Spatial heterogeneity distributions and seasonal variations of microplastic contaminations in surface waters and sediments and microplastic pollution level assessments of the inner Gulf of Thailand

Mr. Pathompong Vibhatabandhu

A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy in Hazardous Substance and
Environmental Management
Inter-Department of Environmental Management
GRADUATE SCHOOL
Chulalongkorn University
Academic Year 2021

การกระจายตัวเชิงพื้นที่และการเปลี่ยนแปลงตามฤดูกาลของการปนเปื้อนไมโครพลาสติกในน้ำระดับชั้นผิวและตะกอนดิน และการประเมินระดับมลพิษไมโครพลาสติกของอ่าวไทยตอนใน

นายปฐมพงศ์ วิภาตะพันธุ์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต
สาขาวิชาการจัดการสารอันตรายและสิ่งแวดล้อม สหสาขาวิชาการจัดการสิ่งแวดล้อม
บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2564

Thesis Title	Spatial heterogeneity distributions and seasonal variations of microplastic contaminations in surface waters and sediments and microplastic pollution level assessments of the inner Gulf of Thailand
By	Mr. Pathompong Vibhatabandhu
Field of Study	Hazardous Substance and Environmental Management
Thesis Advisor	Assistant Professor SARAWUT SRITHONGOUTHAI, Ph.D.

Accepted by the GRADUATE SCHOOL, Chulalongkorn University in Partial Fulfillment of the Requirement for the Doctor of Philosophy

-- Dean of the GRADUATE SCHOOL
(Associate Professor YOOTTHANA CHUPPUNNARAT, Ph.D.)

DISSERTATION COMMITTEE

-- Chairman
(Associate Professor EKAWAN LUEPROMCHAI, Ph.D.)
-- Thesis Advisor
(Assistant Professor SARAWUT SRITHONGOUTHAI, Ph.D.)
-- Examiner
(Assistant Professor PENRADEE CHANPIWAT, Ph.D.)
-- Examiner
(Associate Professor Jenyuk Lohwacharin, Ph.D.)
-- Examiner
(Vacharaporn Soonsin, Ph.D.)
-- External Examiner
(Associate Professor Supakij Suttiruengwong, Ph.D.)

ปฐมพงศ์ วิภาตะพันธุ์ : การกระจายตัวเชิงพื้นที่และการเปลี่ยนแปลงตามฤดูกาลของการปนเปื้อนไมโครพลาสติกในน้ำระดับชั้นผิวและตะกอนดิน และการประเมินระดับมลพิษไมโครพลาสติกของอ่าวไทยตอนใน. (Spatial heterogeneity distributions and seasonal variations of microplastic contaminations in surface waters and sediments and microplastic pollution level assessments of the inner Gulf of Thailand) อ.ที่ปรึกษาหลัก : ผศ. ดร.สราวุธ ศรีทองอุทัย

ไมโครพลาสติก หรือ อนุภาคพลาสติกขนาดเล็กกว่า 5 มิลลิเมตร เป็นมลสารชนิดใหม่ที่อาจเป็นปัญหาในระบบนิเวศทางทะเล เนื่องจากพฤติกรรมของไมโครพลาสติกในสิ่งแวดล้อมยังมีความคลุมเครือ การวิจัยนี้มีวัตถุประสงค์เพื่อวิเคราะห์ลักษณะการปนเปื้อนไมโครพลาสติกในน้ำระดับชั้นผิวและตะกอนดินในพื้นที่อ่าวไทยตอนใน โดยเก็บตัวอย่างน้ำระดับชั้นผิวและตัวอย่างตะกอนดินจากพื้นที่ทะเลชายฝั่ง และพื้นที่ปากแม่น้ำแม่กลอง ปากแม่น้ำท่าจีน ปากแม่น้ำเจ้าพระยา และปากแม่น้ำบางปะกง ในฤดูแล้งและฤดูฝนของปี พ.ศ. 2561 ผลการวิเคราะห์พบว่า อิทธิพลของฤดูฝนทำให้การปนเปื้อนไมโครพลาสติกเพิ่มขึ้นจากฤดูแล้ง โดยค่าเฉลี่ยปริมาณไมโครพลาสติกในตัวอย่างน้ำมีค่าเพิ่มขึ้นจาก 8.70±15.34 ชิ้น/ลิตร ในฤดูแล้ง เป็น 34.59±46.02 ชิ้น/ลิตร ในฤดูฝน ขณะที่การปนเปื้อนในตัวอย่างตะกอนดินมีค่าเพิ่มขึ้นจาก 7297±5960 ชิ้น/กิโลกรัม ในฤดูแล้ง เป็น 12216±7079 ชิ้น/กิโลกรัม ในฤดูฝน การกระจายตัวของไมโครพลาสติกแสดงให้เห็นว่า การไหลของน้ำจืดและกระแสน้ำตามฤดูกาลควบคุมการเคลื่อนที่ของไมโครพลาสติกในน้ำ อย่างไรก็ตาม ไมโครพลาสติกมีแนวโน้มที่จะรวมตัวกับสารแขวนลอยและตกตะกอนในพื้นที่ปากแม่น้ำมากกว่าพื้นที่ทะเลชายฝั่ง การระบุชนิดพลาสติกบ่งชี้ว่า โพลีเอทิลีนและโพลีโพรพิลีนเป็นชนิดพลาสติกที่พบได้ทั่วไปในพื้นที่ศึกษาโดยเป็นชนิดพลาสติกที่พบมากที่สุดในตัวอย่างน้ำ ในขณะที่ โพลีเอไมด์และโพลีอะคริโลไนไตรล์บิวทาไดอีนเป็นพลาสติกชนิดหลักที่พบในตัวอย่างตะกอนดิน นอกจากนี้ การวิเคราะห์ยังพบการปนเปื้อนโลหะหนักในตัวอย่างไมโครพลาสติกโดยเฉพาะส่วนคราบตะกอนที่สะสมอยู่กับไมโครพลาสติก การประเมินระดับมลพิษของไมโครพลาสติกแสดงให้เห็นว่า การปนเปื้อนไมโครพลาสติกในตะกอนดินระดับชั้นผิวของอ่าวไทยตอนในอยู่ในระดับปนเปื้อนสูงมาก ขณะเดียวกัน การประเมินความเสี่ยงทางนิเวศวิทยาพบว่า ความเสี่ยงของการปนเปื้อนไมโครพลาสติกอยู่ในระดับปานกลางถึงสูง ดัชนีความเสี่ยงทางนิเวศวิทยาแสดงให้เห็นว่า มอนอเมอร์ของพลาสติกเป็นปัจจัยหลักที่ควบคุมความเสี่ยงของไมโครพลาสติก ขณะที่การปนเปื้อนโลหะหนักในไมโครพลาสติกส่งผลเล็กน้อยต่อความเสี่ยงทั้งหมดที่เกิดจากไมโครพลาสติก การประเมินความเสี่ยงของการปนเปื้อนไมโครพลาสติกที่ได้รับการปรับปรุงในการศึกษานี้สามารถนำไปรวมกับการประเมินความเสี่ยงของการปนเปื้อนสารพิษชนิดอื่นเพื่อประเมินความเสี่ยงทางนิเวศวิทยาที่เป็นไปได้สำหรับการปนเปื้อนในตะกอนดินของพื้นที่ที่ได้รับการพิจารณา

สาขาวิชา การจัดการสารอันตรายและสิ่งแวดล้อม ลายมือชื่อนิสิต ....
ปีการศึกษา 2564 ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

6087817520 : MAJOR HAZARDOUS SUBSTANCE AND ENVIRONMENTAL MANAGEMENT

KEYWORD: Microplastics, Surface water, Sediment, Spatial distribution, Seasonal variation, The inner Gulf of Thailand, Pollution level assessment

Pathompong Vibhatabandhu : Spatial heterogeneity distributions and seasonal variations of microplastic contaminations in surface waters and sediments and microplastic pollution level assessments of the inner Gulf of Thailand. Advisor: Asst. Prof. SARAWUT SRITHONGOUTHAI, Ph.D.

Microplastics or the plastic particles less than 5 mm are the emerging pollutant that may be threat in marine ecosystems. Due to uncertainty in behavior of microplastics in the environment, this research objectives to analyze the characteristics of microplastic contaminations in surface waters and sediments of the inner Gulf of Thailand. The surface waters and sediments in dry season and wet season of 2018 were sampled from the coastal sea and the river estuaries of Mae Klong, Ta Chin, Chao Phraya, and Bang Pakong rivers. The analysis found that the influence of wet season increased contamination of microplastics from dry season. The average abundance of microplastics in water samples was increased from 8.70±15.34 pieces/L in dry season to 34.59±46.02 pieces/L in wet season, while that in sediment was increased from 7297±5960 pieces/kg of dry weight sediment in dry season to 12216±7079 pieces/kg of dry weight sediment in wet season. The distributions of microplastics illustrated the freshwater runoff and seasonal surface current controlled the transportation of microplastics in surface water; however, the microplastics tend to be aggregated with suspended solids and sedimented in the river estuaries more than that in coastal sea. The identification of plastic types indicated that polyethylene and polypropylene were the common plastic types in the study area as they were the most observed plastic types of microplastics in the water samples, while polyamide and poly (acrylonitrile: butadiene) were the major plastic types of microplastics in the sediment samples. In addition, the analysis found the contamination of heavy metals in the microplastic samples, especially in fouling accumulated on microplastics. The pollution level assessment revealed the contamination of microplastics in surface sediments of the inner Gulf of Thailand was in the level of very high contamination, while the ecological risk evaluation found the risk of microplastic contamination was in the moderate to high levels. The ecological risk index represents that the risk of microplastics was mainly regulated by plastic monomer chemicals, while the contaminated of heavy metals in microplastics resulted the small proportion in the total risk of microplastics. The revised risk assessment for the contamination of microplastics in this study could be included to the risk assessment of the contaminations of the other toxic substances for evaluating the potential ecological risk of the contaminations in sediment of the considered area.

Field of Study:	Hazardous Substance and Environmental Management	Student's Signature ....
Academic Year:	2021	Advisor's Signature ....

ACKNOWLEDGEMENTS

This dissertation was fulfilled with the comprehensive advice, continuous guidance, constructive criticism, and encouragement of my adviser, Assistant Professor Sarawut Srithongouthai, Ph. D., throughout the course of my study. His kindness and generosity will always be remembered.

I am deeply gratitude to the members of my dissertation committee, Associate Professor Ekawan Luepromchai, Ph. D., Assistant Professor Penradee Chanpiwat, Ph. D., Jenyuk Lohwacharin, Ph. D., and Vacharaporn Soonsin, Ph. D. for their valuable comments and suggestions in the completion of this dissertation.

This work was supported by the 100 th Anniversary Chulalongkorn University Doctoral Scholarship and the 90 th Anniversary of Chulalongkorn University Fund (Ratchadaphiseksomphot Endowment Fund). Special thanks are gratefully expressed to the research team at the Department of Marine Science, Faculty of Fishery, Kasetsart University for the sample collection and the Department of Environmental Science, Faculty of Science, Chulalongkorn University for laboratory supports and analytical services.

I also extended acknowledges to International Program in Hazardous Substance and Environmental Management, Graduate School, Chulalongkorn University. Finally, I would like to thank the others and my parents for their support, encouragement and understanding throughout graduate study.

Pathompong Vibhatabandhu

TABLE OF CONTENTS

Page

LIST OF FIGURES

Page

CHAPTER I
INTRODUCTION

1.1 Statement of problems

Microplastics (MPs), generally described as the plastics particles that are smaller than 5 mm, are the emerging pollutant that need to be studied. Sourced from degrading of plastics or releasing of manufactured small size plastic products, the MPs tend to be sank in the marine environments. It must admit that contamination status and behavior of MPs are important for accessing the impacts in ecological system and the toxicological risk of this pollutant.

MPs in environment are a long middle of pipe before plastics were degraded to available organic compounds. The contamination of MPs in waters, sediments and biota has been reported. Sourced from manufacturing of small plastic products and weathering of large plastics debris, MPs are distributed into the marine environment via storm sewers, wind, and currents. Formed with microorganism and organic compounds in the environment, MPs have been changed their density and aggregated with natural particle that cause dynamically and vertically spread in surface water, in water column, and in sediment [45, 46]. This can infer that MPs are bioaccessible for marine biota in several habitats.

With limited evidence of this contamination effects under field condition, the concerned problems about environmental impacts of MPs have been raised for individual effects through the ecological effects. Interestingly, MPs affect all level of biota, which is producer to consumer level, in both freshwater and marine biota. MPs are discussed to be either their intrinsic toxicity, which is physical damage, monomer and additives releasing, or the vectors for transportation of heavy metals and persistence organic pollutants to aquatic organism [47-49]. The mechanistic toxicology of MPs was proposed that MPs exposure inhibits various enzymatic and metabolic pathways, and results in food chain perturbations and ecological imbalance [50]. Finally, the potential impacts of tropic level transfer of MPs also have received considerable attention. Although the ecological risk assessment is not fully studied, the effective of the assessment is based on occurrence, quantification, and delineating toxic effects of MPs in the environmental components.

While the impacts of MPs contamination are not well known, the plastic marine debris loading rate of Thailand was determined to 0.15-0.41 million metric tons/year [51]. The recent studies on MPs in Thailand has reported the contamination in surface water [24, 25, 52, 53], bed sediments [17, 25, 35, 41, 52], beach sediments [24, 54], in bivalves [24, 54, 55], and in sessile invertebrates [56]. Because the contamination of MPs and their potential effects are uncertain, this study objectives to assess the influences of seasonal variations on MPs contamination characteristics and rapidly evaluate the impact on ecosystem. Specifically, the spatial and seasonal distribution of MPs in surface waters and that in sediments of the inner Gulf of Thailand (GT), the national resource and accumulation sink of pollution of Thailand, was investigated. The pollution and eco-risk scales were modified to illustrate MPs contamination status. In addition, the sorption of heavy metals, special co-contaminants, on MPs will be used to index contamination in MPs.

1.2 Objective

1) To investigate spatial distributions and seasonal variations of microplastic contaminations in surface waters and sediments of the inner Gulf of Thailand
2) To characterize the physical and chemical properties of microplastics in surface waters and sediments
3) To revise the potential ecological risk assessment model for evaluating the pollution level and risk of microplastics with the co-contamination of heavy metals

1.3 Scope of the study

In this research, microplastics (MPs) refer to the plastics those are particles smaller than 5 mm along their longest dimension, and those have density lower than 1.2 g/cm^3. The study area was the coastal sea of the inner Gulf of Thailand (GT) included the 4 main river estuaries of Mae Klong River (MK), Ta Chin River (TC), Chao Phraya River (CP), and Bang Pakong River (BK) (Figure 1.1). The study area was represented to the pollutant accumulated area influenced by freshwater runoff, anthropogenic activities, and hydro-geological characteristics.

Figure 1.1 The inner Gulf of Thailand, the South China Sea, Pacific Ocean

According to river runoff, the pollution from the activities in the river basin was loaded to the estuaries and discharged to the inner GT. The water of MK was incorporated with the runoff and emission from the agricultural, industrial, and residential areas of the western part of Thailand. Similarly, water of TC was additionally loaded by the activities from the center basin. The large pollutants runoff from agriculture, fisheries, transportation, industries, and domestic consumption could be entered to the riverine water of CP, as this river is the largest river located in the northern and the central, and the river passes the intensive urban area of the metropolis, Bangkok. In the other side, agriculture was the main propose of land utilization in the eastern river basin of BK; however, the urban, tourism, and industry also be expanded. The freshwater runoff and anthropogenic activities in the river estuaries could be source of pollutants entered to the coastal sea of the inner GT.

It must highlight that season of the study area may strongly affect to the hydrological factors, and those factors also regulated the dynamic of the pollutants. In overview, the southwest monsoon increases rainfall from June to September, and the northeast monsoon reduces rainfall and temperature from October to February. The lowest runoffs and extremely high temperatures are mostly observed in the transition period between the northeast monsoon and the southwest monsoon in March to May. The investigation revealed that the river runoff was strongly magnified during the increased rainfall in the wet season, which is the southwest monsoon period. The model and investigation determined that clockwise circulation of the water current was observed during the southwest monsoon period (May–August), while some counterclockwise circulation was observed during the northeast monsoon period (November–January) [57, 58]. This dynamic was considered it may affect both the concentration and distribution patterns of MPs in the Inner Gulf of Thailand.

This study, the runoff water was mainly hypothesized as being the influence controlling contaminations of MPs and the other pollutants. The end of the monsoon transition period (April–May) was chosen to represent the dry season, as rainfall was scarce since the northeast monsoon period, while the results of runoff in the wet season were studied in the southwest monsoon period (July–August). Thus, the water samples and sediment samples were collected in dry season (April-May 2018) and wet season (July-August 2018). Additionally, the surface waters in northeast monsoon period (December 2017) were sampled. All quantification was modified from laboratory method for analysis of MPs in the marine environment: recommendations for quantifying synthetic particles in water and sediment of National Oceanic and Atmospheric Administration, United States [59]. By microscopic count and gravimetrical analysis, MPs was quantified for shapes, and colors. The plastic types of MPs were identified by FTIR spectrum. The data was normalized and analyzed as parametric statistics with 95% confidence intervals (significance level 0.05). The distribution maps were contributed by Inverse Distance Weighting (IDW) interpolation of ArcGIS®. The seasonal variation of study area according to the sampling periods was analyzed by the published research, and that was the secondary data from the analysis of the "Development of Socio-Ecological Based Effective Fishery Management Policy for Good Governance in Sustainable Fishery of the Inner Gulf of Thailand", Faculty of Fisheries, Kasetsart University. The dissertation was consisted of 3 parts including:

1) **Influence of seasonal variation on distribution characteristics of microplastics in surface water**

The contamination of MPs in surface waters of the inner Gulf of Thailand was firstly investigated for the abundance and physicochemical characteristics with the seasonal variation. The fragmentation in MPs structures was observed, and that was critically detailed for the main plastic types of polyethylene and polypropylene. Beside variation in characteristics of MPs, spatial distributions of film-, fiber-, fragment-, foam-, and pellet-MPs were illustrated for MPs in size of 100-300 µm, 300-1000 µm, and 1000-5000 µm. The effects of multi-environmental variates in dry season and wet season on MPs contaminated in surface water were analyzed.

2) Accumulation of microplastics in surface sediment and co-contamination of heavy metals in microplastics

The abundance of MPs in surface sediments was quantified by plastic identification of microscopic FTIR spectrometer, the presented number of MPs was the particles that confirmed to be plastics, in the other words. The physical and chemical characteristics of MPs in surface sediments were comparatively analyzed with those of MPs in surface waters. In addition, the vertical profile of MPs in sediment was investigated, and the relationships of MPs-sediment variables were observed. The analysis of heavy metals (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn) found the contamination in both plastic contents and fouling contents of MPs.

3) Pollution assessment for contamination of microplastics: case study in the inner Gulf of Thailand

The pollution assessment model, potential ecological risk index, of MPs in sediments were revised for integrating with the eco-risk of the other substance contamination in sediment. The heavy metal co-contamination in MPs on eco-risk was included to the assessment. The approached model was applied to assess the risk of MPs in surface sediment of the inner Gulf of Thailand. The assessment illustrated that high risk level of MPs in the considered area was in the moderate to considerable level with the average ecological risk index. The risk from heavy metal co-contamination was less proportion compared with that from plastic contents.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Plastics

‘Plastic’ has been used to describe the molded or shaped substances. In common, all plastic has a large chain-like molecule, or it is a polymer. Varying applicable properties and types, plastics are widely used. There is an estimation that 99.5 million metric ton of disposed plastic products was generated in coastal regions, and 4.8-12.7 million metric ton of those entered to the ocean [51]. Even though plastics have persistent properties, they are possible to be degraded after released to the environment.

2.1.1 Physiochemical properties

Plastics are long chain-like macromolecules repeating of small molecules. In the other word, they are polymer composed of many units of monomers. The structure of polymer molecule has a significant influence on plastic material properties.

Crystallinity of polymer refers to the degree of structural regions where the polymer chains are aligned with one another. The polymer structures termed lamellae are formed as crystalline region, while amorphous regions entangle in the polymer chain and reduce crystallinity (Figure 2.1). By this reason, some part of the polymer is un-crystalline, or it is semi-crystalline. In general, the degree of crystallinity in a plastic directly affects to mechanical, optical, chemical, and thermal properties of plastics. For example, semi-crystalline polymers have higher strength, lower melt viscosity, and higher resistance than amorphous polymers.

In addition, polymeric chain structures and polymer composition also affects the properties of plastics. Providing larger gap between polymer chains, polymer branching reduces the density and mass of material; however, the flexibility of polymer is increased. On the one hand, a smaller number of stemming from the main polymer chain permits tighter chain packing. Similarly, two or more different types of monomers can form to be more complex structures with improved properties. Moreover, combinations of plastic types or polymer blends are produced advantageous properties of plastic materials.

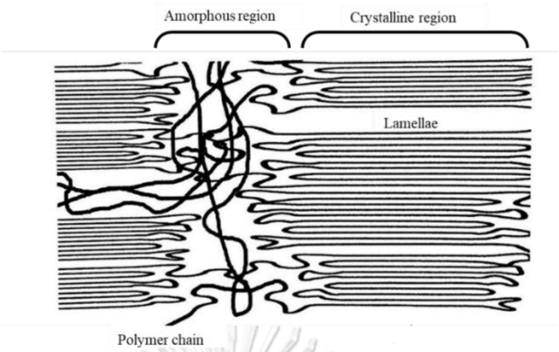


Figure 2.1 Semi-crystalline polymer with lamellae structure, crystalline region, and amorphous region [60]

As results of polymerization, monomer is the main component affected plastics structure. Polymer crystallinity, polymer chain structures, and polymer composition construct plastic molecule more complex structures and change in plastic properties. Because of varied properties, plastic materials become multi-function suited to any common products in daily life.

2.1.2 Common plastics

Resulted to plastic physical and chemical characteristics, variation of polymers and structures make plastics to be a magical material with flexible functions. The plastics have been integrated into most of products in life activities, example, food, drink, and packaging. The code system of common plastics was displayed for identifying plastic types by American Society for Testing and Materials (ASTM). Following ASTM code system, structures and applications of common plastics were shown in Table 2.1. By PlasticEurope, the association of plastics manufacturers and one of the leading European trade associations, European plastics demand inferred to plastic utilization was reported and in order of plastics in the other types (19.3%), PP (19.3%), LD-PE (17.5%), HD-PE (12.3%), PVC (10%), PUR (7.5%), PET (7.4%), and PS (6.7%) [41]. Estimated 18.5% of the world production [42], total plastics converter demand in 2016 was 49.9 million ton, and 39.9% of that was packaging in the main market sector [41].

Table 2.1 Structures and applications of general plastics

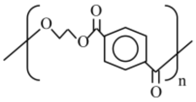
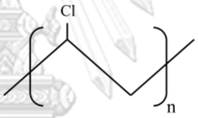
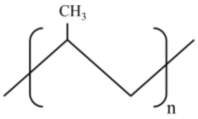
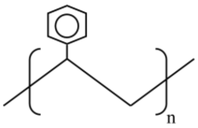
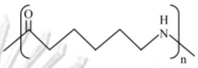
Plastic Code	Name	Density (g/cm^3) [61]	Structure	Typical application
1 PETE	Polyethelene terephthalate (PET)	1.37-1.45		Beverage bottles Food containers Film and sheeting Strapping Fibres / Fleece Filling material
2 HDPE	High density polyethylene (HD-PE)	0.92-0.97		Chemical containers Beverage bottles Food containers Crates / Buckets Tubing / pipes
3 V	Polyvinyl chloride (PVC)	1.16-1.58		Containers Electrical conduct Pipes / Gutters Cladding Window frames Cable insulation
4 LDPE	Low density polyethylene (LD-PE)	0.92-0.97		Bags / Film Squeezable bottles Food packaging Carton lining / mulch shrink wrap Outdoor furniture
5 PP	Polypropylene (PP)	0.9-0.91		Bottle caps / container lids Packaging tape Pipes Rope Automotive Outdoor furniture

Table 2.1 Structures and applications of general plastics (continuous)

Plastic Code	Name	Density (g/cm^3) [61]	Structure	Typical application
6 PS	Polystyrene (PS)	1.04-1.1		Disposable cutlery Tableware Disposable container Packaging foam Thermal insulation
7 OTHER (Example)	Polyamide (PA or nylon)	1.02-1.05		Fibres Bristles Monofilament Bearing Automotive application

2.2 Marine plastic litter

Plastic products that mostly are single use, plastic waste is generated, and it needs to be managed. There is estimation that 31.9 million metric tons of plastics waste were mismanaged; moreover, 4.8-12.7 million metric tons/year of plastic debris were entered to ocean in 2010 [51]. Categized by size, marine plastic litter is included: macroplastics (>25 mm), mesoplastics (25-5 mm), microplastics (5-1 mm), mini-microplastics (1 mm-1 µm), and nanoplastics (<1 µm) [60]. In general, small sizes of plastic debris are from degradation or fragmentation of large plastics by biological and physicochemical process of the ecosystem.

2.2.1 Biotic degradation

In this review, degradation is defined as the deformation processes affected large plastic become smaller in term of polymeric molecular and that in term of material size. Depended on chemical structures of plastics, biological processes may induce plastics to be small fragments or small molecules of residues. To be complete degradable, plastics must undergo a two-stage procedure [60]:

1) The carbon–carbon bonds of the long polymer chains are broken by oxygen, moisture, heat, ultraviolet light or microbial enzymes that results in fragmentation of the plastics;
2) Sufficiently fragmented short carbon polymer chains pass into microbial cell and become food and energy source, before those are transformed to biomass, water, carbon dioxide or methane gases.

Biodegradation of plastics is the best solution for plastic litter in the environment. Polyhydroxybutyrate (PHB), polycaprolactone (PCL), and polylactic acid (PLA) are the most common biodegradable plastic materials [60]. In contrast, they cannot replace the commodity thermoplastics in terms of cost or mechanical properties. Although plastic degrading organisms have been discovered [62], heterotrophic bacteria isolated from sub-merged marine plastic litter cannot degrade polyethylene under agar plate incubation [63].

2.2.2 Abiotic degradation

Chemical additives often be contained in plastics for changing polymer properties, increasing their stability, and protecting against environmental influences and biological attack. In contrast, plastic litter is particularly degraded, but the degradation is not complete. Plastic debris is weathered to small particle by mechanical force, temperature, light, gas, and water after exposed to marine environment.

When released to the aquatic environment, large plastic litter exposes to water currents, waves, and collisions and abrasion from rocks and sand. Over the time, the debris was cracked to smaller prices by mechanical stresses (Figure 2.2). The impact stress, for example, is a high force or shock applied to the plastic over a short period of time that can result in fragmentation. The degree of any effects from these different forces depends upon the mechanical properties of the plastic.

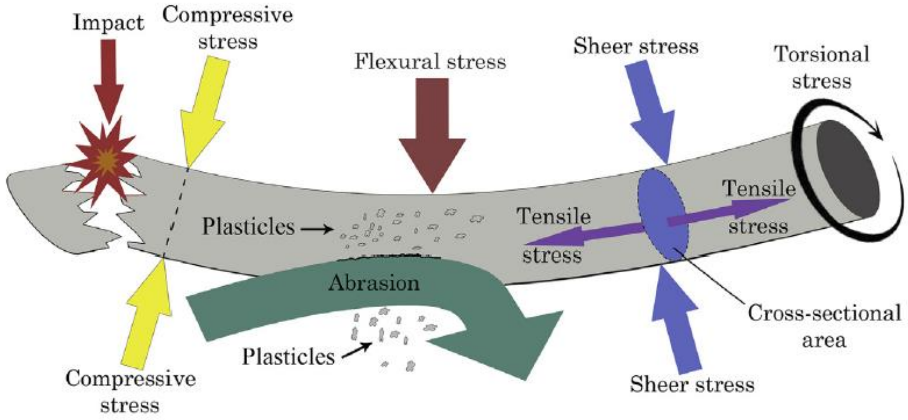


Figure 2.2 The potential forms of stress on a piece of microplastic [60]

The thermal properties of plastic materials indicate the susceptibility to thermal degradation. In the other word, the plastic materials are de-structured by changes in temperature. The degradation by thermal-oxidative reaction at high temperature (Figure 2.3) occurs with three different phases:

1) Initiation, the input of enough energy, in the form of heat, results forming small reactive molecules or radicals by breakdown of long chain polymer;

2) Propagation, the radicals produced from initiation phase react with oxygen to create peroxide radicals, hydroxyl free radicals and alkoxy radicals that react with oxygen and create freer radical like the chain reaction;

3) Termination, the initial energy input, or discontinued oxygen supply, or forming stable non-radical adducts by radical-radical reaction that end self-propagate chain reaction.

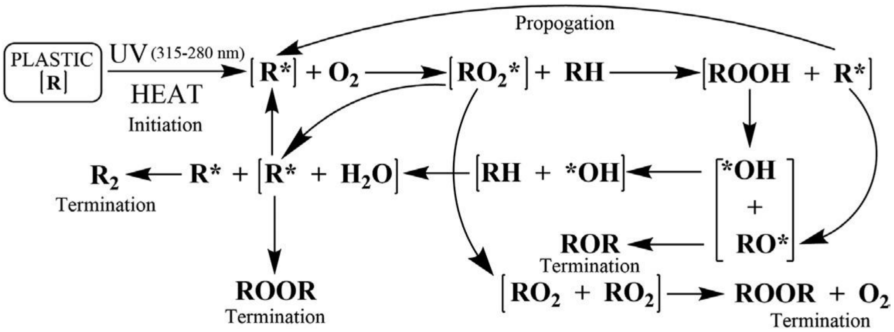


Figure 2.3 Polymer free radical chain reaction [60]

As well as heat, the energy in form of ultraviolet light (UV) can also initiate the chain reaction of thermal degradation. When plastic materials absorb the photons of light, in the region of UV-B (315–280 nm), the photo-oxidative degradation occurs by the free radical polymer chain reaction. Plastic debris on land, such as beach, or on surface water is directly exposed to large amount of sunlight; in the same way, it absorbs high density of UV and fragments by oxidative reaction. The common signs of this reaction are yellowing, hazing, cracking, and embrittlement. In specific, the reaction affects to the polymer matrix, as results of abnormal polymeric functional groups in the presence of C=O and O-O groups.

Following propagation phase of the oxidative chain reaction, presence of oxygen in atmosphere can catalyze the breakdown of plastic materials. However, the decomposition only occurs down to the maximum depth of 1 mm from surface water. The presence of ozone and oxides atmospheric pollutants tends to occur the significant damage by attacking the double bonds of some plastics. In addition, the hydrolysis of some water submerged plastic materials occurs when the water diffuses into the amorphous region of polymer matrix.

The mechanical and chemical processes are reasonable be the main factors for fragmentation of general used plastics. Located in marine environment, plastic litter is specifically susceptible to fragmentation with sunlight, heat, cold, wind, waves, rocks, acids, and enzymes (production from microorganism or ingestion by wildlife), and damage from anthropogenic activities. As a result of abiotic degradation, the plastic litter deterioration to smaller size of particle.

2.3 Microplastics

Microplastics (MPs) are the plastic particles (plasticles) that smaller than 5 mm. Accordingly, plastics in size of 5 mm to 1 μm are described to be MPs, and those of less than 1 μm in size are nanoplastics [60]. Categorized by sources, the less than 5 mm of plasticles since manufacturing are called as primary MPs, while the plasticles fragmented from larger plastic debris are defined as secondary MPs. With no standard sampling and analyzing methods, contamination of MPs have been measured in the environment.

2.3.1 Sample collection and analytical method

To evaluate the impacts and risks of MPs in the environment, contamination monitoring is the best tool for presenting a status of MPs in the environment. Because of that, environmental media samples were collected then MPs were separated and quantified.

In basic, contaminated MPs have been collected using naked eye observation collected by hand or non-plastic equipment. The contamination on beach, for example, was widely studied via collection selected MPs [64-72] or bulk sand samples [29, 54, 64, 73, 74] by using hand, metal spoon and tweezer. Specifically, bed sediment was taken from sea bottom before bulk sample collection [5, 11, 16, 22, 26, 29, 74]. Objectives to sampling MPs in surface water, the water volume reduction by towing 300 µm of neuston net was recommended by National Oceanic and Atmospheric Administration of United States (NOAA) [59]. In addition, bulk water sample was sampled [74], and water pumping into filtration units was applied for surface water sampling [5, 12, 75]. The collected water and sediment samples need preparation before MPs analysis.

By selective sampling, MPs mostly were identified and characterized by naked eyes. However, biogenic materials and the other impurity need to be removed and separated from MPs content in volume reduced or bulk samples. Different reagents (H_2O_2, NaOH, and HCl) were tested for organic content digestion; the H_2O_2 was case-by-case recommended to oxidize a large amount of biogenic organic matter [76]. After that, MPs were separated from the other components by density separation. Because of the density of plastics (Table 2.1), PP, PE, and PS usually be separated by saturated NaCl solution (density 1.2 g/cm^3), but seawater (density 1.003 g/cm^3) also be used [77]. However, NaI (density 1.6-1.8 g/cm^3) [17, 76] and $ZnCl_2$ (density 1.6 g/cm^3) [11, 12] were replaced those for separating denser plastics such as PET and PVC. In addition, samples sieving into certain sizes was recommended [61]. Wet

Peroxide Oxidation process, using H_2O_2 and $FeSO_4$, and density separation by NaCl solution were approved procedure for both water and sediment samples preparation in recommendations of NOAA [59].

To quantifying and confirming supernatant in density separation process are plastics, the number of MPs has been microscopically counted and categorized MPs with the shapes and colors. The plastic visual identification should meet the criteria: 1) no cellular or organic structure are visible; 2) fibers are equally thick throughout their length, and not appear segment or twisted flat ribbons; 3) the colored particles are homogenously colored, and not shiny [22]. Moreover, the plastic shape determination was proposed following Table 2.2. It, however, is important to confirm plastics with their polymer types. Similar with a fingerprint of plastics, the functional groups and structure of the polymer have the specific pattern of varied wavelength light absorption namely spectrum. By spectrophotometry, plastic types mostly be identified by similarity comparison with standard polymer spectrum of Fourier Transform Infrared spectrometer (FT-IR) [5, 22, 26, 29] and Raman spectrometer [56, 74, 75]. In advance, the pyrolysis gas chromatography with mass spectrometer was offered to analyze plastic composition of MPs [78]. The qualitative and quantitative analysis of MPs has been continuously developed for evident fate and transportation of MPs in the environment.

Quality of assurance, quality control, and prevention of the contamination through MPs analytical processes are necessary. The MPs extraction was tested with plasticle recovery from spiked samples. The contamination from air, laboratory coat and all equipment were prevented. Follow above of the concepts for MPs analysis, MPs contamination in environmental media has been characterized.

Table 2.2 Criteria of microplastics' shape identification [60]

Plastic shape	Definition	Shape example
Fiber	A strand or filament of plastic	
Film	A thin sheet or membrane-like piece of plastic	
Foam	A piece of sponge, foam, or foam-like plastic materials	
Fragment	An irregular shaped piece of plastic	
Pellet	A small spherical piece of plastic	

2.3.2 Contamination of MPs

The contamination of MPs in the environments is the evidence of anthropogenic activity. Even though the sample collection and analysis were limited by no standard for size of MPs and no standard for procedures, MPs contamination in waters and sediments has been assessed.

Depended on the study area, the average concentration of MPs in surface water was range of 100-10,200 pieces/m^3 [5, 12, 74, 75]. High MPs concentration was found in the estuaries area with more variation than coastal sea. However, different criteria volume of sampled water and size of MPs had impacts on the concentration. Size distribution of MPs in water samples was limited by the mesh size of sieve or neuston net using in the sample collection. Collected by water filtration pass 333 μm sieve, most MPs were in size of 0.5-1 mm [75], while the major size of MPs was less than 0.5 mm with 35.7-85.5% of the MPs samples collected by 30 μm sieve [5]. Variable color and shape, PE and PP were two majority of plastic types of MPs in surface water [5, 12, 75]. Neither no significant correlation between concentration of MPs and population density, nor extreme meteorological events of Typhoon the concentration of MPs related to hydro-geological dynamics and economic structure of the study area [75].

Results of suspended solids settling to seabed, MPs are integrated to the composition of the shallow sediments. Average concentration of MPs 34-390 pieces/kg of dried sediment was reported [11, 16, 22, 26, 29]. Based on number of MPs, the most prevalent shape of MPs contaminated in bottom sediment was filamentous plastics. No-significant relationship between concentration of MPs and sediment gain size was found [11, 16, 22, 26]. High concentration of MPs was determined in the area where near urban sewage treatment plant [26] and harbors [29], but the concentration of MPs in taking marine protection area was not significantly lower than no taking area and coastal urbanized population area [16]. Similarly, there was no statistical difference between contamination of MPs in beach sediment under the influences of tourism and those that were not tourism [64]. The results can infer MPs may input from land and marine activities, and they were transported to the other area.

The contamination of MPs in waters and sediments links to the accessibility of the organism habited in pelagic and benthic system. As a result, the researchers found MPs in the invertebrates lived in the intertidal zone of the beach [54-56] and pelagic-demersal/ bentho-pelagic carnivorous fish [74, 79]. The interactions between MPs and aquatic environmental components have been seriously investigated.

2.4 Behavior of microplastics in aquatic system

Recognized by monitoring, mismanaged plastic debris has been loaded into marine environment and degraded to be MPs. It is general to say that most plastics float on the water because their density is lighter than water. Surprisingly, the studies found the contamination of low-density plastics such as PE in the bottom sediment [5, 22, 26, 29, 73]. These results confirm that characteristics of MPs are dynamically changed during influence of the environment. In the overview, the research submits the concept that MPs are not only fragmented, but also be transported and transformed after they were entered to the aquatic system (Figure 2.4).

2.4.1 Fate and transportation of microplastics

1) Neustonic interaction

The surface properties of plasticles play an important part for the interaction in the ecosystem. Plastics basically have smooth and hydrophobic surface, but these properties are changed after contaminated in aquatic environment. Substances including nutrients, organic compounds, microbials, and the other contaminants in water column and sediment, are rapidly accumulated on the surface of MPs.

By paradigm of protein corona, the protein coated on nanomaterial in biological fluids, ecocorona refers to the formation of dissolved organic macromolecules on micro- and nanoplastics; moreover, the plasticles retained ecocorona may by attached with organic materials, minerals and the other components of marine snow [45]. The aggregation of those contents is named as biofouling. For instance, microbial biofilm formation was found after 1 week of submerging PE plastic food bags in 2 m below the water surface [63]. The visible settlement cover of diatom and algae communities were observed on plastic sheet (HD-PE and LD-PE) contacted with seawater for 12 weeks [80]. The later experiments have come up with the plankton-plasticles aggregation. The hetero aggregation between MPs and phytoplankton was significantly found in diatom that produced extracellular polysaccharides or transparent exopolymer particles [81, 82].

