a large variety of measures have been used. The coefficient of determination (R^2 or R-squared), sum-of-squared errors (SSE), average relative error, Spearman's correlation coefficient, non-linear chi-square test, and standard deviation of relative errors are some of the error functions that have been employed to study model fit (Alberti et al., 2012; Febrianto et al., 2009; Kajjumba et al., 2018). Most of sorption studies utilized the coefficient of determination (R^2) to validate their models. A validation method is a measure of how low the model error is. The assumptions are that the errors are independent (i.e., random) and they follow the normal distribution (Drapper and Smith, 1998). In our study we have applied the coefficient of determination (R^2) as one of the most used error function in determining the sorption kinetic model. The coefficient of determination can be expressed by the most general formula as following (Drapper and Smith, 1998):

$$R^2 = 1 - (SS_{res}/SS_{tot}) \tag{4.7}$$

where SS_{res} is residuals sum of squares and SS_{tot} is total sum of squares. The residual sum of squares (sum of squares of residuals) and the total sum of squares (proportional to the variance of the data) can be found as following:

$$SS_{res} = \sum_{i=1}^{n} (y_i - \hat{y}_i)^2 \tag{4.8}$$

$$SS_{tot} = \sum_{i=1}^{n} (y_i - \bar{y}_i)^2 \tag{4.9}$$

where y_i represents the actual values or the points; $\hat{y}_i$ represents the prediction or a point on the regression line; $\bar{y}_i$ represents the mean of all the values.

The model predictability performance can be evaluated in terms of R-squared. In the best case, the modeled values exactly match the observed values, which results in $SS_{res}= 0$ and $R^2 = 1$. The coefficient of determination $R^2 \geq 0.50$ is considered a moderate fit for the given model. The fitting of $R^2 \geq 0.75$ is statistically good, but the fitting of $R^2 \geq 0.90$ is most statistically significant and can be used to make conclusions (Drapper and Smith, 1998; Kajjumba et al., 2018). However, it should be noted that a $R^2 \geq 0.90$ for a model does not necessarily show that the model is the appropriate model. This is especially true when the model is fit to only a few data points.

From the literature review, the most common practice to determine the adsorption kinetic parameters, such as rate constants k_1 (PFOM) and k_2 (PSOM), is by using the linear form of the kinetic models. The value of the rate constants k_1 and k_2 can be found from the linear plots of $\ln(q_e - q_t)$ versus time (t) and t/q_t versus time for PFOM and PSOM according to equations (4.2) and (4.6), respectively and best fit line (R_2). In our study, to estimate the value of the rate constants k_1 (PFOM) and k_2 (PSOM) in total 7 (0, 1, 2, 3, 8, 12, and 21 months) and 9 (0, 1, 2, 3, 8, 12, 21, 27, and 38 months) datapoints of triplicated measurements were used from laboratory and field experimental datasets, respectively (Chapter 2, Chapter 3). For the data derived from the field experiments (Chapter 2) and controlled laboratory experiments (Chapter 3) the equilibrium concentrations q_e were determined approximately by the mean of the last two or three concentrations (measurements) in the time-course. However, for the data from the field experiments (Chapter 2) where the equilibrium concentration is dynamic constant, the q_e value can be estimated by extrapolating the experimental data to infinite time $t =\infty$, or by “trial and error”.

Results and Discussion. Kinetic model assumptions and predictions

Predicting the rate of sorption is among the most important factors in sorption studies. Various factors influence the rate of sorption, such as types of trace elements, initial concentration of trace elements, temperature, characteristics of sorbent (e.g., plastic type, particle size of macro- and microplastic). The kinetic model is only concerned with the effect of conditions/parameters of the observable system on the overall reaction rate (Alberti et al., 2012; Febrianto et al., 2009; Kajjumba et al., 2018). As follows from the literature review, pseudo-first-order and pseudo-second-order kinetic models are the most frequently applied model to study the sorption kinetics in soils and sediments (Hu et al., 2021;Kajjumba et al., 2018; Pan and Xing, 2010; Pan et al., 2010).

The interpretation of the results is crucial in sorption studies and the assumptions of each model should not be ignored. Most of sorption studies utilized the coefficient of determination (R^2) combined with q_e (equilibrium concentration/capacity) in their work to validate kinetic modeling. It is very important in the kinetic sorption/desorption experiments to reach equilibrium. Application of the pseudo-first-order and pseudo-second-order kinetic models requires prior knowledge of equilibrium concentration (equilibrium capacity) from the sorption experiments ($q_e=q_{e\ exp}$) for a straight forward estimation of the rate constant by using equations (4.1)-(4.6.) Alternatively, the equilibrium concentration, q_e, could be estimated by extrapolating the experimental data to infinite time $t = \infty$, but this can introduce additional errors. The adsorption studies that did not reach equilibrium (i.e. q_e is unknown) make application of PFOM and PSON kinetic models unsuitable for direct rate constants estimation. However, a kinetic model that properly accounts for all the interactions, could estimate the equilibrium constant if it can be fitted to enough data points.

Equilibrium concentration in sorption is defined as the concentration measured at a time when it no longer fluctuates. We have chosen to use the term “equilibrium concentration” applied by the many authors of the cited sorption studies (Hu et al., 2021; Tourinho et al., 2019; Turner et al., 2015; Wang et al., 2019; Zou et al., 2020). In the long-term (up to 21months) controlled laboratory study on simulation of Cd, Cu, Pb, and Zn sorption by plastic macro- and microparticles deployed in the intertidal sediments and under conditions of constant temperature (T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C) equilibrium was reached in each individual experiment (Chapter 3, Table 3.1). In the long-term (up to 38 months) field experimental study on sorption of trace elements by plastic macro- and microparticles within two contrasting marine intertidal sedimentary environments the concentration of Cd, Cu, Hg, Pb, and Zn in sediments did not reach equilibrium (Chapter 2). Concentration of Cd, Cu, Hg, Pb, and Zn on plastic particles deployed in the intertidal sediments reached equilibrium in the medium (Chapter 2, Table 2.2) that represents a closer approach to the natural conditions in the marine environment which is in accordance with Brennecke et al. (2016), Rochman et al.

(2013), and Rochman et al. (2013). Brennecke et al. (2016) pointed out that the "traditional equilibrium constant can be considered as a dynamic constant considering a continuous fluctuation" of trace elements concentration in the natural conditions.

In this chapter we use data from our field and laboratory experiments to explore the fit of different kinetic models. The aim is to develop kinetic modeling criteria and guiding principles that can predict the degree of Cu, Zn, Pb, Cd, and Hg sorption by a particular type of plastic particles as a function of time and of intertidal sediments characteristics (e. g., grain size distribution, organic matter content). This will provide a kinetic modelling tool that can be used to assess the conditions under which plastic macro- and microparticles pose the greatest threat to the environment as an additional vector of copper, cadmium, lead, mercury, and zinc, exposure into benthic food webs. This can improve ecotoxicological studies which involve understanding the fate and effects of contaminants within natural ecosystems.

4.2.3. Kinetic studies on trace elements (Cd, Cu, Hg, Pb, and Zn) sorption by plastic macro- and microparticles in the intertidal sedimentary environment (field experiments)

The pseudo-first-order (PFOM) and pseudo-second-order (PSOM) kinetic models were used to test the data generated from the long-term field experimental study (up to 38 months) on sorption of trace elements (Cd, Cu, Hg, Pb, and Zn) by plastic macro- and microparticles within two contrasting marine intertidal sedimentary environments with high (MWFCA, OM=15.8%) and low (HB, OM=2.8%) in organic matter content (Chapter 2). The kinetic of trace elements sorption was tested by applying the PFOM and PSOM models given by equation (4.3) and equation (4.6), respectively. The pseudo-first-order (k_1) and pseudo-second-order (k_2) rate constants of Cd, Cu, Hg, Pb, and Zn sorption by plastic macro- and microparticles of PETE and HDPE deployed in the intertidal sediments with low (OM=2.8%) and high (OM=15.8%) organic matter content are shown in Table 4.1. We calculated the coefficient of determination (R^2) for the PFOM and PSOM models applied to our data.

The application of the pseudo-first-order and pseudo-second-order kinetic models demonstrate that in relation to the size of plastic particles, the PFOM and PSOM kinetic models do not perform well (R^2 =0.13-0.70) in fitting experimental data on sorption of Cd, Cu, Hg, Pb, and Zn by micro-PETE (fiber), micro-HDPE (microbeads), and macro-HDPE (polyethylene) and have the most significant values of the coefficient of determination in the range of R^2 = 0.7746 - 0.9676 only for Cd, Cu, Hg, Pb, and Zn sorption by macro-PETE (textile fabric) samples_deployed in the intertidal sediments with low (OM=2.8%) and high (OM=15.8%) organic matter content. In addition, in relation to the type of trace elements, the PFOM and PSOM kinetic models do not perform well (R^2 =0.13-0.70) in fitting experimental data on sorption of Cd, Cu, Pb, and Zn (except Hg) by macro- and microparticles of PETE and HDPE. Only the data on sorption of mercury (Hg) by macro- and microparticles of PETE and HDPE deployed in the intertidal sediments low in organic matter content (OM=2.8%) and by macro- and microparticles of PETE deployed in the intertidal sediments high in organic matter content (OM=15.8%) fitted well both, PFOM and PSOM kinetic models (R^2 =0.7316-0.9676) (Table 4.1). In addition, the rate constants (k_1) were not at all consistent. For instance, for Cd, k_1= 0.7843 for the micro-PETE (fiber) at the HB site but k_1= 0.0074 at the MWFCA site for the same fiber. Even when R^2>0.9, for macro-PETE (textile fabric) k_1= 0.0610 and k_1= 0.2857 for Hg at the HB and MWFCA site, respectively.

These findings are not surprising given that the PFOM and PSOM models only incorporate interactions between dissolved trace elements in the aquatic phase and binding to plastic particles. The models do not account for competitive sorption of trace elements between plastic particles and particles of organic matter in sediments (Wang, 2019; Liu et al., 2019). The high R^2 for Hg can be because Hg concentrations in the intertidal sediments were at low level (0.03-0.05 mg/g) which is in accordance with Kajjumba et al. (2018) and Azizian (2004).

The value of R-squared decreased with increasing organic matter content in the intertidal sediments, supporting the claim that it is necessary to include competition between plastic particles and organic sediments in a kinetic model. Accordingly, high concentration of trace elements (Cd, Cu, Hg, Pb, and Zn) in the surrounding environments and high organic matter content (OM=15.8%) in the intertidal sediments limit the predictability of the PFOM and PSOM kinetic models on trace elements sorption by plastic particles under environmental realistic conditions of intertidal sedimentary environment.

Overall, the analysis of the results of long-term field experimental studies demonstrated that sorption by macro- and microparticles particles of PETE and HDPE data did not fit the PFOM and PSOM well (Table 4.1). It is clear that the pseudo-first-order and pseudo-second-order kinetic models are not applicable to describe properly the mechanism of the trace elements (Cd, Cu, Hg, Pb, and Zn) sorption by plastic macro- and microparticles deployed in the surface layer of the intertidal sediments. The PFOM and PSOM describe the sorption process appropriately only in the system "aqueous phase – solid phase" with low concentration of solid particles. For example, after batch adsorption experiments (solution flasks containing 5 g sediment and 25 mL of solution) the adsorption kinetics of herbicides on sediment were accurately described by the pseudo-second-order kinetic model ($R^2 > 0.900$) (Hu et al., 2021). Contrary to the above, the sorption kinetics in the system "aqueous phase – solid phase" with high concentration of solid particles, as represented in the surface layer of intertidal sediments, cannot be accurately described by the PFOM and PSOM kinetic models. The low and high concentration of solid particles leads to significantly different sorption process in the "aqueous phase – solid phase" system.

Generally, the interaction between solid phase (sorbent) and solute phase (sorbate) is sorption, which can be divided into chemical, physical, or electrostatic terms (Febrianto et al., 2009; Kajjumba et al., 2018; Lagergren, 1898). The pseudo-first-order kinetic model is based on the assumption that the rate of change of solute uptake with time is directly proportional to difference in saturation concentration and the amount of solid uptake with time. It is commonly observed, that this assumption can be applicable over the initial stage of an adsorption process. The pseudo-second-order kinetic model is based on the assumption that the rate-limiting step is chemical sorption and predicts the behaviour over the whole range of adsorption process. In these conditions, the adsorption rate is dependent on adsorption capacity not on concentration of sorbate. However, the results of the field experimental studies (Chapter 2) demonstrated that trace elements-plastic particles interactions within intertidal sedimentary environments may include three periods, such as rapid adsorption (initial period), slow adsorption (reaching of equilibrium state), and a period of desorption (Chapter 2). The process of desorption may occur when the adsorbate-solid surface interactions are weak. To understand the detailed characteristics of the adsorption processes, the combination of two or more steps are necessary to properly model overall reaction rate.

We can conclude that existing PFOM and PSOM kinetic models are not applicable for accurate predictive modeling of trace metals (Cd, Cu, Hg, Pb, and Zn) sorption by micro-PETE (fibre), micro-HDPE (microbeads), macro-PETE (textile fabric), and macro-HDPE (polyethylene chips) in the environmental realistic conditions of intertidal sediments with organic matter content in the range of OM=2.8-15.8%. In light of this conclusion we suggest/propose an alternative approach (modeling framework) in kinetic modeling of the sorption of trace elements by plastic macro- and microparticles within intertidal sedimentary environment.

Table 4.1. Pseudo-first-order (k_1) and pseudo-second-order (k_2) rate constants defining the interaction between trace elements (Cd, Cu, Hg, Pb, and Zn) and plastic macro- and microparticles within intertidal sedimentary environment (field sorption experiments)

Plastic particles			**Pseudo-first order**		**Pseudo-second order**	
		$q_{e, exp}$ (mg/g)	**k_1 (month^{-1})**	**R^2**	**k_2 (g/(mg month))**	**R^2**
HB, OM=2.8%	**Cd**					
micro-PETE (fiber)		0.2201	0.7843	0.4963	1.9500	0.5350
micro-HDPE (microbeads)		0.1565	0.0548	0.7004	0.1700	0.6962
macro-PETE (textile fabric)		0.3158	0.4053	**0.9632**	1.6500	**0.9606**
macro-HDPE (polyethylene)		0.1983	2.3935	0.4863	60.9500	0.4664
MWFCA, OM=15.8%	**Cd**					
micro-PETE (fiber)		0.0991	0.0074	0.1334	0.0150	0.1372
micro-HDPE (microbeads)		0.2585	0.0261	0.2121	0.0090	0.2197
macro-PETE (textile fabric)		0.2986	0.3224	**0.8158**	0.2000	**0.9417**
macro-HDPE (polyethylene)		0.0512	0.0460	0.3624	0.0500	0.3569
HB, OM=2.8%	**Cu**					
micro-PETE (fiber)		4.5099	0.2309	0.6990	0.0674	0.6643
micro-HDPE (microbeads)		1.6602	0.0027	0.1158	2.4809	0.2426
macro-PETE (textile fabric)		9.2492	0.0085	**0.9654**	0.0010	**0.9535**
macro-HDPE (polyethylene)		3.1836	0.3856	0.6355	0.2177	0.6660
MWFCA, OM=15.8%	**Cu**					
micro-PETE (fiber)		1.4332	0.1216	0.0854	9.9816	0.2364
micro-HDPE (microbeads)		4.5395	0.0240	0.3989	0.0023	0.3974
macro-PETE (textile fabric)		1.2563	0.0011	**0.7800**	0.0010	**0.7746**
macro-HDPE (polyethylene)		0.9895	0.0722	0.1999	14.6242	0.2302
HB, OM=2.8%	**Hg**					
micro-PETE (fiber)		0.0330	0.7494	**0.7596**	27.6500	**0.7316**
micro-HDPE (microbeads)		0.0380	0.0747	**0.7581**	1.4000	**0.7575**
macro-PETE (textile fabric)		0.0498	0.0610	**0.9652**	0.9500	**0.9676**
macro-HDPE (polyethylene)		0.0430	0.4117	**0.9161**	20.4200	**0.9646**

Plastic particles		$q_{e,\ exp}$ (mg/g)	Pseudo-first order k_1 (month^{-1})	 R^2	Pseudo-second order k_2 (g/(mg month))	 R^2
MWFCA, OM=15.8%	**Hg**					
micro-PETE (fiber)		0.0353	0.9696	**0.9241**	37.9500	**0.8464**
micro-HDPE (microbeads)		0.0650	0.0150	0.3950	0.0040	0.4083
macro-PETE (textile fabric)		0.0506	0.2857	**0.9191**	6.5000	**0.9155**
macro-HDPE (polyethylene)		0.0468	0.8314	0.5742	35.5000	0.4897
HB, OM=2.8%	**Pb**					
micro-PETE (fiber)		5.2363	0.1086	0.5936	0.1307	0.6250
micro-HDPE (microbeads)		2.5363	0.1097	0.6422	0.0300	0.6213
macro-PETE (textile fabric)		4.1613	0.0197	**0.8700**	0.0004	**0.8857**
macro-HDPE (polyethylene)		4.1164	0.4147	**0.8850**	0.1150	**0.8532**
MWFCA, OM=15.8%	**Pb**					
micro-PETE (fiber)		1.8618	0.0735	0.2537	12.9780	0.1455
micro-HDPE (microbeads)		2.2827	0.1013	0.5012	0.0250	0.4915
macro-PETE (textile fabric)		2.8630	0.0650	**0.9504**	0.0095	**0.9521**
macro-HDPE (polyethylene)		1.0398	0.0232	0.0697	0.0060	0.0737
HB, OM=2.8%	**Zn**					
micro-PETE (fiber)		2.0570	0.8400	0.5123	1.3850	0.4546
micro-HDPE (microbeads)		3.2466	0.0690	0.3198	0.0130	0.3117
macro-PETE (textile fabric)		3.8170	0.0194	**0.9271**	0.0085	**0.9218**
macro-HDPE (polyethylene)		3.4148	1.3660	0.2380	1.4500	0.2023
MWFCA, OM=15.8%	**Zn**					
micro-PETE (fiber)		0.8609	0.0331	0.1970	0.0022	0.2060
micro-HDPE (microbeads)		2.5833	0.0514	0.2408	0.0090	0.2409
macro-PETE (textile fabric)		1.2305	0.5696	**0.8047**	0.5641	**0.8450**
macro-HDPE (polyethylene)		2.1562	0.2665	0.0009	6.5600	0.1594

Note: Pseudo-first-order (k_1) and pseudo-second-order (k_2) rate constants were calculated using the data of long-term (up to 38 months) field experimental study on sorption of trace elements (Cd, Cu, Hg, Pb, and Zn) by plastic particles (macro-PETE (textile fabric), macro-HDPE (polyethylene chips), micro-PETE (fibre), and micro-HDPE (microbeads)) deployed in the intertidal sediments at HB (OM=2.8%) and MWFCA (15.8%) study sites. The detailed description and data analysis of long-term field experimental study is provided in the Chapter 2. The most significant values of the coefficient of determination (R^2) are in the bold text.

4.2.4. Kinetic studies on trace elements (Cd, Cu, Pb, and Zn) sorption by plastic macro- and microparticles in the intertidal sediments under conditions of constant temperature (T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C) (laboratory experiments)

To date, macro- and microplastics study on sorption of trace elements have been conducted as field experiments in aquatic environments, but without or with a minor attention to the temperature as a factor influencing chemical behaviour of the plastic particles (Holmes et al., 2012; Holmes et al., 2014; Rochman et al., 2013; Rochman et al., 2014; Wang et al., 2019). Some published studies on dependence of trace elements sorption on temperature in the terrestrial (soil) environments have reported an increase in loading capacities of trace elements onto plastic surfaces with increasing temperature (Gomez et al., 1999). Accordingly, the effects of the temperature on the process of trace elements sorption/desorption to plastic macro- and microparticles under the conditions of marine sedimentary environments especially in the intertidal area needs further investigation.