The biofouling results plastics have negative buoyant by increasing their density. MPs aggregated algae fouling has higher trend to sink than non-aggregated MPs [81], while the small size of that firstly sink after 12 weeks surface water exposure [80]. With concept of ecocorona, hazardous hydrophobic substances can be included in the adherences on MPs surface. Interestingly, less hydrophobicity surface was found in biofilm formed plastics [83]; by this reason, accumulation of hydrophilic substances in MPs is of concern.

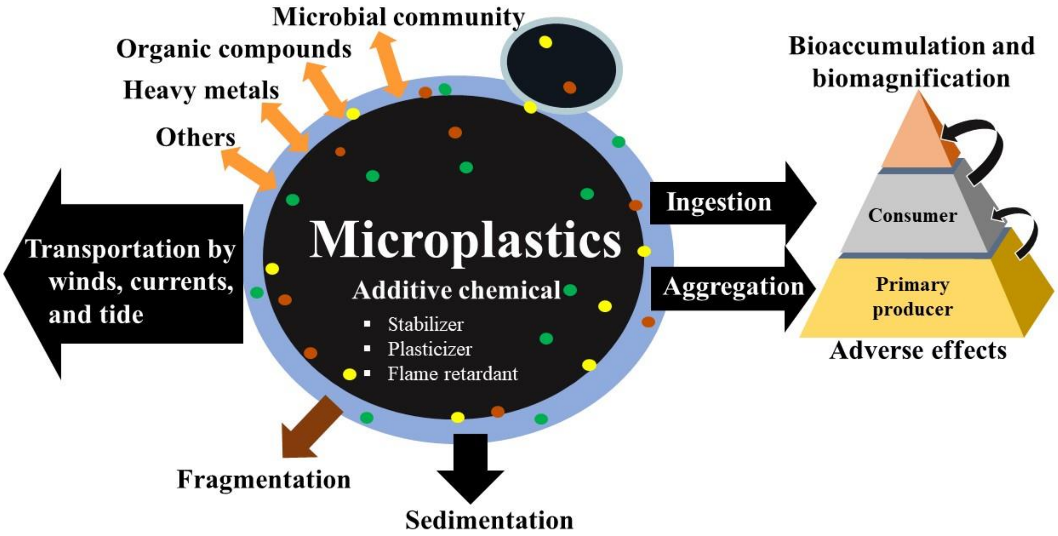


Figure 2.4 The overview of microplastic behavior in aquatic environment

2) Coastal sea transportation

The physical variated properties of MPs are considered for transportation in coastal sea. Like planktonic behavior, the movement of MPs was controlled by water current, tide, and wind. The aggregation of MPs and biogenic matrix affects MPs become denser and sink to the water column. In short, transportation of MPs is an effluence of the hydrodynamic process and biofouling.

Water current and wind direction induce the movement of MPs in horizontal and vertical. Windage, or leeway drift, is the key factor in horizontal transportation of extremely light MPs floating on surface water, PS foam (< 0.05 g/cm^3) and polyurethane (0.08-0.75 g/cm^3), for example [84, 85]. As well as onshore wind and wave, MPs were transported by river discharge, stormwater, surface currents, and tidal currents influences. The turbulent vertical mixing induced by wind and wave can lead MPs to deposition to the sea bed and increase retention of MPs in the sediment [84].

Linked to increasing density, biofouling can settle. Key considered in slightly buoyant plasticles (e.g. PE and PP), biofouling in smaller particle is the faster in fouling up to water density, while the time of fouling was shown to be the same order for films and fibres, and two orders of magnitude higher for spherical particles in the same mass [85]. The accumulation of algae on MPs surface was simulated for modeling vertical transportation. The oscillatory pattern of MPs movement in the water column was presented following:

a) The surface of plasticles is initially attracted by algae biofouling.

b) The plasticles start settle because the biofilm fouling increases their density.

c) The number of algae on plastic surface is fluctuated by collision, respiration, growth, and mortality.

d) The buoyant particles keep moving up and down in the water column.

Following this mechanism, small plastic particles start settle sooner and have more settling velocity; in addition, the different model outcome is affected by temperature, salinity, algae concentration, and thermocline depth [46]. In the same of particle shape, the higher density of plasticles theoretically trend to settle faster than the lower density of those [85]. As the plasticles are of irregular shape, an equivalent spherical diameter (ESD) was used in calculation of sinking rate increased by the biofouling. Characterization of algae aggregated MPs found that the sinking rate of biofouling MPs is forwardly depended on ESD, while the excess density by fouling is inverted with ESD [81].

Same as transportation by oceanographic dynamics and biofouling, attachment, and ingestion of MPs by animals can result they heterogeneously transport in water column thorough the bottom sediment. The attractiveness of MPs on food items can cause misidentified ingestion in many animals. After were exposed, MPs can be accumulated and transported with animal body. In case of ingestion, MPs are possible to be excreted from animal body by condensed with faces and be sedimented. Because plastics are composted of additives for improving their properties, and they can sorb the other substances following the concept of eccorona, the toxic by chemicals of MPs is of concern.

2.4.2 Chemical pollutants

According to plastic properties and environmental dynamics, MPs can be a source and sink of the other contaminants in the environment. In the other word, MPs may be a pollutant or may release contaminants to the environment or may accumulate them from the environment. The organic and inorganic contaminants interaction with MPs have been investigated.

1) Persistent organic pollutants

As MPs are smaller in size, the surface for sorption is more available. By hydrophobic property, plastics can adsorb on organic chemical on their surface. Sorption of hydrophobic organic chemical has been measured in field samples and characterized by experiments.

Collected from beach, plastics were contaminated with persistent organic substances including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCB), total dichloro-diphenyl trichloroethane (DDT and its degradation products), and hexachlorocyclohexanes (HCHs) [86-89]. Accordingly, the measurement shows significant contamination of organic pollutants depended on plastic characters. For example, higher contamination of PCBs and total DDT was found in aged plastics [89], and concentration of PAHs was greater in PS foam samples [86]. The persistence presented in monitored MPs could be sourced form addition during production process and sorption from the environment. The ratio between phenanthrene and anthracene in MPs from the beach near industrial sites and port facilities showed the majority PAHs is from petrogenic source [89]. Besides that, the PAHs contamination in virgin PS was confirmed that the contaminants were added during manufacturing. The high efficiency of organic sorption by plastics was found in the experiments.

The equilibrium of organic substances between solid (MPs) and liquid (water) phases is used to simulate the sorption of organic pollutants on MPs. By experiment, the equilibrium concentration of organic contaminants in MPs (C_{MPs}) and that in water (C_{water}) was measured and simply modeled in the partition coefficient (K_d):

$$K_d = \frac{C_{MPs}}{C_{water}}$$

Described by K_d, the sorption of PAHs was higher in plastics than that in sediment with the order of PE, PS, PVC, and sediment respectively [90]. The adsorption of organic contaminants was specifically explained by non-linear models of Freundlich isotherm and Langmuir isotherm. According to adsorption of antibiotic on MPs, the adsorption was varied depending on hydrophobicity of substances and MPs surface characteristics, including pore structure, specific function groups and surface area that were changed in the environment [91].

The sorption of organic pollutants is complex with variable plastic properties changing and fluctuated environment. Long-term field experiment of PAHs and PCBs sorption on plastic pellets found that the PAHs and PCBs on HD-PE and LD-PE increase over the time during 12 mouth of the measurement [92]. In the other hand, the sorption experiment of twenty-one probe sorbates argued that the sorption was reduced in aged PS because of increase polarity of plastic from the oxygen-containing functional groups during degradation [83].

2) *Heavy metals*

Opposite the hydrophobic properties of plastics that tend to adsorb organic substances, the mixed acid extracts from MPs were detected the contamination of heavy metals that was higher than the contamination of sediment [69, 73]. Similarly, that contamination also be analyzed by field-portable-X-ray fluorescence spectrometry [65]. The heavy metals in MPs structure can be explained by two scenarios: a) heavy metals are added to plastics by the manufacturing process, and b) MPs adsorb heavy metals from the environment.

It is unclear that which scenario above is the main role in the metal contamination of MPs in the environment. Resulting from elemental analysis of visible plastic litter, heavy metals and potentially indicative of hazardous chemicals were measured in the litter [66, 67]. For example, the composition of lead chromates compound that is heat and UV stabilizer in PVC can be referred by the relationship of Pb and Cr in plastics [66]. In addition, heavy metal compounds, were illustrated on surface of adherence removed pellets by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) [70, 73]. The analysis shows that the added chemical during manufacturing process and the adsorption of contaminants in the environment are the source of heavy metals in field collected plastics [69, 71, 73].

Furthermore, the variable change of plasticles characters may induces MPs accumulate heavy metals. After contaminated in the environment, plastics will be fragmented; meanwhile, it also be covered with organic compounds and biofouling. Not only is small particle from plastic litter fragmentation, but it is also polar region from weathering that cases heavy metals accumulation in MPs. FT-IR spectra confirmed the increasing of polarity from chemical weathering MPs with the C=O groups peaks [73]. Moreover, the chlorine in plastics structure, especial in PVC, is the polar group able to adsorb heavy metal ions that result to higher adsorption capacity in aged PVC than virgin PS beads [93]. Extraneous materials on MPs (biofouling and hydrogenous precipitates) are the important partition accumulated heavy metals. As a result of ultra-sonication extraction and mixed acid digestion, the heavy metals in surface adherence of pellet samples were higher than those in pellet content [70, 73]. Non-specific interaction between neutral metals-organic complexes and hydrophobic surface of plastic were discussed for that phenomenon. By polarity and adherence on surface, aged plastics have greater heavy metals accumulation capacity than the virgin plastics [69, 71-73, 93].

Because of polymer structure varying and organic modifying, heavy metals accumulation on MPs was not simply the results of adherence or extraneous materials. The speciation of heavy metals, pH, and salinity in the environment also impact the metal-pellet interaction [72]. The in-situ experiment resulted that the metals on all type of plastics continuously increase after they were deployed for 1 mouth, while the equilibrium of some metal adsorption was not presented in 12 mouths of the experiment [94].

Comparing between organic chemicals and heavy metals, the organic sorption is specific by polymer types, which greater in HD-PE and LD-PE than in PP, PVC, and PET [92], while the metal sorption may not differ [94]. The sorption of pollutants on MPs has been debated that is the vector for transporting those pollutants to biota. Because of high sorption ability, the organic chemical desorption rate is inverse [90]; by this reason, MPs may reduce bioavailability of the organic toxicant. In contrast, heavy metals on plastic may be more sensitive. Physiologically based extraction test using synthetic digestive characteristics of seabird, *Fulmarus glacialic*, showed the inorganic elements in plastic composition was released after 168-220 hours of extraction [65, 67, 68]. The role of MPs in bioaccumulation of toxicants could be concluded:

a) Absorption; plastics ingestion leading to toxic transfer from plastics to organism
b) Cleaning; plastics ingestion leading to increased excretion of toxic from organism
c) Source; plastics acting as a source of toxicants that available for dermal uptake or uptake by gills
d) Sink; plastic accumulating toxic from seawater or organisms
e) Indirect source by dietary; desorption of toxic from plastics to uptake natural particles or pray

However, the accumulation of toxic in organism may not be affected by MPs. The uptake of toxicant is possible to be caused by ingestion of regular dietary or transferred from the other sources than MPs [95]. By field study, observed bioaccumulation is difficult to separately prove that the accumulated toxicants are caused from plastics or the other pathway.

2.5 Pollution indices of microplastic contamination

2.5.1 Overview of pollution indices

As well know, sediment is the source and sink of pollutants in the aquatic system. Pollution assessment may be done by analysis of sediment contamination. Normally, standard limits for the pollutants have been used to represent the level of contaminants. However, it cannot be processed if the standard value was not provided for those pollutants, and it seem to be unfair when compare the pollution level of between areas having different baseline of contamination. Pollution indices can be regarded as a tool and guide for comprehensive geochemical pollution assessment.

In the principle, pollution can be indicated by dose of presented pollutants compared by background or reference concentrations where assume that is no toxic effects. The indices have been widely used for the pollutants from both natural and anthropogenic source, heavy metals, for example. The widely accepted pollution indices for evaluated ecological risk were proposed by Hakanson in 1980 [96]. The indices are consisted of:

1) Contamination factor

To describe the contamination of toxic substances, the contamination factor of contaminant *i* (C_f^i) was defined accordingly:

$$C_f^i = \frac{C_{0-1}^i}{C_{ref}^i}$$

where C_{0-1}^i is the concentration of contaminant i in the superficial sediment (0-1 cm), and C_{ref}^i is the preindustrial reference value for contaminant i, noted that the minimum concentration in sediment layer was used for C_n^i of anthropogenic substances, polychlorinated biphenyl (PCBX), for example. The value of contamination factor indicates the enrichment if $C_{0-1}^i \geq C_{ref}^i$, while the substance will not be characterized as contamination if $C_{0-1}^i \geq C_{ref}^i$. The terminology for grading the contamination is described:

$C_f^i < 1$	low contamination,
$1 \leq C_f^i < 3$	moderate contamination,
$3 \leq C_f^i < 6$	considerable contamination,
$6 \leq C_f^i$	very high contamination.

2) *Degree of contamination*

As the sediment accumulated more than one substance, the complex index namely degree of contamination (C_d) was proposed for assessing the pollution level in sediment of the considered area. In short, the degree of contamination is summation of all contamination factor (C_f^i):

$$C_d = \sum_{i=1}^{n} C_f^i = \sum_{i=1}^{n} \frac{C_{0-1}^i}{C_{ref}^i}$$

With this approach, the degree of contamination can be described to four levels by double value increase for each level. For example, if eight contaminants were considered, eight contamination factors will be calculated, and the value of degree of contamination will be illustrated:

$C_d < 8$	low degree of contamination,
$8 \leq C_d < 16$	moderate degree of contamination,
$16 \leq C_d < 32$	considerable degree of contamination,
$32 \leq C_d$	very high degree of contamination.

3) *Potential ecological risk index*

The principle of potential ecological risk index (RI) is expressed by four compositions: the concentration of substances, the number of considered substances, the toxicity factors, and the sensitivity. The RI-value can be calculated by summation of potential ecological risk factor of considered substances (E_r^i) that derived from toxic-response factor (T_r^i) and contamination factor (C_f^i) of those substances, as following:

$$RI = \sum_{i=1}^{n} E_r^i = \sum_{i=1}^{n} T_r^i \times C_f^i$$

In brief, the compositions may be categorized to factors for dose of contaminants and those for toxic responding of each substance. The contamination factor (C_f^i) and the number of considered substances i to n is represented to the quantitative of contamination, while toxic-response factor

(T_r^i) is expressed by the toxicity factors, and the sensitivity of substance *i* in the sediment system as presented in Table 2.3.

Toxicity factors

Ranking or weighting factors on toxic substances, toxicity factors, were given for the information about the potential transportation and threat of toxic substances to man or ecosystem. The toxic factors of the eco-risk index were credited by “the abundance principle” based on concept that the toxicological effect is proportional to the abundance or the rarity of any substance. The toxicity factors of heavy metals, for example, was firstly evaluated by Hakanson, 1980 [96], and re-assessed by Xu et al. 2008 [97].

Initially, the abundance numbers were determined:

a) The abundance of elements in various media, igneous rocks, soil, fresh water, land plant, and land animals etc., were ranked from highest to lowest concentration.
b) The highest abundance in each media was given the score to be 1.0, and this value will be increased according to ratio of reduced concentration.
c) The “abundance numbers” were calculated by the sum of element score in each media.
d) The numbers were ranked again by division of their minimum value. The result was given in Table 2.3.

In next step, the sink-effect was considered for representing the tendency of metals to be deposited in the sediment. A measure of the sink-effect was calculated by the comparing between natural background concentration in water and preindustrial reference value for sediment. This partition of sink-effect was shown as sink-factors in table 3. The low sink-factor can be implied that the substance tends to be accumulated in sediment rather than that in water. Accounted for sink-effect, the abundance numbers were multiplied with sink-factors, that transformed to “corrected abundance numbers”, however, the range of them was not match the dimensions of contamination factors. The dimension-problem was solved by normalized all "corrected abundance numbers" as divided the lowest value of 57, taken the square-root, emphasized the uncertainty, and described to be sedimentological toxic factors in Table 2.3. The important note is the toxic factor for mercury (Hg) were reduced from 80 to 40 because it is too high value [96], and the factor for manganese (Mn) were assumed to be the same rank with Zinc (Zn) [97]. Finally, the toxic characteristic of substances in sediment was rapidly expressed by the sedimentological toxic factors. Nonetheless, the risk of toxicants is not only from their abundance characteristics, but it is also based on the condition where substances were contaminated.

Sensitivity of the ecosystem

Bioproduction, based on nutrients, plankton, bottom fauna, and morphometry etc., is discussed to be the important factor for quantifying the sensitivity in ecological risk index model. Calculated by the regression of nitrogen (N) and ignition loss organic carbon (IG), bioproduction index (BPI) was proposed for the value of the N-value in the regression line for 10% of IG. According to the relationships with primary production, chlorophyll-A, total phosphorus, total nitrogen, BPI-value can indicate the trophic status and/or degree of production in the ecosystem [96]. Moreover, the content of methyl mercury in fish was proved that it has negative relation with BPI-value [98]. In the potential ecological risk model, negative effects of Hg, Cd, Pb, Cr, Cu, and Zn, are assumed to be increased with decreasing BPI-value. By the idea of the toxic-response factors, the BPI-value was added with the assumptions:

a) BPI values of 5 represented to the intermediate score in normal condition characteristic for moderately eutrophic status.

b) The toxic of Hg was directly inversed with BPI-value.

c) The toxic of As should be independent with the bio-productivity, or it is not related with BPI-value.

d) The other metals should be the same scenario with Hg, but the range should be smaller; thus, the factors of BPI were normalized by square-root.

In summary for eco-risk assessment, the toxic-response factors (Table 2.3) have been established by include toxicity factors from abundance principle and sensitivity from BPI-value. Only sourced from anthropogenic activities, polychlorinated biphenyl (PCB), is the special case that for the toxic-response factor leveling. The sedimentological toxic factor of PCB was safety assumed to be 40 for the same order of magnitude as that of Hg, and the sensitivity also be believed that it directly varied with BPI-value. For all considered substances, potential ecological risk factor of substances *i* ($\mathrm{E_r^i}$) can be assessed by toxic-response factor ($\mathrm{T_r^i}$) and contamination factor ($\mathrm{C_f^i}$), and the potential ecological risk index (RI) were included all risk from all considered substances as illustrated:

$$\mathrm{RI} = \sum_{\mathrm{i=1}}^{\mathrm{n}} \mathrm{E_r^i} = \sum_{\mathrm{i=1}}^{\mathrm{n}} \mathrm{T_r^i} \times \mathrm{C_f^i}$$

The score of potential ecological risk factor of substance i ($\mathrm{E_r^i}$) was described for the risk of single substance. The value of 40 was pined for the low risk of the highest toxic-response factor in the normal condition of ecosystem (BPI=5). The gained value was increased for the new level of risk with the same interpretation of degree of contamination. The description was listed below:

$\mathrm{E_r^i} < 40$	low potential ecological risk,
$40 \leq \mathrm{E_r^i} < 80$	moderate potential ecological risk,
$80 \leq \mathrm{E_r^i} < 160$	considerable potential ecological risk,
$160 \leq \mathrm{E_r^i} < 320$	high potential ecological risk,
$320 \leq \mathrm{E_r^i}$	very high potential ecological risk.

Similarly, the potential ecological risk index (RI) was interpreted by sum of E_r^i of all considered substances in the normal condition (BPI=5), and the safety score with approximately 10% of E_r^i summed score. For instance, the RI interpretation for 8 substances included PCB, Hg, Cd, As, Pb, Cu, Cr, and Zn was described:

$RI < 150$	low ecological risk,
$150 \leq RI < 300$	moderate ecological risk,
$300 \leq RI < 600$	considerable ecological risk,
$600 \leq RI$	very high ecological risk.

The contamination factor, degree of contamination, and potential ecological risk index has a concern to avoid the sediment in dynamic environment such as river and estuary. However, the pollution load index (PLI) was conceptualized for the assessment of heavy metal level in dynamic area, especially the river estuarine system [99]. Regarding the assumption that concentrations of pollutants have high variation and ab-normal distribution in the focused area, the PLI is calculated by geometric average of contamination factors of considered pollutants for *n* sampling points (C_f^n). In easy, the PLI is defined as:

$$PLI = \sqrt[n]{C_f^1 \times C_f^2 \times C_f^3 \times \ldots \times C_f^n}$$

It is important to note that the pollution indices are the philosophical principle for indicating the pollution level that has a limitation. They only show the possibility of risk from the contaminants in the certain area and cannot specify the risk susceptible population. The toxicity assessment with the indicating organism or epidemiological study still be necessary for identifying the effects of the new pollutant, microplastics. Yet, the pollution indices are rapid and easy assessment that is better than non-available process for evaluation.

Table 2.3 Abundance numbers, sink factors, corrected abundance number, sedimentological toxic factors, and toxic-response factors of common contamination assessment for potential ecological risk index

Substance	Abundance number	Sink factor	Corrected abundance number	Sedimentological toxic factor	Toxic-response factor (T_r^i)
Mercury (Hg)	1122	320	359040	40	$40 \cdot \frac{5}{\mathrm{BPI}}$
Cadmium (Cd)	242	200	48400	30	$30 \cdot \frac{\sqrt{5}}{\sqrt{\mathrm{BPI}}}$
Arsenic (As)	125	27	3375	10	10
Lead (Pb)	12	71	852	5	$5 \cdot \frac{\sqrt{5}}{\sqrt{\mathrm{BPI}}}$
Copper (Cu)	3.2	200	640	5	$5 \cdot \frac{\sqrt{5}}{\sqrt{\mathrm{BPI}}}$
Nickel (Ni)	7.8	147	1146.6	5	$5 \cdot \frac{\sqrt{5}}{\sqrt{\mathrm{BPI}}}$
Cobalt (Co)	46.4	47	2181	5	$5 \cdot \frac{\sqrt{5}}{\sqrt{\mathrm{BPI}}}$
Chromium (Cr)	100	2.2	220	2	$2 \cdot \frac{\sqrt{5}}{\sqrt{\mathrm{BPI}}}$
Zinc (Zn)	1	57	57	1	$1 \cdot \frac{\sqrt{5}}{\sqrt{\mathrm{BPI}}}$
Manganese (Mn)				1	$1 \cdot \frac{\sqrt{5}}{\sqrt{\mathrm{BPI}}}$
Polychlorinated biphenyl				40	$40 \cdot \frac{\mathrm{BPI}}{5}$

2.5.2 Pollution assessments of microplastics

Due to persistent structure, contaminations in various media, and contaminated chemicals, MPs have been discussed as a toxic pollution in the environment. The scale of microplastic contamination is necessary for indicating the pollution status of MPs. Dissimilar with common pollutants, the standard limited value or the acceptable minimum concentration of MPs were not provided as same as toxic-performed concentration of them. Rapidly illustrated the pollution level of MPs, the pollution indices were applied by assessments of contamination factor (C_f), pollution load index (PLI), and potential ecological risk factor (E_r^i).

Contamination factor (C_f) and pollution load index (PLI) were used to evaluating pollution of MPs in surface water of Changjiang Estuary, China [18]. With the same concept, the pollution of MPs was assessed for water contamination though the model had been firstly proposed for evaluating pollution in sediment system. The background reference concentration, however, is required for both C_f and PLI calculation. Accordingly, microplastic reference concentration was replaced by the average minimum concentration of MPs from the literature review. By the idea of C_f and PLI, the indices value the quantitative contamination; they do not indicate the toxicity of MPs. Goaled to potential ecological risk assessment, toxic-response factor of MPs must be approached.

'Hazard risk index of polymer', the novel index was proposed for representing toxicity of contaminated MPs [18], and this index was modified as 'toxic-respond factor' in potential ecological risk assessment of MPs in river sediments [32]. The hazard risk index (H_r^{MPs}) was scoped following the framework of abundance and sensitivity:

$$H_r^{MPs} = \sum_{i=1}^{n} \frac{C_n}{C_{total}} \times S_n$$

Included variety of plastic types, PE, PP, and PS, etc., the contamination of MPs was toxic depended on types of plastics. By this reason, quantitative data of each type plastics is inputted to the calculation in the term of the ratio between the concentration of considered plastic polymer type *n* (C_n) and that of the total detected MPs (C_{total}). In addition, hazard ranking score of plastic polymer type n (S_n) was. represented the toxic sensitivity of plastic. Objective to identified environmental and health hazard of plastic polymers, hazard scores of thermoplastic and thermosetting polymers were ranked for monomer chemicals in plastics [8]. To begin with the survey, the plastic monomers were reviewed for their chemicals and the composition ratios in manufacturing. The monomer chemicals were classified into the hazard class with the criteria taken from the Annex VI in the EU classification, labelling and packaging (CLP) regulation, based on the UN Globally Harmonized System (GHS). The hazard level I-V was given to the hazard class: the level V and IV were based on the criteria from the Swedish Chemical Agency for “phase out” substances and “risk reduction” substances, and the criteria for level I-III was developed by evaluating and comparing hazard categories in the Globally Harmonized System (GHS). The hazard grade from 1-10000 was given to each hazard class for level I-V; the score was increased 10 time per level. The lowest hazard level (level I) is scored to be 1 for the minimum, while the score 10000 was given to the chemical in the highest hazard level (level V). In detail, one plastic component may be included more than one monomer, and the chemical in monomer can be classified into various hazard class. The hazard ranking score of plastic (S_n), exampled in Table 2.4, is the summation of the score of each monomer chemical weighted by the ratio of a manufacturing. The sum of the hazard ranking score of plastic polymers (S_n) multiplied by the ratio of plastic in the total contaminated MPs ($\frac{C_n}{C_{total}}$) would be the polymer risk index (H_r^{MPs}) or the toxic-response factor in potential ecological risk assessment for microplastic contamination.

The potential ecological risk factor of microplastic (E_r^{MPs}) is determined by using the contamination factor (C_f^{MPs}) and the polymer risk index (H_r^{MPs}) of contaminated MPs. The initial assessment requires: the concentration of total contaminated MPs, background concentration of MPs, and the concentration of plastic type in detected MPs. However, the toxic of microplastic contamination may be not caused from only monomer chemicals. There are several additive chemicals added to modify plastic properties [100], and the MPs are possible to accumulate the toxicant from the contaminated environment [92, 94]. The pollution assessment of MPs should be complex evaluation for the risk of plastic monomers and the risk of the other co-toxic contaminants.

Table 2.4 Hazard score of plastic polymers based on monomer chemical [8]

Plastic type	Hazard score of plastic polymers (S_n)
Polyacrylonitrile (PAN)	11521
Styrene-acrylonitrile (SAN) copolymer	2788
High-impact polystyrene (HIPS)	1628
Polymethyl methacrylate (PMMA)	1021
Melamine-formaldehyde resin (MF)	882
Polyphenylene oxide (PPO)	400
Polyacrylic acid (PAA)	230
Polyamide 6-nylon-6	50
Expanded polystyrene (EPS)	44
Polystyrene (PS)	30
Low density polyethylene (LDPE)	4
High density polyethylene (HDPE)	4
Polypropylene (PP)	1

2.6 Contamination of microplastics in the inner Gulf of Thailand

The inner Gulf of Thailand (GT), the valuable marine resource for economic and marine-ecological services of Thailand, is the semi-enclose coastal sea bordered by land in 3 sides. The circulation of the inner GT are variated by seasonal monsoon [57, 101]. In short, the counterclockwise circulation in the gulf was influenced by northeast monsoon in period of October to February; on the other hand, southwest monsoon in June to September affected the additional clockwise circulation from western part of the gulf. Passing natural conservation area, agricultural area, urban communities, and industries, four major rivers, including Maeklong, Tachin, Chao-Phraya, and Bangpakong River, are input nutrients and pollutants to the gulf. Briefly, the inner GT is the sink of pollutants loaded from land.

The evidence of MPs contamination in the inner GT were found in sessile invertebrates in the eastern coast, surface water, and bottom sediment. Sampled from beaches in coastal fishery village (Angsila beach), local tourist destination (Bangsaen beach), and the Royal Thai Naval base (Samaesarn beach), three invertebrate species (namely, the striped barnacles *Balanus amphitrite*, the periwinkle *Littoraria* sp., and the rock oyster *Saccostrea forskalii*) were contaminated with MPs at rates of 0.2–0.6 particles/g [56]. Rod shaped and fragmented synthetic fibers of PA and PET particles were significantly detected in the specimen samples, whereas PS particles were detected in lower amounts. The contamination of MPs in surface waters of Chap Phraya River were detected with the abundance in the range of 0.16-120 pieces/m^3 [25, 52, 53]. The investigation found that the tidal cycle of the river estuaries affected the abundance of MPs in surface water, which was directly varied by tidal amplitude [53]. Analysis of MPs in core collected sediments, dated by radio nuclides (^{137}Cs), reveals no contamination of MPs in 44-46 cm layer (1960s), and the contamination of plasticles such as PE, PS, polyacrylates, polycaprolactone, polyethylene propylene copolymer, ethyl vinyl acetate significantly increased in the 6-12 cm layer (1990s) to the surface layer (2000s) [17]. The profile of plastics in sediments suggests that the onset of large plastic consumption in Thailand started in the 1960s and continuously increases. The occurrence and distribution of MPs in surface sediments of the Gulf of Thailand found the abundance of MPs in the average of 150.4 pieces/kg DW with high abundance at the south-east of the inner GT [41].

CHAPTER III

INFLUENCE OF SEASONAL VARIATION ON DISTRIBUTION CHARACTERISTICS OF MICROPLASTICS IN SURFACE WATER

Surface water was proposed to be the main influence in transportation and transformation of microplastics (MPs). In this study, the surface water contamination, and effects of seasonal variation on distribution of microplastics in the inner Gulf of Thailand (GT) were revealed. The surface waters were sampled from the Maklong (MK), Tachin (TC), Chao-phraya (CP), and Bangpakong (BK) river estuaries and coastal sea of the inner Gulf of Thailand (GT) in northeast monsoon period (December 2017), dry season (April-May 2018), and wet season (July-August 2018). The microscopic analysis found total MPs contamination averaged 8.70 piece/L in dry season and 34.59 piece/L in wet season, while that was 9.97 pieces/L in northeast monsoon period. The contamination of MPs was significantly increased in wet season. FTIR microscopic spectrometry confirmed polypropylene, polyethylene, and polytetrafluoroethylene were the main composition of MPs in surface water with proportion of 27%, 20%, and 14%, respectively. More variation of plastic types was observed in wet season. Contaminated MPs were classified to be broken plastics, filamentous plastics, and smooth/spongy plastics. Distribution of MPs showed high accumulation in gyres and strong relation with the seasonal surface current. Oxidative functional groups were observed in the chemical structure of plastics. The results suggest that most MPs may be sourced from land-based activities and transported by river run-off.

3.1 The significance of microplastics contamination in surface water

Plastics are occurred in everywhere. All daily used product can be constructed by plastic materials, and the waste from the end of this plastic product life is needed to be systematic controlled. Mismanage plastic debris was released and contaminated in the environment. At the last, the debris ether from land-based activities or marine-based activities were ended in the aquatic system. Since the plastic debris was entered, it was floated, transported, and transformed by dynamic conditions of the surface water before it was submerged to the water column and the sediment system.

Plastic debris is not only be carried in surface water to the ocean, but it also be fragmented to smaller size of plasticles by physical, chemical, and biological processes of the marine ecosystem. Microplastics (MPs) have been defined as fragmented plastic-particles (plasticles) that less than 5 mm from both manufacturing process (primary MPs) and fragmentation of large plastic debris (secondary MPs). Ubiquitously, both primary and secondary MPs were continuously fragmented. After stirred in saltwater, the tear and crack line on surface of PE-pellets were observed, moreover, a carbonyl group or a marker of oxidation was signed after a 6-week of the exposure [102]. Specifically, the weathering process of was significantly influenced by water, temperature, and oxygen availability [103]. As small as the fragmented particles were, the contamination of MPs seems to be a trouble in ecosystem. For example, contamination of polystyrene micro-particles results inhibition of photosynthesis and respiration of phytoplankton, the primary producer of the aquatic environment [104]. Importantly, persistent organic pollutants and heavy metals tend to be accumulated on MPs surface [105]. The research has a concern that MPs are the vector for toxic transportation.

Contamination of MPs in surface water pose to be the role of their transformation and accumulation in the other area. Addition to photo-degradation and thermal degradation on the beach, tidal current water and wave induced the debris was physically fragmented via collisions and abrasion from rocks and sand. The investigation of MPs on beach suggested that the fragmented small plastics were either backwashed from the beach to the sea [77] or accumulated from the sea to the beach [106]. Moreover, the contaminations in river estuaries and river creeks indicated MPs were transported from sources, especially urban area, by water runoff [12, 21, 107-109]. At the end of the pipe, MPs were transported to the sea. It, however, is not the end of the MPs life, the plastic particles were adhered with biofilm, formed feces pellets, and flocculated suspended solid aggregation. By the experiments, biofouling on plastics surface was formed in 1-2 weeks after submerged plastics to the seawater [63, 80]. Characterization of biofilm colonization of seawater incubated plastics founds pioneer bacteria first layer attachment in 7 days after that the formation of exopolymer substance matrix was observed in 15-22 days [110]. The interaction between MPs and suspended solids in water showed significant aggregation that developed the negative buoyant and caused MPs sunk from surface water [111, 112]. The hetero aggregation of phytoplankton and MPs also be developed after plankton exposed MPs in culture media [81, 82]. These phenomena of MPs were considered for vertical transportation via increasing plastic density that affected plasticles sunk in water column. The experiment founded that sinking of MPs was depended on size, shape, and types of the plasticles which are related to density and buoyancy [112-114]. In general, it is accepted that the horizontal and vertical distributions of MPs are the result of environmental induced factors and that of plastic particle characteristics.

As microplastics in surface water are the initial-transformed phase of the contamination, the dynamic hydro-ecological influences have been discussed that they distributed MPs thorough the marine ecosystem. The inner Gulf of Thailand (GT), semi-enclosed gulf with riverine input and multi-activities, was the significant area for studying the distribution of MPs. The effects of seasonal change on the contamination of MPs were necessary for the knowledge in fate and transportation of MPs. With hypothesis that MPs were loaded from land around the gulf, this work aims to quantify contamination of MPs and characterize effects of environmental factors on spatial and seasonal distribution of MPs in surface water.

3.2 Analysis of microplastic in surface water

3.2.1 Surface water sampling

The surface waters were sampled in dry season (April-May 2018) and wet season (July-August 2018) from Mae Klong (MK), Ta Chin (TC), Chao Praya (CP), Bang Pakong (BK) river estuaries and the coastal sea of the inner Gulf of Thailand (GT) (Figure 3.1). The area coastal sea was categorized into 4 sub-area: north-the inner GT (N-GT), west-the inner GT (W-GT), east-the inner GT (E-GT), and center-the inner GT (C-GT). Additionally, the water samples also be collected in the northeast monsoon period (December 2017), but the sampling area was not included the river estuaries. The surface water samples (0-0.5 m) were collected from 25 sampling stations in northeast monsoon period, 74 sampling stations in dry season, and 70 sampling stations in wet season. The volume reduction of defined mesh size plankton net was used concentrate solid particulate. In detail, water samples of 0.1 m^3 collected by clean bucket were filtered by 80 μm-plankton net, the samples collected by submersible pump were filtered by 22 μm-plankton net, and the volume of pumped samples were calculated by the average of 100-L-water suction flow rates before and after filtration. The filtered solids of samples were transferred to cleaned new polypropylene (PP) bottles. After collected, all samples were kept in cold and dark before analysis.

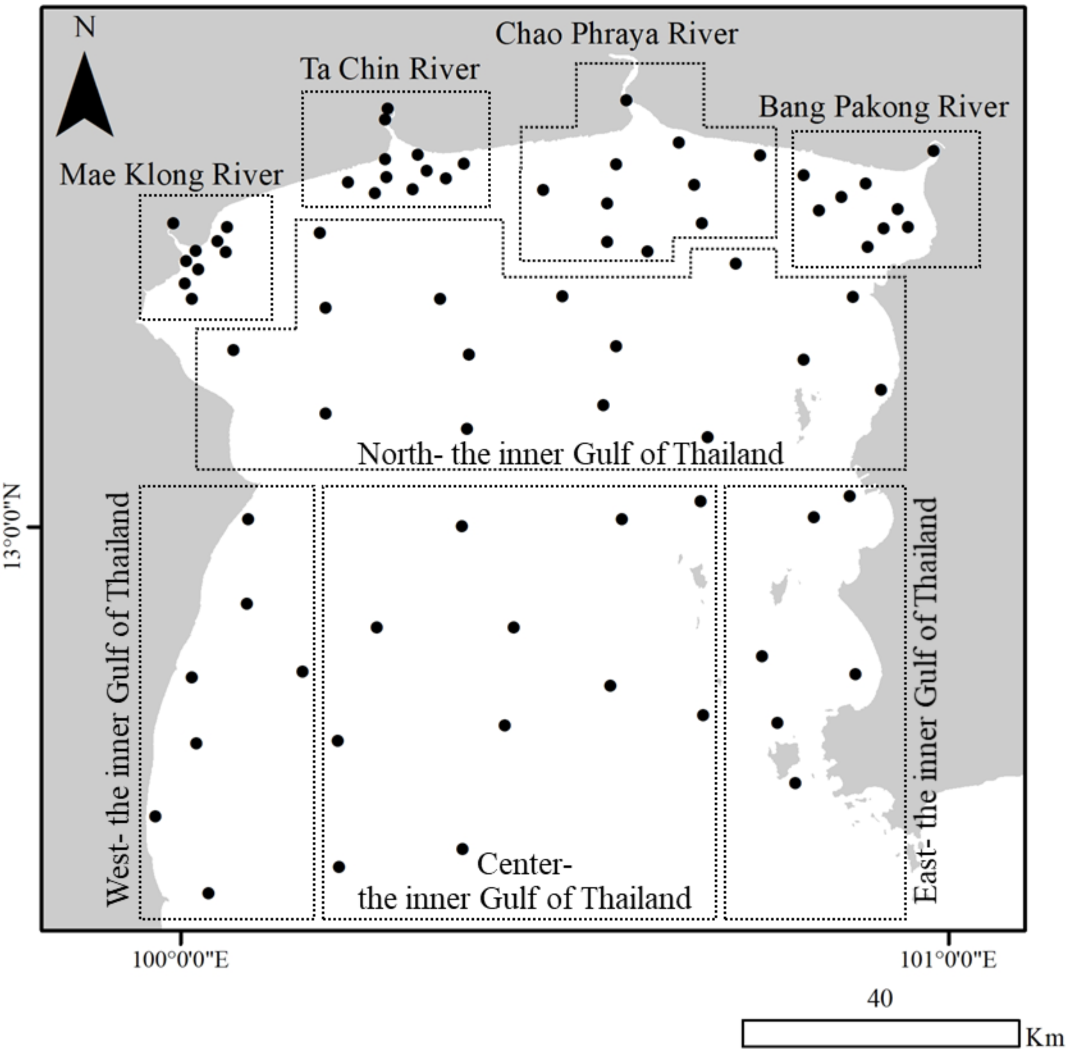


Figure 3.1 Surface water sampling stations of the inner Gulf of Thailand

3.2.2 Quantification of microplastics

The analysis procedure of MPs in this study was applied from National Oceanic and Atmospheric Administration of United States’ the laboratory method for analysis of MPs in the marine environment: recommendations for quantifying synthetic particles in water and sediment [59].