The data generated from laboratory experimental study on trace elements (Cd, Cu, Pb, and Zn) sorption by plastic particles (Chapter 3) were tested by applying the pseudo-first-order and pseudo-second-order kinetic models (Equation (4.3) and Equation (4.6), respectively). Table 4.2 shows the reaction rate constants k_1 (PFOM) and k_2 (PSOM) for Cd, Cu, Pb, and Zn sorption by plastic macro- and microparticles of PETE and HDPE in the intertidal sediments with low (OM=2.8%) and high (OM=15.8%) in organic matter content under conditions of constant temperature (T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C). Statistical criteria used for estimating the goodness of fit of the models to the data were the coefficients of determination (R^2). The differences in the values of the coefficient of determination (R^2) were used as parameters to determine the best model fit for the data.

In general, model fitting of data from laboratory sorption experiments of Cd, Cu, Pb, and Zn resulted in high values of the coefficient of determination (R^2 = 0.80-0.99) (Table 4.2). The lowest significant value of the coefficient of determination in the range of R^2 = 0.7170 – 0.4065 came from experimental data on kinetics of Zn sorption by micro-HDPE (microbeads) under condition of low temperature of T= -4.0°C. Overall, the rate constants k_1 (PFOM) for Cd, Cu, Pb, and Zn sorption decreased with decrease in temperature (T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C). This applied to trace elements sorption by macro-PETE (textile fabric), macro-HDPE (polyethylene chips), micro-PETE (fiber), and micro-HDPE (microbeads) in the surrounding environments of the intertidal sediments with low (OM=2.8%) and high (OM=15.8%) in organic matter content. In contrast to (PFOM) simulations, the rate constants k_2 (PSOM) for trace elements sorption by plastic particles increased with decrease in the temperature of the surrounding environments. Interestingly, the rate constants k_1 (PFOM) and k_2 (PSOM) increased with the increase in organic matter content in the intertidal sediments. This finding suggests that characteristics of sediments such as organic matter content and grain size may significantly affect trace elements (Cd, Cu, Pb, and Zn) sorption by plastic particles of PETE and HDPE than temperatures from T=-4.0°C to T=+18.0°C.

However, for Pb and Zn sorption by plastic particles the PFOM and PSOM models the predicted values of k_1 and k_2 were all over the place for different temperatures and types of plastic particles (Table 4.2). For instance, for Pb sorption by macro-HDPE (polyethylene) and macro-PETE (textile fabric) deployed in sediments with high (OM=15.8%) organic matter content, unexpected increase rate constants k_1 (PFOM) and decrease rate constants k_2 (PSOM) were observed under conditions of T=-4.0°C, respectively. In addition, for Zn sorption by macro-HDPE (polyethylene) in sediments with low (OM=2.8%) organic matter content and by macro-PETE (textile fabric) in sediments with high (OM=15.8%) organic matter the rate constants k_1 (PFOM) and k_2 (PSOM) have opposite trends than expected with change of temperature. This demonstrated the limitation of the current models, since sometimes rates constants, k_1 (PFOM) and k_2 (PSOM), increased with temperature, sometimes they decreased, and sometimes the lowest rates were at +4.0°C. This depended on the type of plastic particles and whether the samples came from intertidal sediments with low (OM=2.8%) or high (OM=15.8%) organic matter content.

An unexpected observation from the analysis of Pb and Zn sorption is the inverse relationship between change in the temperature and rate constants k_1 (PFOM) and k_2 (PSOM). While it is expected that an increase in the temperature should increase rate constants k_1 (PFOM) and decrease rate constants k_2 (PSOM), the opposite trends were observed. These findings demonstrated the limitations of the PFOM and PSOM models for prediction of trace elements sorption by plastic macro- and microparticles. As explained, this is because those models do not factor in competition between plastic particles and sediments.

The analysis reveals that data, derived from laboratory controlled experiments on simulation of trace elements sorption by macro- and microparticles of PETE and HDPE under conditions of constant temperatures (T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C), is generally not well represented by the PFOM and PSOM models (Table 4.2). This is as expected, given the limitations of those model when there is competition in sorption site between sediments and plastic particles. In addition, it is important to remember that a high R^2 value do not mean that those models were appropriate. This is because the models were fitted to only a few datapoints and this can often give high R^2 values even for incorrect models. This was highlighted by the inconsistent values for the rate constants k_1 and k_2 that we got from the fitting the PFOM and PSOM models to our data. This became clear from the predictive modeling of Pb and Zn sorption by plastic micro- and macroparticles under conditions of constant temperature of T=- 4.0°C, T=+4.0°C, and T=+18.0°C in the intertidal sediments with organic matter content in the range of OM=2.8-15.8%. Overall the resulting values for the rate constants when fitting the PFOM and PSOM models to our data suggest that the model is not appropriate to use for our sorption data for all the trace elements, Cd, Cu, Pb, and Zn. It is inaccurate to characterize the mechanisms of kinetic processes using the pseudo-first-order and pseudo-second-order kinetics model equations and the high values of coefficient of determination.

Table 4.2. Pseudo-first-order (k_1) and pseudo-second-order (k_2) rate constants defining the interaction between trace elements (Cd, Cu, Pb, and Zn) and plastic macro- and microparticles in the intertidal sediments under conditions of constant temperature (T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C) (laboratory sorption experiments)

Plastic sorbent	Temperature, °C	$q_{e\ exp}$ (mg/g)	Pseudo-first order k_1 (month^{-1})	 R^2	Pseudo-second order k_2 (g/(mg month))	 R^2
HB, OM=2.8%		**Cd**				
micro-PETE (fiber)	18.0	0.5340	0.3021	0.9888	0.6000	0.9796
micro-HDPE (microbeads)	18.0	0.6880	0.2775	0.9837	0.4025	0.9712
macro-PETE (textile fabric)	18.0	0.3372	0.4950	0.9794	2.3000	0.9783
macro-HDPE (polyethylene)	18.0	0.4580	0.2920	0.9871	0.6000	0.9719
micro-PETE (fiber)	4.0	0.3270	0.2755	0.9649	1.0500	0.9536
micro-HDPE (microbeads)	4.0	0.5825	0.2300	0.9556	0.4250	0.9424
macro-PETE (textile fabric)	4.0	0.2303	0.4350	0.9527	2.9000	0.9664
macro-HDPE (polyethylene)	4.0	0.2675	0.2802	0.9673	2.1500	0.9542
micro-PETE (fiber)	-4.0	0.2370	0.2583	0.9840	1.9500	0.9524
micro-HDPE (microbeads)	-4.0	0.4625	0.2150	0.8853	1.0000	0.9239
macro-PETE (textile fabric)	-4.0	0.1610	0.4235	**0.8563**	3.9000	**0.8758**
macro-HDPE (polyethylene)	-4.0	0.1925	0.2745	0.9262	2.6500	0.9237
MWFCA, OM=15.8%		**Cd**				
micro-PETE (fiber)	18.0	0.5138	0.3387	0.9820	0.8500	0.9703
micro-HDPE (microbeads)	18.0	0.5880	0.4380	0.9647	1.0500	0.9591

Plastic sorbent	Temperature, °C	$q_{e\ exp}$ (mg/g)	Pseudo-first order		Pseudo-second order	
			k_1 (month^{-1})	R^2	k_2 (g/(mg month))	R^2
macro-PETE (textile fabric)	18.0	0.2860	0.3300	0.9379	2.5500	0.9600
macro-HDPE (polyethylene)	18.0	0.4150	0.3450	0.9890	0.9000	0.9765
micro-PETE (fiber)	4.0	0.2675	0.3180	0.9606	2.5500	0.9567
micro-HDPE (microbeads)	4.0	0.4900	0.2700	0.9038	1.0500	0.8558
macro-PETE (textile fabric)	4.0	0.1633	0.2900	**0.8682**	2.9000	**0.8869**
macro-HDPE (polyethylene)	4.0	0.2025	0.2950	0.9464	2.5000	0.9552
micro-PETE (fiber)	-4.0	0.1975	0.2922	0.9865	3.8500	0.9366
micro-HDPE (microbeads)	-4.0	0.4250	0.2600	**0.8392**	1.1000	**0.8460**
macro-PETE (textile fabric)	-4.0	0.1405	0.2720	**0.8043**	7.8000	**0.7987**
macro-HDPE (polyethylene)	-4.0	0.1415	0.2745	0.8879	4.1500	0.9457
HB, OM=2.8%		**Cu**				
micro-PETE (fiber)	18.0	4.5950	0.3019	0.9766	0.0600	0.9802
micro-HDPE (microbeads)	18.0	6.5500	0.2611	0.9858	0.0450	0.9770
macro-PETE (textile fabric)	18.0	3.9875	0.2340	0.9854	0.0550	0.9807
macro-HDPE (polyethylene)	18.0	3.1650	0.2810	0.9855	0.0807	0.9713
micro-PETE (fiber)	4.0	4.2750	0.2650	0.9839	0.0653	0.9728
micro-HDPE (microbeads)	4.0	4.8525	0.2350	0.9748	0.0500	0.9701
macro-PETE (textile fabric)	4.0	3.2250	0.2150	0.9845	0.0750	0.9726
macro-HDPE (polyethylene)	4.0	2.6200	0.1975	0.9057	0.0900	0.9044
micro-PETE (fiber)	-4.0	2.4800	0.2460	0.9809	0.0750	0.9726
micro-HDPE (microbeads)	-4.0	2.6300	0.1565	0.9864	0.0500	0.9830
macro-PETE (textile fabric)	-4.0	1.9750	0.2050	0.9898	0.1500	0.9867
macro-HDPE (polyethylene)	-4.0	1.1700	0.1885	0.9745	0.2500	0.9868
MWFCA, OM=15.8%		**Cu**				
micro-PETE (fiber)	18.0	4.0813	0.3503	0.9873	0.0750	0.9865
micro-HDPE (microbeads)	18.0	5.2600	0.2310	0.9854	0.0450	0.9767
macro-PETE (textile fabric)	18.0	3.1500	0.2180	0.9801	0.0550	0.9681
macro-HDPE (polyethylene)	18.0	2.3250	0.2600	0.9892	0.1000	0.9906
micro-PETE (fiber)	4.0	3.3850	0.3229	0.9926	0.1100	0.9878
micro-HDPE (microbeads)	4.0	3.3800	0.2150	0.9725	0.0600	0.9759
macro-PETE (textile fabric)	4.0	2.3900	0.2050	0.9791	0.1000	0.9695
macro-HDPE (polyethylene)	4.0	2.1700	0.2310	0.9880	0.1200	0.9777
micro-PETE (fiber)	-4.0	2.0900	0.2460	0.9544	0.2450	0.9840
micro-HDPE (microbeads)	-4.0	1.8900	0.2091	0.9593	0.1550	0.9740
macro-PETE (textile fabric)	-4.0	1.3000	0.1950	0.9524	0.2500	0.9762
macro-HDPE (polyethylene)	-4.0	0.8150	0.2250	0.8972	0.9750	0.9606

Plastic sorbent	Temperature, °C	$q_{e\,exp}$ (mg/g)	Pseudo-first order		Pseudo-second order	
			k_1 (month^{-1})	R^2	k_2 (g/(mg month))	R^2
HB, OM=2.8%		**Pb**				
micro-PETE (fiber)	18.0	6.5850	0.4050	0.9563	0.0790	0.9239
micro-HDPE (microbeads)	18.0	7.6750	0.2800	0.9628	0.0320	0.9627
macro-PETE (textile fabric)	18.0	3.9850	0.3050	0.9881	0.0850	0.9813
macro-HDPE (polyethylene)	18.0	5.5750	0.2248	0.9619	0.0350	0.9639
micro-PETE (fiber)	4.0	6.0200	0.2202	0.9572	0.0250	0.9497
micro-HDPE (microbeads)	4.0	6.9600	0.2750	0.9361	0.0550	0.9319
macro-PETE (textile fabric)	4.0	2.7350	0.2795	0.9034	0.1500	**0.8882**
macro-HDPE (polyethylene)	4.0	4.7900	0.2093	0.9856	0.0400	0.9709
micro-PETE (fiber)	-4.0	3.3300	0.2075	0.8375	0.1450	0.8842
micro-HDPE (microbeads)	-4.0	6.0400	0.2500	**0.7629**	0.1125	**0.8238**
macro-PETE (textile fabric)	-4.0	2.0950	0.1405	**0.8443**	0.1550	**0.8144**
macro-HDPE (polyethylene)	-4.0	2.2950	0.1929	0.9834	0.1250	0.9841
MWFCA, OM=15.8%		**Pb**				
micro-PETE (fiber)	18.0	5.1500	0.2757	0.9803	0.0600	0.9843
micro-HDPE (microbeads)	18.0	6.7150	0.3050	0.9192	0.0300	0.9025
macro-PETE (textile fabric)	18.0	3.0450	0.4400	0.9473	0.1650	0.9242
macro-HDPE (polyethylene)	18.0	4.8300	0.1620	0.9719	0.0300	0.9722
micro-PETE (fiber)	4.0	4.8200	0.2415	0.9780	0.0650	0.9820
micro-HDPE (microbeads)	4.0	6.5800	0.2200	0.8922	0.0350	**0.8896**
macro-PETE (textile fabric)	4.0	2.5050	0.3400	0.9283	0.2500	0.9621
macro-HDPE (polyethylene)	4.0	4.1150	0.1600	0.9642	0.0500	0.9567
micro-PETE (fiber)	-4.0	3.5900	0.2250	0.9518	0.1000	0.9648
micro-HDPE (microbeads)	-4.0	6.0500	0.1900	**0.8448**	0.0450	**0.8338**
macro-PETE (textile fabric)	-4.0	1.9700	0.0250	**0.7849**	0.0055	**0.7856**
macro-HDPE (polyethylene)	-4.0	2.0500	0.1800	0.9587	0.0850	0.9368
HB, OM=2.8%		**Zn**				
micro-PETE (fiber)	18.0	4.3200	0.2680	0.9755	0.0500	0.9629
micro-HDPE (microbeads)	18.0	6.3950	0.2755	0.9713	0.0450	0.9725
macro-PETE (textile fabric)	18.0	3.5300	0.3400	0.9858	0.1000	0.9693
macro-HDPE (polyethylene)	18.0	6.1850	0.2507	0.9647	0.0350	0.9728
micro-PETE (fiber)	4.0	4.0200	0.2300	0.9856	0.0550	0.9697
micro-HDPE (microbeads)	4.0	5.1250	0.2500	0.9378	0.0750	0.9294
macro-PETE (textile fabric)	4.0	2.8450	0.2960	0.9828	0.1050	0.9817
macro-HDPE (polyethylene)	4.0	4.6550	0.2321	0.9611	0.0850	0.9785

Plastic sorbent	Temperature, °C	$q_{e\ exp}$ (mg/g)	Pseudo-first order k_1 (month^{-1})	Pseudo-first order R^2	Pseudo-second order k_2 (g/(mg month))	Pseudo-second order R^2
micro-PETE (fiber)	-4.0	2.6300	0.1350	0.9624	0.0650	0.9595
micro-HDPE (microbeads)	-4.0	3.9500	0.2080	**0.7170**	0.0850	**0.6906**
macro-PETE (textile fabric)	-4.0	1.4600	0.2807	0.9828	0.2550	0.9843
macro-HDPE (polyethylene)	-4.0	3.0650	0.0731	0.9457	0.0130	0.9479
MWFCA, OM=15.8%		**Zn**				
micro-PETE (fiber)	18.0	3.8600	0.1929	0.9555	0.0300	0.9619
micro-HDPE (microbeads)	18.0	6.0500	0.2700	0.9665	0.0400	0.9596
macro-PETE (textile fabric)	18.0	2.7700	0.3465	0.9853	0.1450	0.9746
macro-HDPE (polyethylene)	18.0	4.2750	0.3228	0.9788	0.0950	0.9733
micro-PETE (fiber)	4.0	3.1900	0.1629	0.9750	0.0500	0.9580
micro-HDPE (microbeads)	4.0	4.5450	0.2600	**0.8810**	0.0750	**0.8803**
macro-PETE (textile fabric)	4.0	2.3000	0.2141	0.9013	0.1450	0.9313
macro-HDPE (polyethylene)	4.0	3.3200	0.2930	0.9665	0.1850	0.9632
micro-PETE (fiber)	-4.0	1.6800	0.1545	0.9727	0.1000	0.9660
micro-HDPE (microbeads)	-4.0	3.7450	0.2500	**0.4266**	0.0900	**0.4065**
macro-PETE (textile fabric)	-4.0	1.0300	0.2514	0.9267	0.5500	0.9644
macro-HDPE (polyethylene)	-4.0	2.3650	0.2770	0.8948	0.1900	0.9099

Note: Pseudo-first-order (k_1) and pseudo-second-order (k_2) rate constants were calculated using the data of long-term (up to 21 months) controlled laboratory experiments on simulation of trace elements (Cd, Cu, Pb, and Zn) sorption by plastic particles (macro-PETE (textile fabric), macro-HDPE (polyethylene chips), micro-PETE (fiber), and micro-HDPE (microbeads)) deployed in the intertidal sediments low (OM=2.8%) and high (OM=15.8%) in organic matter content and under condition of constant temperature of T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C. The detailed description and data analysis of long-term laboratory experiments is provided in the Chapter 3. The minimum values of R^2 in the bold text. The unacceptable in prediction model fitting rate constant k_1 (PFOM) and k_2 (PSOM) and corresponding values of R^2 are underlined.

4.2.5. Framework for modelling and predicting of the sorption of trace elements by plastic particles within intertidal sediments

To investigate the mechanism of trace elements sorption by plastic macro- and microparticles within two contrasting sedimentary environments, the PFOM and PSOM kinetic models have been used to test the experimental data generated from long-term field and laboratory experiments. However, the PFOM and PSOM kinetic models inaccurately represent the experimentally observed process of trace elements sorption by plastic particles. The existing PFOM and PSOM kinetic models are not acceptable for accurate predictive modeling of sorption processes under condition of intertidal sedimentary environments even if the sorption occur in the surface layer of sediments where re-suspension of solid particles take a place. To better understand and model the process of trace elements sorption by plastic particles within intertidal sediments it would be appropriated to assume that "solute phase (pore water) - solid phase (sediment and plastic particles)" system is complex system with high concentration of solid particles (solid phase). The process of sorption in this system can be described as sorption under condition of marine intertidal sedimentary environment and ignoring this point may lead to a wrong conclusion.

To properly model the kinetics of our system we hypothesize that the transfer of trace elements between solute phase (pore water) and solid phase (intertidal sediment and plastic particles) is governed by reversible reactions. At least two reversible reactions such as sorption and release are generally involved in trace elements exchange between solute phase (pore water) and solid phase (sediment and plastic particles): (a) between pore water (aqua phase) and intertidal sediments (solid phase) and (b) between pore water (aqua phase) and plastic particles deployed in the intertidal sediments (solids phase). These reversible reactions can be represented as follows:

$$Me + S \underset{k_{-2}}{\overset{k_2}{\Leftrightarrow}} Me(S) \qquad (4.10)$$

$$Me + P \underset{k_{-1}}{\overset{k_1}{\Leftrightarrow}} Me(P) \qquad (4.11)$$

where Me is the particular trace element concentration in the aqueous/solute phase; Me(S) is trace element bound to intertidal sediment particles; Me(P) is the trace element bound to the plastic particles deployed in the intertidal sediment; k_1 , k_{-1} , k_2 and k_{-2} are the sorption and desorption rates for reactions (4.1) and (4.2), respectively.

This model considers two reversible reactions for exchange of trace elements that can bind to either the solid phase (sediments (S) or plastic particles (P)). The first one describes a reversible exchange process between dissolved trace elements in pore water and intertidal sediment particles (Me(S)) (Equation 4.10). The second one represents a reversible exchange process between dissolved trace elements in pore water and plastic particles deployed in the intertidal sediments (Me(P)) (Equation 4.11).

The coupled differential equations describing the concentration change in time for these reactions (the evolution of the trace elements in the dissolved phase) can thus be represented by the following differential equations:

$$\frac{d[Me]}{dt} = -k_1[Me]_t[P] + k_{-1}[Me(P)]_t - k_2[Me]_t[S] + k_{-2}[Me(S)]_t \qquad (4.12)$$

$$\frac{d[Me(P)]}{dt} = -k_1[Me]_t[P] + k_{-1}[Me(P)]_t \qquad (4.13)$$

$$\frac{d[Me(S)]}{dt} = -k_2[Me]_t[S] + k_{-2}[Me(S)]_t \qquad (4.14)$$

where [Me] is the concentration of the trace element in the pore water at a given time t; [Me(P)] and [Me(S)] are the concentration of trace element bound to the plastic particles and sediments, respectively. In equation (4.12) the term $(-k_1[Me]_t[P])$ represents the uptake of the trace element by the plastic particles and $(k_{-1}[Me(P)]_t)$ is the release of the trace element from the plastic particles. Similarly, the $(-k_2[Me]_t[S])$ and $(k_{-2}[Me(S)]_t)$ term represent the uptake and release for the sediments. Since this is a closed system, the total amount of trace element is conserved giving:

$$[Me]_t[P] + [Me]_t[S] + [Me] = MT \qquad (4.15)$$

where MT is the total amount of trace element in the "solute phase (pore water) - solid phase (sediment and plastic particles)" system.

At equilibrium $\frac{d[Me]}{dt} = 0$, $\frac{d[Me(P)]}{dt} = 0$, and $\frac{d[Me(S)]}{dt} = 0$ and this gives:

$$(k_1 + k_2)[Me] = -k_1[Me]_t[P] + k_{-2}[Me(S)]_t \qquad (4.16)$$

$$k_2[Me]_t[S] = k_{-2}[Me(S)]_t \qquad (4.17)$$

$$k_1[Me]_t[P] = k_{-1}[Me(P)]_t \qquad (4.18)$$

Taking into account that organic matter content and proportion of fine-grained particles (< 0.063 mm) in grain size distribution of intertidal sediments are important environmental factors with strong influence on trace elements sorption by plastic particles (Chapter 2, Chapter 3), we can further improve the model by separating the sediments into two types. Sediments with non-specific (not organic matter) and specific (organic matter) sorption sites (Ciffroy et al., 2001). In this case equation (4.10) can be split as following:

$$Me + S_1 \underset{k_{-2}}{\overset{k_2}{\Leftrightarrow}} Me(S_1) \tag{4.19}$$

$$Me + S_2 \underset{k_{-3}}{\overset{k_3}{\Leftrightarrow}} Me(S_2) \tag{4.20}$$

This is now gives the following differential equations:

$$\begin{aligned}\frac{d[Me]}{dt} = -k_1[Me]_t[P] + k_{-1}[Me(P)]_t - k_2[Me]_t[S_1] + k_{-2}[Me(S_1)]_t - k_3[Me]_t[S_2] \\ + k_{-3}[Me(S_2)]_t\end{aligned} \tag{4.21}$$

$$\frac{d[Me(P)]}{dt} = -k_1[Me]_t[P] + k_{-1}[Me(P)]_t \tag{4.22}$$

$$\frac{d[Me(S_1)]}{dt} = -k_2[Me]_t[S_1] + k_{-2}[Me(S_1)]_t \tag{4.23}$$

$$\frac{d[Me(S_2)]}{dt} = -k_3[Me]_t[S_2] + k_{-3}[Me(S_2)]_t \tag{4.24}$$

$$[Me]_t[P] + [Me]_t[S_1] + [Me]_t[S_2] + [Me] = MT \tag{4.25}$$

where $Me(S_1)$ is trace element adsorbed by sediments with non-specific binding site (nonorganic particles); $Me(S_2)$ is trace element adsorbed by sediments with specific binding site (organic matter particles). As before, Me(P) is trace element adsorbed by plastic particles deployed in the intertidal sediment; k_1, k_{-1}, k_2, k_{-2}, k_3, and k_{-3} are the sorption and desorption rate constants for reactions (4.11), (4.19), and (4.20), respectively; MT is the total amount of trace element in the “solute phase (pore water) - solid phase (sediment and plastic particles)” system.

The set of coupled differential equations (4.21) - (4.24) can be solved either analytically or numerically. The sorption of trace elements by plastic particles can be calculated as a function of time including period of rapid adsorption (initial period) and period of slow adsorption (reaching of equilibrium) (Chapter 2). The sorption of trace elements by plastic particles would depend on sediment and plastic particles concentrations.

To further improve the model, describing the kinetics of the process of trace elements sorption by plastic particles we can make the rate constants depend on temperature. The model can then be tested against our data collected under conditions of constant temperature of T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C within intertidal sediments. Presumably, the transfer of trace elements between solute phase (pore water) and solid phase (intertidal sediments and plastic particles) is governed by reversible reactions. Therefore we would apply the same approach as previously described (Equation (4.10) - (4.25)). Influence of temperature on sorption of trace elements by plastic particles can be expressed by the rate constants as a function of temperature. A reasonable assumption is to use the Arrhenius equation that gives the dependence of the rate constant of a chemical reaction on the absolute temperature of the surrounding environment. A common form of the Arrhenius equation is:

$$k(T) = Ae^{-\left(\frac{E_A}{RT}\right)} \tag{4.26}$$

Arrhenius equation (4.26) can be rewritten in the logarithmical form as:

$$\ln k(T) = \ln A - (E_A/RT) \tag{4.27}$$

where k is rate constant; A is frequency factor; E_A is activation energy; R is universal gas constant ($R=8.31\ \mathrm{J\ K^{-1}\ mol^{-1}}$); T (Kelvins) is absolute temperature. The activation energy (E_A) is the energy needed to complete the binding. We can assume A and E_A are constant and get the following equation:

$$k(T) = K_0 e^{-\left(\frac{1}{RT}\right)} \tag{4.28}$$

Or equivalently:

$$k(T_2) = k(T_1)e^{-\frac{1}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)} \tag{4.29}$$

4.3. Conclusions

Overall, the PFOM and PSOM models did not fit well to our empirical data on trace elements (Cd, Cu, Hg, Pb, and Zn) sorption (field study). Both too much variation and inconsistency are in the predicted rate constants (Table 4.1). Although the “best” fit was better for the data derived from the laboratory experiments (Table 4.2) the models still suffered from the fact that the predicted rate constants were not consistent, and some went up with temperature while others went down. Since the “best fit” was based on only a few datapoints it is not unusual to get a high R^2 even with an incorrect model. The lack of consistency was not surprising since the underlying assumptions of the PFOM and PSOM models do not apply to our experimental conditions. They don’t take into account the competition of trace element binding between the sediments and the plastic particles.

Therefore, we conclude that existing PFOM and PSOM kinetic models are not applicable for accurate predictive modeling of trace metals (Cd, Cu, Hg, Pb, and Zn) sorption by micro-PETE (fiber), micro-HDPE (microbeads), macro-PETE (textile fabric), and macro-HDPE (polyethylene chips)) in the environmental realistic conditions of intertidal sediments with organic matter content in the range of OM=2.8-15.8% nor in the laboratory experiments that we preformed, where we include sediments from the two sampling sites.

Here we proposed an improved modeling framework that better represent the chemical interactions that are taking place in the intertidal sedimentary system. The model accounts for the kinetics of traces elements sorption by plastic particles under condition of intertidal sedimentary environment. This framework should be a template for future model development for predicting trace elements (Cd, Cu, Hg, Pb, and Zn) sorption by plastic particles within intertidal sediments. The modeling framework is based on two reversible reactions for exchange of trace elements with two elements bound at two different sites on the solid phase: sediment and plastic particles.

References

Alberti, G., Amendola, V., Pesavento, M., & Biesuz R. (2012). Beyond the synthesis of novel solid phases: Review on modelling of sorption phenomena. *Coordination Chemistry Reviews,* 256, 28–45.

Ashton, K., Holmes, L., & Turner, A. (2010). Association of metals with plastic production pellets in the marine environment. *Marine Pollution Bulletin*, 60, 2050-2055.

Azizian, S. (2004). Kinetic models of sorption: a theoretical analysis. *Journal of Colloid and Interface Science,* 276, 47–52.

Bendell, L. I. (2019). Baynes Sound, an Ecologically and Biologically Sensitive Area. In L.I. Bendell, P. Gallaugher, S. McKeachie & L. Wood (Eds.), *Stewarding the Sound; The challenge of managing sensitive ecosystems* (pp.25-40). CRC Press, Taylor and Francis Group, New York.

Brennecke, D., Duarte, B., Paiva, F., Caçador, I., & Canning-Clode, J. (2016). Microplastics as vector for heavy metal contamination from the marine environment. *Estuarine, Coastal and Shelf Science.* 178, 189–195. https://doi.org/10.1016/j.ecss.2015.12.003

Ciffroy, P., Garnier J-M., & Pham, M. K. (2001). Kinetics of the adsorption and desorption of radionuclides of Co, Mn, Cs, Fe, Ag and Cd in freshwater systems: experimental and modelling approaches. *Journal of Environmental Radioactivity,* 55, 71–91.

Davranche, M., Veclin, C., Pierson-Wickmann, A., Hadri, H. E., Grassl, B., Rowenczyk, L., Dia, A., et al. (2019). Are nanoplastics able to bind significant amount of metals? The lead example. *Environmental Pollution,* 249, 940 48. https://doi.org/10.1016/j.envpol.2019.03.087.

Drapper, N.R., & Smith, H. (1998). Applied regression analysis. John Walley & Sons, Inc., New York, NY, USA.

Febrianto, J., Kosasi, A.N, Sunarso, J., Ju, Y., Indraswati, N., & Ismadji, S. (2009). Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: a summary of recent studies. *Journal of Hazardous Materials*, *162*(2-3), 616–645. doi:10.1016/j.jhazmat.2008.06.042.

Fred-Ahmadu O. H., Bhagwat G., Oluyoye, I., Benson, N. U., Ayejuyo O. O., & Palanisami T. (2020). Interaction of chemical contaminants with microplastics: Principles and perspectives. *Science of the Total Environment*, 706. 135978. https://doi.org/10.1016/j.scitotenv.2019.135978

Gomez, C. & Bosecker, K. (1999). Leaching heavy metals from contaminated soil using Thiobacillus ferrooxidans or Thiobacillus thiooxidans, *Geomicrobiology Journal,* 16, 233–244. https://doi.org/10.1080/014904599270613.

Ho Y.S. (2006). Second-order kinetic model for the sorption of cadmium onto tree fern: a comparison of linear and non-linear methods. *Water Research* 40.119–125.

Ho, Y.S., & McKay, G. (1998). Kinetic models for the sorption of dye from aqueous solution by wood. *Process Safety and Environmental Protection, 76*(2), 183-191.

Ho, Y.S., Ng, J.C.Y., & McKay, G. (2000). Kinetics of pollutant sorption by biosorbents: review. *Separation and Purification Methods,* 29, 189–232. https://doi.org/10.1081/SPM-100100009.

Ho, Y. S., & Ofomaja, A. E. (2006). Pseudo-second order model for lead ion sorption from aqueous solutions onto palm kernel fiber. *Journal of Hazardous Materials*, B129 .137–142. doi:10.1016/j.jhazmat.2005.08.020.

Ho, Y.S., Wase, D.A.J., & Forster, C.F. (1996). Kinetic studies of competitive heavy metal adsorption by sphagnum moss peat. *Environmental Science & Technology*, 17, 71–77.

Holmes, L.A. (2013). Interactions of Trace Metals with Plastic Production Pellets in the Marine Environment. (PhD Thesis, University of Plymouth, UK) 199 pp.

Holmes, L.A, Turner, A., & Thompson, R.C. (2012) Adsorption of trace metals to plastic resin pellets in the marine environment. *Environmental Pollution,* 160, 42–48.

Holmes, L.A., Turner, A., & Thompson, R.C. (2014). Interactions between trace metals and plastic production pellets under estuarine conditions. *Marine Chemistry*, 167, 25-32.

Hu, M., Liu, L., Hou, N., Li, X., Zeng, D., & Tan H. (2021). Insight into the adsorption mechanisms of ionizable imidazolinone herbicides in sediments: Kinetics, adsorption model, and influencing factors. *Chemosphere,* 274, Article 129655. https://doi.org/10.1016/j.chemosphere.2021.

Kajjumba, G. W., Emik, S., Öngen, A., Özcan H. K., & Aydın S. (2018). Modelling of adsorption kinetic processes - errors, theory and application. *Advanced Sorption Process Applications*. DOI:http://dx.doi.org/10.5772/intechopen.80495

Moussout, H., Ahlafi, H., Aazza, M., Maghat, H. (2018). Critical of linear and nonlinear equations of pseudo-first order and pseudo-second order kinetic models. *Karbala International Journal of Modern Science*, 4, 244-254. DOI:10.1016/J.KIJOMS.2018.04.001.

Lagergren, S. (1898). About the Theory of so Called Adsorption of Soluble Substances, *Kungliga Svenska Vetenskapsakademiens Handlingar*, 24, 1-39.

Liu, G., Zhu, Z., Yang, Y., Sun, Y., Yu, F., & Ma, J. (2019). Sorption behavior and mechanism of hydrophilic organic chemicals to virgin and aged microplastics in freshwater and sea-water. *Environmental Pollution,* 246, 26–33. https://doi.org/10.1016/j.envpol.2018.11.100.

Miyake, Y., Ishida, H., Tanaka, S., & Kolev, S.D. (2013). Theoretical analysis of the pseudo- second order kinetic model of adsorption. Application to the adsorption of Ag(I) to mesoporous silica microspheres functionalized with thiol groups. *Chemical Engineering Journal,* 218, 350–357. https://doi.org/10.1016/J.CEJ.2012.11.089.

Munier, B. & Bendell, L.I. (2018). Macro and micro plastics sorb and desorb metals and act as a point source of trace metals to coastal ecosystems. *PLoS ONE, 13*(2). Article e0191759. https://doi.org/10.1371/journal.pone.0191759.

Pan, B., & Xing, B.S. (2010). Adsorption kinetics of 17alpha-ethinyl estradiol and bisphenol A on carbon nanomaterials. I. Several concerns regarding pseudo-first order and pseudo-second order models. *Journal of Soils and Sediments,* 10, 838–844. doi:10.1007/s11368-009-0184-8.

Pan, B., Sun, K., & Xing BS. (2010) Adsorption kinetics of 17α-ethinyl estradiol and bisphenol A on carbon nanomaterials. II. Concentration-dependence. *Journal of Soils and Sediments*, 10, 845–854. doi:10.1007/s11368-009-0185-7

Rochman, C.M., Hentschel, B.T., & Teh, S.J. (2014). Long-term sorption of metals is similar among plastic types: Implications for plastic debris in aquatic environments. *PLoS ONE, 9*(1), doi:10.1371/journal.pone.0085433.

Rochman, C.M., Hoh, E., Hentschel, B.T., & Kaye, S. (2013). Long-term field measurement of sorption of organic contaminants to five types of plastic pellets: Implications for plastic marine debris. *Environmental Science & Technology*, *47* (3), 1646-1654. https://doi.org/10.1021/es303700s.

Simonin, J-P. (2016). On the comparison of pseudo-first order and pseudo-second order rate laws in the modeling of adsorption kinetics. *Journal Chemical Engineering.* (May 2016). DOI:10.1016/j.cej.2016.04.079.

Tourinho, P. S., Kocí, V., Loureiro, S., & van Gestel, C. A.M. (2019). Partitioning of chemical contaminants to microplastics: Sorption mechanisms, environmental distribution and effects on toxicity and bioaccumulation. *Environmental Pollution,* 252(Pt B), 1246-1256. doi:10.1016/j.envpol.2019.06.030.

Turner, A., & Holmes, L.A. (2015). Adsorption of trace metals by microplastic pellets in fresh water. *Environmental Chemistry, 12*(5), 600-610.

Wang, F.,Yang,W., Cheng , P., Zhang, S., Zhang, Z., Jiao, W., & Sun Y. (2019). Adsorption characteristics of cadmium onto microplastics from aqueous solutions. *Chemosphere*, 235, 1073-080. https://doi.org/10.1016/j.chemosphere.2019.06.196 0045-6535.

Wright, S.L., Thompson, R.C., & Galloway, T.S. (2013). The physical impacts of microplastics on marine organisms: A review. *Environmental Pollution*, 178, 483-492. https://doi.org/10.1016/j.envpol.2013.02.031.

Zou, J., Liu, X., Zhang, D., & Yuan, X. (2020). Adsorption of three bivalent metals by four chemical distinct microplastics. *Chemosphere*, 248, 1260-1264. https://doi.org/10.1016/j.chemosphere.2020.126064

Chapter 5.

General discussion. Conclusions, implications, and future perspectives

Recently there has been an appreciable increase in the understanding of the occurrence and behaviour of plastic macro- and microparticles in the different environmental compartments (Luo et al., 2022). Most studies have been in marine aquatic environments, reporting on the distribution of macro- and microplastics. However, less is understood about plastic particles in the sedimentary environment, specifically how much macro- and microplastic accumulates in coastal intertidal sediments (Wahyuningsih et al., 2018), possible sources, interaction of plastic particles with the different contaminants, including trace elements, potential ecological impacts, and appropriate analytical techniques for assessing the above.

Despite the growing number of publications on the topic, we have identified some key knowledge gaps that need to be considered to better understand the sorption of contaminants, such as trace elements by plastic macro- and microparticles under conditions of intertidal sedimentary environments. By acknowledging the complexity of many factors influencing the behaviour of macro- and microplastic, the available publications are not covering all of the important aspects in the sorption of trace elements by plastic particles under conditions of intertidal sedimentary environments. Hence, in this thesis I attempted to summarize recent studies and applied combined laboratory, field and modeling approach to investigate sorption of trace elements (Cd, Cu, Hg, Pb, and Zn) by plastic macro- and microparticles within intertidal sediments and under conditions of different constant temperatures.

This study investigated the effect of sediment geochemistry (grain size distribution, organic matter content) and temperature on sorption of trace elements (Cd, Cu, Hg, Pb, and Zn) by plastic particles (micro-PETE (fibre), micro-HDPE (microbeads), macro-PETE (textile fabric), and macro-HDPE (polyethylene chips)) within two contrasting intertidal sedimentary environments, low (HB, OM=2.8%) and high (MWFCA, 15.8%) in organic matter content. The impact of temperature and the presence of organic matter content in the intertidal sediments on trace elements sorption by plastic macro- and microparticles were addressed for the first time.

Since this study on sorption of trace elements sorption by plastic macro- and microparticles within the intertidal sedimentary environments were conducted as long-term field and long-term laboratory experiments, the differences between these two approaches indicated important factors which influencing the results of the study on trace elements–plastic macro- and microparticles interactions.