1) *Size fractionation*

The heterogeneous sizes of suspended solids in water samples were sieved to defined sizes, using nylon sieves in size of 100-300, 300-1000 μm and metal ASTM laboratory test sieve (Endecotts, England) in size of 1000-5000 μm. The sieved particles were rinsed with distilled water for removing dissolved solids in seawater, and those were transferred to oven dry at 60 ºC.

2) *Density separation*

The organic matter in dried solids from water samples that defined sizes was removed by wet peroxide oxidation (WPO) in 75 ºC using H_2O_2 and $FeSO_4$. NaCl powder (6 g of NaCl per 20 mL of solution) was added to the samples after the end of WPO for increasing the solution density. Then, the mixture was transfer to the separation unit for settling the non-plastic residues. The settle partition was discarded. After that, the floating MPs were washed with saturated NaCl solution, while settle residues were discarded 2-3 times. Finally, MPs were filtrated on pre-weight Track-Etched polycarbonate membranes (Whatman, Nuclepore 25 mm, 12 μm).

3) *Quantitative analysis*

After filtration, number of MPs with the shapes (fiber, film, foam, fragment, and pellet) modified from Crawford and Quinn 2017 [60] (Table 2.2) was counted under stereo microscope (Shodensha, NSZ-405J3). The colors of MPs were categorized to be red, blue, green, brown, black, white, transparent, and the others. MPs with membrane were dried at 65 ºC and stored in desiccator. The membrane before and after filtration were gravimetrically analyzed by 5-digit balance (Mettlertoledo, S/N: 1128180269). The MPs in each shape for 3932 pieces for total were picked-up under microscope, and the functional groups of those were analyzed by Fourier-Transform infrared microscope with transmission mode (Bruker, Lumos II). The plastic types of the samples were identified by compare similarity of the analyzed spectrum and the reference plastic spectrum. Accordingly, non-plastic materials, such as cotton and wool, were identified account for 9% of total sampled particles.

Quality control of analysis was operated with blank samples and commercial grade of green polyethylene (G-PE) spiked samples. The blank samples were analyzed by using distilled water passed the sieving unit as same as the method of water sample analysis. The counted and weighted particles in blank samples were used as a background concentration of all water sample analysis. In spited samples, G-PE (106-212 μm) was counted and weighted, then those were spiked to water samples collected by filtrating 100 L of surface water to 22 μm of plankton net. The G-PE was also spiked to distilled water and treated with WPO. No physical changes, both shape and color, were observed in G-PE after treatment. Amount of G-PE in the process samples was counted, weighed, and compared with non-process spike G-PE. Accordingly, the percentage of spiked G-PE recover was 106±11%, indicated the analytical procedure of this study was suitable for separating MPs from water samples.

3.2.3 Related factor analysis

Surface water dynamic were hypothesized that it influenced the spatial distribution of microplastics. Hydrological characteristics, water quality and elementary productions in pelagic food chain of the study area were parallelly investigated with recognized procedures (Table 3.1). Those investigated parameters were published in *Development of Socio-Ecological Based Effective Fishery Management Policy for Good Governance in Sustainable Fishery of the Inner Gulf of Thailand* [58].

Table 3.1 Analysis of hydrological characteristics, water quality and elementary productions in surface water

Parameters	Analytical methods
Average residence time	Remnant function [115]
Surface water current	Delft3D Numerical model
Salinity (Sal) Dissolved oxygen (DO)	Field measurement by multi-parameter water quality monitor (YSI 6600)
Total suspended solids (TSS)	Gravimetric method
Dissolved inorganic-nitrogen (DIN) Ammonium-nitrogen (NH_4^+-N) Nitrate/nitrite-nitrogen (NO_3^--N) Orthro phosphate-phosphorus (PO_4^{3-}-P) Silicate-silicon ($Si(OH)_4$-Si)	Automated nutrient analyzer (Skalar, The SAN^{plus} Segmented flow analysers)
Total particulate phosphorus (TPP) Total dissolved phosphorus (TDP) Total phosphorus (TP) Chlorophyll *a* (Chl)	Spectrophotometry
Abundance of phytoplankton (AP)	15-µm-plankton net filtration and microscopic quantification
Abundance of fish larvae (AFL)	330- and 500-µm-bongo net horizontal towing and microscopic quantification

3.2.4 Contamination characteristic analysis

1) Abundance of microplastics

Number of MPs in total and each shape was calculated in the unit of 'pieces/L'. From gravimetrical analysis, quantitative data was presented in the unit of 'ng/L' for water samples. The size fraction and diversity in shape and color of MPs were calculated by the number of MPs per unit of media and weight of MPs per unit of media, if they were applicable.

2) Oxidative index

According to FTIR spectrum analysis, the oxidative functional groups in plastic structure were observed. Three oxidative indexes were used as the scale for comparing oxidation level. The indexes were calculated as the ratios of integrated intensities for different wavelength as follows:

$$\text{Carbonyl index (CI)} = \frac{I_{1970-1560}}{I_{1540-1450}} \qquad \text{for C=O bonds,}$$

$$\text{Hydroxyl index (HI)} = \frac{I_{3900-3200}}{I_{1540-1450}} \qquad \text{for O-H bonds,}$$

and

$$\text{Vinyl index (VI)} = \frac{I_{940-885}}{I_{1540-1450}} \qquad \text{for C=C bonds.}$$

3) Statistical analysis

Mean value of MPs in pieces/L and that in ‘ng/L’ were represented the contamination. All data were logarithmic transformed for normal distribution and analyzed as parametric statistics. The multi-analysis, including independent student T-test, multi-analysis of covariance (MANOVA) and post-hoc test by Duncan’s equal variances assumed, was performed for describing effects of seasons and sampling areas, and that of size, shapes, and colors of MPs. Factor analysis with factor extraction of Principle Component Analysis (PCA) was performed for composition of MPs characteristics. The relation between MPs detected units (piece/L and ng/L) and that between abundance of MPs (piece/L) and environmental factors were validated using Pearson’s correlation. All statistical analysis was contributed with 95% confidence intervals (significance level 0.05).

4) Spatial data analysis

The spatial distributions of MPs were performed by using geostatistical analysis with Inverse Distance Weighting (IDW) interpolation of ArcGIS®.

3.3 Contamination of microplastics in surface water

The contamination of MPs in actual size of 100-5000 µm was investigated in surface water. Figure 3.2 illustrates the examples of observed MPs for varied shape characteristics. The investigation observed specific characteristics of abundances, characteristics, and distributions of each categorized MPs.

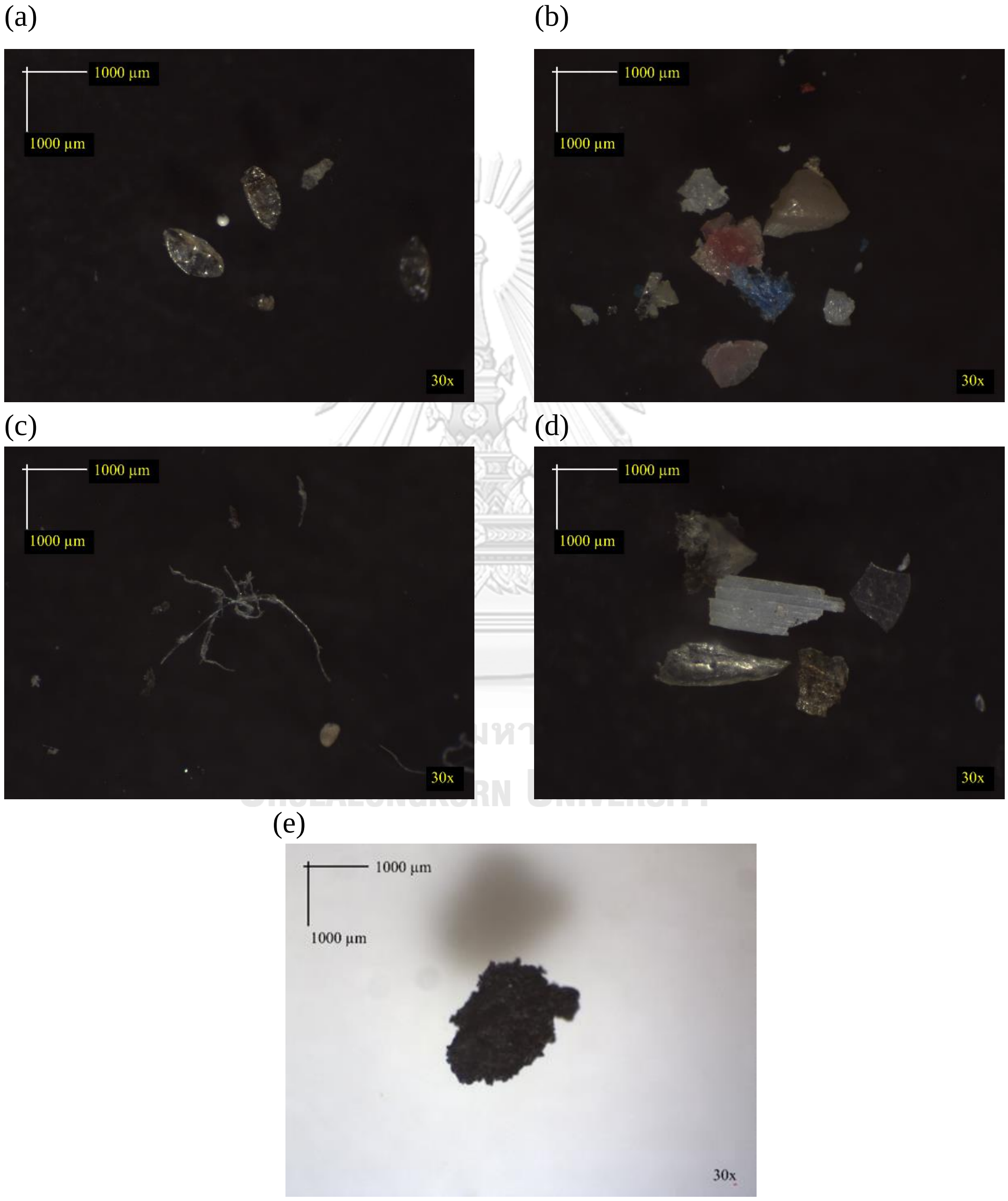


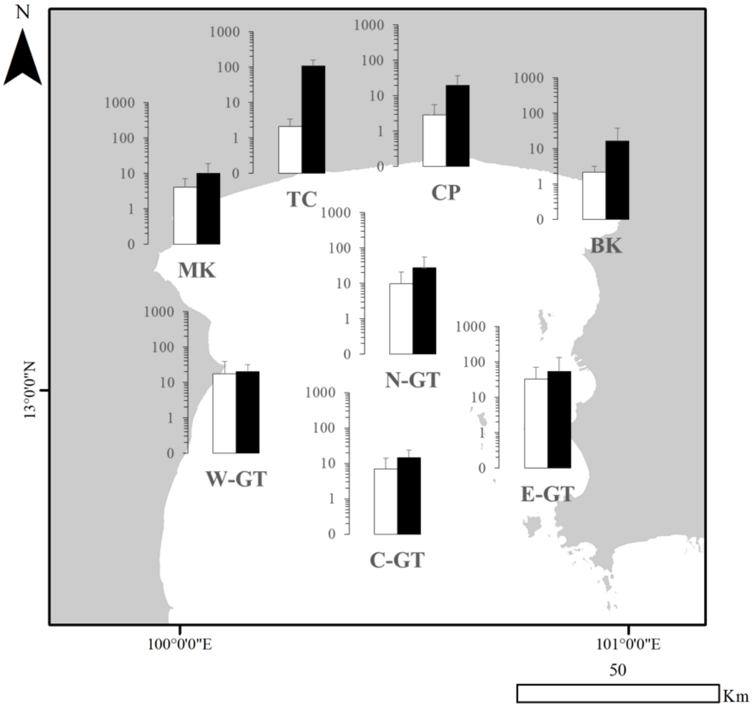
Figure 3.2 Microplastics in surface water of the inner Gulf of Thailand with the shapes of pellet (a), fragment (b), fiber (c), film (d), and foam (e)

3.3.1 Abundance of microplastics

In average, the surface water contamination of total MPs in the overall of the study areas was 21.29±36.21 pieces/L (4±4 ng/L). The contamination was greatly increased from the average of 8.70±15.34 piece/L (4±4 ng/L) in dry season to that of 34.59±46.02 pieces/L (5±4 ng/L) in wet season. The statistical analysis found the total MP concentration in “pieces/L” was found to be significantly higher in the wet season ($p < 0.01$), the significant positive relationship between the unit of ‘piece/L’ and ‘ng/L’ (R=0.357, p<0.01). Compared to the contamination in the northeast monsoon period (December 2017), the concentration of MPs during the monsoon transition period (the dry season) decreased non-significantly from 9.97±18.55 pieces/L to 8.70±15.34 pieces/L ($p > 0.05$). It could be inferred that the contamination of MPs in northeast monsoon period were similar level with the dry season. The contaminations of MPs between dry and wet seasons were specified for the effects of seasonal variation.

The difference of the contamination in each estuary and costal sea zone was found in both seasons (Figure 3.3). In dry season, total MPs in river estuaries (MK, TC, CP, and BK) were not statistically differ, while the slightly accumulating of MPs in costal GT (N-GT, E-GT, W-GT, and C-GT) was significantly higher for the number of plasticles. On the opposite in wet season, the contamination was magnified in the estuaries. The critical area of contamination was TC with the average concentration of 108.77±52.33 piece/L (6±3 ng/L). However, the similar in difference patterns of both seasons seems to be observed in the gravimetric weight of plasticles, but that more significantly fluctuate in the costal sea.

(a)



(b)

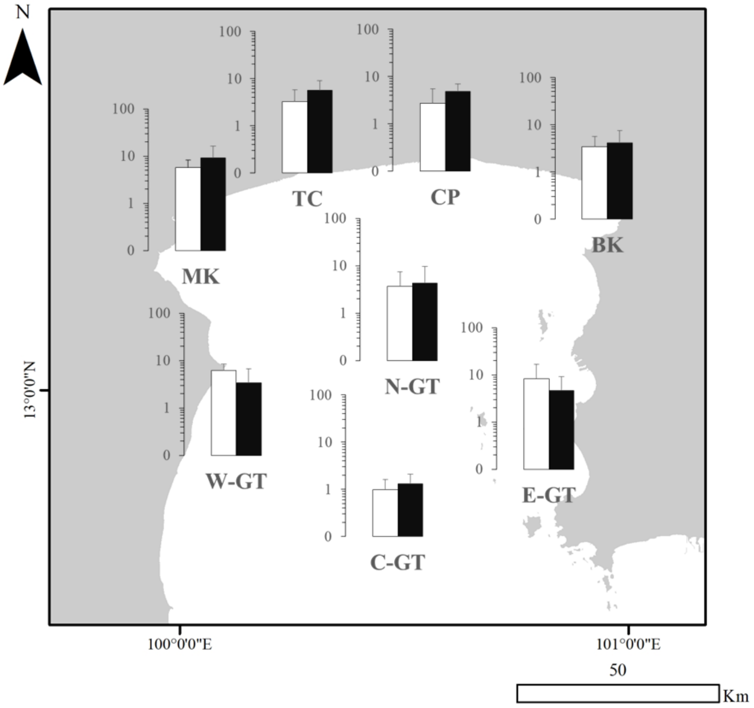


Figure 3.3 Total microplastics in surface water of dry season (☐) and wet season (■) of the inner Gulf of Thailand for the number of plasticles (a) and gravimetric weight of plasticles (b)

The contamination of MPs depended on the study area, and it is strongly related by the detectable size of them. The comparison of the contamination of MPs between the different areas needs to be carefully attended because there is no standard procedure for MPs analysis. This study suggests that the sampling methods and the minimum of detectable size in the investigation should be reported in the comparison. As the concentration of detected MPs were revealed in Table 3.2, the contamination of MPs in the inner GT seems to be higher than the other area though it is essential to note that there was the difference in size of detected MPs. The minimum detectable size of MPs directly impacts their abundance detected in the samples. According to the mesh size of sampling net, the detected MPs in net tow sampling were relatively lower than that in grab or pump sampling. For example, the total abundance of MPs in Bohai sea, China was increased with 4 orders of magnitude when the detected size of MPs was reduced from 330 µm to 5 µm [14, 42]. If considered about detectable size variation, the abundance of MPs between different area cannot be competed, but the trend of the investigation should be considered. This study suggests that the minimum size of detected MPs should be regulated for the standard. The concentrations of MPs can be more accurately determined if smaller sized MPs are analyzed. However, the detectable size of MPs is limited by sampling and analytical procedures. Accordingly, the minimum size of detection may be reduced, but the abundance of MPs should be reported for the size of 300 µm and lower than 300 µm as it can be compared with the most study that use 300 µm neuston nets for water sampling.

The abundance of MPs presents the number of plasticles. In deep, the characteristics of MPs are important to be reported. As same as the variety of plastic materials, the fragmentation of MPs may result different physical and chemical characteristics. The quantitative details of MPs may specify the properties of them, and those may be inferred to the plastic products or the sources of MPs.

Table 3.2 The comparison of microplastics abundance in surface waters

Contamination area	Sampling method	Average abundance (pieces/L)	Minimum size (μm)
Garonne River, France [1]	500-μm mesh net tow	1.5×10^{-4}	500*
Tokyo Bay, Japan [10]	350-μm mesh net tow	3.98×10^{-3}	100
Southern Ocean [15]	350-μm mesh net tow	3.1×10^{-5}	100
Bay of Breast, France [4]	335-μm mesh net tow	2.4×10^{-4}	335
Kingston Harbour, Jamaica [27]	335-μm mesh net tow	7.6×10^{-4}	335
Chabahar Bay, Iran [38]	333-μm mesh net tow	4.9×10^{-4}	100
Southeastern coast of Korea [39]	333-μm mesh net tow	0.26-1.56	330
Balearic Islands, Spain [40]	333-μm mesh net tow	3.19×10^{-3}	333
East China Sea, China [12]	333-μm mesh net tow	1.67×10^{-4}	500
Bohai sea, China [42]	330-μm mesh net tow	3.5×10^{-4}	330*
Tampa Bay, USA [20]	330-μm mesh net tow	4.5×10^{-3}	330*
Chao Phraya River, Thailand [25]	300-μm mesh net tow	0.08	30
Benoa Bay, Indonesia [43]	300-μm mesh net tow	6.2×10^{-4}	200
Guanabara Bay, Brazil [44]	300-μm mesh net tow	7.1×10^{-3}	355
The southern North Sea [30]	100-μm mesh net tow	0.03	11
Southeastern coast of Korea [39]	50-μm mesh net tow	6.2×10^{-4}-0.86	50

*The mesh size of net or filter was defined as the minimum size of MPs because no minimum size was report

Table 3.2 The comparison of microplastic abundance in surface waters (continuous)

Contamination area	Sampling method	Average abundance (pieces/L)	Minimum size (µm)
Charleston Harbor, USA [3]	Surface microlayer collection apparatus	6.6	63
Winyah Bay, USA [3]	Surface microlayer collection apparatus	30.8	63
North Yellow Sea, China [5]	Pump and filtration	0.55	30
Nordic Seas [7]	Pump and filtration	1.19-2.43	50*
Changjiang estuary, China [12]	Pump and filtration	4.14	51
South Yellow Sea, China [13]	Pump and filtration	4.5-6.5	50*
Bohai sea, China [14]	Grab sampling and filtration	2.2	5*
Ciwalengke River, Indonesia [6]	Grab sampling and filtration	5.85	50
Urban estuary in Gulf of Mexico, Mexico [19]	Grab sampling and filtration	151	10
Tampa Bay, USA [20]	Grab sampling and filtration	0.94	1.2*
Small-scale estuaries, Shanghai, China [21]	Grab sampling and filtration	27.84	10*
Surabaya, Indonesia [23]	Grab sampling and filtration	0.49	200*
Kuaka Nerus, Malaysia [28]	Grab sampling and filtration	0.13-0.69	20*
Kuantan, Malaysia [28]	Grab sampling and filtration	0.14-0.15	20*
Nakdong River, South Korea [36]	Grab sampling and filtration	0.29-4.8	20*
Monas River Basin, China [37]	Grab sampling and filtration	14-17	100
Tapi-Phumduang River, Thailand [24]	Grab sampling and filtration	0.33-1.77	0.33*
The inner Gulf of Thailand (this study)	Pump and filtration	8.70-34.59	100

*The mesh size of net or filter was defined as the minimum size of MPs because no minimum size was report

3.3.2 Characteristics of microplastics

Characteristics of MPs including sizes, shapes, colors, and polymer types were investigated for the composition of them in dry and wet seasons (Figure 3.4). The dominant plasticles in surface water were in actual size of 100-300 μm (65-66%), in color of transparent (72-90%), and in proportion of polypropylene (26-28%) in both seasons. However, the majority shape of MPs was film (64%) in dry season while that were fiber (57%) in wet season. Although PP was the main plastic type of both seasons, the number of plastic types increased from 32 in the dry season to 42 in the wet season. The variation of MPs properties was found in each season. Moreover, these characteristics have been discussed in fate and transportation of MPs even though that in their impacts in the aquatic environment.

Size of particles is the key characteristic for indicating MPs. The small size of MPs is defined as the result of manufacturing process (primary-MPs) and that of environmental fragmentation (secondary-MPs). Likewise, the large size of MPs is tended to be fragmented. In this study, the size fractions of the MPs in both seasons were similar form that were high abundance in small size of 100-300 μm, then the fraction was reduced in larger size (Figure 3.4 (a)). However, it is necessary to note that the size of MPs reported in this study is the actual size of MPs, the size of MPs with fouling and aggregation. Small MPs are probably to be sticked on solid particle, and they may be ingested by biotas; as a result, MPs were accumulated into large particles. The evidence of aggregation of MPs with the other particle was revealed in this study by detected smaller size of MPs than the sieved size of MPs sample. However, the decreasing size of plasticles during WPO process also be possible. To detect the real size of MPs, disaggregation process before sieve is required, or the size of MPs might be re-measured after the finish the organic digestion. Similarly, the other visually observed characteristics of MPs should be investigated after the organic content was removed.

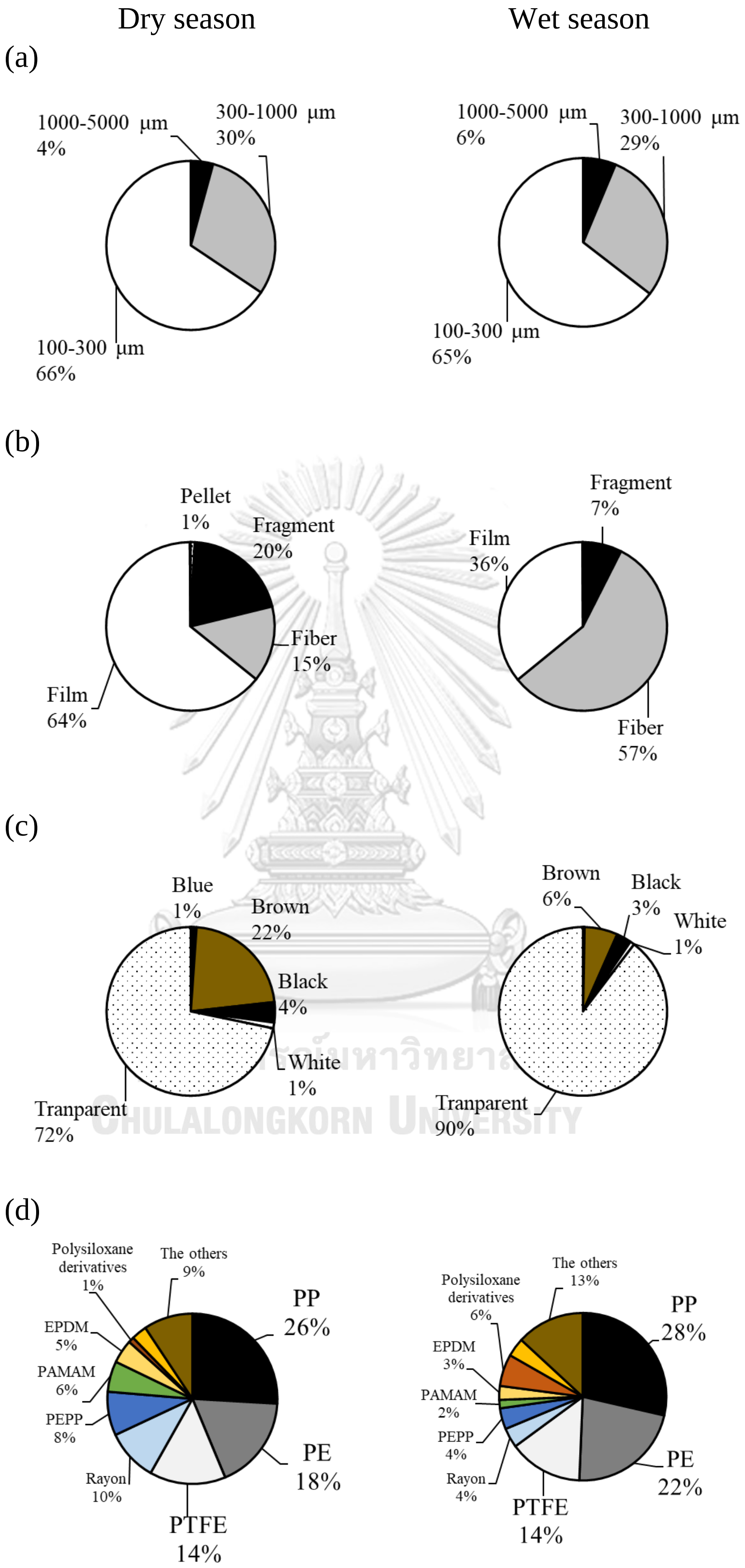


Figure 3.4 The composition of sizes (a), shapes (b), colors (c), and polymer types (d) of microplastics in surface water of the inner Gulf of Thailand

Shape of MPs (Figure 3.4 (b)) may roughly refer to plastic products. The FB-MPs is possible to be sourced from fibrous material such as the synthetic fiber in clothing products and the fishing accessories. While the PL-MPs, a smooth surface MPs, may be indicated to new MPs or the primary MPs, the FR-MPs may be referred to broken-plastic or the secondary MPs, in the other word. Beside the shape, the color (Figure 3.4 (c)) also be briefly represented the age of plastics. The white or transparent colors with smooth surfaces of MPs represented to the new plastics, while the pale or brown colors with a cracked surfaces were often referred to the aged plastics [106]. In fact, the aging properties, distribution, and toxic of plastics also be proportionally related with the chemical structures of them.

Plastic type, polymeric structure, was addressed the plastic materials although it is not evidently and precisely accounted the specific plastic products. For instance, the polyethylene film-MPs might be sourced from plastic bag or film-like products. However, the polymeric investigation of marine MPs may not represent to the accurate sources of the contamination at this time. Importantly, the polymer type is mainly response to the plastic density influenced the fate, transportation, and toxic from additive chemicals of MPs. In short, the plastics with the density higher than the density of water (1.0 g/cm^3) should be settled to water column and sediment system.

The characteristics of MPs represent the specificity in plastic transformation and transportation. The increase in large MPs with transparent color indicates that new MPs were more discharged in wet season. The variation in shapes and polymer types infers to the difference in plastic utilization and discharging in each season. In short, the transportation of MPs may be regulated by environmental based factors (season and area) and plasticle based factors (size, shape, color, and plastic type).

1) *Physical characteristics*

The effects of seasons, stratified areas, and physical characteristics on the abundance of MPs were significance. Based on seasons and areas, the interaction between observed characteristics on abundance of MPs were statistical significance for: 1) sizes and shapes (*p*=0.020), and 2) shapes and colors (*p*=0.000). In the other words, the sizes of MPs contaminated in each season and zone were linked with the shape, and those shapes were specific in colors, but the colors of MPs were the same proportion in all categorized sizes.

Quantity of MPs detailed in shape and size was varied on the contamination zones and seasons (Figure 3.5 and Figure 3.6). In both seasons, the number of MPs were inversed with the size of particles in most shape categories. While film-, fragment-, and fiber-MPs were the major shapes of MPs, pellet- and foam-MPs (100-1000 µm) were abundant in surface water of river estuaries in dry season. Dissimilarly in wet season, the contamination characteristic was diverted. MPs in wet season was enhanced, significantly in all river estuary and in some coastal area. Fiber-MPs were dramatically raised in Ta Chin River estuary and East-the inner GT. Pellet-MPs in particle 1000-5000 µm were increased in Ta Chin River estuary while those in particle 100-1000 µm were reduced. In addition, pellet contaminations were slightly shifted to coastal sea zones. The contamination characteristic of shapes and sizes reveled the heterogenous of MPs was affected by area-based sources and seasons. However, that of shapes and colors also indicated the variety of physical properties in MPs.

High variety of colors was evidently found in fragment-MPs and fiber-MPs although transparent, brown, white, and black were the dominant color of MPs (Figure 3.7 and Figure 3.8). In the river estuaries and center-the inner GT, more colored MPs were contaminated in dry season than those were in wet season. Additionally, the proportion of transparent MPs, especially fiber-MPs, was increased in wet season. In this study, it is important to note that the colors are depended on personal detection sensitivity of analyst, and they were reported as qualitative characteristics for contamination. The main factors of MPs characteristic influenced by seasonal dynamic were mainly focused on the shapes and sizes.

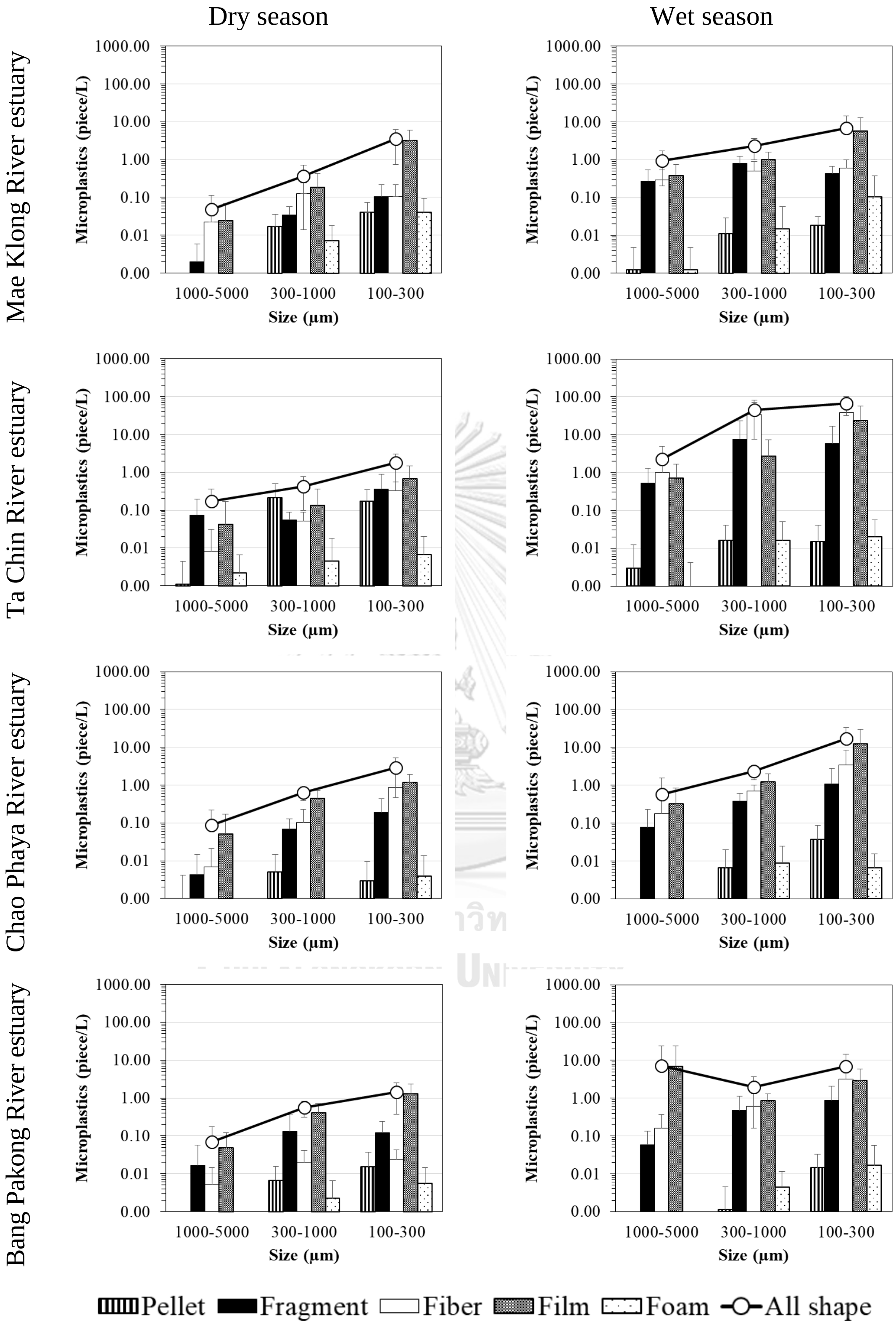


Figure 3.5 Shape and size characteristics of microplastics in surface water of the river estuaries, the inner Gulf of Thailand

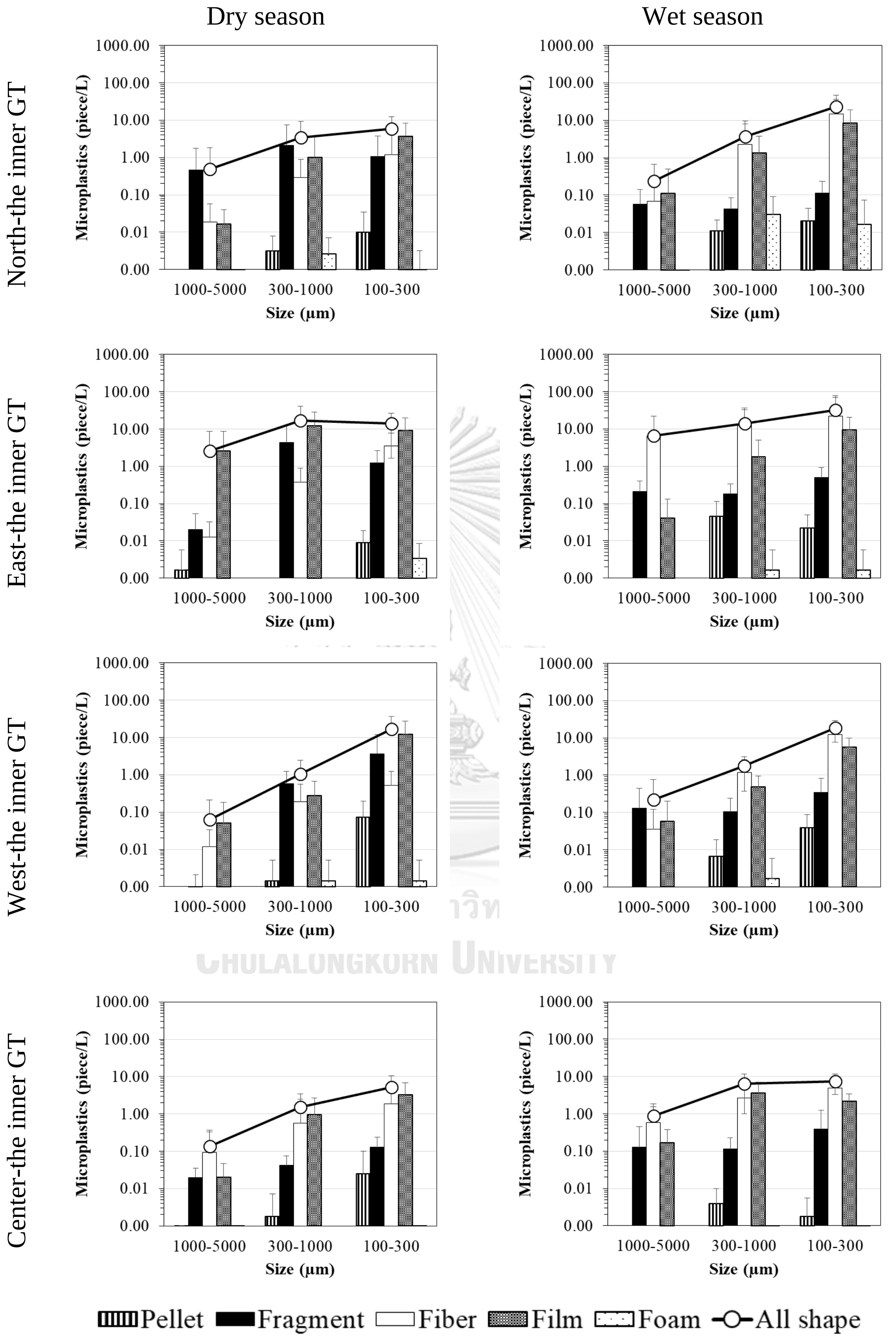


Figure 3.6 Shape and size characteristics of microplastics in surface water of the coastal sea, the inner Gulf of Thailand