5.1. Key findings

5.1.1. Sorption of trace elements (Cd, Cu, Hg, Pb, and Zn) by macro- and microplastic in the marine intertidal sedimentary environment

The results of this field research indicates that interaction between trace elements (Cd, Cu, Hg, Pb, and Zn) and plastic macro- and microparticles within contrasting intertidal sediment environments may include a period of rapid adsorption (initial period), a period of slow adsorption (reaching equilibrium state), and a period of desorption or two of them, depending on the rate of trace elements accumulation by plastic particles and plastic materials degradation. The formation of new peaks (FTIR spectra) supported the fact that continuing degradation and aging of plastic materials under condition of the intertidal sedimentary environment influence the process of trace elements-plastic particles interactions (Endo et al., 2005; Wang et al., 2018).

Organic matter content and proportion of fine-grained particles (< 0.063 mm) in grain size distribution of intertidal sediments have dominated influence on interaction of trace elements and plastic macro- and microparticles. Sorption of Cu, Zn, Pb, Cd, and Hg by plastic macro- and microparticles of HDPE and PETE decreased with increase of the organic matter concentration in sediments. Plastic macro- and microparticles play a minor role in trace elements (Cu, Zn, Pb, Cd, and Hg) sorption within intertidal sedimentary environments in the presence of organic matter at high concentrations (OM=15.8%). These results can be explained as a phenomenon of competitive adsorption between plastic macro- and microparticles and particles of organic matter in the intertidal sediments which is in accordance with Gomez et al. (1999).

In relation to plastic type, sorption behaviour/capacity of macro- and microparticles of PETE towards trace elements (Cd, Cu, Pb, Zn, and Hg) are more dependent on organic matter concentration in the intertidal sediments and exhibit greater adsorption capacity compare to the plastic particles of HDPE. In the intertidal sedimentary environments plastic particle size can affect sorption rate, equilibrium concentration, and time of reaching equilibrium (Wang et al., 2018). In addition, sorption rate of trace elements (Cu, Zn, Pb, Cd, and Hg) by macro- and microparticles of PETE and HDPE increased with decrease of particle size. This phenomenon may be due to increasing the specific surface area, resulting in an increase in sorption sites on the surface of solid particle and the amount of sorbed trace elements is also increased which is in accordance with Ashton et al. (2010) and Wang et al. (2018).

The distribution/partition of trace elements under conditions of intertidal sedimentary environment was related to the characteristics of intertidal sediments and plastic particles which is in accordance with Wang et al. (2018). The value of $\log[(K_{sed\text{-}wp})_e/(K_{pl\text{-}wp})_e]$ for concentration of Cu, Zn, Pb, Cd, and Hg in macro-HDPE (polyethylene chips), macro-PETE (textile fabric) and micro-HDPE (microbeads) and micro-PETE (fibres) increased with increasing of the organic matter concentration in sediments as a results of competition in sorption site between plastic particles and organic matter particles of sediments (Gomez et al., 1999). In relation to the plastic particle size, partitioning of Cu, Zn, Pb, Cd, and Hg between sediments and plastic macroparticles of PETE and HDPE is more dependent on organic matter concentration in sediments compare to the microparticles of PETE and HDPE. Importantly, that in relation to the polymer type, partitioning of Cu, Zn, Pb, Cd, and Hg between sediments and plastic macro- and microparticles of PETE are more dependent on organic matter concentration in sediments compare to plastic particles of HDPE. This suggests that PETE has a higher affinity and faster sorption rate with most of trace elements (Cu, Zn, Pb, Cd, and Hg) which is in accordance with Alimi et al. (2018) and Wang et al. (2018). In relation to the type of trace elements, partitioning of Cu, Zn, Pb between plastic macro- and microparticles and sediments have higher dependence on sedimentary characteristics compare to Cd, and Hg with lower dependence.

Temperature significantly influences all of the characteristics of plastic materials and has impact on their sorption/desorption behaviour towards trace elements which can be defined as temperature-dependent. In the second part of this project (Chapter 3), the sorption of Cd, Cu, Pb, and Zn by plastic macro- and microparticles of PETE and HDPE were studied under laboratory controlled conditions of different constant temperatures (T=- 4.0°C, T=+4.0°C, and T=+18.0°C) within two contrasting intertidal sediments with low (HB, OM = 2.8%) and high (MWFCA, OM = 15.8%) in organic matter content.

The results of this experimental study indicate that the interaction between Cd, Cu, Pb, and Zn and plastic macro- and microparticles in the intertidal sediments under laboratory-controlled conditions of three constant temperatures can be described as the process of trace elements accumulation over time which include two periods such as, period of rapid adsorption (initial period) and period of slow adsorption (reaching equilibrium state). In general, sorption of Cd, Cu, Pb, and Zn in plastic macro- and microparticles of HDPE and PETE was higher and reached the state of equilibrium and equilibrium concentration faster under conditions of higher temperature T=+18.0°C (8-12 months) compare to that at lower temperature T=- 4.0°C (12-21 months).

The characteristics of intertidal sediments (organic matter content, grain size distribution) have greater influence on sorption of trace elements compare to the influence of temperature (T=- 4.0°C, T=+4.0°C, and T=+18.0°C) applied in our simulation experiments. The sorbed concentrations of Cd, Cu, Pb, and Zn on plastic macro- and microparticles of HDPE and PETE deployed in sediments low in organic matter (OM = 2.8%) was higher compare to that in sediments high in organic matter content and under conditions of constant temperature (T=- 4.0°C, T=+4.0°C, and T=+18.0°C) of the surrounding environments.

The partitioning of trace elements (Cd, Cu, Pb, and Zn) between sediments and plastic macro- and microparticles is higher under condition of high temperature (T=+18.0°C) compare to that at low temperature (T=-4.0°C). In general, the value of $\log[(K_{sed\text{-}wp})_e/(K_{pl\text{-}wp})_e]$ for concentrations of Cd, Cu, Pb, and Zn on macro- and microparticles of HDPE and PETE is decreasing when the value of constant temperature (T=- 4.0°C, T=+4.0°C, and T=+18.0°C) increases in both, intertidal sediments low (OM=2.8%) and high (OM=15.8%) in organic matter content. Under laboratory controlled conditions the temperature of T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C have minor influence on the partitioning of Cu, Pb, and Zn, except of Cd, between plastic particles and intertidal sediments compare to the influence of organic matter of OM=15.8%. It was found that at high temperature of T=+18.0°C only Cd can partition to plastic particles more readily than to sediments high in organic matter (OM=15.8%).

5.1.2. Kinetic studies on trace elements (Cd, Cu, Hg, Pb, and Zn) sorption by polymeric macro- and microparticles within intertidal sediments

There are various factors influencing the behaviour of trace elements in the marine intertidal sedimentary environments with plastic particles component and kinetic study can be appropriate approach for identifying their sorption and partition mechanisms. In the third part of this project (Chapter 4), to investigate the sorption of trace elements (Cd, Cu, Pb, Zn and Hg) by plastic macro- and microparticles within two contrasting sedimentary environments, the pseudo-first-order (PFOM) and pseudo-second-order (PSOM) kinetic models have been used to test data derived from the long-term field study (Chapter 2) and controlled laboratory experiments (Chapter 3).

Overall, the pseudo-first-order (PFOM) and pseudo-second-order (PSOM) kinetic models did not fit well to our empirical data on trace elements (Cd, Cu, Hg, Pb, and Zn) sorption well (field study). We can conclude that too much variation and inconsistency are in the predicted rate constants (Table 4.1). Although the “best” fit was better for the data derived from the laboratory experiments (Table 4.2) the models still suffered from the fact that the predicted rate constants were not consistent, and some went up with temperature while others went down. Since the “best fit” was based on only a few datapoints it is not unusual to get a high R^2 even with an incorrect model. This was not surprising since the underlying assumptions of the PFOM and PSOM models do not apply to our experimental conditions. They don’t take into account the competition of trace element binding between the sediments and the plastic particles.

Therefore, we conclude that existing pseudo-first-order (PFOM) and pseudo-second-order (PSOM) kinetic models are not applicable for accurate predictive modeling of trace metals (Cd, Cu, Hg, Pb, and Zn) sorption by micro-PETE (fiber), micro-HDPE (microbeads), macro-PETE (textile fabric), and macro-HDPE (polyethylene chips)) in the environmental realistic conditions of intertidal sediments with organic matter content in the range of OM=2.8-15.8% nor in the laboratory experiments under conditions of constant temperature (T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C).

We propose an improved modeling framework that better represent the chemical interactions that are taking place in the intertidal sedimentary system. The model accounts for the kinetics of traces elements sorption by plastic macro- and microparticles under condition of intertidal sedimentary environment. This framework should be a template for future model development for predicting trace elements (Cd, Cu, Hg, Pb, and Zn) sorption by plastic particles within intertidal sediments. The modeling framework is based on two reversible reactions for exchange of trace elements with two elements bound at two different sites on the solid phase: sediment and plastic particles.

5.1.3. Comparison of field and laboratory studies

Most of studies on sorption of trace elements by plastic macro- and microparticles are conducted under controlled laboratory conditions. In the field, environmental conditions can vary considerably, such as trace elements concentration (sea water, intertidal sediments and pore water), temperature, and intertidal sediments composition. In addition, plastic materials degradation, biofilm formation, and the presence and possible competition of sorbates (organic matter and plastic particles) can also affect the processes and rates of the sorption of trace elements by plastic macro- and microparticles (Ashton et al., 2010; Fotopoulou et al., 2012; Holmes et al., 2012; Wang et al., 2019). The results of this study (Chapter 2 and Chapter 3) demonstrate that the aging (environmental degradation) of the synthetic plastic macro- and microparticles under conditions of the intertidal sedimentary environments is an important factor influencing trace elements-plastic particles interaction.

Previous study on sorption of trace elements by macro- and microplastic indicated the difference in sorption process in the laboratory and field studies (Holmes et al., 2012; Rochman et al., 2013; Rochman et al., 2014). Results of our study indicated, that one the main difference between laboratory and field sorption experiments is different periods of sorption and desorption in the process of trace elements-plastic particles interaction within intertidal sediment. In the field study (Chapter 2) the interaction between Cd, Cu, Hg, Pb, and Zn and plastic macro- and microparticles within contrasting intertidal sediment environments may include three periods, such as period of rapid adsorption, a period of reaching equilibrium state, and a period of desorption or two of them, depending on the rate of trace elements accumulation by plastic particles and plastic materials degradation. However, the interaction between Cd, Cu, Pb, and Zn and plastic macro- and microparticles in the intertidal sediments under laboratory-controlled conditions of constant temperatures (T=- 4.0°C, T=+4.0°C, and T=+18.0°C) can be described as the process of trace elements accumulation over time which include two periods such as, period of rapid adsorption and period of reaching equilibrium state. We can conclude that stability and temporal changes of environmental factors and differences in the continues degradation and aging of plastic materials under laboratory and field conditions have influence on the process of interaction between trace elements (Cd, Cu, Hg, Pb, and Zn) and plastic macro- and microparticles in the intertidal sediments that is partially in accordance with Holmes et al. (2012) and Rochman et al. (2014).

Another difference between laboratory and field experiments is the equilibration time. The results of our study indicated, that equilibrium is reached much faster under laboratory conditions (Chapter 3, Table 3.1) compare to that in the field experiments (Chapter 2, Table 2.2). Some study on sorption of trace elements by microplastic indicated that equilibrium can be reached within hours or days under laboratory conditions, while it takes several months in the field environment (Rochman et al., 2014; Zhan et al., 2016; Holmes et al., 2012). The possible explanations of this difference include the lower sorbate (trace elements) concentrations in the field environment (Rochman et al., 2014) compare to the concentration of sorbate which is usually applied in laboratory experiments (Zhan et al., 2016).

The results of our study clearly demonstrate that process of trace element sorption by plastic macro- and microparticles in the intertidal sediments observed under laboratory and field conditions have some differences. Laboratory approach of study is very important to find and indicate the processes separately. However, the differences between laboratory and field experiments have to be defined to be able to transfer the results of the study to realistic environmental conditions. Thus, the connection between the results of the laboratory studies and the field measurements needs to be established (Guo et al., 2021).

5.2. Implications of key findings, limitations, and future directions

The main objectives of this thesis/study were to investigate the sorption of trace element (Cd, Cu, Hg, Pb, and Zn) by plastic macro- and microparticles as influenced by intertidal sediment geochemistry and temperature and contribute with a set of guiding principles and criteria as frameworks for the future development in modeling and predicting of trace elements sorption by plastic particles within intertidal sedimentary environment. The findings of this thesis may have some areas of research that need further consideration.

The results of field studies has shown that the sorption of Cd, Cu, Hg, Pb, and Zn by plastic particles under conditions of marine intertidal sedimentary environments is influenced by various factors including characteristics of intertidal sediments, initial concentration of trace elements, and plastic materials composition and degradation. The concentration of organic matter in the intertidal sediments and proportion of fine-grained particles (< 0.063 mm) in grain size distribution have dominated influence on trace elements-plastic particles interaction. Plastic macro- and microparticles play a minor role in trace elements (Cu, Zn, Pb, Cd, and Hg) sorption because trough the competition for sorption site sediments high in organic matter (OM=15.8%) may reduce trace elements accumulation by macro- and microplastics as compared to sediments low in organic matter (OM=2.8%). It would be beneficial to study the sorption of trace elements by plastic particles within intertidal sedimentary environment with wide range of organic matter content in sediments.

Macro- and microparticles of PETE are more dependent on organic matter concentration in sediments compare to particles of HDPE. This suggests that PETE has a higher affinity and faster adsorption rate with most of trace elements (Cu, Zn, Pb, Cd, and Hg) which is in accordance with Wang et al., (2018). In addition, the formation of new peaks (FTIR spectra) in the composition of macro- and microplastic of PETE and HDPE supported the fact that continuing degradation and aging of plastic materials influence the process of trace elements-plastic particles interaction and partition under conditions of the intertidal sedimentary environment. The process of plastic particles degradation requires further study. It would be beneficial to investigate the role plastic particles degradation in partitioning of trace elements because this is related to their bioavailability. Outcomes of this study will add to our knowledge base on the risks that plastic particles present to intertidal environments and the role they play on the movement of these contaminants through intertidal food webs.

The results of laboratory of the studies has shown that temperature has a minor influence on the partitioning of Cu, Pb, and Zn, except of Cd, between plastic particles and intertidal sediments compare to the influence of organic matter concentration of OM=15.8%. It was not expected results of study. Therefore, there is a need for more research with more wide range of the temperature and organic matter concentration in sediments to better understand the impact of temperature on trace elements sorption by plastic particles and their partitioning between compartments of intertidal sedimentary environments. In addition, the long-term field experiments on trace elements sorption by plastic particles are more preferable, because they provide valuable information on sorption process under realistic environmental conditions.

In Chapter 4, the kinetic studies on trace elements (Cd, Cu, Hg, Pb, and Zn) sorption by plastic macro- and microparticles within intertidal sediments were applied. To the best of our knowledge, this is the first study on the application of pseudo-first-order (PFOM) and pseudo-second-order (PSOM) models as predictive kinetic models of trace element (Cd, Cu, Hg, Pb, and Zn) sorption by plastic macro- and microparticles as influenced by sediment geochemistry and temperature. Results indicated, that existing PFOM and PSOM kinetic models not perform well for accurate predictive modeling of Cd, Cu, Hg, Pb, and Zn sorption by micro-PETE (fibre), micro-HDPE (microbeads), macro-PETE (textile fabric), and macro-HDPE (polyethylene chips)) in the environmental realistic conditions of intertidal sediments with organic matter content in the range of OM=2.8-15.8% (Table 4.1). The better fit was for the data derived from the laboratory experiments (Table 4.2), but the models still suffered from the fact that the predicted rate constants were not consistent, and some went up with temperature while others went down. This can be explained that PFOM and PSOM models do not take into account the competition of trace element binding between the sediments and the plastic particles. Therefore, we can conclude that existing PFOM and PSOM kinetic models are not applicable for accurate predictive modeling of trace metals (Cd, Cu, Hg, Pb, and Zn) sorption by micro-PETE (fiber), micro-HDPE (microbeads), macro-PETE (textile fabric), and macro-HDPE (polyethylene chips)) in the environmental realistic conditions of intertidal sediments with organic matter content in the range of OM=2.8-15.8% and temperature of T=- 4.0°C, T=+ 4.0°C, and T=+18.0°C

We propose an improved modeling framework that better represent the chemical interactions that are taking place in the intertidal sedimentary system. The model accounts for the kinetics of traces elements sorption by plastic particles under condition of intertidal sedimentary environment. The modeling framework is based on two reversible reactions for exchange of trace elements with two elements bound at two different sites on the solid phase: sediment and plastic particles. This framework should be a template for future model development for predicting trace elements (Cd, Cu, Hg, Pb, and Zn) sorption by plastic particles within intertidal sediments.

References

Ashton, K., Holmes, L., & Turner, A. (2010). Association of metals with plastic production pellets in the marine environment. *Marine Pollution Bulletin*. 60. 2050-2055.

Azizian, S. (2004). Kinetic models of sorption: a theoretical analysis. *Journal of Colloid and Interface Science,* 276, 47–52.

Fotopoulou, N. K., & Karapanagioti, K. H. (2012). Surface properties of beached plastic pellets. *Marine Environmental Research*, 81, 70–77.

Gomez, C. & Bosecker, K. (1999). Leaching heavy metals from contaminated soil using Thiobacillus ferrooxidans or Thiobacillus thiooxidans, *Geomicrobiology Journal,* 16, 233–244. https://doi.org/10.1080/014904599270613.

Guo, X., & Wang, J.L. (2021).Projecting the sorption capacity of heavy metal ions onto microplastics in global aquatic environments using artificial neural networks. *Journal of Hazardous Materials,* 402. 123709. https://doi.org/10.1016/j.jhazmat.2020.123709

Holmes, L.A, Turner, A., & Thompson, R.C. (2012) Adsorption of trace metals to plastic resin pellets in the marine environment. *Environmental Pollution,* 160, 42–48.

Kajjumba, G. W., Emik, S., Öngen, A., Özcan H. K., & Aydın S. (2018). Modelling of adsorption kinetic processes—errors, theory and application. *Advanced Sorption Process Applications*. DOI:http://dx.doi.org/10.5772/intechopen.80495

Koelmans, A.A., Besseling, E., & Foekema, E.M. (2014). Leaching of plastic additives to marine organisms. *Environmental Pollution*, 187, 49–54. doi:10.1016/j.envpol.2013.12.013.

Liu, G., Zhu, Z., Yang, Y., Sun, Y., Yu, F., & Ma, J. (2019). Sorption behavior and mechanism of hydrophilic organic chemicals to virgin and aged microplastics in freshwater and sea-water. *Environmental Pollution*, 246, 26–33. https://doi.org/10.1016/j.envpol.2018.11.100.

Luo, H. W., Liu, C.Y., He, D., Xu, J., Sun, J., Li, J., & Pan, X. L. (2022). Environmental behaviors of microplastics in aquatic systems: A systematic review on degradation, adsorption, toxicity and biofilm under aging conditions. *Journal of Hazardous Materials, 423*(8). DOI: 10.1016/j.jhazmat.2021.126915

Rochman ,C.M., Hentschel, B.T., & Teh, S.J. (2014). Long-term sorption of metals is similar among plastic types: Implications for plastic debris in aquatic environments. *PLoS ONE, 9*(1). doi:10.1371/journal.pone.0085433

Rochman, C.M., Hoh, E., Hentschel, B.T., & Kaye, S. (2013). Long-term field measurement of sorption of organic contaminants to five types of plastic pellets: Implications for plastic marine debris. *Environmental Science & Technology*, *47*(3), 1646-1654. https://doi.org/10.1021/es303700s.