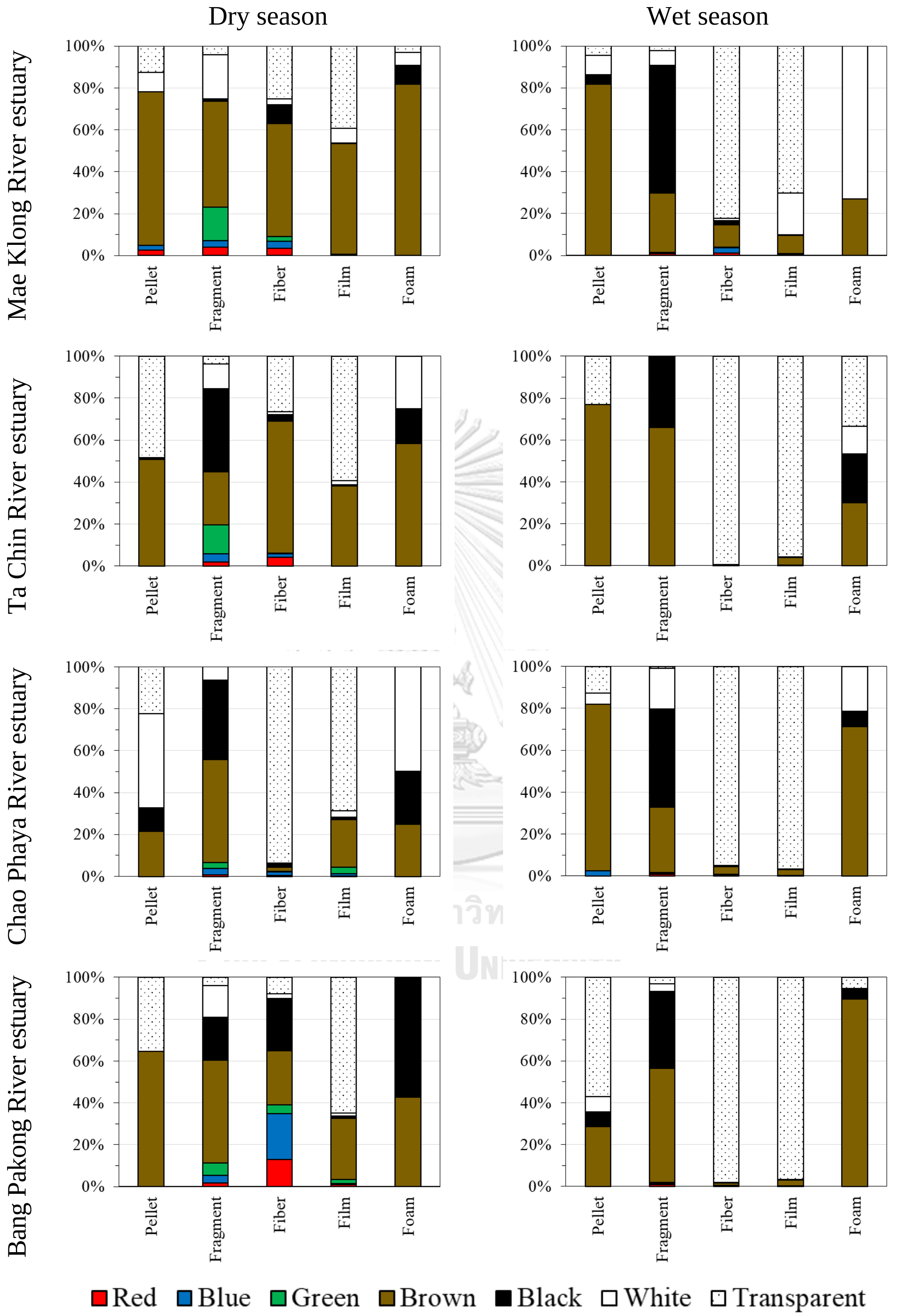


Figure 3.7 Shape and color characteristics of microplastics in surface water of the river estuaries, the inner Gulf of Thailand

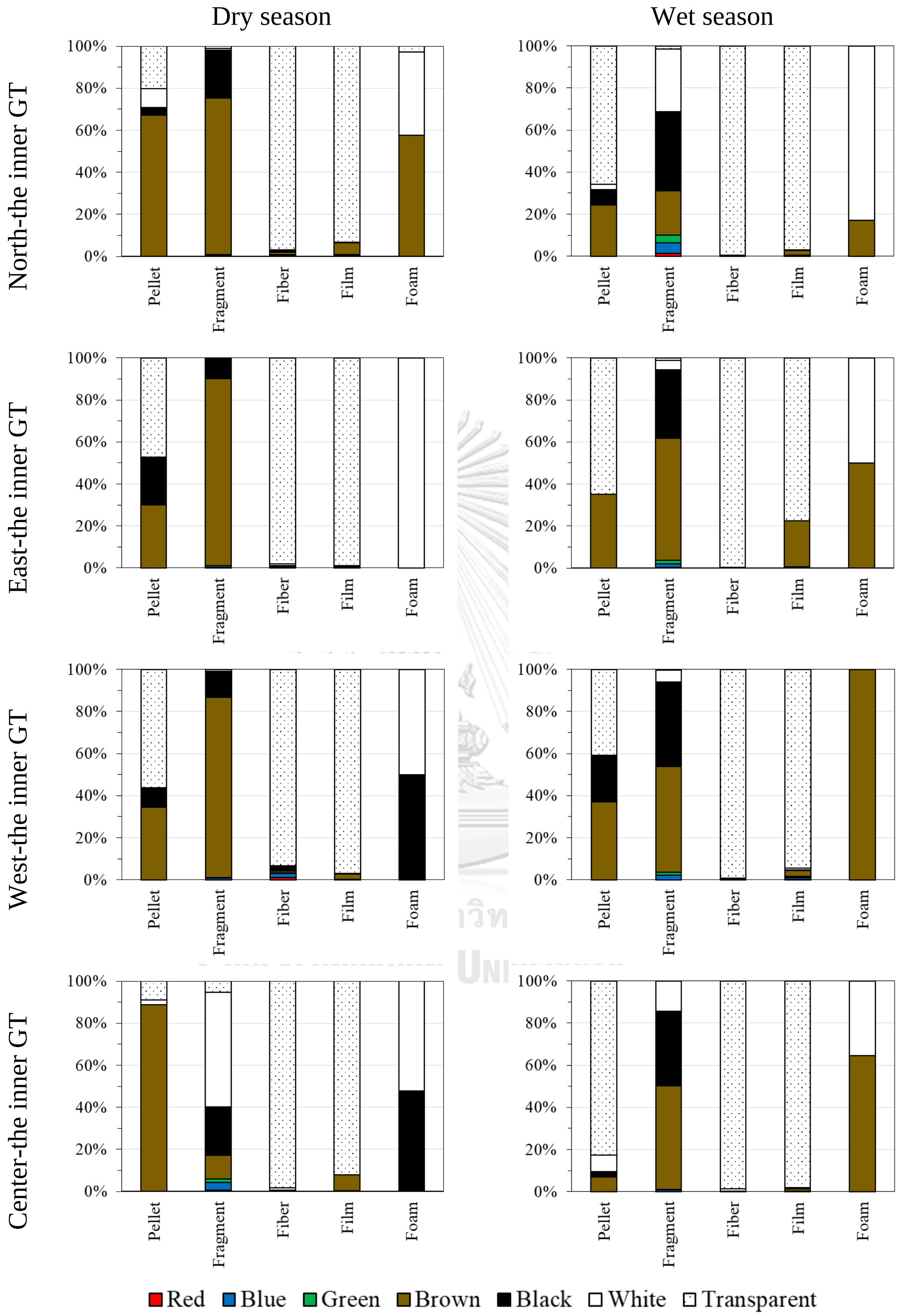


Figure 3.8 Shape and color characteristics of microplastics in surface water of coastal sea, the inner Gulf of Thailand

2) Chemical characteristics

Plastic type compositions of MPs were hypothesized that they were related with the shapes of MPs. The polymer compositions of different shapes of MPs are presented in Figure 3.9. Polypropylene (PP) and polyethylene (PE) were the common plastic types occurred in all shape of the samles although only PP was observed in PL- and FM- samples. It is generally to said that PP was ingredient of various plastic products, and it migh be fragmented to different shapes depened on the product characteristics and the induced forces. However, PE was the major plastic type in FR-MPs with 29% and 43% in dry season and wet season, respectively. In addition, PP was the main composition of FB-MPs in both seasons (39-51%), and the rayon fiber was clearly more identified in dry season. Interestingly, FI-MPs was the most variable in plastic types and polytetrafluoroethylene (PTFE) was mostly observed in FI-MPs samples with 33% for dry season and 28% for wet season. The observation of PTFE could be confiremed the effecficiency of density separation method because its density (2.2 g/cm^3) was greater than separated solution (NaCl solution, 1.2 g/cm^3). Because of the density of plastic, PTFE should be observed in sediment, as the investigation in Arctic deep-sea sediment [31]. However, the contamination of PTFE also be found in this study and in the water columns of the West Pacific Ocean and the East Indian Ocean [116]. The finding was discussed because they may be fragmented by anti-abrasives, which can consist of a protective layer of floating electronic debris, or the coatings applied on ships. It could be discussed that fragmented PTFE may be floated by the buoyancy of film characteristics. PP, PE, and PTFE were majority plastic type in MPs samples for FR, FB, and FI. PL- and FM-MPs were varied for more the other types of plastics, styrene-ethylene-butyl-styrene (SEBS), fibrous mixed plastic materials, polystyrene (PS), for example. The effects of seasonal change on MPs plastic type were discussed in the next topic (see 3.3.3. influence of seasonal variation on contamination of microplastics). Acccouted for more than 90% of MPs samples, the plastic proportions of FR-, FB-, and FI-MPs were analyzed for illustrating effects of plasticle sizes on polymeric composition.

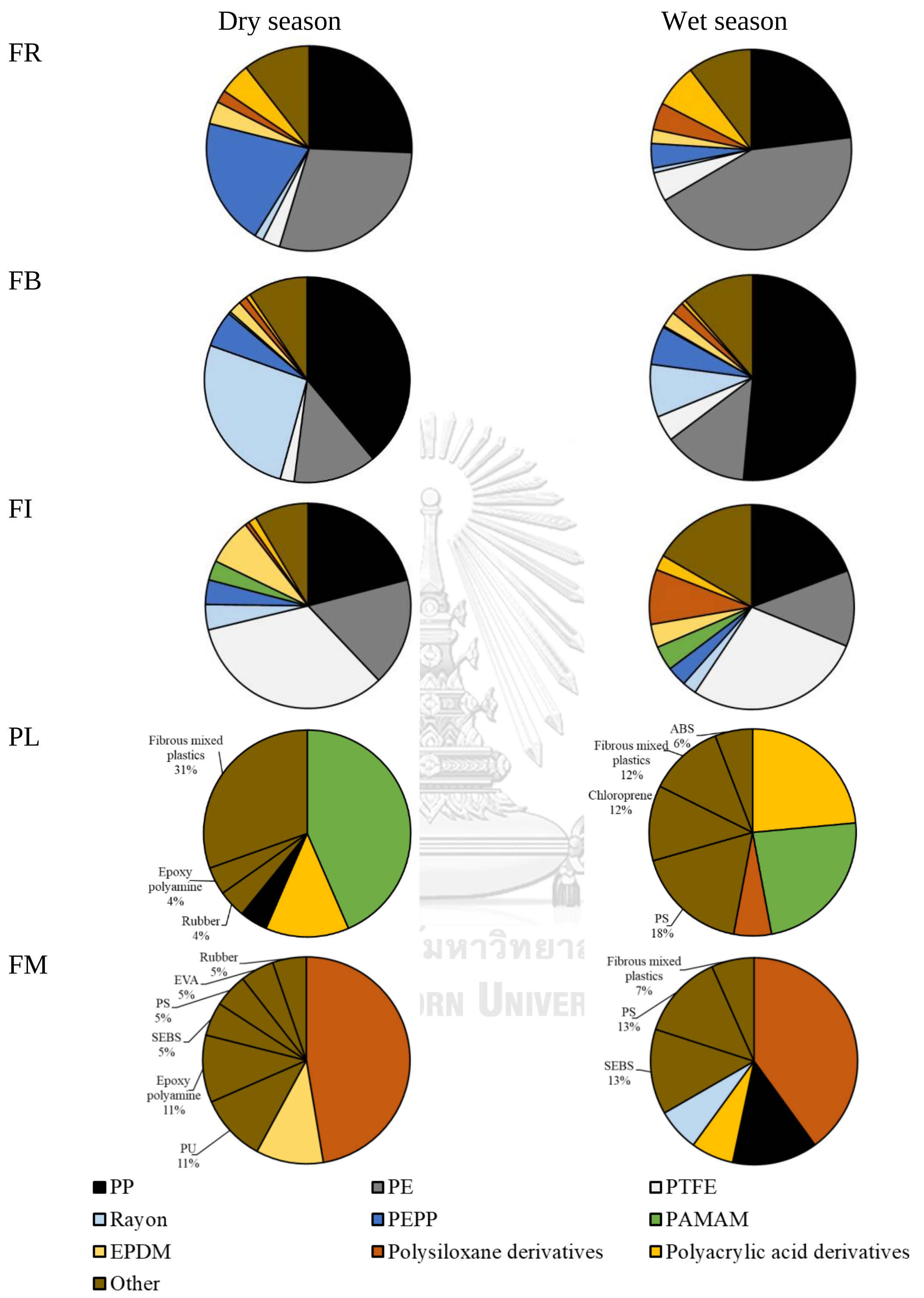


Figure 3.9 Polymer types of fragment-, fiber-, film-, pellet-, and foam-microplastics (FR, FB, FI, PL, and FM respectively) in surface water

The plastics compositions varied for 100-300, 300-1000, and 1000-5000 μm of actual sizes of MPs for FR-, FB-, and FI-MPs in estuarine water and coastal seawater were illustrated in Figure 3.10. In FR-MPs samples from esturies, PP fraction was reduced in wet season. While PP fraction in sample from costal sea in both seasons was a bit smaller than that from esturies, the fractions of varous plastic types were increased, for example, PE, polyethylen/propylene copolymer (PEPP), and poly acrylic acid derivatives.

The polymer composition may infer that PP-fragment possible to be released from the rivers, and the other plastics also be runoff during wet season as their fractions were increased. However, the reduction of PP fraction in coastal sea could be resulted from either the other plastics from the coastal sea that may be more generated or the selectively settling of PP in the water column. The inverse fraction characteristic was found in FB-MPs. High proportion of PP was detected in the large size MPs (1000-5000 μm) from the coastal sea, while that was detected in the small size MPs (100-300 μm) from the river estuaries. It should be represented the small fibrous plastic materials were mostly sourced from river, but the large plastic fibers were from the activities in the sea. In addition, the PP fiber was more released from the esturies in wet season. The result must be noted that these fibers, either large or small, were blended in both estuaries and costal sea by the hydrodynamic characteristics. According to plastic type composition of FI-MPs, the variation of plastics was observed, and it was amplified in wet season. But there was no clear pattern between river esturies and coastal sea. It is reasonable to said that the sources of FI-MPs could not be specified for river or sea. The polymer types of MPs indicated the plastic materials that entered to the environment before they were physicochemically transformed to MPs.

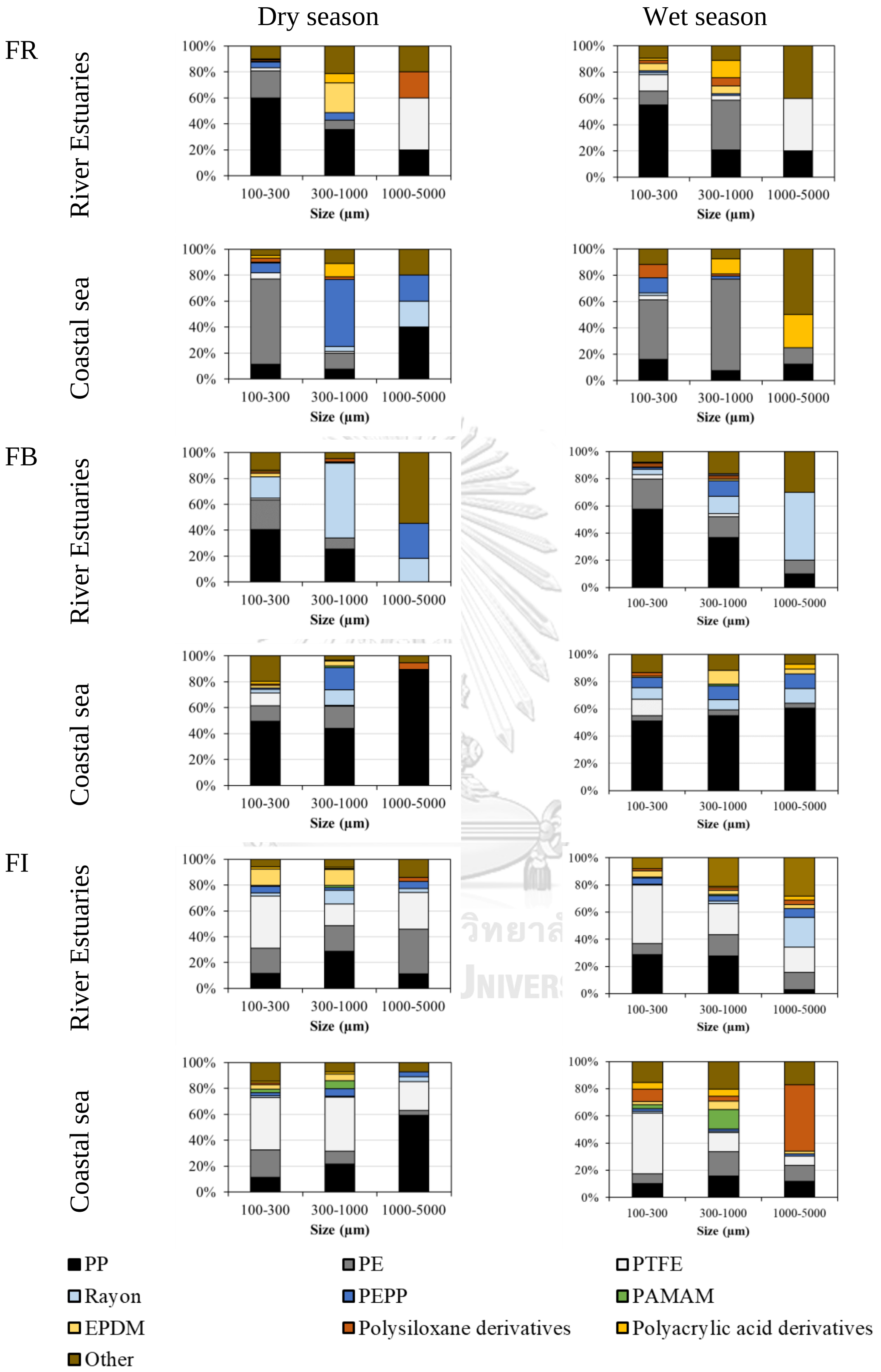


Figure 3.10 Polymer types of size varied fragment-, fiber-, and film- microplastics (FR, FB, and FI, respectively) in surface water of river estuaries and coastal sea, the inner Gulf of Thailand

The chemical structures of MPs were detailed for the plastic polymer types and the transformation of them after contaminated in the environment. The FT-IR spectrums (Figure 3.11) represent to the chemical structures of PP and PE in raw materials of commercial plastics and those of MPs samples. The structure of acyclic alkane hydrocarbon in PP and PE was indicated by the peaks at wave number of 3000-2840 cm^{-1} for C-H stretching. The structure of PP was specified by the peaks at wave numbers of 1450 cm^{-1} and 1375 cm^{-1} for -CH$_3$ bending, the structure of PE was presented by the peaks at wave numbers of 1460-1450 cm^{-1} for -CH$_2$ bending and 750-700 cm^{-1} for C-H bending. Additionally, the peaks at wave numbers of 1167-1168, 998, 973 and 841 cm^{-1} were the fingerprint of PP, while those of 730 and 719 cm^{-1} were the characterized peaks of PE. The new functional groups of hydroxyl group (-OH) (a broad peak of O-H stretching at 3200-3500 cm^{-1}) and ether alkene group or carbonyl group (medium to weak peaks of C=C or C=O stretching at 1680-1625 cm^{-1}) were observed in polymeric structures of MPs samples. The additional functional groups of PE in MPs tend to be similar with the aged PE by the water exposed experiment that found the oxidized groups of hydroxyl group (-OH) and carbonyl groups (C=C and C=O) in the region of 3370-3330 cm^{-1} and 1630-1600 cm^{-1}, respectively [102, 103]. These oxidative functional groups linked to the age of plastic materials and may resulte to the change in color of the plastics.

To evaluate the oxidation of PE [103], three oxidative indexes were calculated as the ratios of integrated intensities for different wavelength as follows:

$$\text{Carbonyl index (CI)} = \frac{I_{1970-1560}}{I_{1540-1450}} \quad \text{for C=O bonds,}$$

$$\text{Hydroxyl index (HI)} = \frac{I_{3900-3200}}{I_{1540-1450}} \quad \text{for O-H bonds,}$$

and

$$\text{Vinyl index (VI)} = \frac{I_{940-885}}{I_{1540-1450}} \quad \text{for C=C bonds.}$$

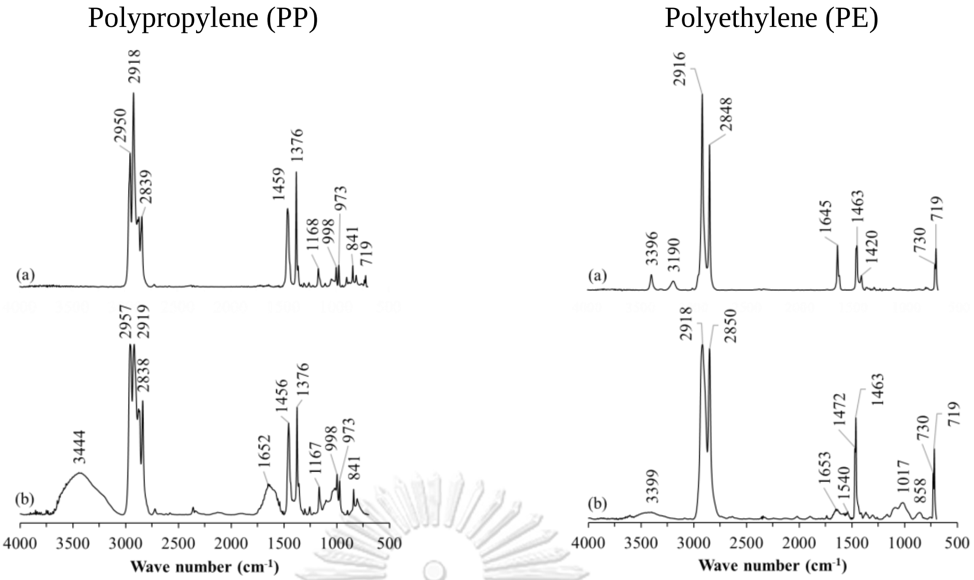


Figure 3.11 FT-IR spectrums of polypropylene (PP) and polyethylene (PE) for raw plastic materials (a) and those for microplastics in surface water (b)

These three indexes were applied for evaluating the oxidation of PP and PE in MPs samples as they were main component account for 44% in dry season and 50% in wet season. CI, HI, and VI of MPs sample had a similar trend in each categorized shapes of PP and PE (Figure 3.12-3.14). There was no significant difference of oxidative indexes between the contamination in estuaries and coastal sea (p>0.100); however, the oxidative indexes of both PP and PE in large MPs significantly less than those of smaller MPs (p<0.010). The indexes of fiber-PP and film-PP were parallel increased in wet season while those of fragment-PP were decreased in wet season. the oxidative indexes of all shape of PE were inversed to that of PP. Additionally, the oxidation of fragment-PP was slightly higher than that of fiber-PP and film-PP, but the oxidation of fiber-PE was greater than the oxidation in film-PE and fragment-PE. The oxidation of MPs might be inferred as the indicator of aging plastics due to their chemical structure transformation. Accordingly, the oxidative indexes of MPs samples represented that more oxidized fiber-PP, film-PP, and fragment-PE were contaminated in wet season. It is possible to be that the fragmentation of MPs was related with polymer types and plastic materials resulting different physical characteristics. The transformation of chemical structures, however, needs to be identified for the other plastics.

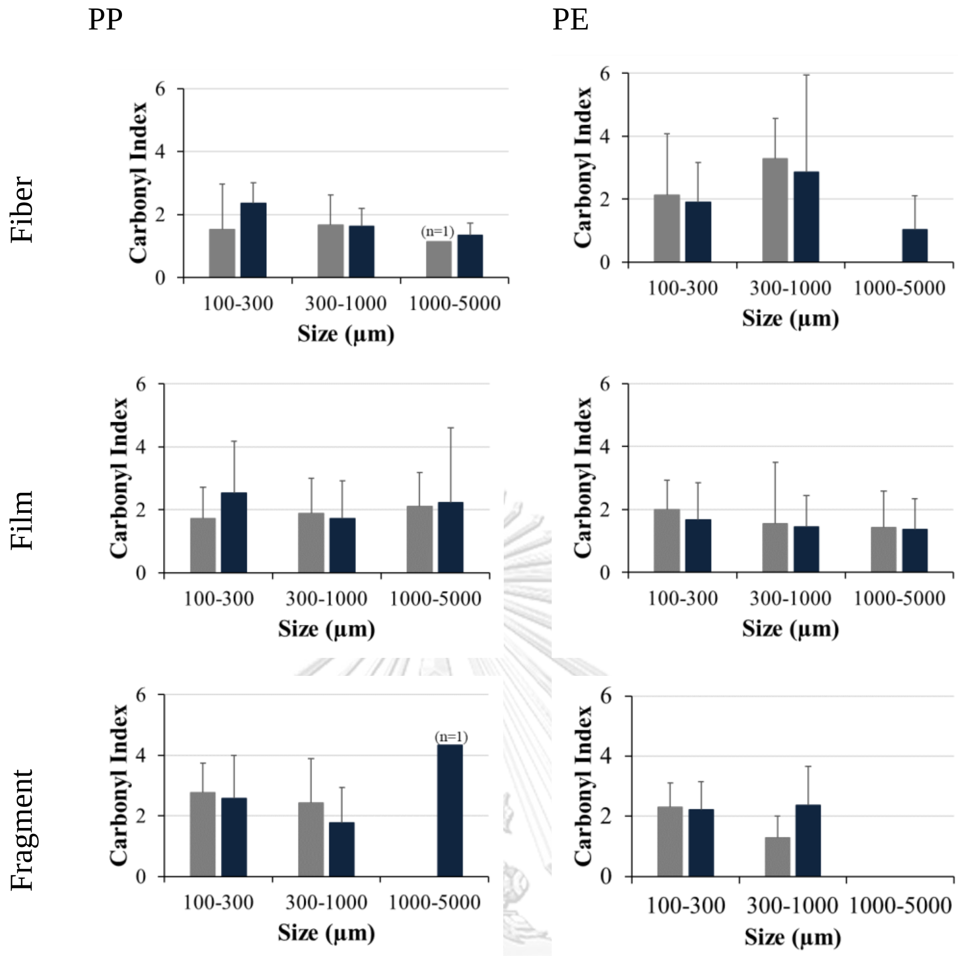


Figure 3.12 Carbonyl index of polypropylene (PP) and polyethylene (PE) in microplastic samples in dry season (■) and wet season (■)

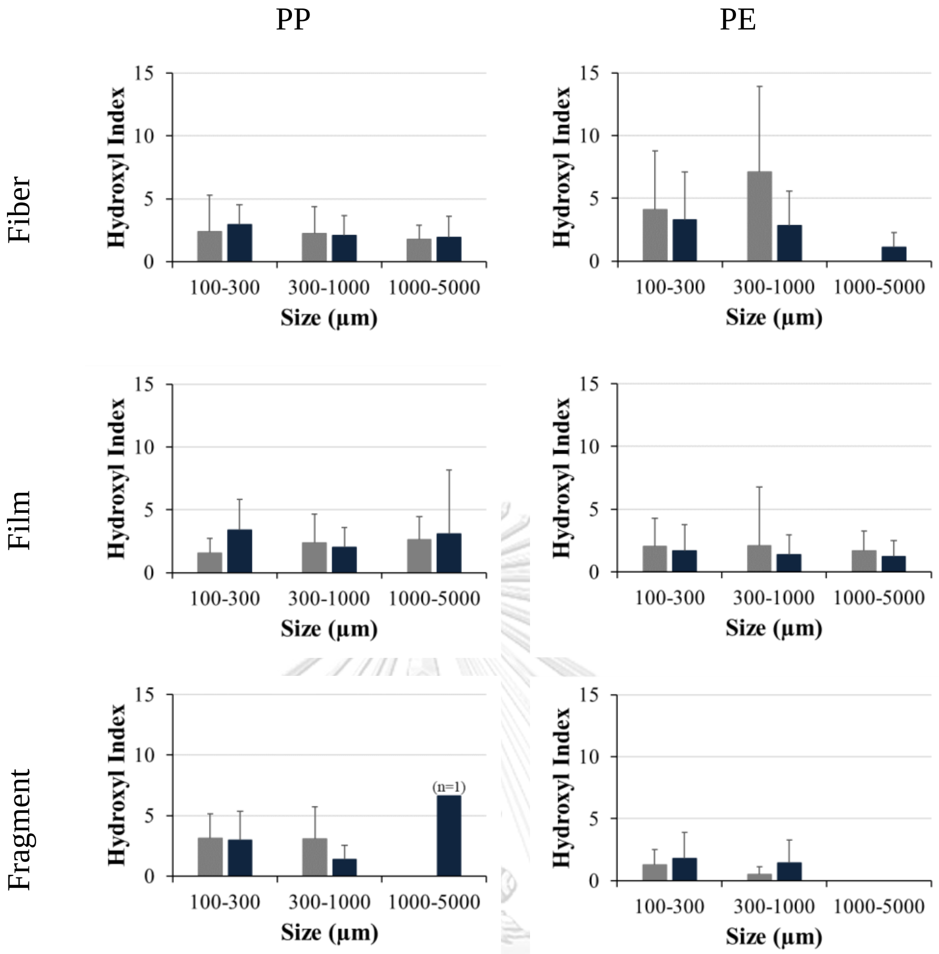


Figure 3.13 Hydroxyl index of polypropylene (PP) and polyethylene (PE) in microplastic samples in dry season (■) and wet season (■)

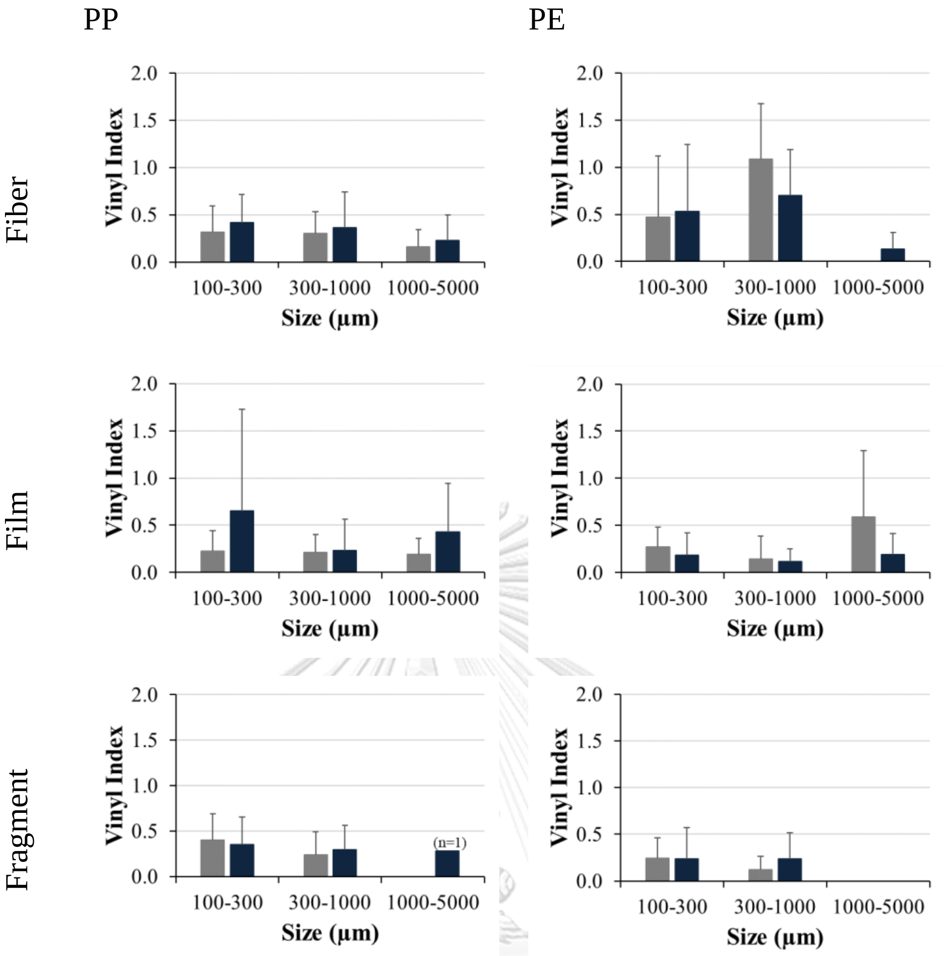


Figure 3.14 Vinyl index of polypropylene (PP) and polyethylene (PE) in microplastic samples in dry season (■) and wet season (■)

The oxidized carbonyl groups (C=C and C=O) and the hydroxyl group (−OH) in the structures of PE and PP in the artificial photo-oxidation were found in the accelerated aging plastics [102, 103, 117]. The energy from UV light absorbed in the C−C and C−H bonds and induced the formation of free radicals. After that, the radicals were reacted with oxygen, then the carbonyl, carboxyl, hydroxyl, or peroxide groups were introduced into the polymer chain [118]. Addition to the UV exposure, the physical surface cracks in the plastic samples also be driven by mechanical abrasion [119]. The CI was applied to represent the degree of weathering or the surface oxidation [102, 103, 117, 119-121]. The index value was referred to the age of the plastics [106]. Similarly, the increase in the hydroxyl and vinyl groups were evaluated by HI and VI [102, 103]. After exposure to UV, the CI of PP rapidly increased in 2 months, while that of PE demonstrated a linear increase [119]. The CI of plastic waste was also investigated, as it significantly increased by the age of disposal for PP waste, although this was slightly decreased for PE waste [120].

The results of this study suggested that plastic weathering may be regulated by polymeric type and shape. The different degrees of weathering between fiber, film, and fragment shapes were presented by oxidative indexes. Two distinct behaviors were proposed for understanding the fragmentation of MPs: (1) The flat parallelepipeds floated at the surface of the water were fragmented on the one face exposed to the sun and (2) The cubic piece that tended to roll at the surface of water resulted in biofilm prevention, more erosion, and faster fragmentation than parallelepipeds [121]. It can be inferred that the fragment MPs were rotated, and the film MPs were parallelly floated, in surface water. Furthermore, the oxidation indexes of fiber differ slightly compared to those of film and fragment. The results may indicate that the fragmentation of the fiber was a blend of flat and rotating behaviors along its longest dimension. The oxidation of plastic materials notably depended on plastic chemical structures and additive chemicals such as antioxidants, and photo-stabilizers [118]. Conversely, the physicochemical deterioration and transportation of MPs may continuously occur. The characteristics of contaminated MPs indicated the transformation that occur in plastic debris generated from non-specific sources.

3.3.2 Distribution of microplastics in surface water

The distribution of MPs in the dry and wet seasons (Figure 3.15) illustrated that MPs were sourced from both riverine water and unidentified sourced activities, then those were dispersed in the coastal sea. The investigation found high abundance of MPs in estuarine waters, but the contamination level fluctuated in the gulf. Notably in the Ta Chin River, the distribution map clearly confirmed the river transported MPs in the wet season, (Figure 3.15 (b)). Nonetheless, addition to the river transportation, MPs in the dry season may be generated by the unidentified sources, which are likely to be marine activities, or the coastal activities (Figure 3.15(a)). It could be discussed that the surface circulation in the gulf influenced the spreading and accumulating of MPs.

The investigations found surface water concentrated the contamination of MPs [7, 42, 122], and the volume of water was found to controlled the concentration of MPs [12, 13, 75, 108]. As observed during the sample collection of this study, the influence of seawater current from the south, the middle Gulf of Thailand, induced the seawater flowed up north in both seasons (Figure 3.16) [58]. In the dry season, an anticlockwise circulation was found in the northern part of the gulf, while dynamic gyres were occurred on the east and west sides. Dissimilar circulation pattern, clockwise circulation, was observed in the wet season. According to high contamination in the eastern and western regions of the gulf in dry season, it can be referred that the surface water current distributed MPs to condense in the gyre. Additionally, it also can be said that low MP concentration in the southern and northern areas might be the result of a dilution from high volume of seawater flowing up to the gulf. On the other hand, in the wet season, the riverine transportation affected a high concentration of MPs.