Seidensticker, S., Zarfl, C., Cirpka, O.A., Fellenberg, G., & Grathwohl, P. (2017). Shift in mass transfer of wastewater contaminants from microplastics in the presence of dissolved substances. *Environmental Science & Technology*, 51, 12254-12263.

Tourinho, P. S., Kocí, V., Loureiro, S., & van Gestel, C. A.M. (2019). Partitioning of chemical contaminants to microplastics: Sorption mechanisms, environmental distribution and effects on toxicity and bioaccumulation. *Environmental Pollution,* 252(Pt B), 1246-1256. doi:10.1016/j.envpol.2019.06.030.

Wahyuningsih, H., Bangun, A. P., & Muhtadi, A. (2018). The relation of sediment texture to macro- and microplastic abundance in intertidal zone. *IOP Conference Series: Earth and Environmental Science*, 122. doi:10.1088/1755-1315/122/1/012101

Wang, F.,Yang,W., Cheng , P., Zhang, S., Zhang, Z., Jiao, W., & Sun Y. (2019). Adsorption characteristics of cadmium onto microplastics from aqueous solutions. *Chemosphere*, 235. 1073-080. https://doi.org/10.1016/j.chemosphere.2019.06.196 0045-6535

Wang, F., Wong, C.S., Chen, D., Lu, X., Wang, F., & Zeng, E. Y. (2018). Interaction of toxic chemicals with microplastics: A critical review. *Water Research*, 139, 208-219.

Zhan, Z., Wang, J., Peng, J., Xie, Q., Huang, Y., & Gao, Y. (2016). Sorption of 3, 30 ,4, 40 - tetrachlorobiphenyl by microplastics: a case study of polypropylene. *Marine Pollution Bulletin, 110*(1), 559-563. doi: 10.1016/j.marpolbul.2016.05.036.

Appendix A.

Supporting Information for Chapter 1

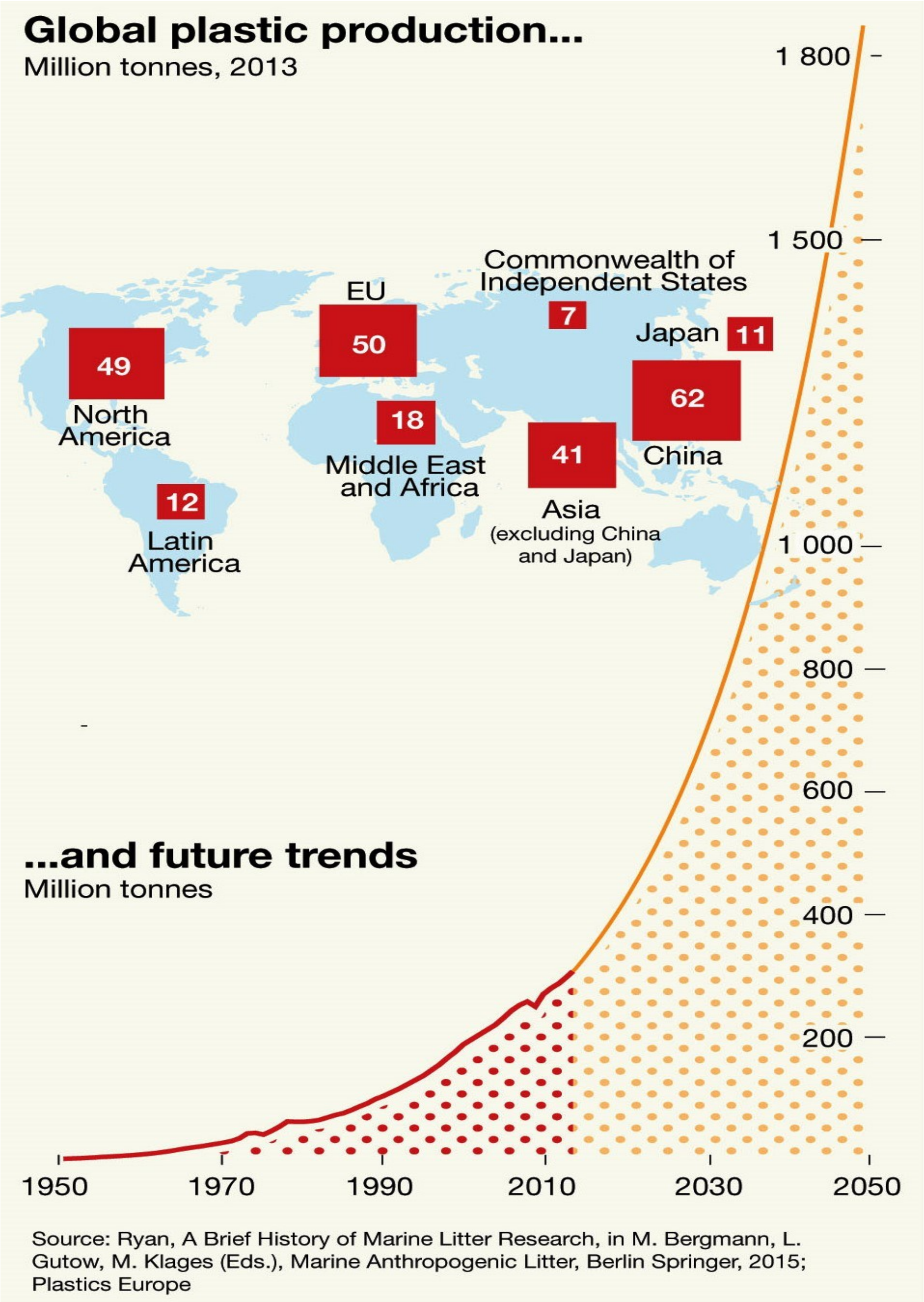


Figure A1. Global plastic production and future trends
Graph source: UN GRID-Arendal. From collection: Marine Litter Vital Graphics.
Cartographer: Maphoto/Riccardo Pravettoni.
Source: Retrieved from https://www.grida.no/resources/6933

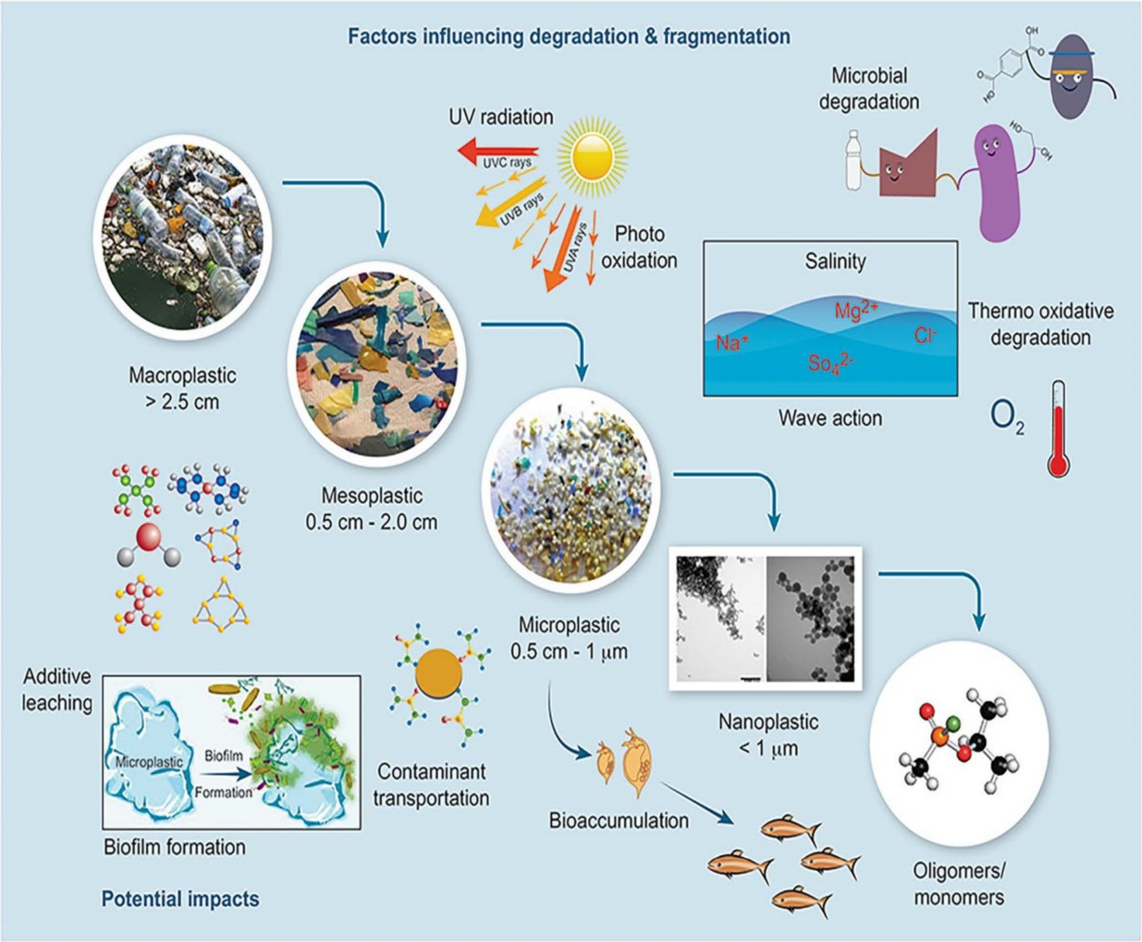


Figure A2. Fate and effects of plastic materials in the environment

Source: Atugoda, T., Vithanage, M., Wijesekara, H., Bolan, N., Sarmah, A. K., Bank, M. S., You, S., & Ok, Y. S. (2021). Interactions between microplastics, pharmaceuticals and personal care products: Implications for vector transport. Environment International.149, 106-137. https://doi.org/10.1016/j.envint.2020.106367.

Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

Table A1. Density of synthetic plastic materials and their application

Chemical name	Density, g/cm^3	Application example
Polypropylene (PP)	0.895 – 0.920	Rope, bottle caps, netting, folders
Low-density polyethylene (LDPE)*	0.917 – 0.930	Plastic bags, pack rings, bottles, netting, wire cables
High-density polyethylene (HDPE)*	0.930 – 0.970	Milk and juice jugs; detergent bottles; containers, trays
Polystyrene (PS)	0.960 – 1.050	Plates, cups, bottles, containers
Polyamide (Nylons) (PA)*	1.150	Fishing nets, clothing, traps
Cellulose Acetate (synthetic fiber)	1.220 – 1.240	Cigarette filters
Polyvinyl chloride (PVC)	1.160–1.380	Plastic film, bottles, cups, boots, medical equipment, packaging
Polyester (PES)	1.350	Clothing
Polyethylene terephthalate (PET)*	1.370 – 1.390	Plastic bottles, carpet, clothing
Polyester resin + glass fibre	>1.350	Textiles, boats
Rayon	1.500	Clothing
Organic matter*	0.90 – 1.30	
Clay*	1.70 – 2.68	
Beach sand*	2.65	

Note:* Material density measured in the laboratory (presented study)

Source: Adapted from: Andrady, 2011; Plastics Europe, 2015; Plastics Europe, 2019; Harris, 2020; Hidalgo-Ruz et al., 2012; Ziccardi et al., 2016.

Table A2. Interactions of plastic particles with marine biota: impact and effects

Organism	Plastic particles	Effect	References
Whales *(Balaenoptera physalus, Mesoplodon mirus, Megaptera novaeangliae)*	Polyethylene, polypropylene, polyvinyl chloride nylon	Ingestion, accumulation in liver, elevation of respiration rates	Lusher at el. (2015)
Sea turtles	Polypropylene, polyethylene	Accumulation	Caron et al. (2016)
Shore crab *(Carcinus maenas)*	Microspheres (polystyrene)	Retention through gills	Watts et al. (2014)
Marine fish	Microbeads (polyethylene, polystyrene)	Pathological stress, lipid accumulation in liver	Rochman et al. (2013)
Pelagic fish species (mackerel, herring, cod, dab, flounder	Polyethylene	Ingestion	Rummel et al. (2016)
Mussel *(Mytilus edilus)*	Microbeads (polyethylene, polystyrene)	Vector for accumulation of POPs	Browne et al.(2008)
Brown shrimp *(Crangon cragon)*	Microplastics	Ingestion	Devriese et al. (2015)
Bivalves	Microbeads	Accumulation in soft tissues	Van Cauwenberghe et al. (2014)
Zooplankton *(Centropages typicus, Daphnia magna)*	Microbeads (polystyrene)	Decreased algal feeding, causes immobilization	Cole et al. (2013)
Copepod *(Calanus helgolandicus, C. cristatus, Euphasia pacifa)*	Polystyrene	Reduced feeding, decreased reproduction, fewer egg productions	Cole et al. (2016) Desforges et al.(2015)
Microalgae	Polystyrene	Affected	Sjollema et al. (2015)

Appendix B.

Supporting Information for Chapter 2

Table B1. Selective concentration (µg/g dw) of Cd, Cu, Pb, Zn, and Hg in sea water, intertidal sediments, and macro- and microparticles at different residence time at HB and MWFCA study sites.

Site location	Time, months	Water, µg/mL	Sediment	micro-PETE fiber	macro-PETE textile fabric	micro-HDPE microbeads	macro-HDPE polyethylene
Cd (ISQG marine sediment: 0.7 µg/g dry weight)							
HB	0	0.0023	0.7030	0.0608	0.1196	0.3478	0.0931
	1	0.0008	0.6000	0.0944	0.16	0.5713	0.2133
	3	0.0207	0.5200	0.1643	0.26	0.6630	0.2918
	12	0.0022	0.4000	0.2216	0.2776	0.3317	0.1955
	38	0.0098	0.3300	0.2555	0.3025	0.1225	0.2286
MWFCA	0	0.0051	0.3540	0.0608	0.1196	0.3478	0.0931
	1	0.0098	0.3480	0.2013	0.14	0.3687	0.1424
	3	0.0157	0.4370	0.3932	0.19	1.0555	0.2382
	12	0.0093	0.3060	0.1036	0.2841	0.3383	0.0543
	38	0.0045	0.2100	0.0974*	0.3130*	0.2381*	0.0467*
Cu (ISQG marine sediment: 18.7 µg/g dry weight)							
HB	0	0.0206	12.19	0.1429	0.2601	0.2070	0.1330
	1	0.0032	12.95	1.3439	0.8	4.7739	0.8936
	3	0.0123	11.77	2.4680	1.3	3.5288	2.1716
	12	0.0065	14.70	8.1569	2.2062	6.7278	3.9964
	38	0.0125	10.51	4.3500	10.3639	1.4365	3.1800
MWFCA	0	0.0114	13.65	0.1429	0.2601	0.2070	0.1330
	1	0.0247	14.51	4.7615	0.5	3.9430	2.6877
	3	0.0103	15.50	2.0979	0.7	5.7084	3.0760
	12	0.0029	14.58	1.7189	0.6045	1.1860	1.2786
	38	0.0085	16.63	1.4055	5.80	0.2377	0.9277
Hg (ISQG marine sediment: 0.130 µg/g dry weight)							
HB	0	0.0000003	0.1105	0.0105	0.0320	0.0678	0.0152
	1	0.0000003	0.1207	0.0135	0.0340	0.0870	0.0302
	3	0.0000003	0.1225	0.0254	0.0380	0.0940	0.0370
	12	0.0000003	0.1214	0.0253	0.0430	0.0500	0.0380
	38	0.0000003	0.1555	0.0320	0.0500	0.0380	0.0430
MWFCA	0	0.0000003	0.1208	0.0105	0.0320	0.0678	0.0152
	1	0.0000003	0.1501	0.0240	0.0330	0.0880	0.0280
	3	0.0000003	0.1622	0.0370	0.0460	0.0950	0.0580
	12	0.0000003	0.1723	0.0380	0.0500	0.0830	0.0650
	38	0.0000003	0.1685	0.0340	0.0506	0.0650	0.0390

Site location	Time, months	Water, µg/mL	Sediment	micro-PETE fiber	macro-PETE textile fabric	micro-HDPE microbeads	macro-HDPE polyethylene
			Pb (ISQG marine sediment: 30.2 µg/g dry weight)				
HB	0	0.1000	9.25	1.2929	1.6645	5.0725	0.1640
	1	0.0910	9.50	3.3352	2.30	8.4746	0.6263
	3	0.1770	10.13	3.7626	2.90	7.8291	3.9061
	12	0.0230	9.10	5.1778	2.5317	2.4746	3.1918
	38	0.1300	10.79	5.1378	5.0700	2.1365	4.1567
MWFCA	0	0.1730	13.43	1.2929	1.6645	5.0725	0.1640
	1	0.1520	13.20	6.0658	1.80	5.7494	2.1253
	3	0.2080	13.70	5.9002	2.00	4.9167	1.9638
	12	0.0350	14.50	1.7465	2.5506	1.9534	1.3087
	38	0.0630	17.61	1.7531*	2.7599*	2.1429*	0.9616*
			Zn (ISQG marine sediment: 124.0 µg/g dry weight)				
HB	0	0.0009	44.91	0.6572	0.3798	3.4910	1.7530
	1	0.0008	43.10	1.3420	1.37	4.6305	2.8253
	3	0.0015	40.10	2.1865	1.80	9.5553	6.7882
	12	0.0050	43.00	2.5499	2.9707	2.9243	2.9296
	38	0.0007	36.13	1.9866	4.7895	2.6785	3.7855
MWFCA	0	0.0002	87.85	0.6572	0.3798	3.4910	1.7530
	1	0.0017	76.50	0.9913	0.87	4.1572	2.4468
	3	0.0011	77.20	2.8220	1.10	9.3129	4.6650
	12	0.0009	73.90	1.2943	1.0986	2.4226	2.1139
	38	0.0010	46.91	0.6936	1.3565*	2.8031*	2.1122*

Note:*data are obtained for the residence time of 28 months

Table B2. Summary output of liner regression models (*lm*)

Statistical parameters	micro-PETE fiber	micro-HDPE microbeads	macro-PETE textile fabric	macro-HDPE polyethylene chips
Cd: Horseshoe Bay (OM=2.8%)				
Residuals: min	-0.069	-0.206	-0.074	-0.109
max	0.080	0.223	0.066	0.106
Residual standard error ((n-2), df=25)	0.052	0.105	0.044	0.059
t value	4.613	-6.921	5.471	5.420
p-value	<0.001	< 0.05	<0.001	0.049
Cd: Maplewood Flats Conservation Area (OM=15.8%)				
Residuals: min	-0.187	-0.353	-0.050	-0.106
max	0.174	0.442	0.062	0.114
Residual standard error ((n-2), df=25)	0.064	0.077	0.035	0.072
t value	-2.991	-3.234	9.601	-3.771
p-value	<0.05	< 0.05	< 0.05	<0.001

Statistical parameters	micro-PETE fiber	micro-HDPE microbeads	macro-PETE textile fabric	macro-HDPE polyethylene chips
Cu: Horseshoe Bay (OM=2.8%)				
Residuals: min	-3.291	-3.699	-1.080	-1.593
max	3.962	3.742	0.874	1.800
Residual standard error ((n-2), df=25)	0.061	0.058	0.056	0.072
t value	3.744	-1.834	30.903	4.424
p-value	<0.001	0.048	< 0.05	<0.001
Cu: Maplewood Flats Conservation Area (OM=15.8%)				
Residuals: min	-2.348	-3.180	-1.464	-2.314
max	2.790	2.649	1.385	1.446
Residual standard error ((n-2), df=25)	0.062	0.061	0.081	0.071
t value	-2.622	-3.989	9.518	-2.902
p-value	0.117	<0.001	< 0.050	< 0.050
Hg: Horseshoe Bay (OM=2.8%)				
Residuals: min	-0.010	-0.019	-0.003	-0.010
max	0.011	0.020	0.003	0.009
Residual standard error (df=25)	0.005	0.013	0.002	0.006
t value	4.088	-6.840	14.260	4.696
p-value	<0.001	< 0.05	< 0.05	< 0.050
Hg: Maplewood Flats Conservation Area (OM=15.8%)				
Residuals: min	-0.016	-0.024	-0.008	-0.030
max	0.014	0.023	0.006	0.021
Residual standard error ((n-2), df=25)	0.008	0.011	0.005	0.016
t value	2.925	-4.258	5.651	-2.026
p-value	0.066	<0.001	< 0.050	0.097
Pb: Horseshoe Bay (OM=2.8%)				
Residuals: min	-1.714	-3.124	-0.700	-1.648
max	1.807	3.613	0.598	1.946
Residual standard error ((n-2), df=25)	0.048	0.074	0.057	0.064
t value	4.573	-5.054	13.430	4.905
p-value	<0.001	<0.001	< 0.05	<0.001
Pb: Maplewood Flats Conservation Area (OM=15.8%)				
Residuals: min	-3.868	-2.498	-0.372	-1.345
max	4.559	3.079	0.401	1.042
Residual standard error ((n-2), df=25)	0.039	0.091	0.039	0.655
t value	-3.231	-4.121	10.420	-2.084
p-value	0.003	<0.001	< 0.050	0.047
Zn: Horseshoe Bay (OM=2.8%)				
Residuals: min	-1.090	-3.774	-0.732	-2.598
max	1.081	4.288	0.729	3.338
Residual standard error ((n-2), df=25)	0.053	0.047	0.040	0.036

t value	2.802	-3.099	16.430	2.308
p-value	0.043	0.005	< 0.05	0.076
Zn: Maplewood Flats Conservation Area (OM=15.8%)				
Residuals: min	-0.938	-2.592	-0.316	-1.927
max	1.313	3.457	0.278	2.172
Residual standard error ((n-2), df=25)	0.061	0.070	0.063	0.049
t value	-2.542	-2.857	6.570	-2.031
p-value	0.017	< 0.05	< 0.050	0.053

Note: The summary output of the liner regression models *(lm)* are combined for three time periods of field sampling “short -term”(0-2 months), “mid-term” (3-12 months) and “long-term” (21-38 months). Differences in concentration of trace elements among study sites versus plastic type and particle size.

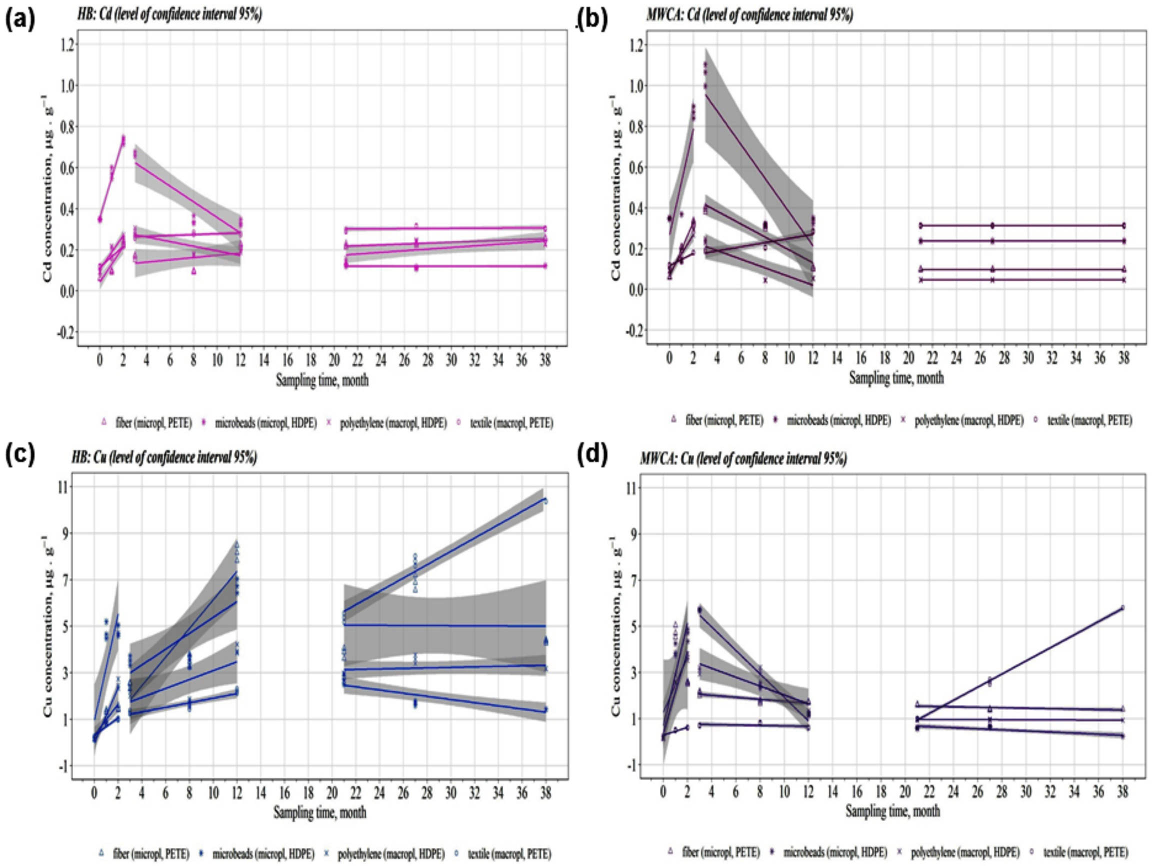


Figure B1. **Liner relationship (95% CI) between concentrations of Cd (a, b) and Cu (c, d) (dependent variables) and residence time of macro- and microparticles in the intertidal sediments (independent variable) at HB and MWFCA study sites.**

Note: Concentration of Cd (a, b) and Cu (c, d) were measured in micro-PETE (fiber), micro-HDPE (microbeads), macro-PETE (textile fabric), and macro-HDPE (polyethylene chips) deployed in the intertidal sediments at HB (a, c) and MWFCA (b, d) study sites. Output of liner regression models *(lm)* combined for three time periods of field sampling “short -term” (0-2 months), “mid-term” (3-12 months) and “long-term” (21-38 months). Shading represents 95% confidence intervals for predictions from a linear model (*lm*).

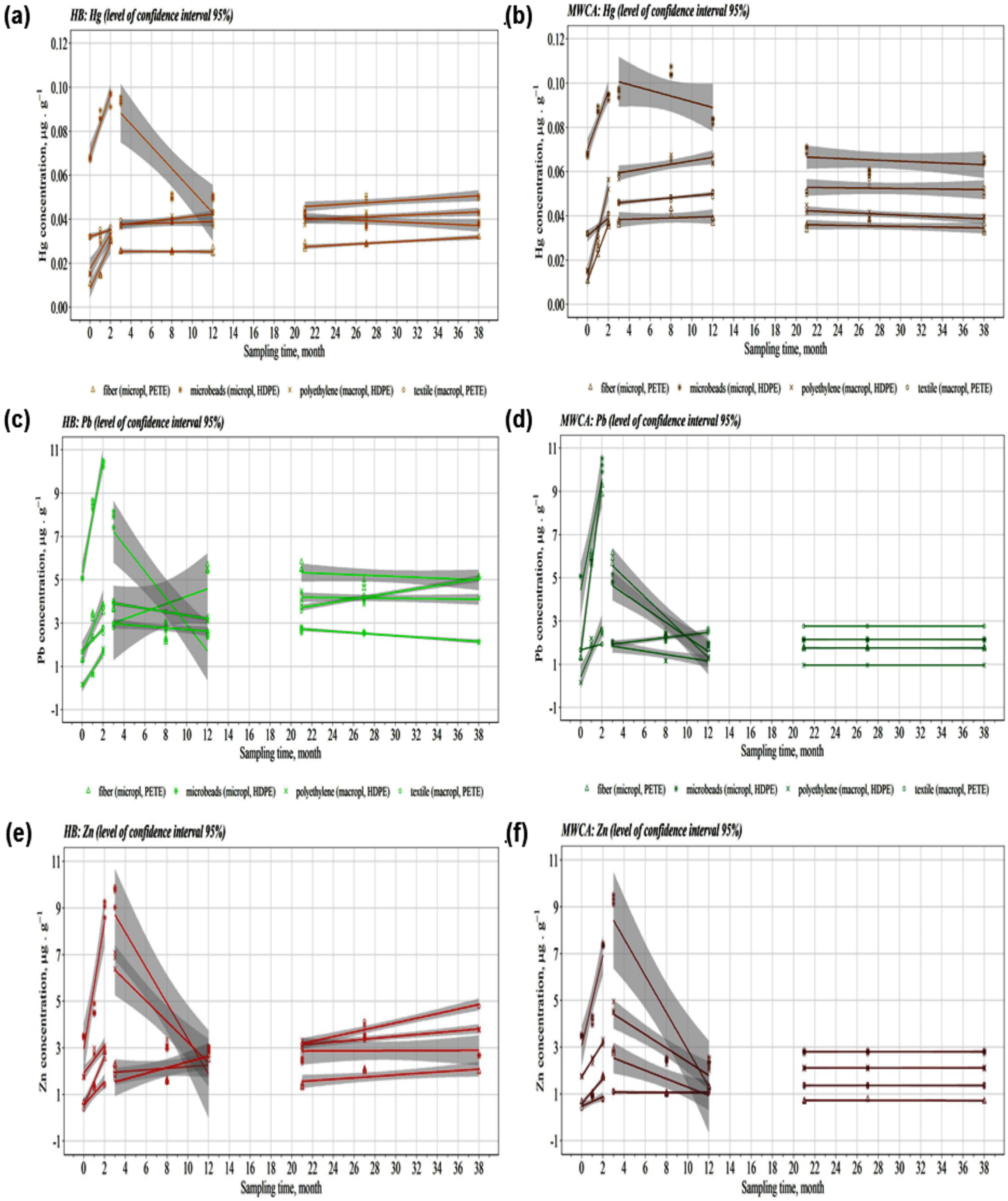


Figure B2. **Liner relationship (95% CI) between concentrations of Hg (a, b), Pb (c, d), and Zn (e, f) (dependent variables) and residence time of macro- and microparticles in the intertidal sediments (independent variable) at HB and MWFCA study sites.**

Note: Concentration of Hg (a, b), Pb (c, d), and Zn (e, f) were measured in micro-PETE (fiber), micro-HDPE (microbeads), macro-PETE (textile fabric), and macro-HDPE (polyethylene chips) deployed in the intertidal sediments at HB (a, c) and MWFCA (b, d) study sites. Output of liner regression models *(lm)* combined for three time periods of field sampling “short -term” (0-2 months), “mid-term” (3-12 months) and “long-term” (21-38 months). Shading represents 95% confidence intervals for predictions from a linear model (*lm*).

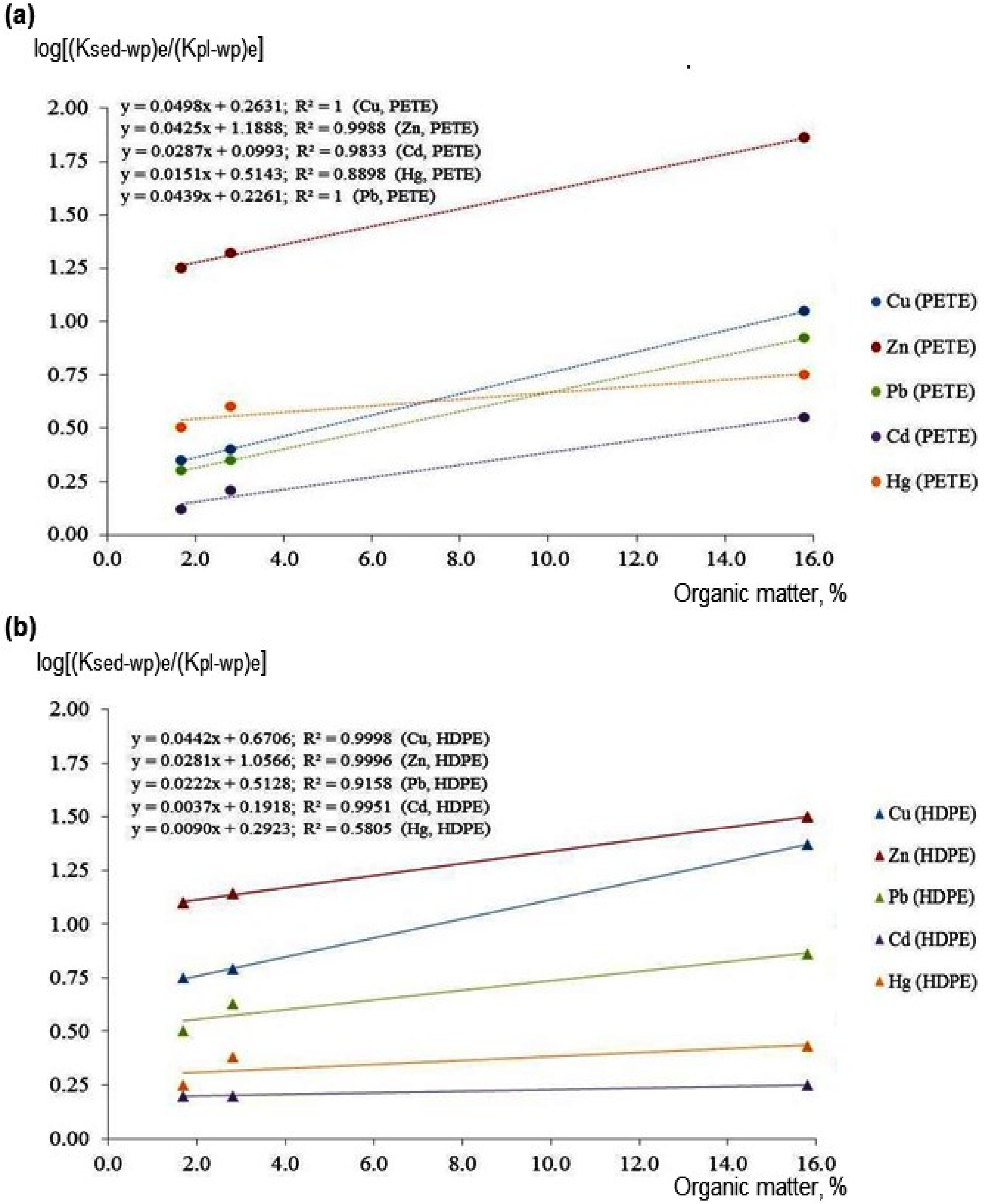


Figure B3. The relationship between value of log[$(K_{sed\text{-}wp})_e/(K_{pl\text{-}wp})_e$] of Cd, Cu, Hg, Pb,and Zn for micro-PETE (fiber) (a) and micro-HDPE (microbeads) (b) and organic matter content in the intertidal sediments withing Burrard Inlet coastal area.

Note: Data on organic matter content in the intertidal sediments were obtained for Cates Park (OM = 1.7%), Horseshoe Bay (OM = 2.8%), and Maplewood Flats Conservation Area (OM = 15.8%) study sites.

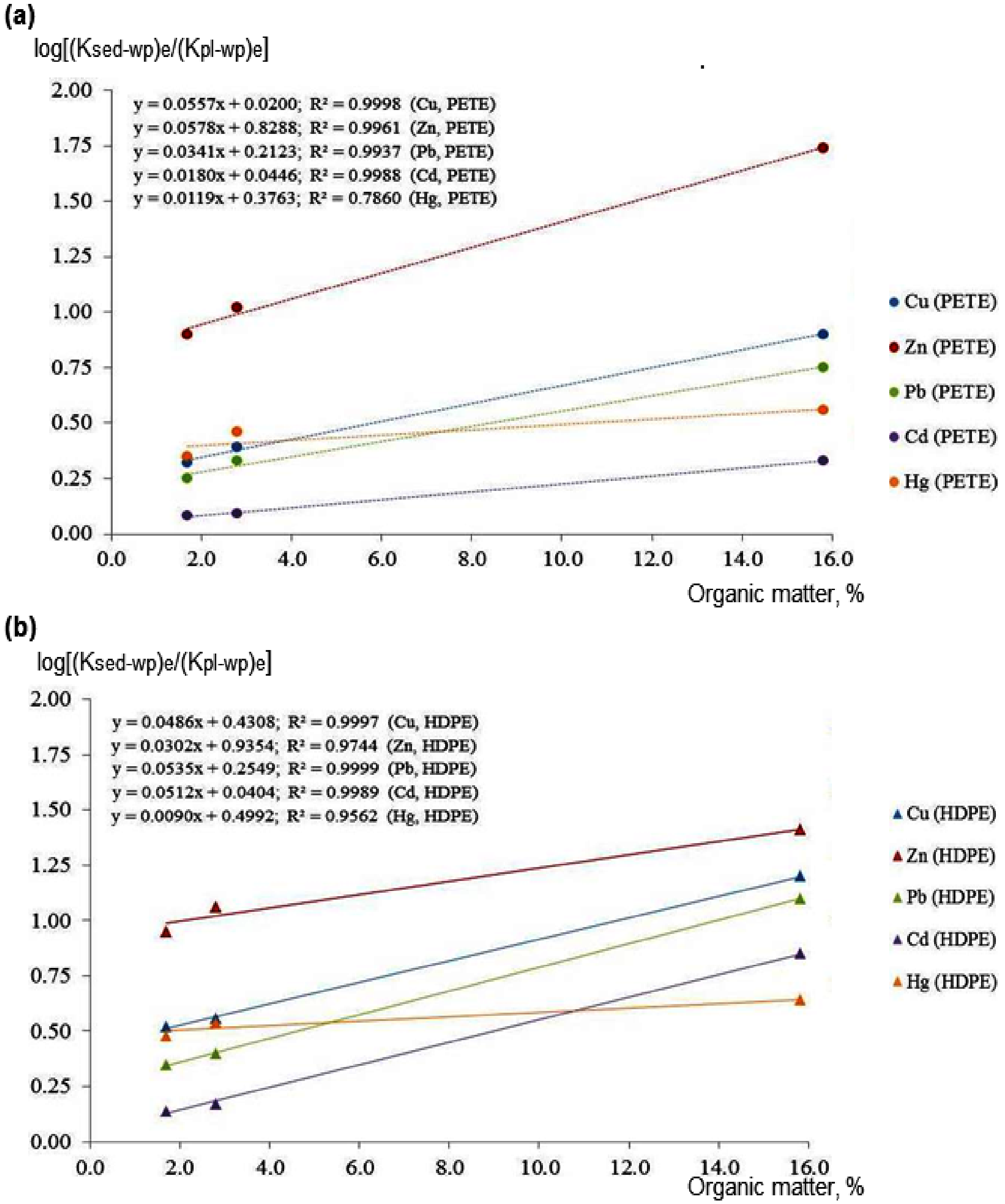


Figure B4. The relationship between value of log $[(K_{sed\text{-}wp})_e/(K_{pl\text{-}wp})_e]$ of Cd, Cu, Hg, Pb,and Zn for macro-PETE (textile fabrice) (a) and macro-HDPE (polyethylene chips) (b) and organic matter content in the intertidal sediments withing Burrard Inlet coastal area.