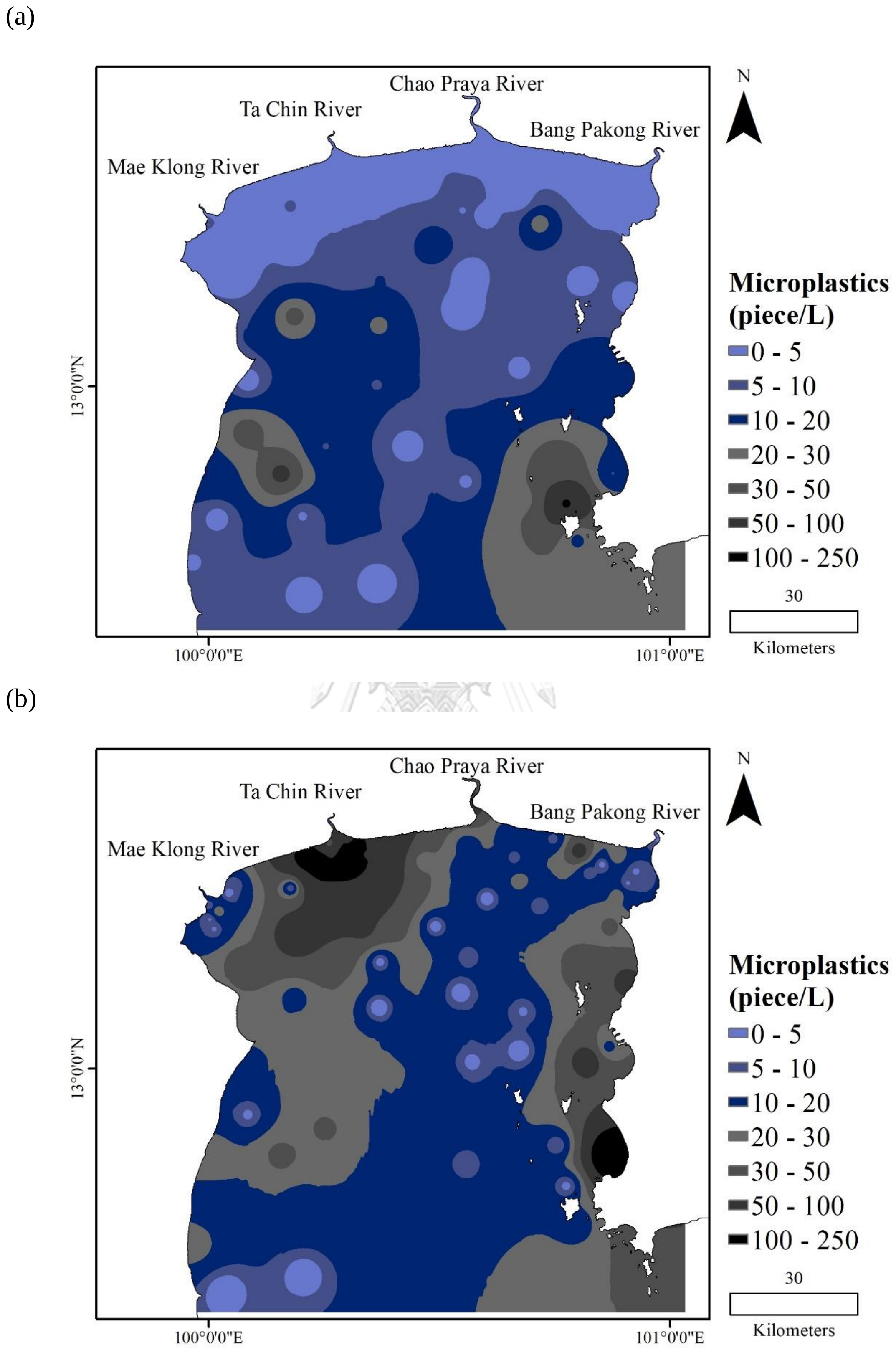


Figure 3.15 Spatial distribution of total microplastics in surface water of dry season (a) and wet season (b)

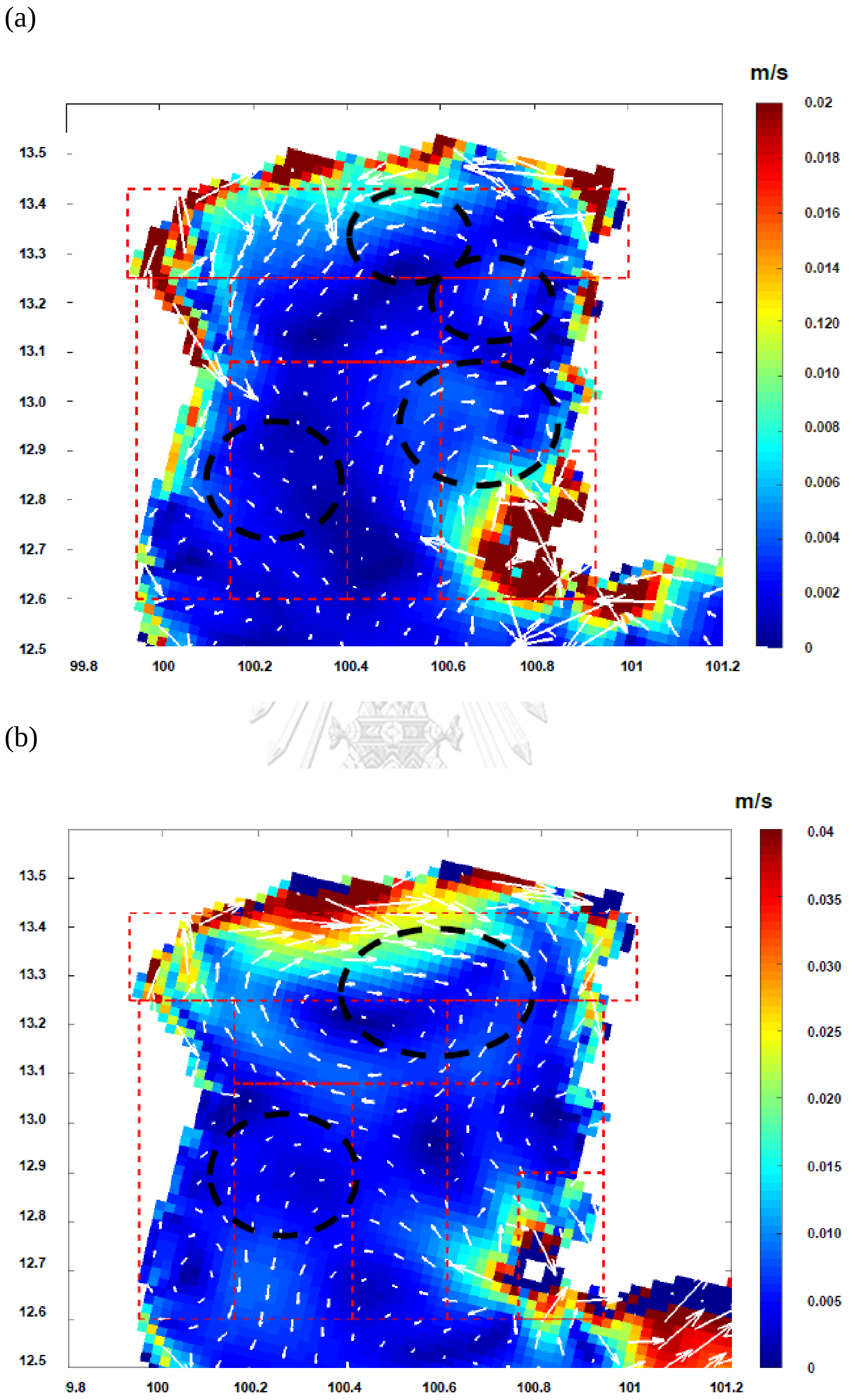


Figure 3.16 Current velocity and direction in the surface water of the inner Gulf of Thailand in the dry season (a) and the wet season (b) of 2018 [58]

As MPs’ shapes were categorized as film, fiber, fragment, pellet, and foam, their distributions were specified. The distributions of MPs with the specified shapes of film (Figure 3.17), fragment (Figure 3.18), and fiber (Figure 3.19), reveal a high abundance in the estuaries and gyre. However, greater contaminations in the large size of pasticles were observed in the southern area, fiber-MPs in size of 1000–5000 μm for the beast example. It can be said that certain compositions of MPs were generated from the middle Gulf of Thailand, south of the study area, from where the seawater current flows up into the study area. Additionally, the contaminations of pellet-MPs (Figure 3.20) and foam-MPs (Figure 3.21), occurred in some estuaries or some area of the coasts, represented to the various sourced in non-specific area. As the distribution of MPs was a snapshot of their transportation, the sources of contamination have been hypothesized to be activities along the coastal area.

When compared with previous study, more plastic fragments were extensively found in the coastal sea of the bay area than in the open oceans [123]. The observation showed the urbanization drove contamination of MPs [1]. Accordingly, the abundance of MPs was discussed that it was sourced from widespread human, commercial, and tourism activities [21]. There was a proposed that MPs came from nearby area landfills through airborne and leachate contamination [43]. However, the distance from the coast inversely related to the concentration level of plastic particles [40]. The river runoff was focused as an important role regulated MPs entering to the coastal sea [21, 109]. In this study, anthropogenic activities could not be identified due to the characteristics of the coastal sea. However, the distribution maps of the investigation suggested that the contamination of MPs might be from riverine transportation depending on their shapes and sizes.

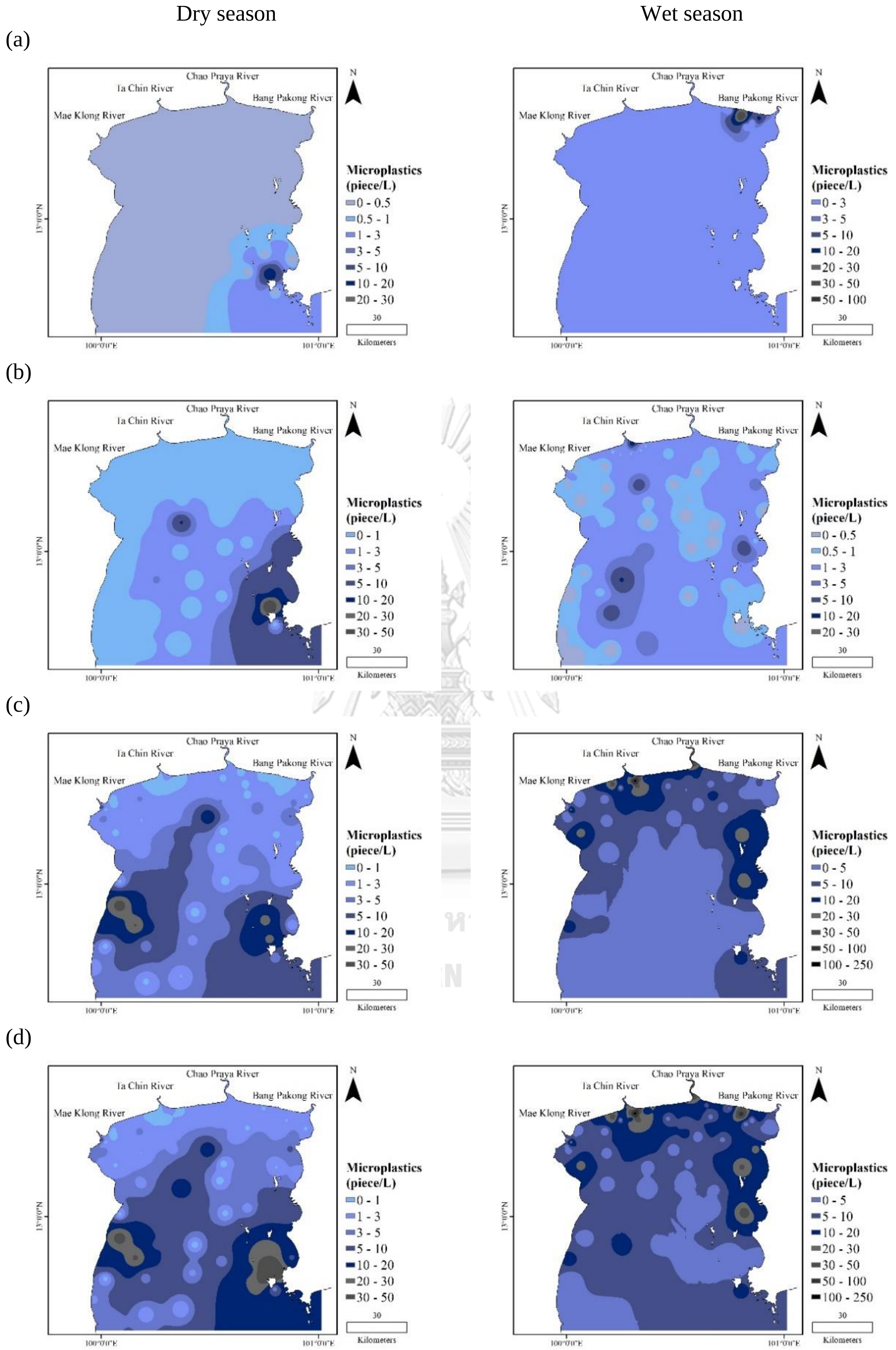


Figure 3.17 Distributions of film-microplastics in surface water: (a) 1000-5000 µm, (b) 300-1000 µm, (c) 100-300 µm, and (d) total film-microplastics

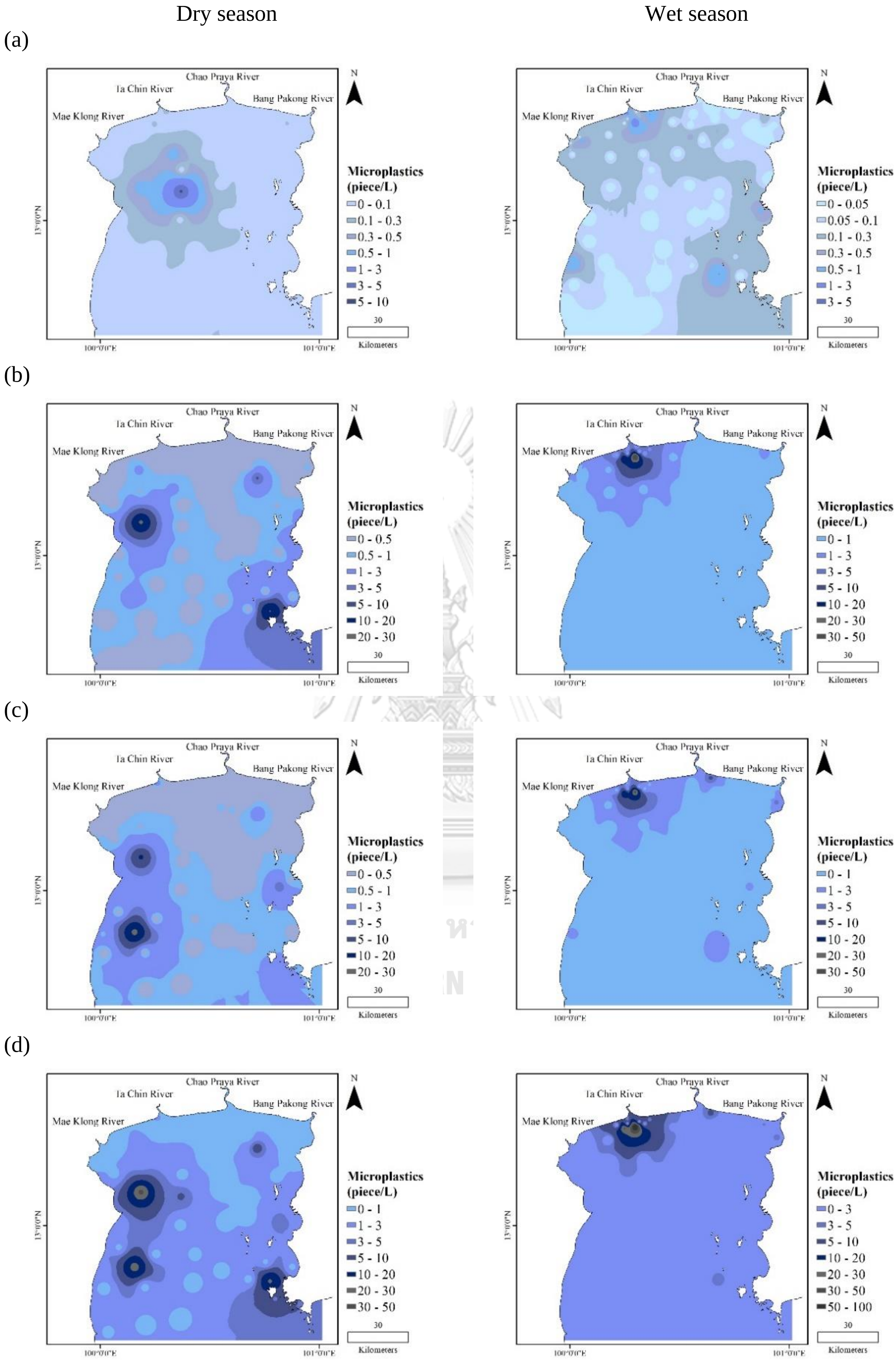


Figure 3.18 Distributions of fragment-microplastics in surface water: (a) 1000-5000 µm, (b) 300-1000 µm, (c) 100-300 µm and (d) total fragment-microplastics

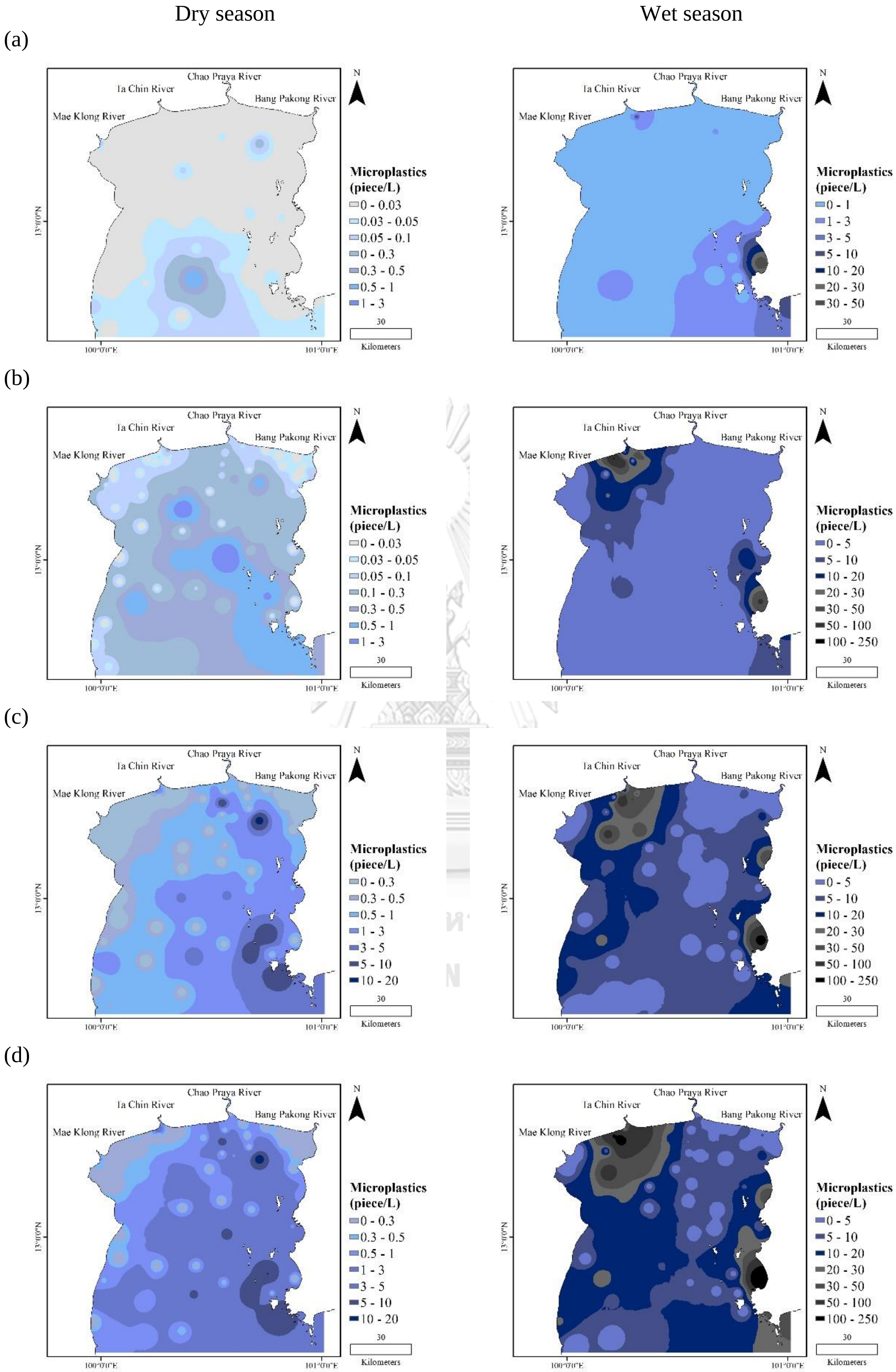


Figure 3.19 Distributions of fiber-microplastics in surface water: (a) 1000-5000 µm, (b) 300-1000 µm, (c) 100-300 µm and (d) total fiber-microplastics

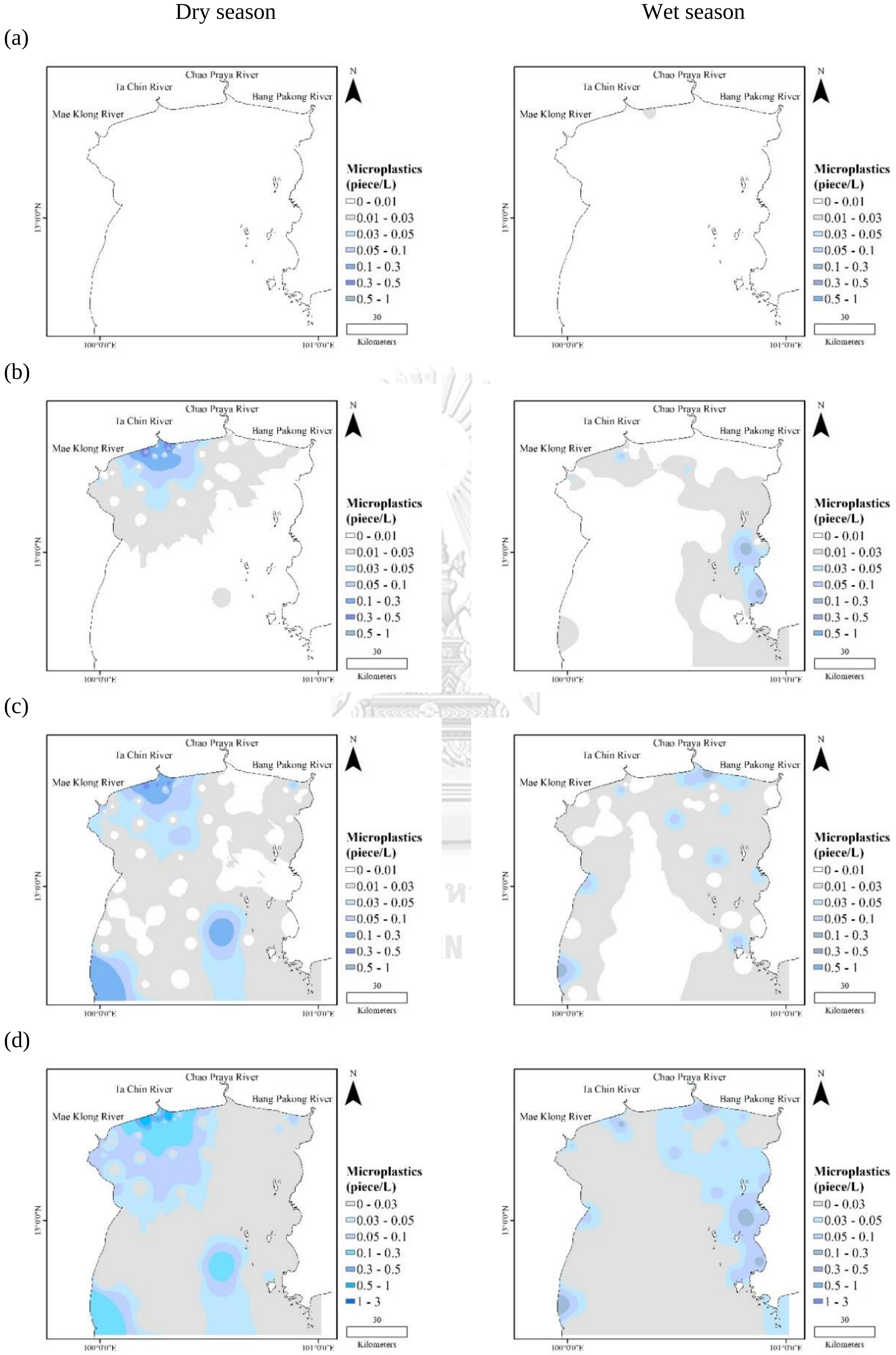


Figure 3.20 Distributions of pellet-microplastics in surface water: (a) 1000-5000 µm, (b) 300-1000 µm, (c) 100-300 µm and (d) total pellet-microplastics (d)

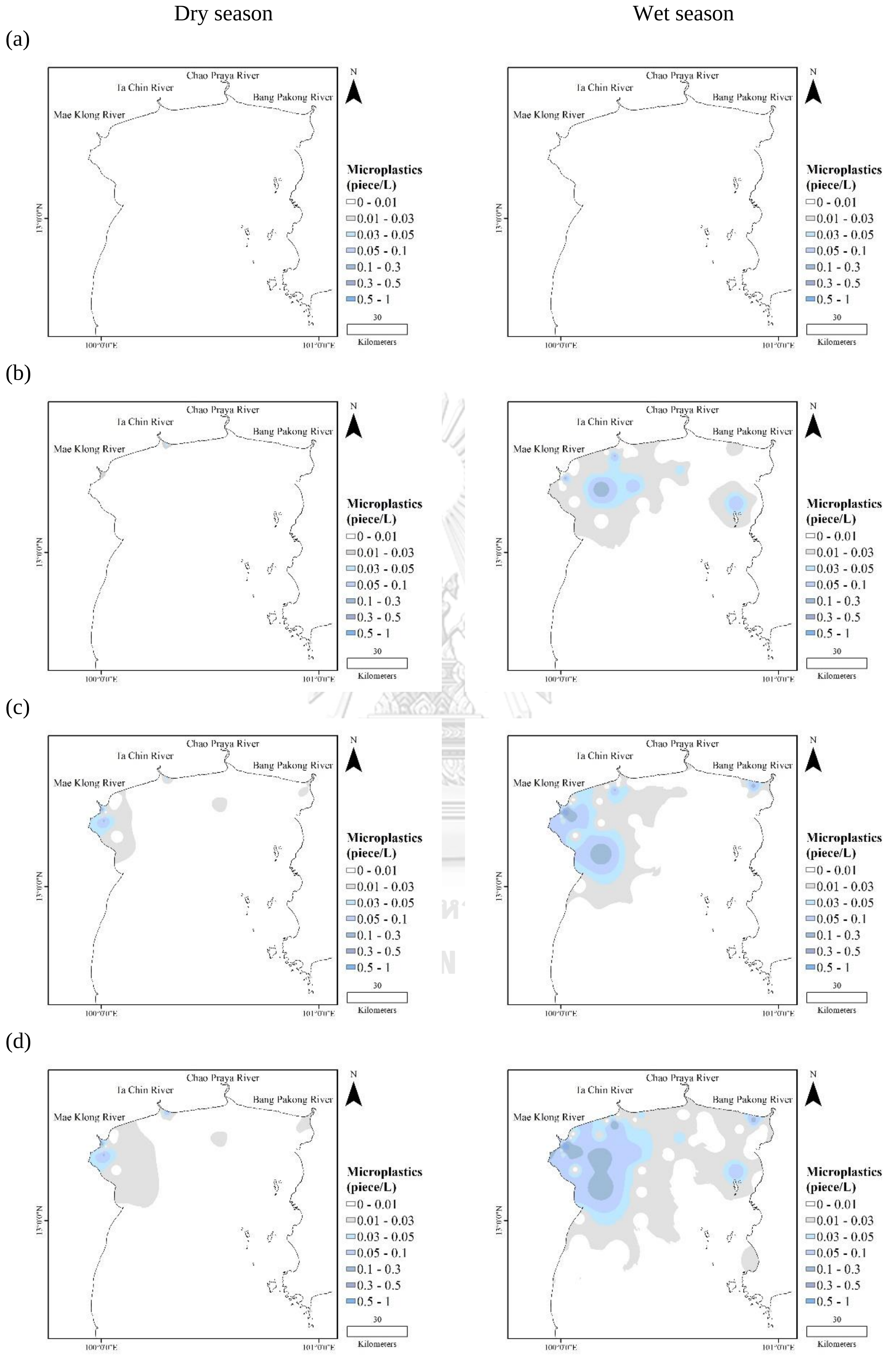
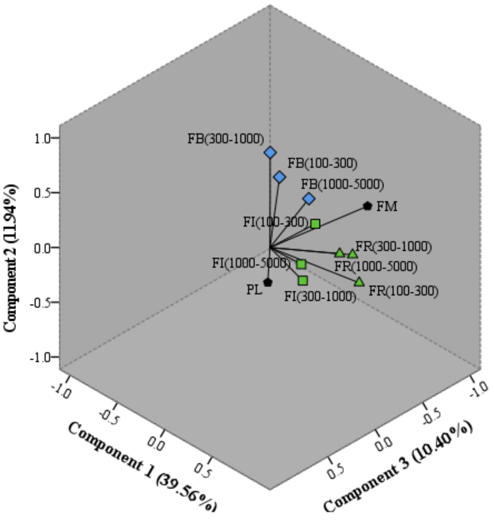


Figure 3.21 Distributions of foam-microplastics in surface water: (a) 1000-5000 µm, (b) 300-1000 µm, (c) 100-300 µm and (d) total foam microplastics

The distribution plot of MPs suggested that the different characteristics of MPs from the sources were transported in water. Addtion to the oxidative funtional groups, physical characteristics of MPs including size, shape, and color were physically observed that showed the results of plastic fragmentation. Principle Component Analysis (Figure 3.22) proposed that distribution of MPs in surface water were categorized to three components with a 61.90% cumulative percentage of variance: (1) Broken plastics (fragment and film), (2) Filamentous plastics (fiber), and (3) Smooth and spongy surface plastics (pellet and foam). The broken plasticles, can be categorized to be secondary MPs. The filamentous particles was possible to be generated from fibrous material through either fragmentation or production. While the new and non-fragmented plastics (primary MPs) could be represented by smooth surface, the third component may sourced from the specific activities generated in certain areas because it was not only a group of pellet-MPs but also included the foam-MPs. The sources of the debris and their weathering process may affect the difference in the physical characteristics of MPs. In the other side, the different characteristics of MPs from the sources were transported in water and they were related to hydro-ecological parameters.



Shape	Size (µm)	Component*		
		1 (🟢)	2 (🔵)	3 (●)
FR	100-300	**.824**	.028	-.118
FR	300-1000	**.779**	.272	-.094
FR	1000-5000	**.696**	.267	-.040
FI	1000-5000	**.605**	.283	.275
FI	300-1000	**.600**	.120	.253
FI	100-300	**.536**	.509	.056
FB	300-1000	.036	**.902**	.034
FB	100-300	.209	**.800**	.108
FB	1000-5000	.407	**.646**	-.003
FM	100-5000	.122	-.012	**-.909**
PL	100-5000	.439	.127	**.463**

*Cumulative percentage of variance = 61.90%

Figure 3.22 Component plot and rotated component matrix of factor loading for microplastic shape and size

3.3.3 Influence of seasonal variation on contamination of microplastics

The main difference between the dry and wet seasons of the inner Gulf of Thailand was the freshwater inflow from the rivers. It is normally to accepted that the rainfall in the wet season enhanced the volume of freshwater. Amount of freshwater loaded from the estuaries to the gulf in the wet season was amplified approximately double in the Ta Chin River estuary and seven to eight times in the Chao Phraya River and the Bang Pakong River estuaries as compared to the dry season (Table 3.3). Addition to the spatial distribution plot, riverine transportation of MPs from the land to the sea was confirmed by the abundance of MPs that was directly magnified by the increasing of freshwater load during rainfall in the wet season.

The observation of this investigation was similar with the results mostly reported in previous studies that the increases in precipitation and discharged water in the wet season regulated the high abundance of MPs in surface water [10, 36, 37, 42, 108, 122]. However, more contamination of MPs in water caused by sediment resuspension also be discussed [36]. Moreover, mechanical breakdowns induced by strong winds at the end of the hurricane season might rise the fragmentation of plastics, and that might result to increasing in amount of MPs [19]. In contrast, no significant change in MP abundance before and after typhoons was discussed that magnified water volume and vertical mixing could reduce the plasticles from the surface water [75]. In some study, the MPs was also suggested they were contaminated from non-seasonal event parameters, for example, the discharged leachate or heavy air pollution [43]. The other parameters besides river flow were believed that they could affect abundance of MPs [13].

Table 3.3 Average runoff water, average residence time, and average one-day-loaded water from the river estuaries to the inner Gulf of Thailand [58]

River estuaries	Average runoff water (m^3/s)		Average residence time (day)		Average water loading to the inner Gulf of Thailand ($x10^3$ m^3/day)	
	Dry	Wet	Dry	Wet	Dry	Wet
Mae Klong	753.15	369.75	2.96	3.00	21996	10649
Ta Chin	180.50	174.00	2.96	1.21	5272	12442
Chao Phraya	160.13	417.39	2.96	0.96	4677	37630
Bang Pakong	80.31	222.26	1.50	0.58	4626	32920

This study revealed the relationships between the investigated hydro-ecological parameters and the abundance of MPs (total MPs and the categorized MPs according to PCA classification (Table 3.4). It could be proposed the viewpoint for the coordinate releasing of MPs and the other parameters. The salinity, TSS, and nutrients (nitrogen, phosphorus, and silicon) were the indicators of the river runoff, as low salinity, high TSS, and concentrated nutrients were investigated in the river estuaries. The statement of the river transported MPs or plastic waste from the upper area of the gulf to the study area could be confirmed by the significantly negative relationship between MPs and salinity, as well as the positive relationship between MPs and nutrients. The evident was clearly illustrated in the broken plastics or the component of film- and fragment-MPs, with the significant correlation coefficient at the 0.01 level (99% confidence). However, no significant relation between filamentous plastics and salinity was presented, although the relationships of filamentous plastics and some nutrients were significant. These relations supported the idea that the fibers were generated from both riverine and marine activities, following the distribution maps of fiber-MPs (Figure 3.19). Inversely, the smooth and spongy surfaces plastics were not significantly related to any of the considered factors; as a results, it could be inferred that the sources of this components were possible to be the coast, river estuaries, or others.

Table 3.4 Pearson's correlation between environmental parameters and categorized microplastics

Parameter	Total MPs	Broken MPs	Filament MPs	Smooth-spongy MPs
Sal	0.093	-0.365**	-0.029	-0.008
DO	-0.199*	-0.453**	-0.372**	-0.061
TSS	0.062	0.455**	0.426**	-0.069
NH_4^+-N	0.017	0.600**	0.293*	0.178
NO_3^--N	-0.132	0.366**	0.205	0.053
DIN	-0.032	0.558**	0.266	0.150
$Si(OH)_4$-Si	-0.097	0.439**	0.198	-0.128
TDP	-0.234	-0.137	-0.174	-0.184
TPP	0.005	0.076	0.083	-0.310
TP	-0.262	-0.122	-0.286	-0.100
PO_4^{3-}-P	-0.079	0.474**	0.286*	0.098
Chl	0.014	0.242	0.272	-0.047
AP	0.077	0.061	0.241	0.100
AFL	0.189*	0.281	0.148	0.120

** Correlation is significant at the 0.01 level (2-tailed).
* Correlation is significant at the 0.05 level (2-tailed).

The chemical transformation and the microbial activities on the surface of MPs may indirectly shape the water quality. The relationship between MPs, nutrients, and dissolved oxygen (DO) were the case for example. The oxygen consisted of C−O bonds, which are the new functional groups in the MPs' chemical structures, thus it usually contributed in the oxidation process of plastic polymer [118]. The photo-chemical oxidation also resulted in dissolved organic carbon from plastics. Furthermore, the bioassay found the rapidly bioavailable carbon that released from plastics [124]. As result of DO reducing by the activated bacterial metabolism, the microcosm experiment confirmed microorganism on the surface of MPs could release nutrient and it also consumed oxygen from the environment [125]. The suggested idea was that the microbial activity and oxidation process on MPs indirectly regulated the negative relationship between MPs and DO indirectly. This interaction of

MPs-microbials might be implied by the inverse relations with DO for total MPs, broken plastics, and filamentous plastics. In the case of smooth, spongy plastics, the non-significant relationship between DO and MPs is probable to be indicated less biofouling or new plastics, in the other words. It is important to note that the MPs and physicochemical factors from field investigation were included the effects of co-released substances and the effects of the substances induced by MPs. Both pollution releasing sources and the simulated activities of MPs could influence the relationship between MPs and hydro-ecological parameters. The study could recommend that the season induced the difference in hydro-ecological characteristics, and it also regulated the variation in MPs contamination.

3.4 Summary of microplastic contamination in surface seawater

The effects of seasonal variations on the contamination of MPs in surface water of the inner Gulf of Thailand were investigated. The physical and chemical properties of plastic materials were transformed and fragmented to be MPs. The detected MPs in the water samples were classified into three groups: 1) broken plastics, 2) filamentous plastics, and 3) smooth and spongy surface plastics. While PP and PE were the most plastic types observed in the sample, the oxidative functional groups, indicators of polymer weathering, also be observed in the polymeric structures. Oxidative indexes, or the degree of weathering, depended on the shape of MPs suggested the oxidation characteristics varied different physical movement. Qualification, quantification, and the relationship with hydrological parameters suggested that rivers and surface current were the main regulated factors resulted MPs transportation. Diversity and quantity of MPs in surface water posed to be directly varied by freshwater runoff, as they were increased in wet season. The shape of MPs combined with the environmental factors were discussed that they regulated the distribution pattern and the interaction of MPs. It is reasonable to say that the MPs in surface water will be vertically moved and settle to accumulation in the sediment system. The physicochemical transformation and environmental interaction of MPs need to be understanded for answer the concern about ecological impacts of them.

CHAPTER IV

ACCUMULATION OF MICROPLASTICS IN SURFACE SEDIMENT AND CO-CONTAMINATION OF HEAVY METALS IN MICROPLASTICS

Emerging pollutants of microplastics, less than 5 mm plastic particles, were ubiquitously contaminated in various media of the environment. While the microplastics were observed in surface waters of the inner Gulf of Thailand, the accumulation of them in sediment of the river estuaries and the coastal sea was investigated in this section. The results found abundance of microplastics in range of 1284-22752 pieces/kg of dry weight sediment. While high contamination was detected in estuaries, wet season influenced microplastics more dispersed to accumulated in the coastal sea sediment. Polyamide and poly (acrylonitrile: butadiene) were the main plastic type observed in sediment. Accumulation of microplastics directly reversed by depth of sediment. The analysis of contamination of heavy metals (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn) in microplastics revealed they were mainly consisted in the fouling content. High concentrations of the heavy metals were investigated in microplastics; however, those were the small faction in the total mass of sediments.

4.1 Importance of microplastic accumulation in sedimentological system

The microplastics (MPs), plastic particle smaller than 5 mm, is contaminated in everywhere. The chapter III illustrates the clear evident and the specific characteristics of MPs contamination in the surface seawater. It is general to accepted that MPs in surface water will be settled to the sea bottom. Thus, the sedimentological system is finally enriched microplastics, and it is the sink of plastic pollution.

The gravimetrical density of MPs is the main factor discussed it is affected MPs vertically transported in water column and sedimented to the seabed. Based on sea water density (1.02-1.03 g/cm^3), the plastics that have higher density than seawater theoretically submerge in water column and settled to the sediment, while the plastics that have lower density than seawater should float on the surface sea. However, the light plastics could be deposited by the adherence aggregation. The experiment found formation of biofilm was observed on submerged PE after submerged it into surface seawater [63]. The aggregation of MPs and suspended sediments induced negative buoyant of MPs-sediment matrix [111, 112]. The interaction between MPs and phytoplankton also affected the density of MPs as the phytoplankton was aggregated with MPs by extracellular polysaccharides [81, 82]. The adhesion on coral surface was pointed as a major role of the settling of MPs [126]. Addition to the attachment of MPs, shape, size, and mechanical properties of them were controlled the buoyancy, and those resulted to the settling of MPs [80, 113, 114]. Followed the concept of substance attachment on MPs, the effects did not only induce the vertical transportation and sedimentation of MPs, but it also be that either fouling on MPs or plastic content of MPs could accumulate pollutants from the environment.