Note: Data on organic matter content in the intertidal sediments were obtained for Cates Park (OM = 1.7%), Horseshoe Bay (OM = 2.8%), and Maplewood Flats Conservation Area (OM = 15.8%) study sites.

Appendix C.

Supporting Information for Chapter 3

Table C1. Summary output of liner regression models (*lm*)

Statistical parameters	micro-PETE fiber	micro-HDPE microbeads	macro-PETE textile fabric	macro-HDPE polyethylene chips
Cd: Horseshoe Bay (OM=2.8%); T=-4.0°C				
Residuals: min	-0.050	-0.046	-0.024	-0.038
max	0.046	0.040	0.019	0.034
RSE ((n-2), df=19)	0.038	0.029	0.012	0.024
Multiple R-squared	0.794	0.758	0.695	0.790
t value	5.412	4.062	2.768	5.420
p-value	<0.001	< 0.05	0.041	0.001
Cd: Horseshoe Bay (OM=2.8%); T=+4.0°C				
Residuals: min	-0.050	-0.064	-0.053	-0.062
max	0.046	0.072	0.049	0.056
RSE ((n-2), df=19)	0.038	0.053	0.028	0.041
Multiple R-squared	0.794	0.754	0.710	0.684
t value	5.413	5.480	3.535	4.567
p-value	<0.001	<0.001	0.004	<0.001
Cd: Horseshoe Bay (OM=2.8%); T=+18.0°C				
Residuals: min	-0.051	-0.107	-0.094	-0.102
max	0.046	0.122	0.076	0.116
RSE ((n-2), df=19)	0.038	0.075	0.053	0.082
Multiple R-squared	0.790	0.788	0.658	0.736
t value	5.412	5.165	3.894	5.338
p-value	<0.001	<0.001	0.002	<0.001
Cd: Maplewood Flats Conservation Area (OM=15.8%); T=-4.0°C				
Residuals: min	-0.044	-0.030	-0.014	-0.024
max	0.036	0.031	0.012	0.019
RSE ((n-2), df=19)	0.028	0.020	0.007	0.012
Multiple R-squared	0.749	0.750	0.659	0.679
t value	5.468	3.836	2.305	3.600
p-value	<0.001	0.002	0.039	0.004
Cd: Maplewood Flats Conservation Area (OM=15.8%); T=+4.0°C				
Residuals: min	-0.044	-0.035	-0.021	-0.042
max	0.036	0.034	0.018	0.036
RSE ((n-2), df=19)	0.028	0.024	0.012	0.026
Multiple R-squared	0.749	0.828	0.726	0.767
t value	4.468	7.578	3.346	4.302
p-value	<0.001	<0.001	0.005	0.001

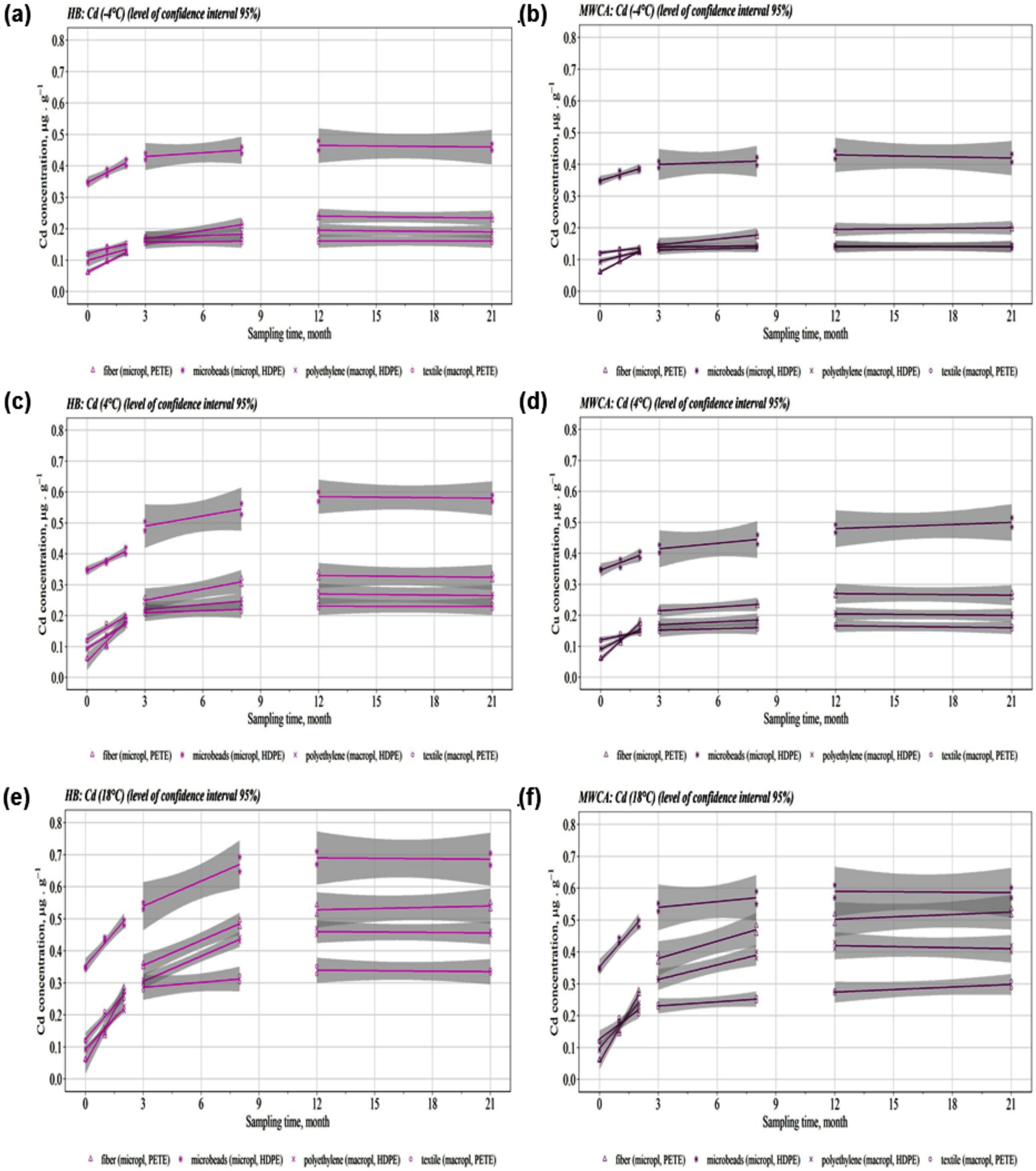
Statistical parameters	micro-PETE fiber	micro-HDPE microbeads	macro-PETE textile fabric	macro-HDPE polyethylene chips
Cd: Maplewood Flats Conservation Area (OM=15.8%); T=+18.0°C				
Residuals: min	-0.044	-0.105	-0.063	-0.111
max	0.036	0.086	0.055	0.096
RSE ((n-2), df=19)	0.028	0.061	0.030	0.075
Multiple R-squared	0.792	0.678	0.725	0.697
t value	5.460	3.779	5.437	4.698
p-value	<0.001	0.002	<0.001	<0.001
Cu: Horseshoe Bay (OM=2.8%); T=-4.0°C				
Residuals: min	-0.560	-0.047	-0.446	-0.296
max	0.787	0.569	0.418	0.230
RSE ((n-2), df=19)	0.047	0.037	0.033	0.020
Multiple R-squared	0.771	0.863	0.757	0.794
t value	6.357	8.664	6.114	5.842
p-value	<0.001	< 0.001	< 0.001	< 0.001
Cu: Horseshoe Bay (OM=2.8%); T=+4.0°C				
Residuals: min	-0.560	-1.103	-0.783	-0.485
max	0.787	1.128	0.801	0.741
RSE ((n-2), df=19)	0.047	0.092	0.028	0.038
Multiple R-squared	0.771	0.755	0.760	0.864
t value	6.357	6.079	5.790	8.132
p-value	<0.001	<0.001	< 0.001	<0.001
Cu: Horseshoe Bay (OM=2.8%); T=+18.0°C				
Residuals: min	-0.560	-1.674	-0.930	-0.821
max	0.787	1.532	0.924	0.961
RSE ((n-2), df=19)	0.047	0.075	0.068	0.071
Multiple R-squared	0.771	0.788	0.799	0.731
t value	6.357	5.665	6.876	5.462
p-value	<0.001	<0.001	<0.001	<0.001
Cu: Maplewood Flats Conservation Area (OM=15.8%); T=-4.0°C				
Residuals: min	-0.673	-0.534	-0.306	-0.270
max	0.398	0.499	0.227	0.193
RSE ((n-2), df=19)	0.037	0.033	0.020	0.630
Multiple R-squared	0.728	0.786	0.765	0.775
t value	5.528	5.128	5.768	4.247
p-value	<0.001	<0.001	<0.001	0.001
Cu: Maplewood Flats Conservation Area (OM=15.8%); T=+4.0°C				
Residuals: min	-0.670	-0.688	-0.544	-0.489
max	0.368	0.716	0.658	0.516
RSE ((n-2), df=19)	0.038	0.055	0.040	0.040
Multiple R-squared	0.729	0.862	0.772	0.767
t value	5.528	7.065	5.517	6.159
p-value	<0.001	<0.001	<0.001	<0.001

Statistical parameters	micro-PETE fiber	micro-HDPE microbeads	macro-PETE textile fabric	macro-HDPE polyethylene chips
Cu: Maplewood Flats Conservation Area (OM=15.8%); T=+18.0°C				
Residuals: min	-0.643	-1.184	-0.721	-0.556
max	0.398	1.248	0.840	0.496
RSE ((n-2), df=19)	0.038	0.061	0.053	0.039
Multiple R-squared	0.729	0.778	0.788	0.798
t value	5.528	6.340	6.519	6.598
p-value	<0.001	< 0.001	<0.001	<0.001
Pb: Horseshoe Bay (OM=2.8%); T=-4.0°C				
Residuals: min	-0.820	-0.443	-1.132	-0.573
max	1.043	0.451	1.176	0.520
RSE ((n-2), df=19)	0.064	0.031	0.093	0.043
Multiple R-squared	0.729	0.741	0.754	0.739
t value	3.633	3.072	5.881	5.818
p-value	<0.05	< 0.05	<0.001	<0.001
Pb: Horseshoe Bay (OM=2.8%); T=+4.0°C				
Residuals: min	-0.821	-0.631	-0.421	-1.159
max	1.043	0.608	0.473	1.420
RSE ((n-2), df=19)	0.063	0.047	0.033	0.541
Multiple R-squared	0.724	0.761	0.719	0.961
t value	3.413	4.375	3.470	6.180
p-value	<0.05	<0.001	<0.05	<0.001
Pb: Horseshoe Bay (OM=2.8%); T=+18.0°C				
Residuals: min	-0.851	-0.750	-0.767	-1.189
max	1.046	0.728	0.666	1.411
RSE ((n-2), df=19)	0.038	0.052	0.050	0.048
Multiple R-squared	0.729	0.758	0.784	0.973
t value	3.412	5.721	5.101	6.702
p-value	<0.050	<0.001	<0.001	<0.001
Pb: Maplewood Flats Conservation Area (OM=15.8%); T=-4.0°C				
Residuals: min	-0.731	-0.434	-0.094	-0.549
max	0.663	0.432	0.139	0.724
RSE ((n-2), df=19)	0.038	0.028	0.046	0.041
Multiple R-squared	0.749	0.860	0.786	0.875
t value	5.064	4.905	6.631	5.753
p-value	<0.001	<0.001	<0.001	< 0.001
Pb: Maplewood Flats Conservation Area (OM=15.8%); T=+4.0°C				
Residuals: min	-0.731	-0.519	-0.362	-1.083
max	0.664	0.543	0.242	1.377
RSE ((n-2), df=19)	0.051	0.034	0.040	0.089
Multiple R-squared	0.800	0.799	0.758	0.768
t value	5.064	5.271	4.295	5.715
p-value	<0.001	<0.001	0.001	<0.001

Statistical parameters	micro-PETE fiber	micro-HDPE microbeads	macro-PETE textile fabric	macro-HDPE polyethylene chips
Pb: Maplewood Flats Conservation Area (OM=15.8%); T=+18.0°C				
Residuals: min	-0.730	-0.590	-0.580	-0.971
max	0.663	0.813	0.472	1.192
RSE ((n-2), df=19)	0.038	0.044	0.039	0.039
Multiple R-squared	0.769	0.819	0.748	0.758
t value	5.058	4.412	3.395	7.877
p-value	<0.001	< 0.001	<0.01	<0.001
Zn: Horseshoe Bay (OM=2.8%); T=-4.0°C				
Residuals: min	-0.441	-0.216	-0.358	-0.218
max	0.564	0.214	0.252	0.391
RSE ((n-2), df=19)	0.031	0.041	0.043	0.051
Multiple R-squared	0.852	0.740	0.781	0.931
t value	8.300	3.751	5.062	12.740
p-value	<0.001	< 0.005	<0.001	<0.001
Zn: Horseshoe Bay (OM=2.8%); T=+4.0°C				
Residuals: min	-0.442	-0.569	-0.661	-1.004
max	0.563	0.608	0.544	0.708
RSE ((n-2), df=19)	0.030	0.039	0.049	0.064
Multiple R-squared	0.872	0.849	0.794	0.776
t value	8.413	4.718	5.891	5.022
p-value	<0.001	<0.001	<0.001	<0.001
Zn: Horseshoe Bay (OM=2.8%); T=+18.0°C				
Residuals: min	-0.442	-0.884	-1.025	-1.118
max	0.537	0.717	1.005	1.133
RSE ((n-2), df=19)	0.031	0.057	0.058	0.076
Multiple R-squared	0.865	0.779	0.766	0.797
t value	8.341	5.713	4.680	6.783
p-value	<0.001	<0.001	<0.001	<0.001
Zn: Maplewood Flats Conservation Area (OM=15.8%); T=-4.0°C				
Residuals: min	-0.269	-0.180	-0.274	-0.241
max	0.298	0.242	0.241	0.203
RSE ((n-2), df=19)	0.021	0.034	0.047	0.049
Multiple R-squared	0.784	0.727	0.768	0.814
t value	6.233	2.118	3.971	4.300
p-value	<0.001	<0.001	<0.001	0.001
Zn: Maplewood Flats Conservation Area (OM=15.8%); T=+4.0°C				
Residuals: min	-0.230	-0.386	-0.384	-0.592
max	0.298	0.407	0.595	0.469
RSE ((n-2), df=19)	0.032	0.056	0.040	0.037
Multiple R-squared	0.769	0.762	0.846	0.834
t value	6.528	4.347	8.109	4.558
p-value	<0.001	<0.001	<0.001	<0.001

Statistical parameters	micro-PETE fiber	micro-HDPE microbeads	macro-PETE textile fabric	macro-HDPE polyethylene chips
Zn: Maplewood Flats Conservation Area (OM=15.8%); T=+18.0°C				
Residuals: min	-0.270	-0.778	-0.825	-0.844
max	0.2 98	0.780	0.653	0.682
RSE ((n-2), df=19)	0.037	0.053	0.057	0.056
Multiple R-squared	0.764	0.782	0.863	0.769
t value	6.528	5.671	4..582	6.934
p-value	<0.001	< 0.001	<0.001	<0.001

Note: The summary output of the liner regression models (*lm*) are combined for three time periods of field sampling “short -term”(0-2 months), “mid-term” (3-8 months) and “long-term” (12-21 months). Differences in concentration of trace elements among study sites versus plastic type and particle size.


(a) HB: Cd (-4°C) (level of confidence interval 95%)

(b) MWCA: Cd (-4°C) (level of confidence interval 95%)

(c) HB: Cd (4°C) (level of confidence interval 95%)

(d) MWCA: Cd (4°C) (level of confidence interval 95%)

(e) HB: Cd (18°C) (level of confidence interval 95%)

(f) MWCA: Cd (18°C) (level of confidence interval 95%)

Figure C1. **Liner relationship (95% CI) between concentrations of Cd (dependent variables) and residence time of macro- and microparticles in the intertidal sediments (independent variable) under conditions of constant temperature of T= -4.0°C (a, b), T=+4.0°C (c, d), and T=+18.0°C (e, f).**

Note: Concentration of Cd were measured in micro-PETE (fibre), micro-HDPE (microbeads), macro-PETE (textile fabric), and macro-HDPE (polyethylene chips) deployed in the intertidal sediments at low (OM=2.8%) (a, c, e) and high (OM=15.8%) (b, d, f) in organic matte content. Output of liner regression models (lm) combined for three time periods of field sampling “short -term” (0-2 months), “mid-term” (3-8 months) and “long-term” (12-21 months). Shading represents 95% confidence intervals for predictions from a linear model (*lm*).

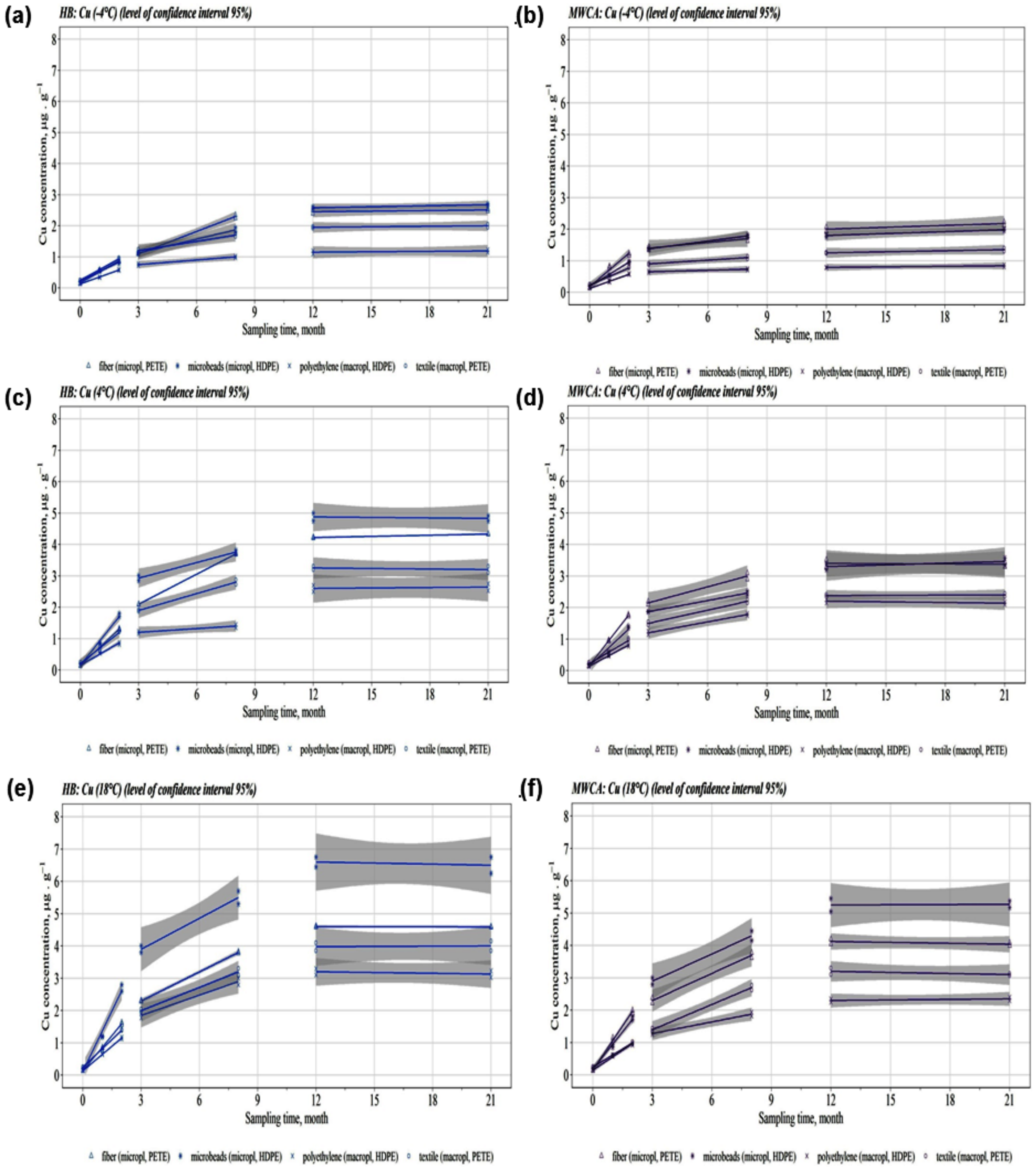


Figure C2. Liner relationship (95% CI) between concentrations of Cu (dependent variables) and residence time of macro- and microparticles in the intertidal sediments (independent variable) under conditions of constant temperature of T= -4.0°C (a, b), T=+4.0°C (c, d), and T=+18.0°C (e, f).

Note: Concentration of Cu were measured in micro-PETE (fibre), micro-HDPE (microbeads), macro-PETE (textile fabric), and macro-HDPE (polyethylene chips) deployed in the intertidal sediments at low (OM=2.8%) (a, c, e) and high (OM=15.8%) (b, d, f) in organic matte content. Output of liner regression models (lm) combined for three time periods of field sampling "short -term" (0-2 months), "mid-term" (3-8 months) and "long-term" (12-21 months). Shading represents 95% confidence intervals for predictions from a linear model (*lm*).

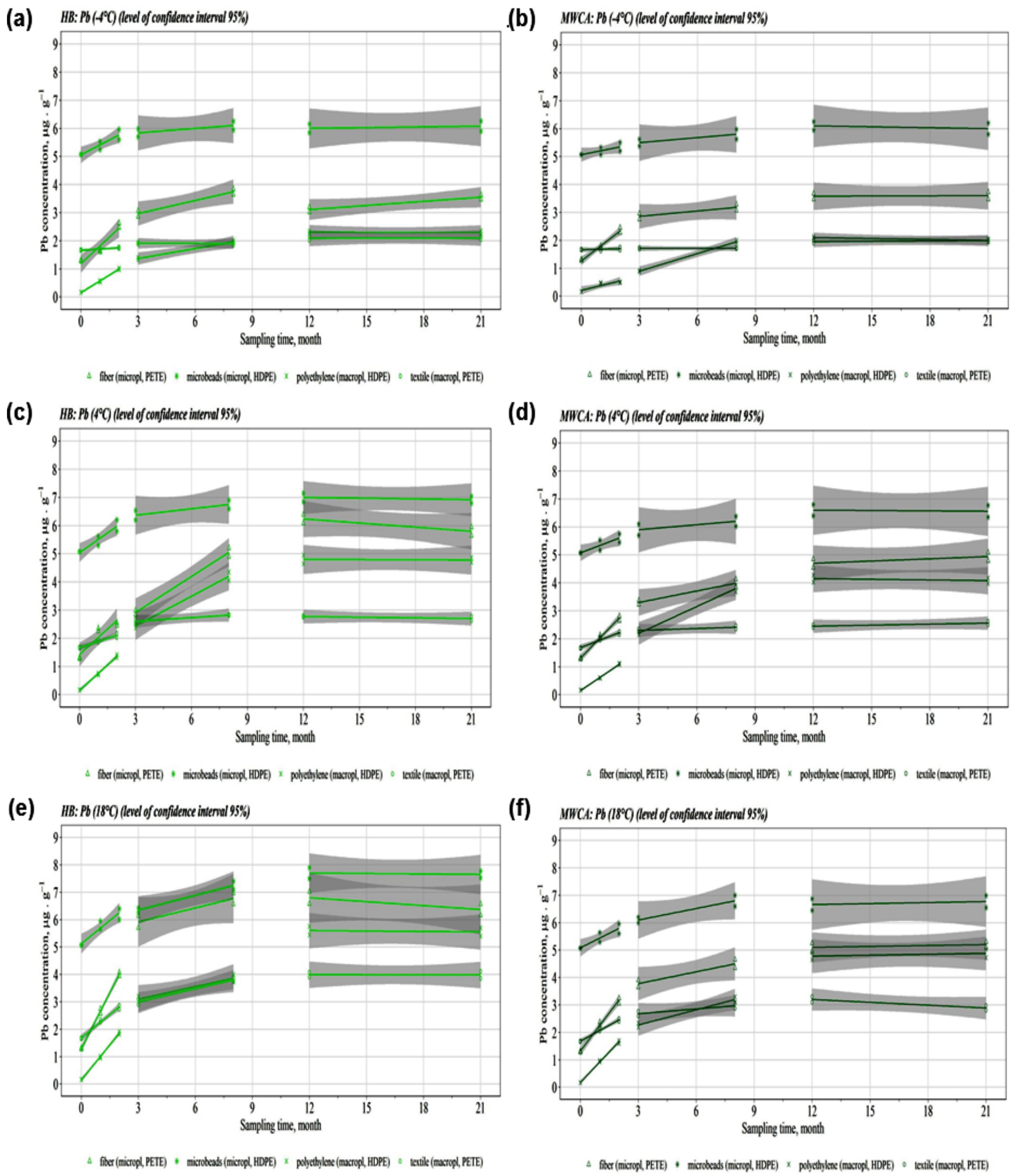


Figure C3. **Liner relationship (95% CI) between concentrations of Pb (dependent variables) and residence time of macro- and microparticles in the intertidal sediments (independent variable) under conditions of constant temperature of T= -4.0°C (a, b), T=+4.0°C (c, d), and T=+18.0°C (e, f).**

Note: Concentration of Pb were measured in micro-PETE (fibre), micro-HDPE (microbeads), macro-PETE (textile fabric), and macro-HDPE (polyethylene chips) deployed in the intertidal sediments at low (OM=2.8%) (a, c, e) and high (OM=15.8%) (b, d, f) in organic matte content. Output of liner regression models (lm) combined for three time periods of field sampling “short - term” (0-2 months), “mid-term” (3-8 months) and “long-term” (12-21 months). Shading represents 95% confidence intervals for predictions from a linear model (*lm*).

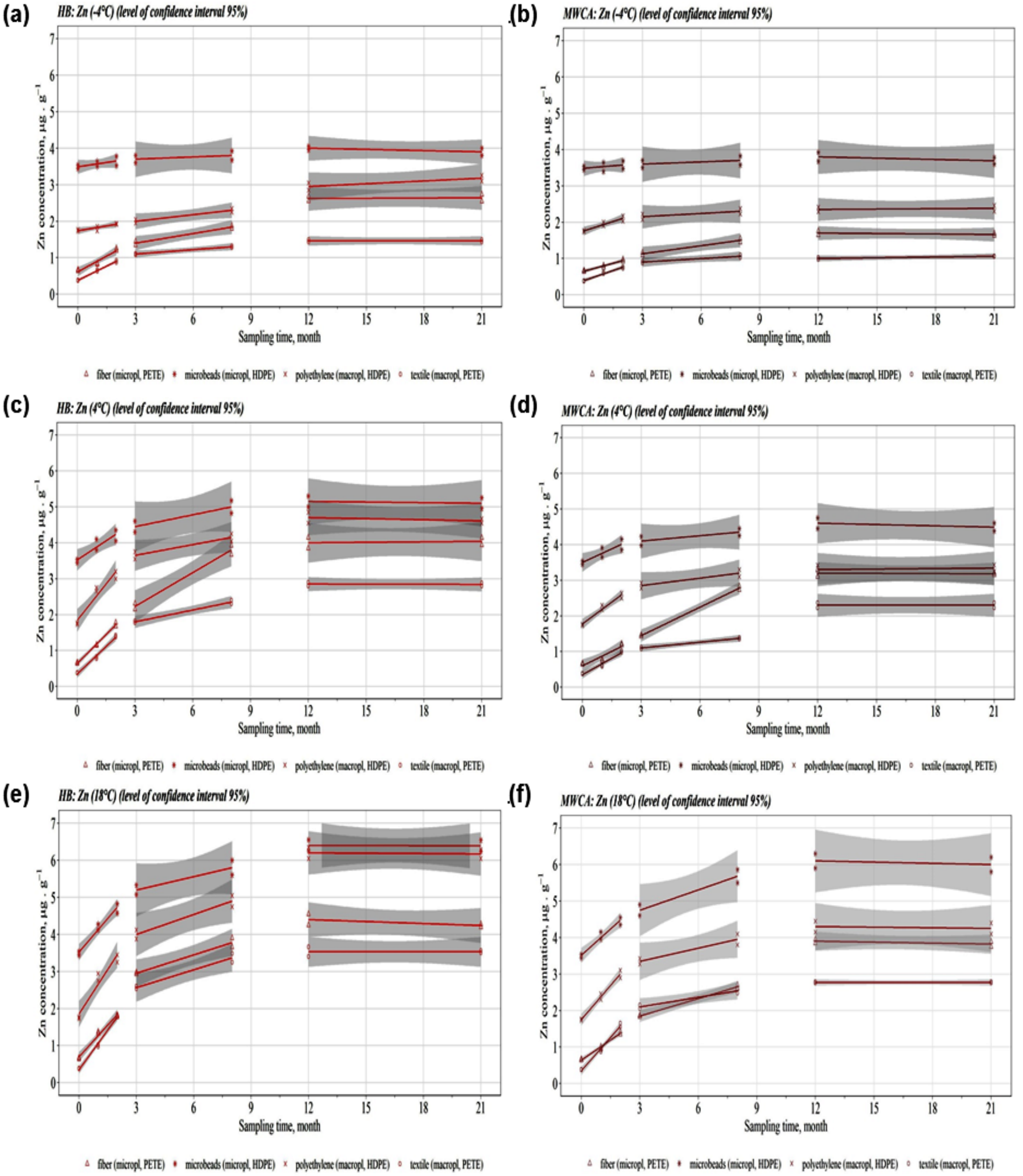


Figure C4. Liner relationship (95% CI) between concentrations of Zn (dependent variables) and residence time of macro- and microparticles in the intertidal sediments (independent variable) under conditions of constant temperature of T= -4.0°C (a, b), T=+4.0°C (c, d), and T=+18.0°C (e, f).

Note: Concentration of Zn were measured in micro-PETE (fibre), micro-HDPE (microbeads), macro-PETE (textile fabric), and macro-HDPE (polyethylene chips) deployed in the intertidal sediments at low (OM=2.8%) (a, c, e) and high (OM=15.8%) (b, d, f) in organic matte content. Output of liner regression models (lm) combined for three time periods of field sampling “short - term” (0-2 months), “mid-term” (3-8 months) and “long-term” (12-21 months). Shading represents 95% confidence intervals for predictions from a linear model (*lm*).

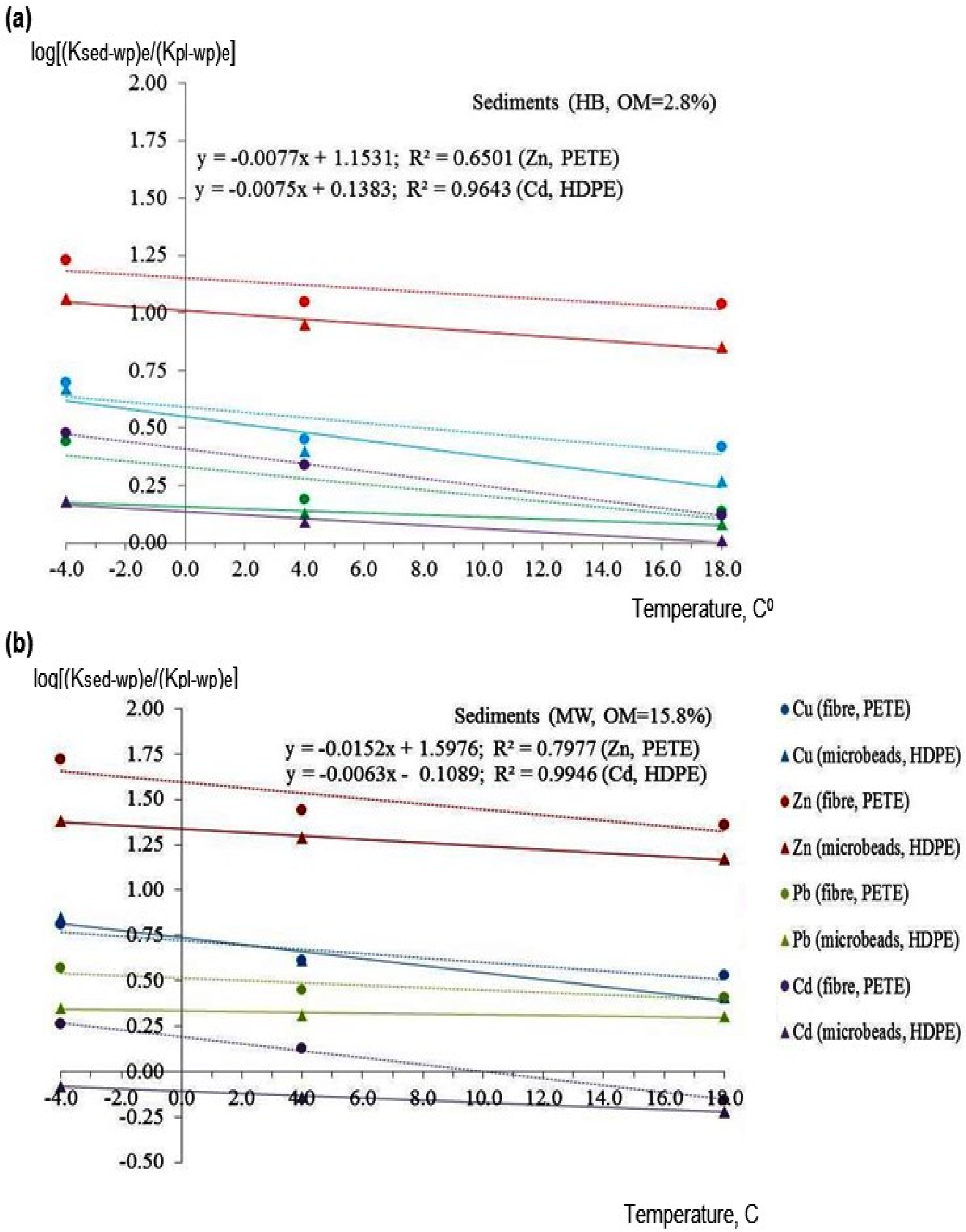


Figure C5. **The relationship between value of log [$(K_{sed\text{-}wp})_e/(K_{pl\text{-}wp})_e$] of Cd, Cu, Pb,and Zn for microparticles of PETE and HDPE and constant temperature.**

Note: Micro-PETE (fiber), micro-HDPE (microbeads) were deployed in the intertidal sediments low (OM=2.8%) (a) and high (15.8%) (b) in organic matter content under conditions of constant temperature of T=- 4.0°C, T=+4.0°C, and T=+18.0°C.

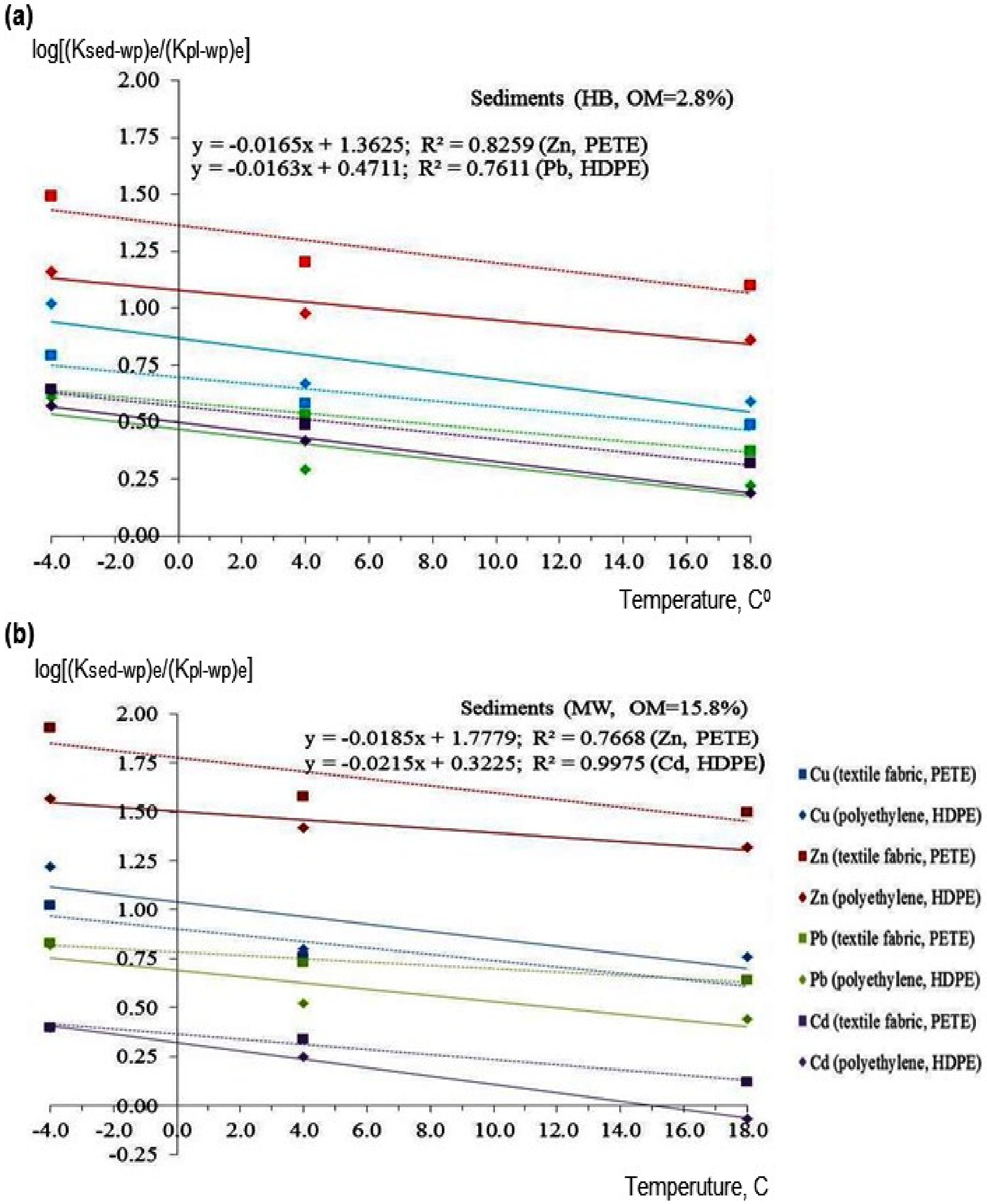


Figure C6. **The relationship between value of log [$(K_{sed\text{-}wp})_e/(K_{pl\text{-}wp})_e$] of Cd, Cu, Pb,and Zn for macroparticles of PETE and HDPE and constant temperature.**

Note: Macro-PETE (textile fabric), and macro-HDPE were deployed in the intertidal sediments low (OM=2.8%) (a) and high (15.8%) (b) in organic matter content under conditions of constant temperature of T=- 4.0°C, T=+4.0°C, and T=+18.0°C.