The analysis of contamination in MPs confirmed that MPs could accumulate toxic substances. The sorption experiments, either in situ or ex situ, and the investigation found the substances surrounding MP were adsorbed to the plasticles [69, 72, 90-94, 105, 127, 128]. By field investigations, the hazard elements, Br, Cd, Cr, F, and Pb for example, were detected in plastic composition [65-68, 70, 71, 73]. Parallelly, the analysis also found the contamination of persistent organic pollutants in plastic debris [86-89]. The extraction by synthetic digestive fluid showed the releasing of heavy metals from plastics [65, 67, 68, 129]. Previous research could support the statement that heavy metals and organic persistent pollutants were consisted in plastic particles, and those are possible to be released.

According to MPs characteristics in surface water, it is possible to said that MPs contamination in sediment may related with the shape of plastics, adhesion aggregation, as well as the pollutant accumulation. In this research, the accumulation of MPs in surface sediment of the inner GT and the contamination of heavy metals in MPs were investigated. The effects of dry and wet seasons were analyzed with the hypothesis that the MPs were trapped in estuaries, and the river runoff which in wet season affected high contamination and more variation of MPs in sediment.

4.2 Analysis of microplastics contamination in sediment

4.2.1 Sediment sampling

Surface sediments (0-5 cm) were collected from the area of the inner Gulf of Thailand in dry season (May 2018) and wet season (August 2018). The sampling sites were included the river estuaries (Mae Klong (MK), Ta Chin (TC), Chao Phraya (CP), and Bang Pakong (BK)) and the coastal sea of the inner Gulf of Thailand (GT) (Figure 4.1). Ekman grab sampler and Smith McIntyre grab sampler were used to collect sediments from the sampling sites. Approximate 0.5-1 kg of sediments from grab samplers were sampled by scooping to clean PE storage bag and sealed to vacuum. Addition to surface sediment collection, sediment profile was sampled from station GT26 in dry season. The sediment layers classified to 0-5, 5-10, 10-15, 15-20, 20-25, 25-30, 30-35, and 35-40 cm were taken by vertical gravity core sampler. All of samples were kept in cold and dark before analysis.

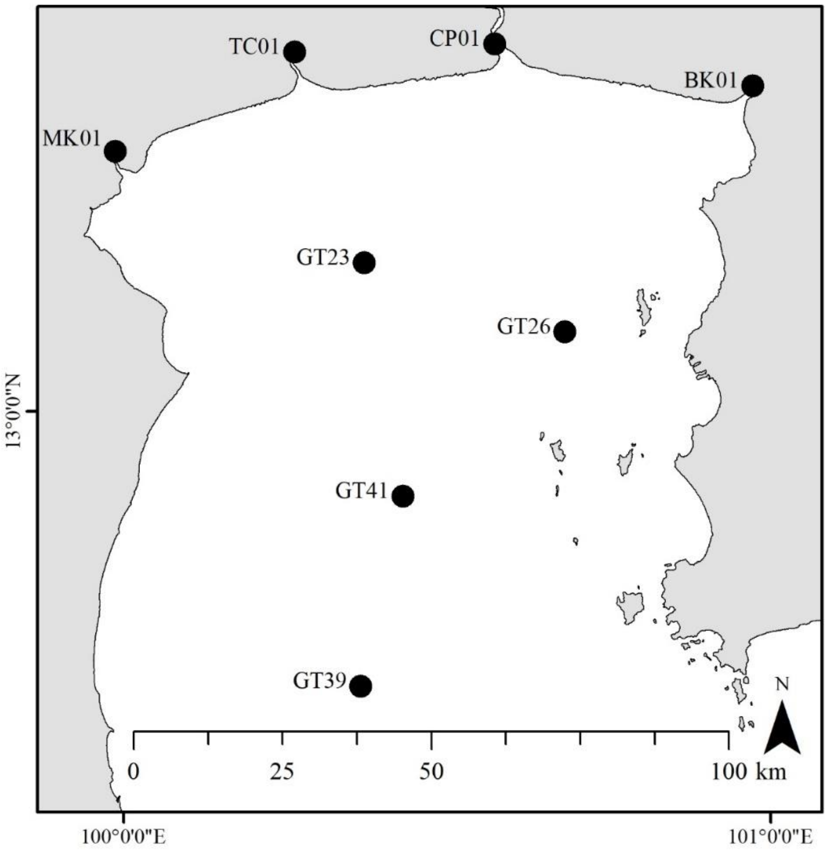


Figure 4.1 Sediment sampling stations of the inner Gulf of Thailand

4.2.2 Microplastics quantification

The MPs analysis procedure was applied from laboratory method for analysis of MPs in the marine environment: recommendations for quantifying synthetic particles in water and sediment [59].

1) *Microplastics separation*

Nearly 100 g of wet sediments was placed to aluminum containers and oven dried at 60°C. The dried weight (DW) of sediments were measured, after that the samples were disaggregated by mixing with 5% Calgon solution (the solution of $Na_6P_6O_{18}$ and Na_2CO_3). Then, heterogenous particles were sieved for the size 16-5000 μm, and those were mixed with saturated NaCl solution. Amounts of sediment samples for MPs analysis were reduced by using the supernatant solids in NaCl solution. Finally, the collected solids were treated by WPO and NaCl density separation as same as water samples. The separated MPs with NaCl solution were placed in test tubes and rap with aluminum foil.

2) *Characterization and quantification of microplastics*

The MPs were filtered on Aluminum oxide (Al_2O_3) membrane filter with the pore size of 0.2 µm (Anodisc^{TM} 25, Whatman). Amounts of particle was counted under stereo microscope (Shodensha, NSZ-405J3) for shape and color categorization. Similar with the contamination in water samples (Chapter III), the shapes were categorized to fiber, film, foam, fragment, and pellet, while the colors were included red, blue, green, brown, black, white, transparent, and the other. The samples were air dried and stored in desiccator. The microplastics on filters were quantified by find particle and mapping technic of microscopic Fourier-transform Infrared spectrophotometer, micro-FTIR (Bruker, Lumos II). In short detail, all particles-like on Al_2O_3 filter were positioned by image and qualified with transmission mode of FTIR. While the size of particle was investigated by the contrast of the image, the resulted spectrums were identified for the chemical compounds by compare with the reference data bases. The MPs were counted by the number of the spectrums that confirmed to by plastics with higher than 60% of the similarity due to the comparison of plastic polymer reference spectrum. Only particles that confirmed to be plastics were reported as the abundance of MPs in the unit of plastic pieces per weigh of dried sediment (pieces/kg DW).

3) *Quality control analysis*

The sample were stored and analyzed follow the controlled container for preventing plastic contamination. The new plastic bags were considered to use in sample collection and those were storage in cool and dark condition for minimized the fragmentation process. During the analysis, non-plastic containers were used, additionally the containers were covered with aluminum foil to reduce the contact of airborne plastics.

Importantly, the blank sediments were tested follow the MPs separation by using the settle sediments in NaCl solution. Accordingly, the commercial grade of green polyethylene (106-212 μm) was spiked to the blank sediment and analyzed as the sediment sample; 94.55±17.14% of spiked plastics was recovered. In principle, the blank sediment should be not contaminated with MPs because the plastics were removed by the density of NaCl solution. However, it is accepted to note that the detected plastic in blank sediments may be the result of separation efficiency. Thus, the report of MPs abundance was normalized by the number of each size and polymer types of plastics in blank sediments.

4.2.3 Environmental variable analysis

The abundance of MPs in sediments of estuaries and coastal sea in the details of physicochemical characteristic were comparatively analyzed with the contamination in surface water. The sedimental variables of the investigation period, including heavy metals and nutrients, of the sampling site were analyzed with standard methods (Table 4.1). the relation of those parameters and MPs were evaluated by Pearson’s correlation coefficient.

Table 4.1 Analysis of heavy metal contamination and sedimentological parameters in the surface sediment

Parameters	Analytical methods
Cadmium (Cd, mg/kg DW) [130]	Hydrofluoric acid and aqua regia digestion in high performance microwave digester, detected by inductively couple plasma optical emission spectroscopy
Lead (Pb, mg/kg DW) [130]	
Copper (Cu, mg/kg DW) [130]	
Cobalt (Co, mg/kg DW) [130]	
Nickel (Ni, mg/kg DW) [130]	
Manganese (Mn, mg/kg DW) [130]	
Zine (Zn, mg/kg DW) [130]	
Aluminum (Al, mg/kg DW) [130]	
Chromium (Cr, mg/kg DW) [131]	Hydrofluoric acid and aqua regia digestion in high performance microwave digester, detected by flame atomic absorption spectrophotometer
Total organic matter (TOM, %) [130]	Loss of ignition process
Total organic carbon (TOC, mg/kg DW) [130]	Total organic carbon analyzer
Total phosphorus (TP, mg/kg DW) [130]	Acid molybdate-ascorbic method
Acid volatile sulfide (AVS, mg/kg DW) [130]	Colorimetric gas detection tubes
Water content (%) [130]	Gravimetrical analysis

4.2.4 Microplastics contamination analysis

The MPs were classified to the plastics content and the fouling content. After dry sediments were weighed, those were mixed with 5% Calgon solution for disaggregation. The particles in the samples were sieved to the size of 16-5000 µm. MPs were separated from heterogenous solid particles by density of NaCl solution. The fouling contents on plastic particles were extracted by ultra-sonication (BANDELIN, SONOPLUS UW 2070). After that, the fouling contents were separated from plastics content by NaCl solution and filtered on pre-weighted glass fiber filter (Whatman GF/C). The fouling contents were gravimetrical quantified. While the plastic contents were filtrated on Aluminum oxide (Al_2O_4) membrane filter (Anodisc^{TM} 25, Whatman), the plastic polymer were identified by microscopic Fourier-transform infrared spectrophotometer, micro-FTIR (BRUKER, LUMOS II) follow the procedure of MPs quantification.

The fouling contents and plastic contents were acid digested by aqua regia (HNO_3:HCl 3:1) in high performance microwave digestion system (MILESTONE, ETHOS One). HNOs (69%, QReC) and HCl (37%, QReC) were used for preparing the aqua regia, while the 18 mΩ-ultrapure water was performed for sample dilution. The sample solutions were filtrated pass 0.45 µm of cellulose acetate disposable membrane filter (ADVANTEC, DISMIC-25CS). The contaminations of heavy metals (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn) in both fouling contents and plastic contents were investigated by inductive couple plasma optical emission spectrophotometer, ICP-OES (Analytikjena, PlasmaQuant PQ 9000 Elite) and atomic absorption spectrophotometer, AAS (Agilent, 240AA). All glassware were deeply cleaned by acid wash and rinsed with deionized water. The heavy metal contamination of the samples was neutralized by the concentration detected in blank filter for fouling contents and blank sediment for plastic contents.

4.3 Accumulation of microplastics in sediment

4.3.1 Abundance of microplastics

The contamination of MPs was clearly observed in the sediment of the inner GT! Figure 4.2 illustrates difference shapes of MPs detected in the surface sediment of the inner GT. The abundance of total MPs, all shape and size of MPs contaminated in sediment, was range from 1284-22752 pieces/kg DW (average 9757±6813 pieces/kg DW). Overall, the abundance of MPs of the study area was enhanced from 7297±5960 pieces/kg DW in dry season to 12216±7079 pieces/kg DW in wet season. In detail, the abundance in the estuaries was increased from 4355 pieces/kg DW in dry season to 8216 pieces/kg DW in wet season, while that in the coastal sea was dramatically enhanced from 1200 pieces/kg DW in dry season to 6118 pieces/kg DW in wet season (Figure 4.3). There was a significance to confirm that this investigation illustrates the confidential abundance of MPs although it is higher than the other area.

Table 4.2 shows the comparative value of the contaminated MPs in surface sediment. The abundance of MPs according to the detection of this study was in the level of very high contamination compared with the other areas. The quantification methods were mainly influenced to the abundance of MPs, addition to the limitation in detected sizes and density of separated solutions. Although the most study presented the abundance of MPs by detection of microscopic count with the examination of particles to plastic identifications, the quantitation of MPs for FTIR identification each particle may result more accurate of the abundance of MPs, as it could defined chemical structure of each particle. The literature review (Table 4.2) illustrated that the quantification by FTIR identification results higher abundance of MPs than that by microscopic count. Addition to the identification methods, the size of detectable MPs also affected to the abundance. More abundance posed to be reported when the detected size was smaller than 100 µm.

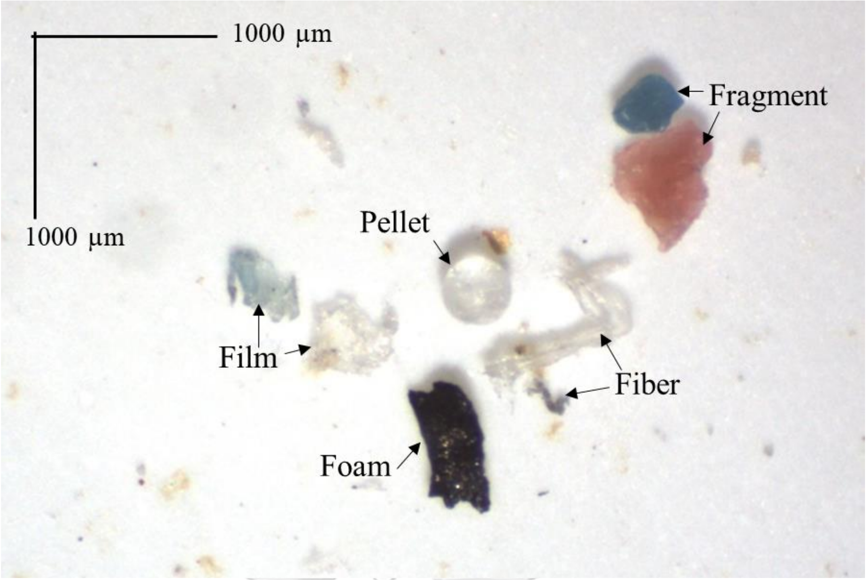
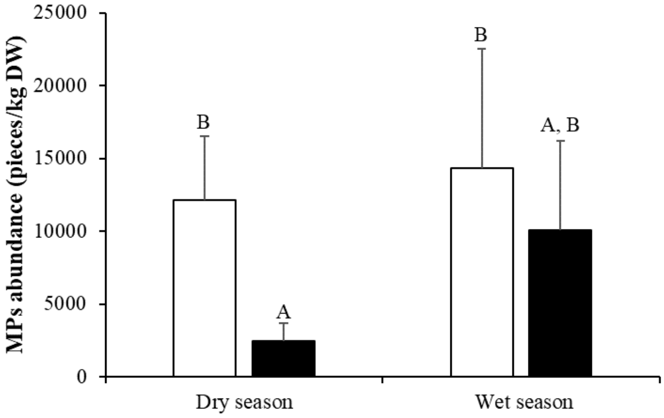


Figure 4.2 Microplastics in surface sediment of the inner Gulf of Thailand



* A and B show the statistically significant at the confidence level of 95% (p=0.05)

Figure 4.3 Average microplastics abundance in sediment of river estuaries (☐) and coastal sea (■) of the inner Gulf of Thailand

Table 4.2 The comparison of microplastics abundance in surface sediments

Contamination area	Solution for density separation	Quantification	Abundance (pieces/kg DW)	Minimum size (µm)
Bay of Breast, France [4]	NaCl and Na_2WO_4	Visual sort and Raman identification	0.97	Not report
North Yellow Sea, China [5]	NaI and NaCl	Microscopic count	37	30
Ciwalengke River, Indonesia [6]	NaCl	Microscopic count	30.3	50
Baltic sediment, Russia [11]	ZnCl2	Microscopic count	34	175
Coastal mangroves, Singapore [22]	NaCl	Microscopic count	36.8	Not report
Tapi-Phumduang River, Bandon Bay, Thailand [24]	NaCl	Microscopic count	79*	Not report
Chao Phraya River, Thailand [25]	NaI	Microscopic count	91	50
Changjiang Estuary, China [26]	NaCl	Microscopic count	120	1
Urban estuary in Gulf of Mexico, Mexico [19]	$ZnCl_2$	Microscopic count	121	Not report
Bloukrans River, South Africa [33]	NaCl	Microscopic count	160.1*	Not report
Bohai sea, China [14]	NaCl and $ZnCl_2$	Microscopic count	256.3*	20
Tampa Bay, USA [20]	NaI	Microscopic count	280	Not report
Bang Yai canal, Phuket, Thailand [35]	NaCl	Microscopic count	450*	Not report

* The highest abundance of MPs of the investigation

Table 4.2 The comparison of microplastics abundance in surface sediments (continuous)

Contamination area	Solution for density separation	Quantification	Abundance (pieces/kg DW)	Minimum size (µm)
Iceland shelf [2]	Deionized water	Microscopic count	768*	63
Guanabara Bay, Brazil [9]	NaCl	Microscopic count	528*	15
Mediterranean Sea [16]	Distilled water	Microscopic count	900*	63
Straights of Johor, Malaysia [17]	NaI	FTIR identification	300*	315
Belgian coast, Belgium [29]	NaCl	FTIR microscope	390	38
The southern North Sea [30]	ZnCl2	FTIR identification	1188.8*	11
Durban Bay (South Africa) [17]	NaI	FTIR identification	1900*	315
HAUSGARTEN, Arctic [31]	ZnCl2	FTIR microscope	4356	11
Sakurada-bori Moat at the Imperial Palace in Tokyo, Japan [17]	NaI	FTIR identification	7228*	315
Amsterdam canal, the Netherlands [34]	NaCl	FTIR microscope	10500*	10
the Gulf of Thailand, 2004 [17]	NaI	FTIR identification	328*	315
The Gulf of Thailand, 2010-2011 [41]	NaCl	Microscopic count	150.4	100
The inner Gulf of Thailand, 2018 (This study)	NaCl	FTIR identification	9757	16

* The highest abundance of MPs of the investigation

4.3.2 Characteristics of microplastics

The abundance of MPs, or the total MPs, was presented to the summation of MPs with variety physical and chemical characteristics. Figure 4.4 presents the overall detail of characteristics of MPs in dry and wet seasons. While the film was the major shape of MPs in dry season, the proportions of fiber and fragment were increased in wet season. The new MPs, inferred by the colors of red, green, blue, white, and transparent, pose to be reduced according to the influences of wet season. The size composition of MPs in both seasons was similar with the most detected MPs were in the size of 16-100 µm; however, the MPs in size of 300-5000 µm were enhanced in dry season. The plastic types of polyamide (PA), polypropylene (PP), polyethylene (PE), poly (acrylonitrile: butadiene), acrylate ethylene copolymer (AEM), poly (alkyl methacrylate) and polystyrene (PS) were identified for MPs accounting 74%, and 79% of all detected plastics in dry and wet seasons, respectively. The other types of plastics were included polycyclohexanone, polyester, and ethylene butyl acrylate copolymer, for example. The proportion of PA was enlarged from 12% in dry season to 64% in wet season. As the number of total MPs was significantly difference between area and season, shape, color, size, and plastic type of plasticles may result the specific in the sedimental accumulation of MPs although there was not statistical difference between seasons (*p*=0.415) and settled areas (*p*=0.871).

1) Shape, color, and size

Similar with the shape of MPs in surface water (Chapter III), film, fiber, and fragment were the dominant shape of MPs observed in the surface sediment, while the pellet and foam were mostly found in the river estuaries (Figure 4.5). Accumulation of fiber-MPs in sediment tend to be increased in wet season parallel to the contamination in surface water. In addition, the fragment-MPs also be raised in wet season of estuaries.

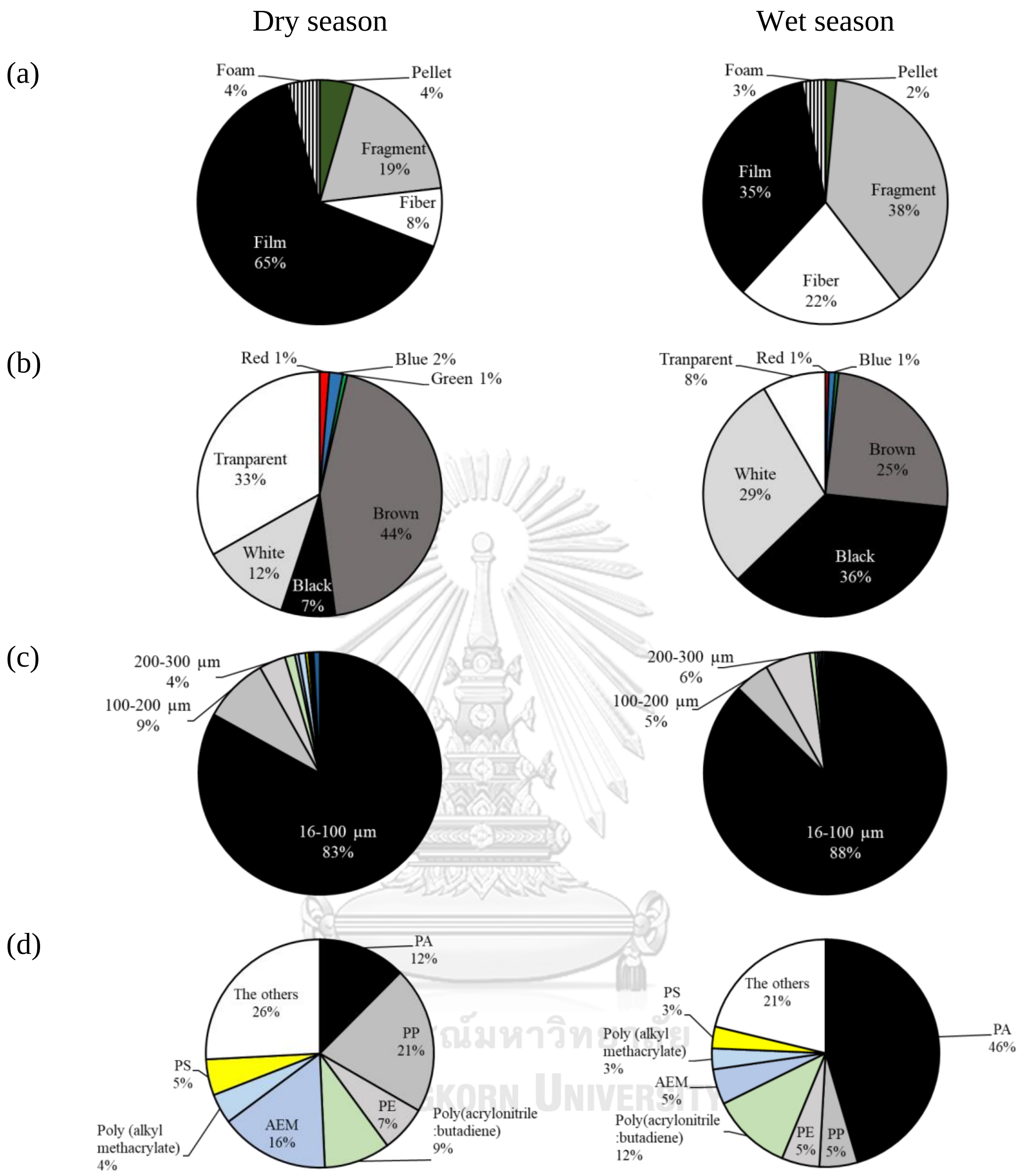
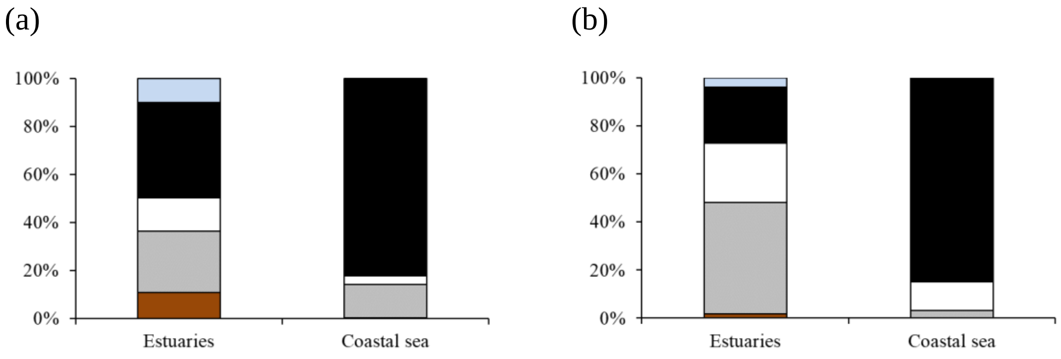


Figure 4.4 Proportions of shape (a), color (b), size (c), and plastic type (d) of microplastics in surface sediments in dry season and wet season

Informationally, the major colors of MPs in surface sediment (49-62 %) were back and brown (Figure 4.6). The investigation showed that back and brown fraction were magnified in wet season whereas the fraction of transparent-MPs in surface water was increased in wet season. The colorful MPs (red, blue, and green) in both surface water and surface sediment were likely to be more detected in the estuaries, however. In contrast with the surface water, the enhanced fraction of brown and back colors of MPs, inferred to aged MPs in wet season could be discussed that the high riverine runoff in wet season may interrupt MPs sedimentation.

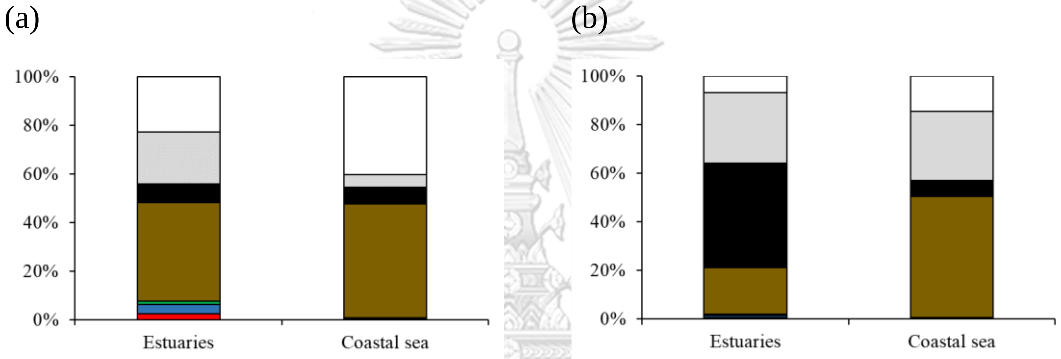
The shapes, and colors of MPs in the estuarine sediment were more variety than that in the sediment of coastal sea dissimilar with the size of MPs. The detected MPs was dominant in the size of 16-100 µm that accounted for 81-88% in estuaries and 86-93% in coastal sea (Figure 4.7). The small fraction of MPs was distributed in the range 100-1000 µm in both river estuaries and coastal sea, while larger size MPs (>1000 µm) mostly be observed in the estuaries. The dynamic variation from wet season probably reduced the proportion of large MPs in the size of 100-5000 µm though the proportion of MPs in size of 200-300 µm was increased in the coastal sea, especially in GT26. It is important to note that the size of MPs contaminated in sediment of this investigation is smaller than the size of MPs in surface water. The results of both surface water and surface sediment could be referred that the size of most detected MPs was less than 300 µm. Interestingly, the fraction of large size MPs in sediment was reduced in wet season, while that in surface water was enlarged. This observation may represent the small MPs likely trend to be formed with natural solids and sedimented rather than large MPs that may be transported to other area by water current.

The investigation of shape, size, and color of MPs suggested the river runoff water and turbulation in water column might be regulating factors for MPs movement from surface water to sediment. The contaminations of MPs in both water and sediment were enlarged by increased surface runoff. The composition of MPs in water may link to that in sediment by the reason that MPs were firstly released to the hydrosphere. By the small size of plasticles, the MPs could be aggregated with the other suspended solids and sunk to the sea bottom. However, new MPs with large size pose to be floated on water and transported by the dynamic current. The buoyancy of different shapes was pointed that it influenced the sinking rate of MPs [114]. The sedimentation of MPs also be additionally controlled by the density of plastics themself.



(🟫) Pellet, (▨) Fragment, (□) Fiber, (■) Film, and (🟦) Foam

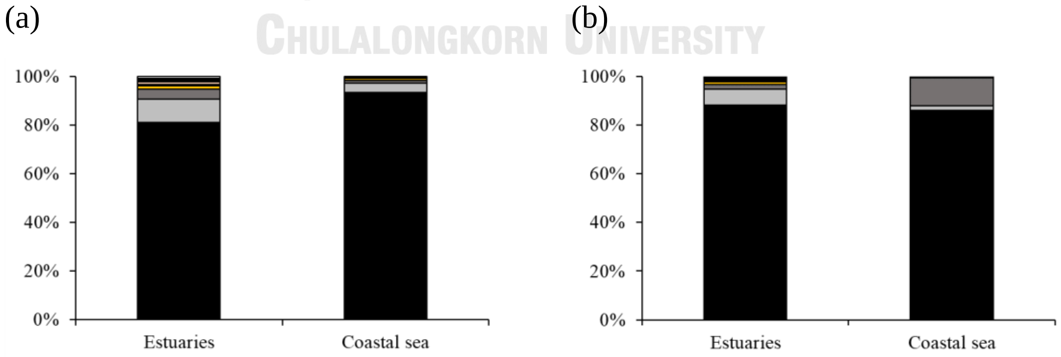
Figure 4.5 Shape composition of microplastics in surface sediment of dry season (a) and wet season (b)



(🟥) Red, (🟦) Blue, (🟩) Green, (🟫) Brown, (■) Black,

(▨) White, and (□) Transparent

Figure 4.6 Color composition of microplastics in surface sediment of dry season (a) and wet season (b)



(■) 16-100 µm, (▨) 100-200 µm, (▨) 200-300 µm, (🟧) 300-400 µm,

(▨) 400-500 µm, (🟧) 500-600 µm, (▨) 600-700 µm, (🟦) 700-800 µm,

(🟨)800-900 µm, (🟦) 900-1000 µm, and (□) >1000 µm

Figure 4.7 Size composition of microplastics in surface sediment of dry season (a) and wet season (b)

2) Plastic types

Polyamide (PA), polypropylene (PP), and polyethylene (PE) were observed in the composition of plastic types in the surface sediment of all sampling station (Figure 4.8). The plastic type composition of MPs accumulated in sediment related to the seasons and contaminated areas; moreover, it was clearly different from that in surface water.

PA was the predominant plastic in sediment in wet season accounted for 40% in estuaries and 54% in coastal sea. The plastic types of PP, PE, poly (acrylonitrile: butadiene), acrylate ethylene copolymer (AEM), poly (alkyl methacrylate) and polystyrene (PS) tend to be more accumulated in estuarine sediments, and those fractions were increased in dry season. According to density of sea water (1.02-1.03 g/cm^3), it is common to observed that the plastics that have density higher than sea water density, PA (1.02-1.05g/cm^3) and poly (acrylonitrile: butadiene) (1.06-1.08 g/cm^3), for example. However, PE (0.88-0.96 g/cm^3) and PP (0.855-0.946 g/cm^3), the dominant plastic types in surface water having lower density than seawater also be detected in the sediment samples. The results of high abundance of MPs in estuaries sediment and high portion of MPs with lower density compared to seawater could suggest that the estuarine geological characteristics influence MPs co-aggregrated with suspended solids and settling to the seafloor. Additionally, the detected low density plastic types may link to the polymer production. For example, the composite materials, $CaCO_3$ filler in PP structure, may resulted MPs vertically transported to the sediment due to the density of $CaCO_3$. According to FTIR analysis, the settling of plastic composite with $CaCO_3$ in sediment were indicated by the spectrum of $CaCO_3$ in the samples although the samples were washed with 1 HCl before analysis. Importantly, it must be noted that the detected MPs was not included the PTFE (2.2 g/cm^3), that was the component of MPs in water samples, because the characteristic peaks of it was interfered by the spectrum Al_2O_3. The analysis of MPs (>500 µm) by FTIR with attenuated total reflection (ATR) detected PTFE in the sediment of Arctic deep-sea sediment; however, the smaller MPs also cannot be identified as it was a limitation of the analysis [31]. It could be appropriated to accepted that PTFE were settle to the seabed, but the this may be less impact as its monomer was not classified in the hazard classification of the UN Globally Harmonized System (GHS) [8]. The sedimentation of MPs was discussed that it was influenced by the specific density of plastic polymers and the aggregation of surrounding substances. In the other word, the physical and chemical properties of MPs, modified by natural induced process, resulted dynamic in fate and transportation of MPs.

The oxidative functional groups were observed in the plastic chemical structures of MPs in sediment, PA, PE, and PP, for example of plastic that detected in all sample (Figure 4.9). As the structure of alkane hydrocarbon of PA, PP and PE, the peaks at wavenumber of 3000-2840 cm^{-1} for C-H stretching. The amide structure of PA was indicated by N-H strectching at 3250-3310 cm^{-1} and C=O streching at 1650 cm^{-1}. The wavenumbers of 1450 cm^{-1} and 1375 cm^{-1} for $-CH_3$ bending indicate the structure of PP, while wave numbers of 1460-1450 cm^{-1} for $-CH_2$ bending was presented to PE structure. The new functional groups were observed additionally from the raw plastic structure. A broad peak of O-H stretching at 3200-3500 cm^{-1} was clearly detected in PA spectrum, while it was the weak peaks in the spectrum PP and PE. The oxidized groups of C=O stretching at 1700-1740 cm^{-1} was found in all exampled spectrum of PA, PP, and PE while that of the weak peaks of C=C or C=O stretching at 1680-1625 cm^{-1} could be refered only in the spectrums of PE and PP. The functional groups of MPs confirmed the transformation of plastic structure; as a result, the properties of MPs were modified.

The accumulation of various types of MPs including seawater-higher density plastics and seawater-lower density plastics confirmed that the sediment is the susceptible system for MPs settling in the marine ecosystem. The dynamic environment variables may cause the transformation of MPs physical and chemical structures. Then, MPs were induced to be settled from the surface water to the seafloor.

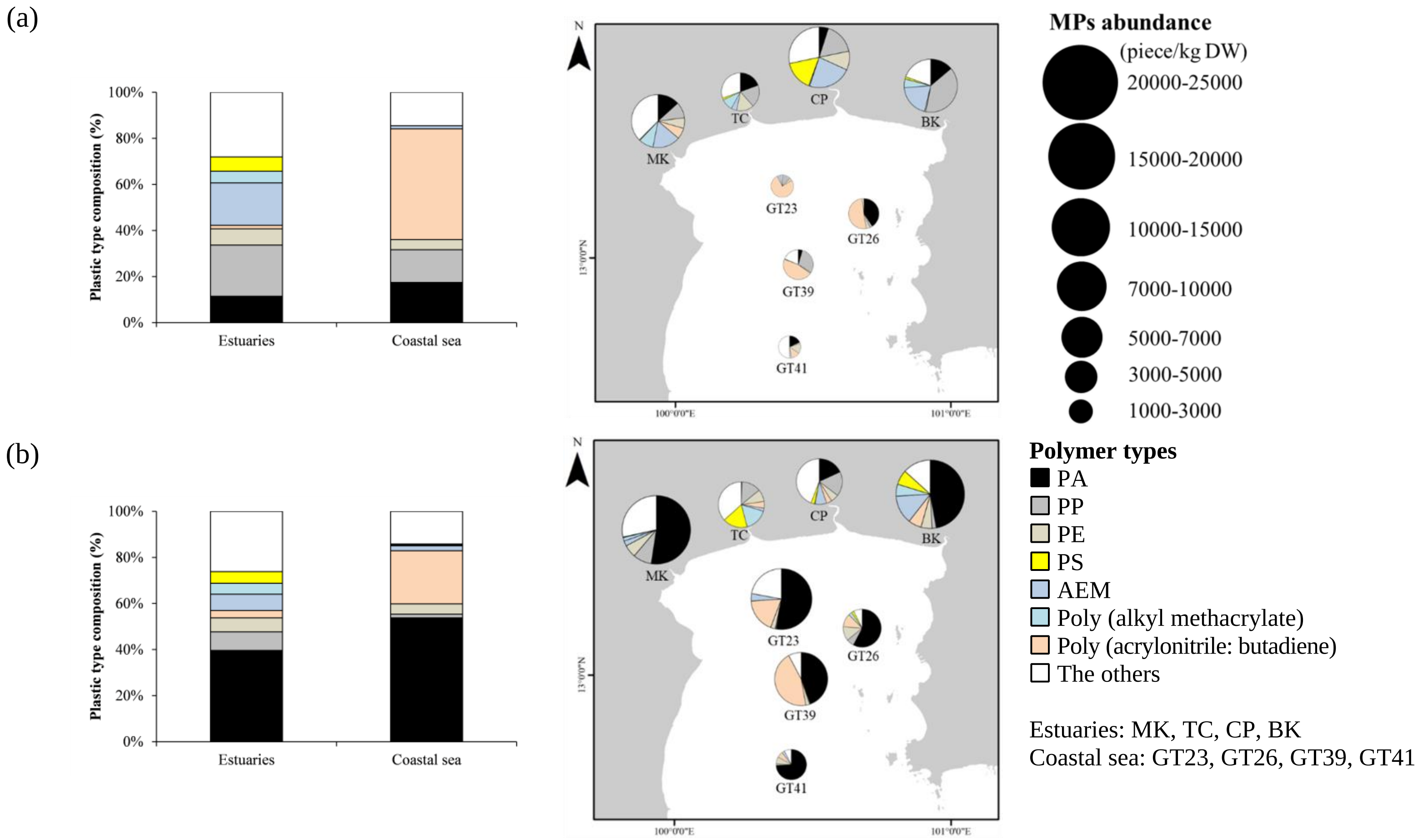


Figure 4.8 Abundance of microplastics with plastic type composition in surface sediment of the river estuaries and the coastal sea of the inner Gulf of Thailand in dry season (a) and wet season (b)

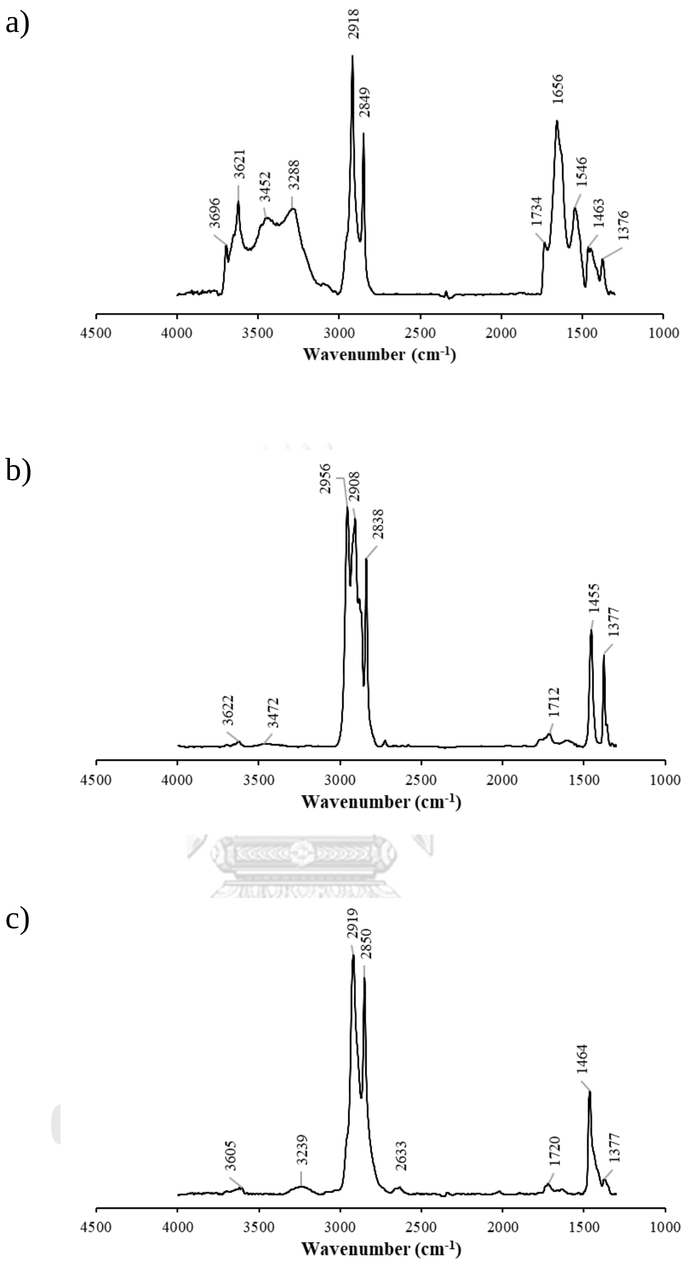


Figure 4.9 FTIR spectrum of detected microplastics: polyamide (a), polypropylene (b), polyethylene (c)

4.3.3 Microplastics in sediment profile

The sediment can indicate the history of the substance accumulation as the sediment was theoretically increased by time of settling of suspended solids. In the other word, the sediment at deeper from the surface represents the older status of suspended solids, as well as microplastics or plasticles.

The profile of sediment in GT26 (Figure 4.10) showed vertical distribution of MPs that was highest abundance in the surface layer of sediment (0-5 cm). In layer 5-40 cm, the abundance and the polymer types of MPs were fluctuated; however, both tend to be reduced varied by depth. The overall of the vertical distribution of MPs in sediment profile in this study was the same trend with the profile of the other area, which the abundance of MPs was higher in surface sediment and reduced in the deeper sediments [41]. The decrease of abundance and diversity of MPs in layer of 10-15 cm might be the results of sediment turbation, while the small contamination in the deep sediment, especially in the layer of 35-40 cm, might be represented to the vertical transportation of MPs in the sediment.

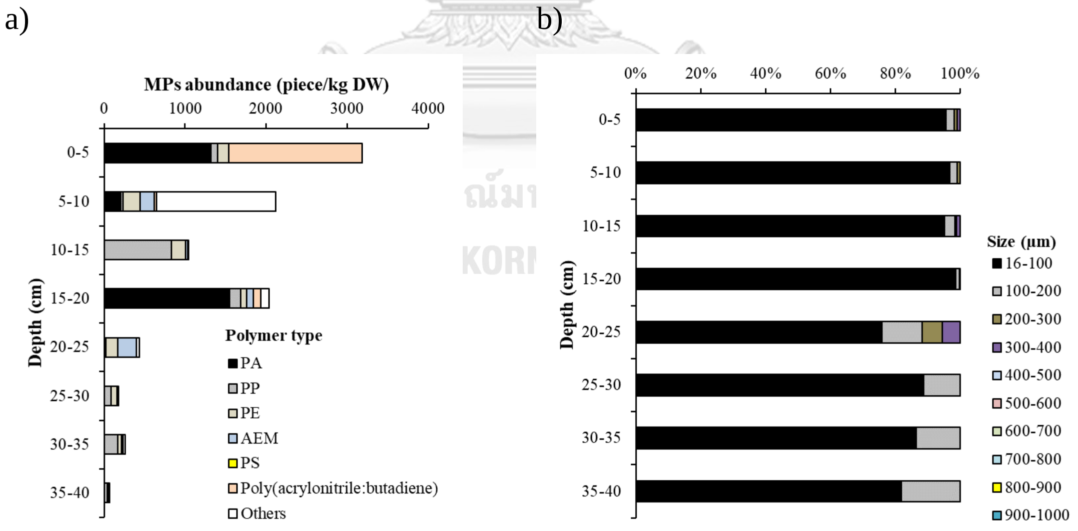


Figure 4.10 Distribution (a), and size composition (b) of microplastics in vertical sediment of sampling station GT26, the inner Gulf of Thailand

The oscillated abundance of MPs in 0-25 cm of the sediment profile could be considered the effects of surface sediment disturbance. The interactions of the towed demersal fishing gears, the seabed, and the ambient water mechanically altered surface sediment with defined edges, berms, and backfilling of settled sediments [132]. It is possible to said that the bottom trawling in the past may migrate the sediment from the collected area or that may resuspend sediment to water interphase. MPs may be removed from the sediment by the floatation in water turbulence, as the MPs abundance in the layer of 10-15 cm was less than that in the deeper layer of 15-20 cm. The resuspended sediment with included MPs were settle back to the seafloor at the same time with the MPs contaminated in the bottom water. This investigation could be inferred to the back-settling of resuspended MPs-sediment aggregation. The results of enlarged MPs abundance from the layer of 10-15 cm to the surface layer and the enhanced MPs in size of 16-100 µm in the upper layer of 20-25 cm sediment may be inferred to the back-settling of resuspended MPs-sediment aggregation. However, the fragmentation of plastic materials in fishing gear also be considered that it could affect the contamination of larger size MPs (200-400 µm) in the sediment at the layer 20-25 cm.

In contrast, the contamination in deep sediments, especially in the layer of 35-40 cm might be considered that was the result of transportation of MPs in sediment. The column experiment investigated that vertical transportation of MPs was increased by decreasing particle size as the small particles have great mobility in porous media, as well as the decreasing in hydrophobicity of MPs that can induce the particles downward migration with infiltration of water. In addition, the vertical motion of MPs in the sand column also be regulated by the density of plastics. The experiment revealed that PP (0.833 g/cm^3) were hindered infiltration on surface column that PE (0.893 g/cm^3) [133, 134]. Beside the higher density, the hydrophilic functions of PA were discussed that results accessibility of water and contributed to great mobility [133]. Accordingly, the formation of MPs-titanium dioxide nanoparticles heteroaggregates increased MPs deposition, while the MPs transportation was decreased in the quartz sand under all examined conditions [135]. Although the evident of the vertical movement of MPs in marine sediment still be unclarified, it is acceptable to said that the MPs were aggregated with the suspended sediment and those were settled to accumulated in the seabed.

The contamination of MPs in sediment represents to the history of anthropogenic activities as the plastics was man-made materials. The small number of detected MPs in the layer of 38-40 cm, date to 1950s, in the sediment profile of Tokyo, Japan [17]. This founding was discussed that the plastics were produced when the industrial production were started. Dating sediment profile of the inner GT in the previous study estimated that the layers of 44-46 cm and 6-12 cm in 2006 were deposited in the 1950s and 1990s, respectively [136]. The sediment in the layer of 35-40 cm in this study might be approximately dated between 1950s-1990s, as well as MPs, although the sedimentation rate of MPs-sediment aggregation need to be evaluated.

4.3.4 Microplastics and sedimental variables

The correlation between MPs and sedimentological parameters indicated that plasticles were incorporated to be a part of sediment as almost of them have positive relation with the sediment parameters (Table 4.3). Significant relations with some heavy metals or some nutrients were observed for the total MPs (TMPs) and the varied types of plastics, excepted poly (acrylonitrile: butadiene). It, however, is necessary to note that the light density of MPs like PE significantly relate with heavy metals and the other parameters (Cd, Pb, Cu, Co, Ni, Mn, Al, TOC, TP, AVS, and water content). The relationship between MPs and sediment parameters could be inferred to the behavior of plasticles as they are a part of settled solids

In fact, the persistent and numerous densities of plastic properties are the massive difference between MPs and sediment although both can be settled to the sediment. The light density plastics tend to be suspended in the surface water, while the heavy density plastics are sunk to the water column and seabed. The hydrophilic structures in polymer were induced via photo-oxidative reaction; at the same time, plastics were fragmented. As the oxidative functional groups were observed in the results of FTIR spectrum in the water samples of chapter III and that in the sediments, the plastics could be adsorbed the charged compounds such as heavy metals and nutrients. In addition, the aggregation with biofouling and the other substances also increases the density of plasticles and affects the vertical transportation or the sedimentation of them.

In contrast, the non-significant relation between plastics and the considered factors of sediment may infer that the sedimentation of plastics was not regulated by the settled sediment. The observed relation between plastics with some substances in sediment may be caused by those substances were consisted in plastic chemicals. The contamination of some substances in sediment may be mainly affected by the abundance of plastics.

The significantly positive correlation between MPs, especially PE, and the sediment parameters may be predicted that the plasticles may accumulate those substance in the water column and settle as the sediment. Due to light density of plastics, it can say that the sedimentation of plastics request time for aggregating with several compounds. Inversely, the heavy density plastics may be settled before the surface fouling was formed, and this may affect no relation between MPs and sediment parameters. Because some sediments consisted of MPs, the detected substances in sediments are probably to be sourced from the additive chemicals or accumulated substances in MPs contents.

Table 4.3 Pearson's correlation between environmental parameters and categorized microplastics in total microplastics (TMPs), polyamide (PA), polypropylene (PP), polyethylene (PE), poly (acrylonitrile: butadiene) (PAB), acrylate ethylene copolymer (AEM), poly alkyl methacrylate (PAMA), polystyrene (PS), and the others

Parameters	TMPs	PA	PP	PE	PAB	AEM	PAMA	PS	The others
Cd	0.678**	0.444	0.469	0.755**	-0.393	0.536*	0.476	0.373	0.653**
Pb	0.585*	0.507*	0.210	0.705**	-0.369	0.089	0.398	0.203	0.760**
Cu	0.334	0.210	0.062	0.589*	-0.280	0.055	0.318	0.408	0.506*
Co	0.718**	0.480	0.425	0.601*	-0.343	0.521*	0.604*	0.492	0.693**
Ni	0.673**	0.433	0.345	0.618*	-0.295	0.453	0.551*	0.559*	0.678**
Mn	0.213	0.106	-0.183	0.479	0.025	0.194	0.278	0.614*	0.115
Zn	0.325	0.134	0.219	0.396	0.003	0.110	0.282	0.329	0.351
Al	0.499*	0.154	0.275	0.778**	-0.381	0.593*	0.184	0.720**	0.626**
TOM	0.513*	0.341	0.359	0.358	-0.185	0.269	0.455	0.190	0.554*
TOC	0.402	0.238	0.203	0.600*	-0.335	0.131	0.524*	0.279	0.572*
TP	0.535*	0.141	0.582*	0.586*	-0.495	0.633**	0.620*	0.493	0.636**
AVS	0.540*	0.084	0.457	0.819**	-0.391	0.739**	0.297	0.941**	0.567*
Water content	0.336	0.003	0.487	0.253	-0.418	0.414	0.634*	0.331	0.509

** Correlation is significant at the 0.01 level (2-tailed).
* Correlation is significant at the 0.05 level (2-tailed).

4.4 Heavy metal contamination in microplastics

Beside MPs-substance compound aggregation in sediment, MPs were consisted of the plastic materials and the adherence or fouling on surface of plastic particles. This study, the fouling content and plastic content were extracted the component of MPs. The contamination of heavy metals (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn) in both contents was analyzed. The results found that the fouling content, accounted for 87-99% of total mass of extracted MPs, was more contaminated with heavy metals than that of plastic content.

The proportion of heavy metals in MPs shows contamination in both fouling content and plastic content (Figure 4.11). The fouling on surface of MPs played the important role in heavy metals accumulation; however, the plastic content was contained with some heavy metals, Ni, As, Pb, and Cu, for example. The heavy metals in fouling content might be regulated by the adsorption of active functional groups in fouling substances, while the contamination in plastic content poses to be sourced by plastic additive chemicals. But the oxidative groups in MPs could be considered that they can be active groups for heavy metal adsorption, the small size of MPs also increased the active surface area, in addition. The adsorption experiments showed that the surface charge and oxidized functional groups of aged MPs could increase heavy metal sorption, compared to the virgin microplastics [69, 72, 105]. The fouling contaminations analysis showed that the adhesion components were the key for pollution accumulation on MPs. The results were similar with the higher concentration of heavy metals detected in extraneous solids than that in plastic pellets from beaches [70]. A concern about MPs with the toxic substances such as heavy metals may be the releasing of toxic after MPs were ingested.

The MPs were the accumulate substrates for heavy metals as the concentration of heavy metals in MPs was significantly magnified from the sediment with 1 to 6 orders of magnitude, compared between mass of MPs and mass of sediment (Figure 4.12). No statistical difference of most heavy metals contamination in MPs between season were observed with 95% confident level (p>0.05). Interestingly, this study observed the heavy metal contaminations in MPs were in very low level when considering by weight of sediment that MPs were contaminated. However, the contaminations by weight of MPs still be in the high level that have the similar trend with the previous study. The analysis of heavy metals in MPs from littoral zone revealed that the contamination was greater than that in sediment [65, 73]. Comparison between field collected samples and recently manufacturing samples observed that the Cu and Pb were more contaminated in field samples, while Zn and Cd were recently manufacturing samples [71]. The determination represented that the sorption and desorption were depended on plastic types and species of heavy metals.

The exposure of MPs may course adverse effects from heavy metals than that of sediment. The weak acid (0.1 M HNO_3) could be desorbed Cd that adsorbed on MPs [127]. The mobilization test resulted that Cd was released from plastic-sediment mixture greater than that from sediment alone [129]. The physiologically based extraction tests presented that the heavy metals in MPs could be released under the synthetic digestive characteristics of seabird [67, 68]. It must be noted that the extraction was the simulation results for MPs selective ingestion. The accumulation and releasing of heavy metals in MPs may relate to the adsorption mechanism either physical adsorption of the increasing surface area of MPs or/and chemical adsorption of oxidative function group in MPs structures. Considering the whole ecological system, the contamination of heavy metals in MPs may be a small fraction in the contamination of sediment. Thus, this contamination may give a minor risk to the ecosystem, but it may be increased when the contamination of MPs was amplified.

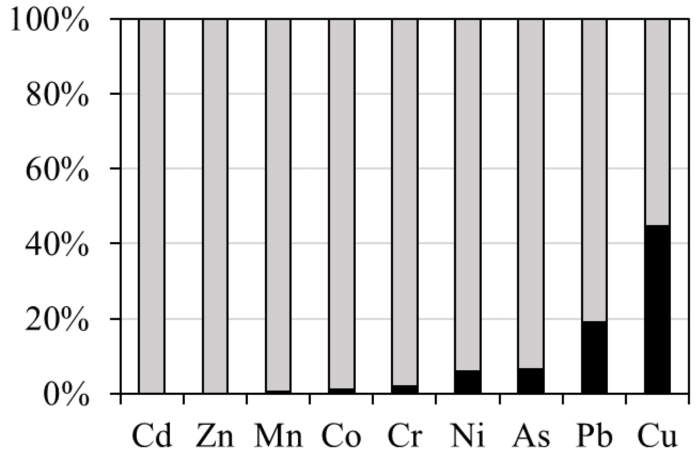


Figure 4.11 Proportion of heavy metals by weight of MPs in plastic content (■) and fouling content (□) of microplastics

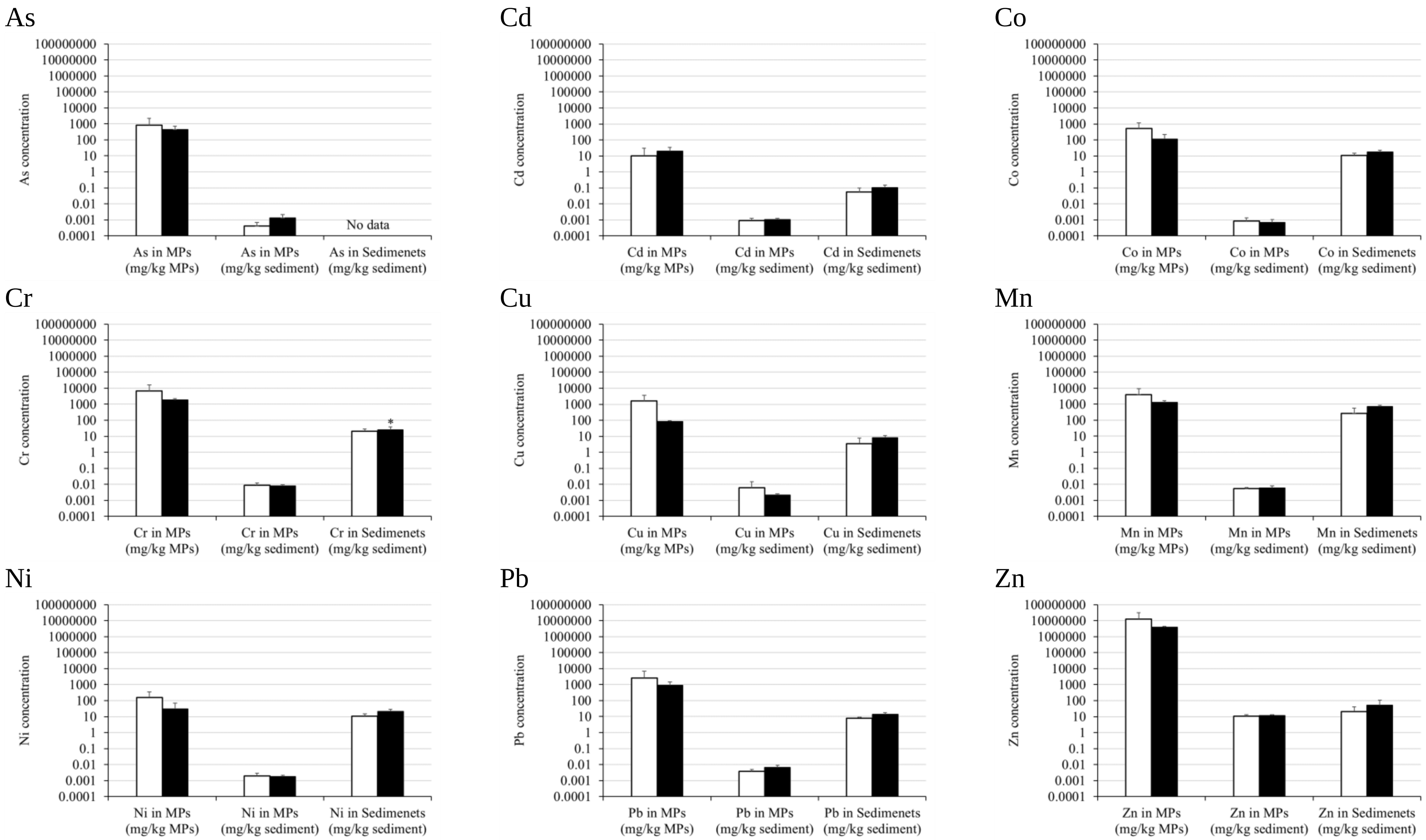


Figure 4.12 Concentration of heavy metals (As, Cd, Co, Cr*, Cu, Mn, Ni, Pb, and Zn) in microplastics and sediments

* Concentration of Cr in wet season was investigated in July 2017

4.5 Summary of microplastics accumulation in sediment

Variation of MPs were investigated in the sediment of the inner GT. High contamination in the river estuaries showed MPs were trapped according to high sedimentation rate of the geo-hydrological characteristics. PA and poly (acrylonitrile: butadiene), seawater-higher density plastics, were the most common MPs in the surface sediment; however, the seawater-lower density plastics of PE and PP also observed. Wet season affected the contamination of MPs increasingly dispersed to the coastal sea, and that decreased the proportion of light density plastics. The relationship between MPs and sediment parameters suggested that either hetero aggregation of plastics-suspended solids and the density of plastics may result MPs accumulate in the bed sediment. Significantly, the contamination of heavy metals in MPs were magnified from that in the sediment, but the contamination seems to be a minor compared to the weight of sediment. It may be probable to state that the contamination of heavy metals in MPs does not affect the risk of MPs contamination in the sediment ecosystem.

CHAPTER V

POLLUTION ASSESSMENTS FOR CONTAMINATION OF MICROPLASTICS: CASE STUDY IN THE INNER GULF OF THAILAND

The pollution indexes of contamination factors, pollution load index, polymer hazard risk index, and ecological risk index were modified for the pollution assessment of microplastics with the co-contamination of heavy metals in sediment of the inner Gulf of Thailand. The assessment showed that the contamination level of MPs is in the level of very high abundance with the high polymer hazard risk index. The ecological risk of MPs in the study area was in the moderate-risk level in dye season and that was in the high-risk level in the wet season. However, the risk from heavy metal contaminated in MPs resulted small faction compared with the total sediment. The revised ecological risk model for MPs assessment can be integrated to the potential ecological risk index for evaluating the total risk of toxic substances in the ecosystem.

5.1 Limitation in assessing ecological impacts of microplastics

After plastic debris entered to the aquatic environment, it could be fragmented to small size of microplastics (MPs) and mixed with suspended solid in the water system. The accumulation of surrounding chemicals and formulation with microorganism have been hypothesized as a cause of MP contamination in sedimentary system. The contaminations of MPs, however, are confirmed by environmental monitoring, it is important to answer how those impact to the ecosystem.

The potential ecological risk index was modeled for accuracy, simplicity, and rapidity in evaluated impacts or risk of contaminants in ecosystem [96]. In simply, the model firstly assessed the contamination factors (C_f) of toxic substances by using concentration of contaminants in the samples and that in natural background. The toxic response factor of the toxicants was used for calculated ecological risk factors (E_r) of those substances. Finally, the potential ecological risk index (RI) was scaled the risk in contamination by summing all E_R of considered toxicants. Calculated risk for plastics, the polymer hazard ranking score was proposed [8]. The value of that is included the hazard score from plastic monomer mass composition. Evaluating ecological risk of MPs, the polymer hazard ranking score was used in RI model as toxic respond factor of the MPs [18, 32].

Realistically, MPs may physically entangle and reduce food consumption; however, the toxicity of MPs has been viewed that it was course of plastic monomer chemicals, additive chemicals, and adsorbed environmental toxicants. Calculated for polymer hazard score, some plastic monomers were carcinogenic and mutagenic [8]. In addition, the functional additive chemicals, colorants, filler, and reinforcement that used to improve plastic properties and their function were toxic substances such as organic and metal compounds [100]. Moreover, plastics have tendency in accumulated both persistence organic pollutants [86-89] and heavy metals [69, 71-73, 93] from the environment, and that may be increased because of high active surface area of small size oxidized MPs. Releasing toxics from MPs, has been focused that MPs may be vector for transporting toxicants to organism. By these reasons, physical characteristics, monomer composition, and toxic substances accumulation in MPs should be used in impact evaluation. In the other site, the evaluation of eco-risk on MPs by using all characters of plastics is very limited because: 1) there is no evident to confirm that how the MPs affect to the ecological system, 2) it is no clear standard definition for the factor that may affect the toxic characteristics of MPs, especially for physical characteristics of MPs, such as sizes, shapes, and colors, 3) the background concentration, or the threshold concentration of MPs, is not investigated, and 4) the criteria for scaling the risk is not clearly developed.

Previous research proposed the modified eco-risk model for assessing plastic monomer chemical risk of MPs contaminated in surface water and sediment. Importantly, the other toxic substances in MPs should be integrated in the risk evaluation. The physiological-based extraction test, simulation of bird digestive characteristics, presented heavy metals in plastics significantly released after ingested by seabirds [65, 67, 68]. Thus, this study, plastic monomer chemicals and heavy metals, which are plastic additives and adsorbed toxicants, were analyzed and included in the risk assessment of MPs contamination in sediment of the inner GT. The quantity of plastic types and heavy metals (Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn) in

MPs were analyzed. The universal models of contamination factor, contamination degree, pollution load index and ecological risk assessment were modified.

5.2 Model approach for microplastics pollution indexes

This study focused on the pollution of MPs in sedimentological system where the pollutants were long-term accumulated in the concerned area. The model approach was applied from the previous studies that based on Hakanson's models included:

5.2.1 Contamination factor (C_f)

The contamination level of MPs in sediment was assessed by modified contamination factors (C_f) of heavy metals contamination in sediment of Hakanson [96]. All MPs with any chemical types and any varied sizes were considered as a one type of substance namely MPs; the C_f (equation 1) could be accounted for relative comparison of MPs in the focused area with background concentration.

$$C_f^i = \frac{C_{0-1}^i}{C_{ref}^i} \quad (1)$$

Where C_f^i is contamination factor of the pollutant,
C_{0-1}^i is concentration of the pollutant in surface sediment,
C_{ref}^i is reference concentration of the pollutant.

C_{ref} value for heavy metals and MPs were listed in Table 5.1. Because this model was modified from assessing heavy metal pollution model, C_{ref} originally is background concentration of those pollutants in non-anthropogenic influenced sediment. Meanwhile, C_{ref} for anthropogenic substances should not be available. However, the minimum concentration of non-natural source substance like polychlorinated biphenyl (PCB) was used in the model [96]. By this reason, it is possible to use the minimum concentration of MPs in sediment profile as the reference concentration by assume the environmental impacts were non-significant in that concentration. According to the lowest abundance of MPs in the vertical profile of the chapter IV, the value of C_{ref} in this study was proposed to be 70 pieces/kg DW.

5.2.2 Pollution load index (PLI)

Pollution load index (PLI) objectives to assess and compare pollution level in different dynamic area, especially the river estuarine system [99]. According to C_f of MPs, the pollution load index of MPs could be assessed (equation 2).

$$\mathrm{PLI_{Area}} = \sqrt[n]{\mathrm{C^i_{f,1}} \times \mathrm{C^i_{f,2}} \times \ldots \times \mathrm{C^i_{f,n}}} \qquad (2)$$

Where $\mathrm{PLI_{Area}}$ is pollution load index of the pollutant in the area A,

$\mathrm{C^i_{f,n}}$ is contamination factor of pollutant in station n of the considered area.is contamination factor of the pollutant in station n of the considered area.

As the following terminology of PLI was the geometrical average of C_f, the output value should be the same interpretation. Based on the background of the model, the contamination level of heavy metals, PCB, and MPs was showed in Table 5.2. The first describing for C_f was proposed for heavy metal and PCB pollution by Hakanson, 1980. However, the risk scale of MPs was given for the value of PLI by Pei Xu, et al., 2018. The risk category for MPs was followed the hazard score that used in plastic chemical hazard ranking.

Table 5.1 Reference concentrations of heavy metals, polychlorinated biphenyl, and microplastics in sediment

Substance	Reference concentration, C_{ref}	Unit
Zn[96]	175	mg/kg DW
Mn[137, 138]	540	mg/kg DW
Cr[96]	90	mg/kg DW
Co[137, 138]	10	mg/kg DW
Cu[96]	50	mg/kg DW
Ni[139]	5	mg/kg DW
Pb[96]	70	mg/kg DW
As[96]	15	mg/kg DW
Cd[96]	1.0	mg/kg DW
Hg[96]	0.25	mg/kg DW
PCB[96]	0.01	mg/kg DW
MPs (This study)	70	piece/kg DW

Table 5.2 Contamination level and risk level criteria of heavy metal, polychlorinated biphenyl, and microplastics pollution

Contamination factor (C_f) and pollution load index (PLI)		Contamination level (Risk category)
Heavy metals and PCB [96]	Microplastics [18]	
<1	<10	Low (I)
1-3	10-20	Moderate (II)
3-6	20-30	Considerable (III)
>6	>30	High (IV)

5.2.3 Potential ecological risk index (RI)

Due to plastic monomer chemical and contaminated chemicals (additives and adsorbed pollutants), risk index of MPs in considered station i ($\mathrm{E_r^{MPs}}$) should be calculated from the eco-risk factors ($\mathrm{E_r^{Pl}}$) of plastic content and co-contaminant content ($\mathrm{E_r^{Cont,i}}$) (equation 3).

$$\mathrm{E_r^{MPs}} = \textstyle\sum_{i=1}^{n} \mathrm{E_r^{Cont,i}} + \mathrm{E_r^{Pl}} \qquad (3)$$

The eco-risk factor of plastic monomer chemical ($\mathrm{E_r^{Pl}}$) and that of contaminants ($\mathrm{E_r^{Cont}}$) were conceptually described followed toxic-response factors and contamination factors.

1) Potential eco-risk from contaminated heavy metal in MPs

As the eco-risk model was proposed for, the considered toxicants accumulated in MPs (heavy metals, or persistent organic pollutants) were analyzed and calculated for the eco-risk factor from the co-contamination in MPs ($\mathrm{E_r^{Cont,i}}$, equation 5).

$$\mathrm{E_r^{Cont,i}} = \mathrm{T_r^{Cont,i}} \times \mathrm{C_f^{Cont,i}} \qquad (5)$$

Where $\mathrm{T_r^{Cont,i}}$ is toxic response value of the contaminant,

$\mathrm{C_f^{Cont,i}}$ is contamination factor of the contaminant in MP (mg/kg DW sediment).

The toxic response factors ($\mathrm{T_r^{Cont,i}}$) could be taken from Hakanson [96] and Xu et al. [97]. For example, the $\mathrm{T_r^{Cont,i}}$ of heavy metals was listed in Table 5.3. Bioproduction index (BPI) was assumed to be 5 represented to the intermediate score in normal condition characteristic for moderately eutrophic status.

Table 5.3 Toxic response factors of heavy metals and polychlorinated biphenyl

Substance	Toxic response factors (T_r^{cont})
Zn[96, 97]	$1 \cdot \sqrt{5}/\sqrt{BPI}$
Mn[97]	$1 \cdot \sqrt{5}/\sqrt{BPI}$
Cr[96, 97]	$2 \cdot \sqrt{5}/\sqrt{BPI}$
Co[97]	$5 \cdot \sqrt{5}/\sqrt{BPI}$
Cu[96, 97]	$5 \cdot \sqrt{5}/\sqrt{BPI}$
Ni[97]	$5 \cdot \sqrt{5}/\sqrt{BPI}$
Pb[96, 97]	$5 \cdot \sqrt{5}/\sqrt{BPI}$
As[96, 97]	10
Cd[96, 97]	$30 \cdot \sqrt{5}/\sqrt{BPI}$
Hg[96, 97]	$40 \cdot 5/BPI$
PCB[96, 97]	$40 \cdot BPI/5$

The ecological risk level of heavy metals and polychlorinated biphenyl according to Hakanson's model was illustrated in Table 5.4. The ecological risk level was considered by E_R of the most toxic substance in the normal condition (BPL=5 for PCB or Hg, T_r=40) and no contamination from the considered substance (C_f=1). Thus, E_R was 40 for the low-risk level. The higher risk levels were defined by geometric sequence by 2 multiplied for each stage of E_r. Scaling risk index (RI) was the summation of E_r for all considered substance in the same condition for scaling E_r with adding margin of uncertainty. It must be noted only 8 substances (Zn, Cr, Cu, Pb, As, Cd, Hg, and PCB) were considered in the proposed model. Mn, Ni, and Co were additionally considered after the T_r of them was calculated by Xu, 2008. However, the RI scale still be in the same margin, when the new pollutants were added to the model. The potential eco-risk from contaminated heavy metal in MPs was the summation of contaminated substance' E_r

Table 5.4 Ecological risk criteria of heavy metals and polychlorinated biphenyl [96]

Ecological factor ($E_r^{Cont,i}$)	Risk index (11 substances) $\sum_{i=1}^{11} Er_i^{Cont}$	Risk level
<40	<150	Low ecological risk
40-80	150-300	Moderate ecological risk
80-160	300-600	Considerable ecological risk
160-320	600-1200*	High ecological risk
>320	>1200*	Very high ecological risk

* The scale of high risk and very high-risk level were modified from the proposed model for balancing scale of risk index and ecological factor

2) Potential eco-risk from plastic monomer composition

The risk assessment of MPs using monomer chemicals was modified by Peng et al. [32] and Xu et al. [18] (equation 5). The concentration of MPs and quantitative monomer composition in the samples might be used. The hazard ranking score of each detected monomer can be taken from Lithner et al. [8] (Table 5.5).

$$H_r^{Pl} = \sum_{i=1}^{n} \frac{C^{Pl,i}}{C^{MPs}} \times S^{Pl,i} \qquad (5)$$

Where H_r^{Pl} is hazard risk index of plastic chemicals,
$C^{Pl,i}$ is concentration of plastic monomer type i,
C^{MPs} is concentration of total MPs,
$S^{Pl,i}$ is hazard ranking score of plastic chemical type i.

The concentration of total MPs was used to calculated ecological risk of plastic monomer i (E_r^{Pl}, equation 6).

$$E_r^{Pl} = H_r^{Pl} \times C_f^{MPs} \qquad (6)$$

Where E_r^{Pl} is eco-risk index of monomer chemicals,
H_r^{Pl} is hazard risk index of plastic chemicals,
C_f^{MPs} is contamination factor of MPs.

The criteria for ecological risk of MPs were showed in Table 5.6. Xu et al. 2018 had provided the risk scale of MPs was provided for polymer index (referred as hazard risk index of this study) and pollution load index (or the contamination factor, in the same concept). Peng et al. were proposed the concept of ecological risk factor that presented in equation 6. H_r^{Pl} can be referred to toxic response factors of MPs.

This study calculated the eco-risk criteria using Peng's ecological risk equation and following the Hakanson's concept. However, using the maximum toxic response factors, or hazard risk index for plastic, ($H_r^{Pl} = 10000$) with the condition of the lowest risk of contamination (C_f=10) results non-balance scale with the eco-risk scale for heavy metal pollution assessment (Table 5.6). The hazard ranking score of plastic chemicals (S^{Pl}) was developed by hazard grade of the hazard classification score, taken from the Annex VI in the EU classification, labelling and packaging (CLP) regulation which is based on the UN Globally Harmonized System (GHS) [8]. The human health risk, carcinogenicity, and germ cell mutagenicity, for example, was included in the hazard grade for scoring S^{Pl}. Considering the level of ecological risk, the risk index of MPs should be higher than 10000 for represent the moderate risk as the scale was followed Peng's ecological risk equation. In contrast, the moderate risk of the toxic substances like heavy metals and PCB was considered while the eco-risk index was higher than 40 followed Hakanson's eco-risk model. In the hazard ranking of plastic score calculation [8], it is acceptable that the maximum score of ten thousand (10000) can be the comparative value for human risk, but this value was over scale for the ecological risk compared with PCB. Because of the large area of ecological system, it might be reasonable to say the sensitivity in ecological risk was less than human risk. In short, the plastics should have lower risk than the pure anthropogenic toxicants like PCB. The scale in sensitivity of plastic risk for eco-risk evaluation should be adjusted to be the same scale with the other pollutants. Thus, the ecological risk factor of plastics (E_r^{Pl}) was divided by 10000, the maximum hazard ranking score (equation 7).

$$E_r^{Pl} = \frac{1}{10000} \times H_r^{Pl} \times C_f^{MPs} \quad (7)$$

Accordingly, the maximum value for low risk of plastics was reduced to be 10. The ecological risk criteria of MPs pollution were revised for the risk from plastic monomers:

$E_r^i < 10$	low potential ecological risk,
$10 \leq E_r^i < 20$	moderate potential ecological risk,
$20 \leq E_r^i < 40$	considerable potential ecological risk,
$40 \leq E_r^i < 80$	high potential ecological risk,
$80 \leq E_r^i$	very high potential ecological risk.

The criteria for risk index (RI) of the potential ecological risk in the considered area are summarized in Table 5.6. The risk scale was included the risk from MPs and the other contaminants of heavy metals (As, Cd, Cu, Co, Cr, Cu, Hg, Mn, Ni, Pb, Zn) and PCB.

Table 5.5 Hazard ranking score of plastic chemicals

	Polymer	ID chemical	Hazard score (S^{Pl}) [8]
Acrylic resin	Polyacrylonitrile (PAN) and copolymers	Polyacrylonitrile	11521
		Polyacrylonitrile with vinyl acetate	10599
		Polyacrylonitrile with methyl acrylate	10685
		Polyacrylonitrile with methyl methacrylate	10681
		Polyacrylonitrile with acrylamide	12379
		Modeacrylic with vinylidene chloride	6957
		Modeacrylic with vinyl bromide	10913
		Modeacrylic with vinyl chloride	10913
	Polymethyl methacrylate (PMMA)	Poly (methyl methacrylate); 2-Propenoic acid, 2-methyl-, methyl ester, homopolymer	1021
Fluoropolymer	Polytetrafluorethylene (PTFE)	Polytetrafluoroethylene	Not classified
	Polyvinylidene fluoride (PVDF)	polyvinylidene fluoride	Not classified

Table 5.5 Hazard ranking score of pastic chemicals (Continuous)

	Polymer	ID chemical	Hazard score (S^{Pl}) [8]
Polyamide (PA) (aliphatic), nylon	Polyamide 6 - Nylon 6	Caprolactam polymer, Polyamide 6, Nylon 6; Poly[imino(1-oxo-1,6-hexanediyl)]	50
	Polyamide 6.6 – Nylon 6.6	Nylon 66, Polyamid 6,6; Poly[imino(1,6-dioxo-1,6-hexanediyl)imino-1,6-hexanediyl]	63
	Polyamide 6.10 – Nylon 6.10	Poly(hexamethylene sebacamide); Decanedioic acid, polymer with 1,6-hexanediamine	47
	Polyamide 11 – Nylon 11	Undecanoic acid, 11-amino-, polyamide	not classified
	Polyamide 12 – Nylon 12	Polyamide 12; Poly[imino(1-oxo-1,12-dodecanediyl)]	not classified
Polyamide (aromatic), aramides	Poly(m-phenyleneisophtalamide) (MPD-I) (Nomex®)	m-aramid; 1,3-Benzenedicarbonyl dichloride, polymer with 1,3-benzenediamine	1187
	Poly(p-phenyleneterephtalamide) (PPD-T) (Kevlar® and Twaron®)	p-aramid fibrils	829

Table 5.5 Hazard ranking score of plastic chemicals (Continuous)

	Polymer	ID chemical	Hazard score (S^{Pl}) [8]
Polyesters	Polylactic acid (PLA)	polylactide; Propanoic acid, 2-hydroxy-, homopolymer	not classified
	Polybutylene terephtalate (PBT)	Poly(butylene terephthalate); 1,4-Benzenedicarboxylic acid, polymer with 1,4-butanediol	not classified
	Polycarbonates (PC)	Polycarbonate, phosgene; carbonyl chloride	1177
		Polycarbonate, Diphenyl carbonate	610
	Polyethylene terephthalate (PET)	Poly(ethylene terephthalate); Poly(oxy-1,2-ethanediyloxycarbonyl-1,4-phenylenecarbonyl)	4

Table 5.5 Hazard ranking score of plastic chemicals (Continuous)

	Polymer	ID chemical	Hazard score (S^{Pl}) [8])
Polyethylenes	Low-density polyethylene (LDPE)	Polyethylene; Ethene, homopolymer	11
	Linear-low-density polyethylene (LLDPE)	Ethene-1-butene copolymer (LLDPE); 1-Butene, polymer with ethene	10
	High-density polyethylene (HDPE)	Polyethylene; Ethene, homopolymer	11
	Ethylene vinyl acetate (EVA) and ethylene vinyl alcohol (EVOH)	ethylene vinyl acetate	not found
Styrenic resins	Polystyrene (PS)	Polystyrene; Benzene, ethenyl-, homopolymer	30
	Expanded polystyrene (EPS)	Polystyrene; Benzene, ethenyl-, homopolymer	44
	High-impact polystyrene (HIPS)	Styrene-1,3-butadiene copolymer; Benzene, ethenyl-, polymer with 1,3-butadiene	1628
	Acrylonitrile-butadiene-styrene (ABS) terpolymer	acrylonitrile-butadienestyrene terpolymer; 2-Propenenitrile, polymer with 1,3-butadiene and ethenylbenzene	6552

Table 5.5 Hazard ranking score of plastic chemicals (Continuous)

	Polymer	ID chemical	Hazard score (S^{Pl}) [8]
Styrenic resins	Styrene-acrylonitrile (SAN) copolymer	Styrene-acrylonitrile copolymer; 2-Propenenitrile, polymer with ethenylbenzene	2788
Other thermoplastics	Polyoxymethylene (POM) and copolymers	polymer POM, homopolymer	1500
		POM, copolymer with ethylene oxide	871
		POM, copolymer with dioxolane	103
	Polyphenylene ether (PPE), also called Polyphenylene oxide (PPO)	Phenol, 2,6-dimethyl-, homopolymer	400
	Polyphenylene sulphide (PPS)	Polyphenylene sulfide; Benzene, 1,4-dichloro-, polymer with sodium sulfide (Na2S)	897
	Polypropylene (PP)	Propylene polymer; 1-Propene, homopolymer	1
	Polyvinyl acetate (PVAc) and polyvinyl alcohol (PVOH)	Poly (vinyl acetate)	1

Table 5.5 Hazard ranking score of plastic chemicals (Continuous)

	Polymer	ID chemical	Hazard score (S^{Pl}) [8]
Other thermoplastics	Polyvinyl chloride (PVC)	PVC, rigid	10001
		PVC, plasticised most toxic plasticiser (BBP)	10551
		PVC, plasticised least tox (Nc) plasticiser	5001
Thermoplastic elastomer	Thermoplastic polyurethanes (TPU) (linear polyurethanes)	Thermoplastic polyurethanes (TPU) polyester based soft example	556
		Thermoplastic polyurethanes (TPU) polyester based rigid example	1094
Amino plastics (resin)	Melamine-formaldehyde resin (MF)	Melamine-formaldehyde polymer; 1,3,5-Triazine-2,4,6-triamine, polymer with formaldehyde	882
	Urea-formaldehyde resin (UF)	Carbamic acid, butyl ester, polymer with formaldehyde	750

Table 5.5 Hazard ranking score of plastic chemicals (Continuous)

	Polymer	ID chemical	Hazard score (S^{Pl}) [8]
Epoxy resins	Epoxy resins	Epoxy resins (low mw, most tox curing agent MDA)	7139
		Epoxy resins (low mw, least tox curing agent DDS)	4513
Phenol formaldehyde resins (PF)	Phenol formaldehyde resins (PF)	Phenol, polymer with formaldehyde with novolacs reaction	1450
		Phenol, polymer with formaldehyde with resol reaction	1500
Polyurethanes (PUR) (Three-dimensional)	Polyurethanes (PUR) (Three-dimensional)	polymer, flexible PUR, example with polypropylene glycol	13844
		polymer, rigid foam, example with polypropylene glycol	7384

Table 5.5 Hazard ranking score of plastic chemicals (Continuous)

	Polymer	ID chemical	Hazard score (S^{Pl}) [8]
Unsaturated polyester (UP)	Unsaturated polyester (UP)	UP ex with propylene glycol, phtalic and maleic anhydride and styrene	1117
		UP ex with propylene glycol, phtalic and maleic anhydride and methyl methacrylate	1414
Polyelectrolyte	Polyacrylic acid (PAA), superabsorbent polymer	polyacrylic acid	230

Table 5.6 Ecological risk criteria of microplastic pollution assessment

Plastics					Heavy metals		
Hazard ranking score [8] (S^{Pl})	Hazard risk index* [18] (H_r^{Pl})	Contamination factor* [18] (C_f)	Peng's ecological risk factor** [32] (E_r^{Pl})	This study ecological risk factor (E_r^{Pl})	Ecological risk factor for single co-contaminant (E_r^{HMs})	Risk index	Risk level (Risk category)
1	<10	<10	<10000	<10	<40	<150	Low (I)
10	10-100	10-20	10000-20000	10-20	40-80	150-300	Moderate (II)
100	100-1000	20-30	20000-40000	20-40	80-160	300-600	Considerable (III)
1000	1000-10000	30-40	40000-80000	40-80	160-320	600-1200	High (IV)
10000	>10000	>40	>80000	>80	>320	>1200	Very high (V)

* The scale was modified by geometric and arithmetic sequence following the concept of Xu, 2018

** The scale was calculated following the concept of risk scale by Hakanson, 1980

5.3 Case study in the inner Gulf of Thailand

The pollution of MPs in surface sediments of the inner Gulf of Thailand (GT) was assessed by using the principle of contamination factor, pollution load index, and potential ecological risk index. According to modified model, the concentration of MPs, and the concentration of heavy metals in MPs were sourced from the results of the chapter IV, MPs in sediment of the inner GT. The study area was categorized the river estuaries (Mae Klong (MK), Ta Chin (TC), Chao Phraya (CP), and Bang Pakong (BK)) and the coastal sea (GT23, GT26, GT39, and GT41). There are three components in the eco-risk evaluation of MPs: 1) quantity of MPs contamination, 2) polymeric types of MPs, and 3) heavy metals as the additional chemicals.

5.3.1 Risk from dose of contaminated microplastics

The contamination factor (C_f) of MPs showed the status of very high contamination in surface sediment of the most sampling station although the contamination in some stations in dry season were in moderate and considerable level (Figure 5.1). Overall, C_f of the study area show the status of very high contamination with the arithmetically mean for the value of 104 in dry season, and average was increased to 175 in wet season. The geometrical mean value of C_f, Pollution load index (PLI), also indicated very high contamination for the value of 72 in dry season and 150 in wet season. The C_f value of this research was in the higher range compared to the previous research due to the analysis methods and the sampling sites.

Because the C_f was the value for ratio between the sediment contaminated toxicants in present and that in pre-industrial age, the contamination in the part without or very less anthropogenic influences was used as a baseline for the natural substances. The lowest concentration of anthropogenic substances in sediment profile was accepted to verified as a background of the contamination. Thus, the very high contamination of MPs according to the criteria of contamination factor was the result of the high abundance of MPs in surface sediments and the very low concentration for the compared reference dose. As the result presented in chapter IV, the abundance of MPs detected by this study, concentration of the surface sediment (C_i), was higher than the other investigation. In contrast, the reference concentration (C_{ref}) was in the same order with that in the assessment of the previous study. This study, the background concentration of MPs was revised to be 70 pieces/kg DW with the plastic confirmed MPs in size of 16-5000 µm. The lowest concentration of MPs reported in Thailand, 39.5 pieces/kg DW in the beach sand, was used for the risk assessment of beach contamination [140]. The minimum concentration in sediment core of the inner GT, 82 pieces/kg DW, was reported for MPs in the size of 315-5000 µm [17]. Based on the literature, the predicted no effect concentration in marine sediment was derived to be 540 pieces/kg DW, however [141]. Although the reference concentration was a bit different than previous assessment, it is necessary to state that the efficiency of quantification strongly affects to C_f. Informationally, the very high level of the contamination may be results of the intensive sources of MPs and the suitable factors inducing MPs settle.

The C_f and PLI of MPs contamination in surface sediments of the inner GT revealed the very high level of contamination in surface sediment. These values are representing to the dosage of MPs in the present compared with the reference concentration or the dose of MPs that might have minimum toxic effect. In trust, the toxic of MPs is not only related to the quantity of contamination, but also linked to the quality of MPs or the plastic polymer chemicals.

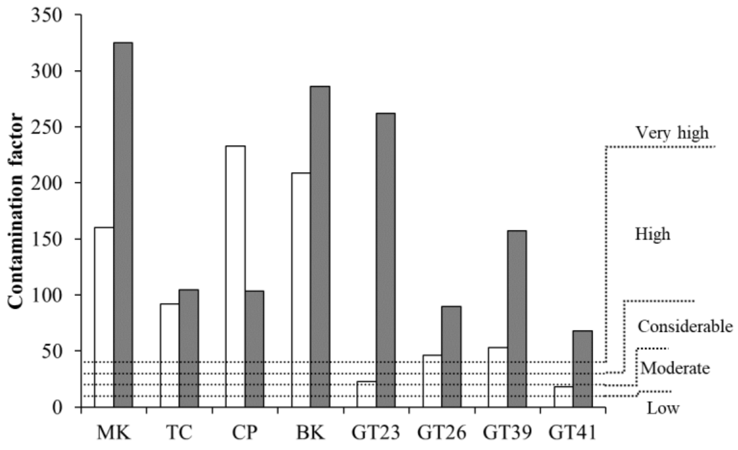
5.3.2 Risk from plastic chemicals

Polymer hazard risk index for contamination of MPs in sediment of the inner GT fell in the category of considerable to high risk (Figure 5.2). The average hazard risk index was 3189 in dry season, and that was reduced to be 1716 in wet season. Accordingly, the coastal sea tends to accumulate risky plastic than the river estuaries with the higher value of polymer hazard risk index. The major proportion in MPs of the coastal sea sediment, poly (acrylonitrile: butadiene), mainly increased the polymer risk index. On the other hand, the low hazard scores of PE and PP affect less polymer risk index in estuaries although their contamination was larger than poly (acrylonitrile:

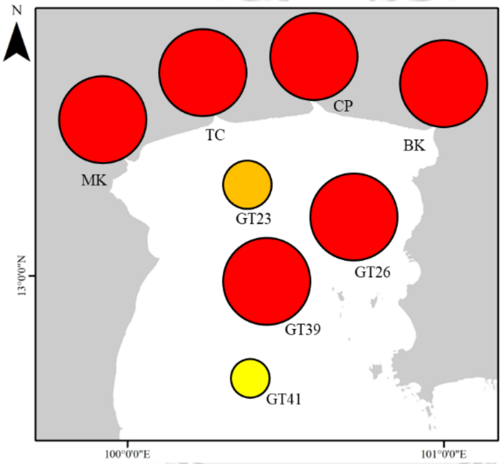
butadiene). It could be inferred that the risk from plastic chemicals in MPs is directly varied by the plastic types and their proportion.

As the plastics are used as a multifunctional material of ubiquitous products, the plastic chemical structures are particularly varied. For example, in the group of polyamides (PA) or nylon that observed in all sample, there are five different grades and are different in polymerization methods for a common commercially available plastic: PA6, PA6.6, PA6.10, PA11, and PA12. Several properties were explored by polymeric structure as well as their risk. Accordingly, the polymerization reagents were included additionally to the monomer chemicals in the hazard score calculation. The hazard score of 63 for PA6.6 were integrated the hazard grades of methanal as medium for salt precipitation and the monomers of adipic acid and hexamethylenediamine, while the hazard class of its monomer, 11-aminoundecanoic acid, was not classified; as a result, the hazard score for PA11 was not found [8]. This study used the maximum hazard score of each group of plastic in the risk evaluation for the worst case of contamination. Because there was no report hazard score for poly (acrylonitrile: butadiene), the main plastic type in samples, the highest score of polyacrylonitrile and copolymer (polyacrylonitrile with acrylamide) was applied. However, it is important to note that some copolymers in small fraction were not included in the evaluation due to no quantitative data of the blending composition. The polymer hazard risk index of MPs was the summation of hazard score of each plastic type with their fraction.

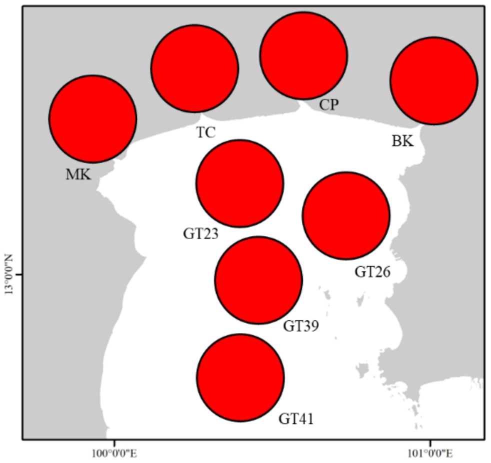
The plastic risk of MPs was conducted by polymer hazard risk index of each plastic in the plastic type composition of MPs. The great value of this index according to the investigation of this study was affected by the highest hazard score of poly (acrylonitrile: butadiene) and the quantity of detected PA in the sample. Notably, the hazard index was the comparative scale for plastic type proportion in the total MPs.



Dry season



Wet season



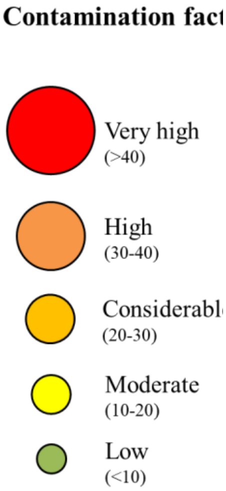
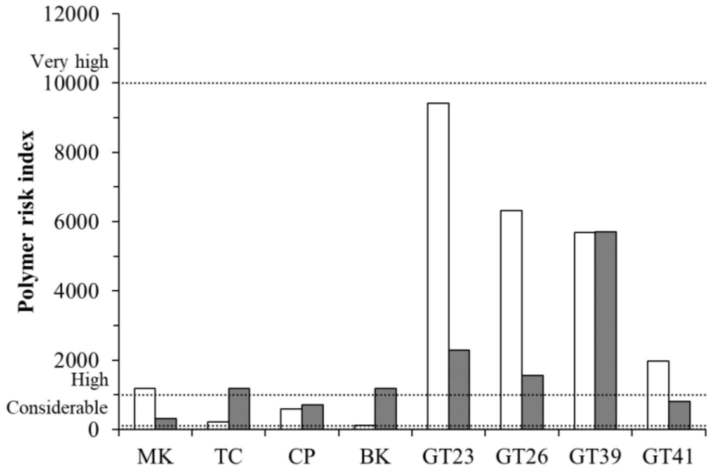
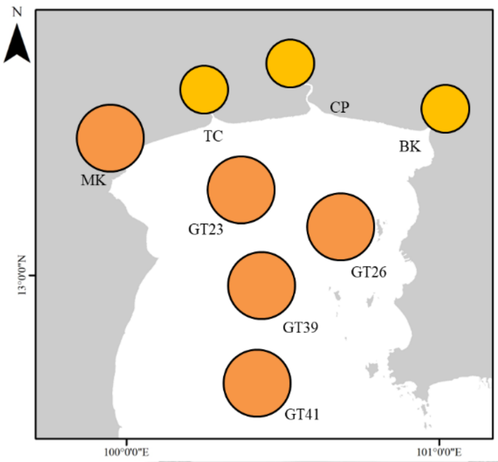


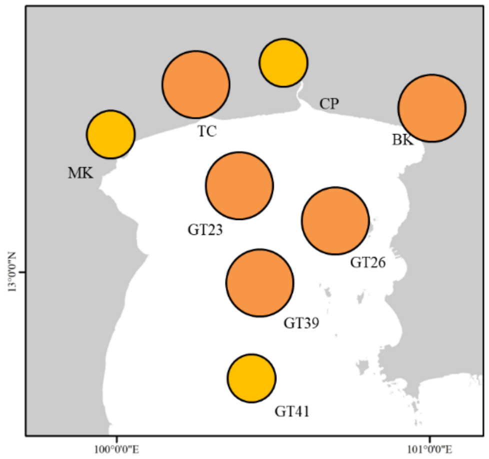
Figure 5.1 Contamination factor (C_f) of microplastics in dry season (☐) and wet season (■) of the river estuaries (MK, TC, CP, and BK) and the coastal sea (GT23, GT26, GT39, and GT41), the inner Gulf of Thailand



Dry season



Wet season



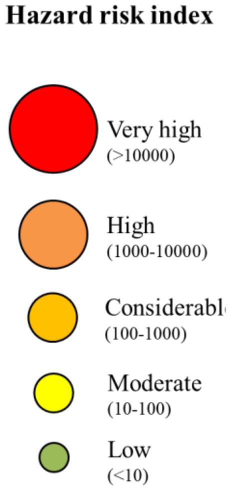


Figure 5.2 Hazard risk index of plastic chemicals (H_r) in dry season (☐) and wet season (■) of the river estuaries (MK, TC, CP, and BK) and the coastal sea (GT23, GT26, GT39, and GT41), the inner Gulf of Thailand

5.3.3 Risk from heavy metal contamination

Addition to the polymer chemicals, the other substances are ingredients in plastic products for improving the properties of materials. There is a concern that some additives may be toxic substances and those may be released according to the fragmentation process. Moreover, it is possible to be that MPs, the outcome of broken plastics, can accumulate the toxic substances from the environment. The ecological risk of toxic substances in plasticles was examined for the case of heavy metals.

The heavy metal accumulation in MPs resulted very low risk as the ecological risk was in the range of 0.07-0.13 due to the amount of the contamination in sediment of the coastal sea (GT23, GT26, GT39, and GT41) (Figure 5.3). The unit for quantifying heavy metals in MPs relatively affects the scale of risk index. As the results in chapter IV, the contamination of heavy metals in MPs (mg/kg MPs) was higher than that in sediment (mg/kg dry sediment). However, the small weigh-fraction of MPs in sediment gave exceedingly low concentration when calculate the MPs' heavy metals as weigh of heavy metal by weigh of dry sediments (mg/kg). To assess the eco-risk of heavy metals in MPs, the contamination by weigh of MPs is not acceptable as MPs was not the main component of sediment weight. MPs Thus, the contaminations by weigh of dry sediment should be used in the evaluation of risk of heavy metals in MPs with objective for presenting the status of the pollution in sediment.

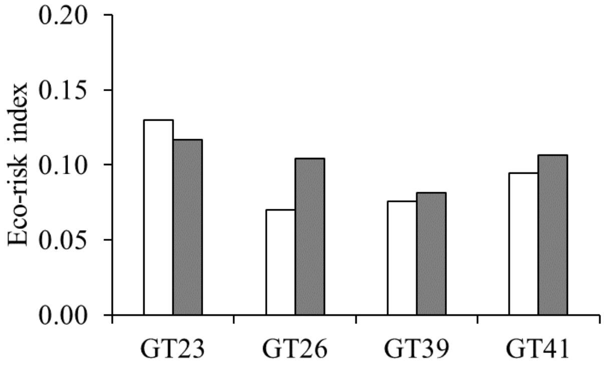


Figure 5.3 Ecological risk index (E_r) of heavy metals in microplstics for dry season (☐) and wet season (■) of the coastal sea, the inner Gulf of Thailand

5.3.4 Ecological risk of microplastics

A concern about risk of MPs is considered it was the effects of their persistence, their monomer chemicals, and their additional chemicals. This study, the ecological risk index of MPs was revised for the combination of risk from dose of MPs (contamination factor of MPs), risk from monomer chemicals (polymer hazard risk index), and risk from contaminated heavy metals (toxic response factor for heavy metals).

The proportion of ecological risk index for plastic chemicals and contaminated heavy metals in MPs revealed that the risk from heavy metals were small fraction in the total risk of MPs (0.2-2.5%) (Figure 5.4). It is reasonable to assume that there was no risk from the heavy metal contamination in plasticles. Thus, the eco-risk of MPs in estuarine sediments were acceptable to be assessed without the addition of the risk from heavy metals. Overall, the risk of MPs in the sediment of the inner GT was in the moderate level with the average eco-risk index value of 15 in dye season, and that was in the considerable level with the average eco-risk index value of 29 in wet season. Specifically, the ecological risk index of MPs was varied from the value of 2 for the low risk to 90 for the very high risk, depending on the seasons and area of contaminations (Figure 5.5). Because the contamination in estuaries was in the same level of the contamination factors, the polymer hazard risk index was the main factor controlling the different risk scale. The contamination of MPs in river estuaries resulted low to moderate risk, however, the risk in BK river estuary was increased to considerable level in wet season due to high contamination and high polymer risk index. The risk of MPs in the coastal sea was more fluctuated from the low risk (E_r=4) to very high risk (E_r=90). In the opposite with the estuaries, the quantities of MPs in the coastal sea promoted risk index, addition to the same levels of polymer risk index along the sampling station. The seasonal variation affected increasing risk index to high and very high levels in GT23 and GT39, while that was reduced in GT26, and that was not different risk level in GT41. Amount of sediment contaminated MPs and plastic type composition of MPs are the major factors initiated the ecological risk assessment of MPs.

The ecological risk assessment of MPs contamination in surface sediment of the inner GT reported the moderate risk level of the contamination. According to the assessment in previously study, the lower eco-risk level of MPs was evaluated in the shore of Rayong province, Thailand, but it must be illustrated only 3 types of plastic (PP, PE, and PS) were assessed with the reference concentration from the literature review [140]. This study, the several types of plastics were detected and used to assess the eco-risk. The modified MPs-risk assessment model was balanced for the eco-risk of MPs with the other contamination risk assessment in sediment, and the reference concentration of MPs with the minimum detectable size was proposed. The risk of MPs was primarily involved from the plastic monomer chemicals, while that was a little linked to the contaminated substances. Importantly, the risk index of MPs can be integrated the assessment of the other substances as they could be polluted in the ecosystem. The potential ecological risk index of the concerned area is the summation of ecological risk indexes of all considered substance.

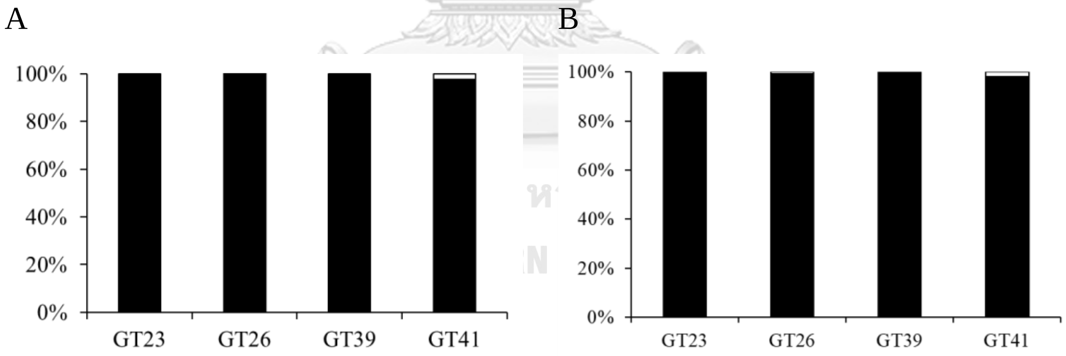
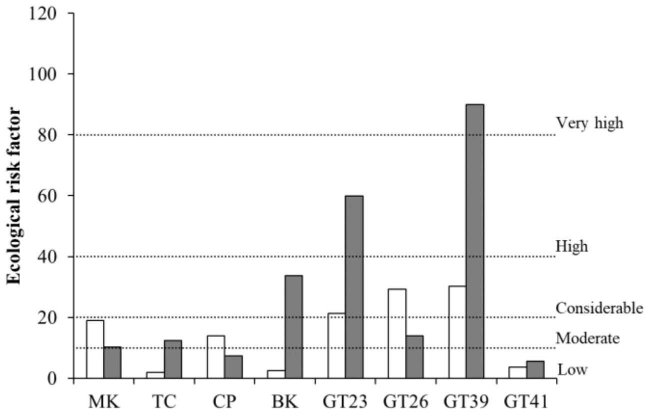
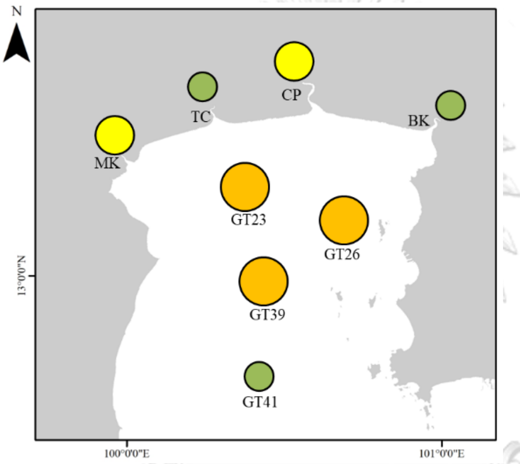


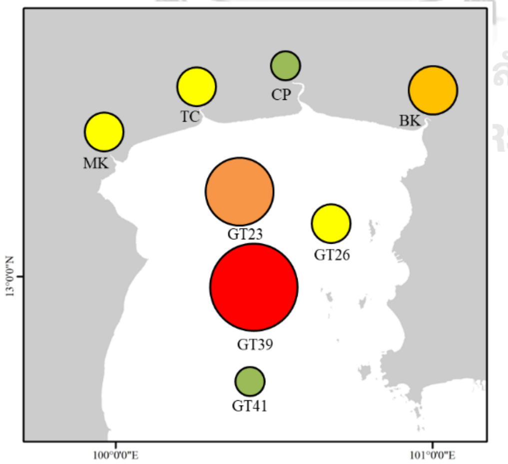
Figure 5.4 Proportion of ecological risk index (E_r) for plastic chemicals (■) and contaminated heavy metals in microplstics (☐) in dry season (a) and wet season of the coastal sea, the inner Gulf of Thailand



Dry season



Wet season



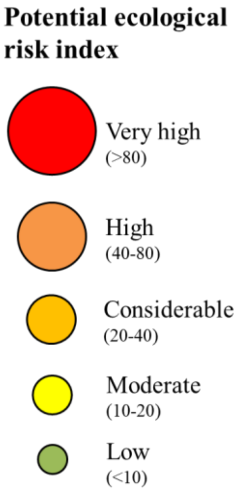


Figure 5.5 Ecological risk index (E_r) of microplastics in dry season (☐) and wet season (■) of the river estuaries (MK, TC, CP, and BK) and the coastal sea (GT23, GT26, GT39, and GT41), the inner Gulf of Thailand

5.4 Conclusion and recommendation in microplastics pollution assessment

The model of ecological risk assessment of MPs in surface sediments was revised for combination with the assessment of the risk from the other substances. The contamination of MPs in surface sediments of the inner GT was a case study for ecological risk assessment. The results revealed the moderate risk level and suggested that the risk of MPs was the predominant from plastic monomer chemicals rather than heavy metals as the co-contaminants. The risk of MPs was varied by the quantity and plastic types of MPs that related to the specific characteristics of contaminated area and seasonal variation. The recommendation in pollution assessment of MPs was included:

5.4.1 Quantification of microplastics

The ideal requirement in MPs analysis was the quantitative measurement in the unit of pieces (or items) per dry weight of sediment for each plastic polymer chemicals. Various procedures are possible to separate MPs from sediment sample because standard method for MPs separation had not been developed. In principle, plastics would be floated from sediment by using high density solution. For example, NaCl solution (1.2 g/cm^3) was recommended for economic and environment friendly, while NaI solution (1.6 g/cm^3) was suggested for separated high density plastics. However, metal solutions, such as $ZnCl_2$ solution (1.6-1.7 g/cm^3), are not recommended if the contamination of heavy metals in MPs will be analyzed and included in the ecological risk index. Similarly, the wet peroxide oxidation process (WPO) also be not recommended for removing organic fouling from MPs in case that contaminant in MPs will be analyzed. This study suggested the minimum requirement for risk assessment of MPs is the quantity of MPs contaminated in surface sediment (pieces/kg), the background concentration of MPs, and the proportion of plastic types in MPs. Essentially, the plastic type of MPs is the important component that need to be identified for at least 30 pieces in one MPs sample or all detected particle if applicable.

5.4.2 Co-contaminants analysis

The co-contaminated toxic substances in MPs pose to be the considerable property of MPs addition to the stability of the plastic's structure. The persistent organic pollutants (POPs) should be investigated and included to the risk evaluation of MPs; however, the extraction process and analytical procedure are needed to be calibrated with the certified reference materials. Only hydrophilic pollutants, heavy metals, were added to the risk assessment. Thus, the risk assessment of the co-contaminations of the other substances in MPs, especially POPs, still be necessary to be investigated according to hydrophobic properties of plastic chemicals.

5.4.3 Assessment of the potential ecological risk

The potential ecological risk index is the summation of the ecological risk index of the considered toxic substances. MPs was the new substance added to this index. In fact, the eco-risk index calculation showed the small fraction of risk from MPs' heavy metals. Thus, the risk of heavy metals as the co-contaminants in MPs can be omitted. and those can be evaluated in the contamination in the whole sediment. The potential ecological risk index (RI) could be revised to be the summation of eco-risk index of toxic substances including heavy metal and PCB ($\mathrm{E_r^{Toxic}}$), and plastic chemical in MPs ($\mathrm{E_r^{Pl}}$) (equation 8).

$$\mathrm{RI} = \sum \mathrm{E_r^{Toxic}} + \sum \mathrm{E_r^{Pl}} \qquad (8)$$

CHAPTER VI
CONCLUSIONS AND SUGGESTIONS

Microplastics (MPs), less than 5 mm of plastic particles, were investigated in surface waters and sediments of the inner Gulf of Thailand, the semi-enclosed gulf with multifunctional service. The variation in dry season and wet season influenced abundances and characteristics of MPs. This research observation could be inferred to specific evidence in transportation of MPs although some behavior needs to be clarified with more intensive field investigations or more exclusive experiments.

Abundance and distribution of MPs suggested plasticles were sourced from land-based activity. The increasing freshwater runoff in wet season enhanced contamination and dispersion of MPs in both surface waters and sediments. Physicochemical characteristics of MPs were roughly linked to fragmentation-oxidation process. Polyethylene (PE) and polypropylene (PP) were common plastic types contaminated in both surface water and sediment; however, polyamide (PA) and poly (acrylonitrile: butadiene) were major plastic types in sediment. Density of plastics compared with seawater was the important difference between plastic in surface water and sediment. The functional groups of hydroxy, carbonyl, and vinyl were observed in the chemical structure of MPs confirmed the oxidation of plastics. In addition, the fouling content of extracted MPs indicated that MPs were aggregated with the other substances. The contamination of heavy metals in MPs was magnified from that in sediment due to light weight and the formation of fouling and oxidative functional groups of MPs, but the contamination in MPS seems to be a small proportion in that in sediment. As the model for ecological risk assessment of MPs was revised for combination with the eco-risk of the other substances, the major risk of MPs was originated from the plastic monomer chemicals. This study captured a little component of the fate and transportation of MPs and proposed the perspective of ecological risk evaluation for the contamination of new pollutants, MPs. Necessarily, the knowledge about dynamic of MPs still needs to be improved.

Parallel to understand the pollution of MPs, the plastic waste management seems to be the first action to prevent the generation of plastic debris. The results of this study confirmed that there is contamination of MPs in the ecosystem, and this contamination is driven by the mismanagement in plastic debris. The shape of MPs and the plastic types detected in this study may indicate the plastic products that should be managed the disposal of them. For example, PE in shape of film MPs is possible to be generated by fragmentation of plastic bag, so the management should be focused on the plastic bag in the waste. However, it must be highlight that the contamination of MPs in this study was investigated before the coronavirus disease pandemic in 2019 (COVID-19). The contamination of MPs may be magnified by increasing single use plastic products. In addition, the characteristics of MPs, either shape, color, or plastic type, is possible to be changed by the properties of those products. Long-term investigation may be required for monitoring the contamination status and illustrating the dynamic of MPs in the ecosystem. The removing MPs from the point source emission may control the releasing of MPs, while the site remediation is the last steps for reduce the adverse effects of the contamination. Notably, the actions on the contamination of MPs are precaution for the uncertainty of its effects on the ecosystem.

The understanding in behavior of plastic particles may be the initiation for evaluating the impacts of the contamination of MPs. The fate and transportation of them could be described the transformation in physicochemical structure and movement in the ecosystem. It may be the significant impacts if the vertical distribution of MPs was defined. The sedimentation of MPs-aggregate and the resuspension of MPs may be investigated in water column and sediment interface for comprehensive study in the movement of MPs. The interaction between plastics and the other substances should be considered as the additional factor regulated the transportation of MPs. However, the effects of MPs exposure still be the most important data in the toxicity assessment.

6.1 Suggestion in study of microplastics

This study revealed the diversity of MPs. The source identification of MPs contaminated in marine environment still be the problem because of non-specific linkage between MPs and plastic products. Various mechanism may result difference characteristic in fragmented plastic particle. Importantly, it seems to be that the variation in physical and chemical characteristics of MPs controlled the fate and transportation of them. As a concern about plastic particles in terms of toxicity and risk, the factor of sizes, shapes, colors, and polymer types should be included in the research about MPs following the topics:

1) The rate, regulating factors, byproducts, and transformed structure during the fragmentation of plastic materials,
2) Vertical movement and resuspension in water column and sediment,
3) Interaction between MPs and microorganism as it may result MPs settling,
4) Accumulation and discharge of substances in MPs,
5) Effects or toxicity of MPs contamination included the co-contamination,
6) Accumulation and magnification of MPs in food web,
7) Remediation of MPs in the environment.

The influences of numerous environmental variations and the impacts of MPs in the ecosystem are uncertain. The behavior of MPs can be deeply explained by experiment; in the other hand, that can be evidently observed by field monitoring. It may be benefit for managing plastic debris if the loading of MPs to the ecosystem were identified and estimated. Critically, the qualitative and quantitative analysis even though the sample collection of MPs was the essential part, especially for field investigation.

6.2 Suggestion in sample collection for microplastics analysis

Various sample collection methods have been used in previous. With the objective for collect MPs in the mixture of solids particle, the soluble contents in samples need to be eliminated before the analysis of MPs. By this reason, the water sampling either collected by grab water or pumping water could be used as well as the plankton net throwing. The grab water sampling was recommended for sample collection from the water column. The water sampling methods for MPs analysis need to be comparatively analyzed due to there was no guideline for acceptable sampling methos of sampling of MPs in water samples. However, the samples should be storage in non-plastic container for preventing the plastic contamination. In contrast, the grab sediment sampler or sediment corer still be the technic for collecting mixed solids of bed sediment samples. The concern is that mesh size of net or filter for retaining solid part in samples. The minimum mesh size may result more abundance of MPs as the particles were more analyzed, but the size of particle also be depended on the detection limit of the analysis.

6.3 Suggestion in microplastics analysis

It is reasonable to say that the diversity of MPs is dramatically variated, as it has series of difference in sizes, shapes, colors, and plastic polymer types. At least, the analysis of MPs should report quantification method, plastic particle size, and abundance of MPs.

The separation process performed for extracting MPs from the mixture of solid particles in the samples. The organic content removing should be done due to the biofouling may the component in plastic particle. Wet peroxide oxidation process (WPO) was recommended as it was proposed by National Oceanic and Atmospheric Administration (NOAA), and it was mostly used in previous research. However, the oxidative reagents or enzymatic digestion also could be used before the separation process. The separation of MPs basically operated by the density of plastics. The NaCl solution with the density of 1.2 g/cm^3 was accepted for floating MPs because the large productions of low-density plastic types were assumed that was the main proportion in the plastic composition of MPs. Environmentally friendly reagent and economical cost also be considered for using NaCl solution. However, the higher density solution such as $ZnCl_2$ (1.6-1.7 g/cm^3) and NaI (1.6 g/cm^3) could be applied for the increasing density of the solution. The observation of PTFE (2.2 g/cm^3) by using NaCl solution in separation process in this study could be suggested the floatation of MPs may relate to the other factors, and NaCl solution is suitable for separating MPs. The separated MPs should be place on filter before the analysis

The MPs should be generally identified for size, shape, colors, and plastic types. The shapes and colors of MPs were quantified under microscope. The categories of shape and color were based on personal decision. This study suggested groups of shapes should be included fragment fiber and pellet, while the groups of colors should be colorful, white, transparent, brown, and black. The most important in MPs analysis is the plastic quantification and identification. At least, the number of particles should be identified under stereomicroscope. Non-plastic should not be counted as MPs, and it should be removed from the filter although the excellent skill is required. The extracted particles should be confirmed that they were plastic materials by FTIR spectrum. In detail, the FTIR technic for MPs identification should be chemical imaging or chemical mapping of the particle on Al_2O_3 filter although it cannot detect the functional groups in wave number lower than 1300 cm^{-1}. The reported abundance of MPs should be the number of plastics identified by chemical imaging or chemical mapping. The sampling particles to analyzed via FTIR also be acceptable, but the proportion of plastic and non-plastic materials must be reported. All analytical process needs to be driven by quality control analysis.

It is general to say that all analysis has the error in accuracy and precision according to the heterogeneity of the samples. The quality control analysis improves the reliability of the detected value, especially for the abundance of MP. Herein, the minimum requirement for quality control in analysis of MPs were suggested:

1) the containers and equipment for sample collection and analysis need to be cleaned and avoided the plastic materials.
2) The contamination from airborne plastic should be prevented by cover the sample containers.
3) The blank sample should be analyzed, and the detected MPs in the samples should be normalized by blank.
4) The spike plasticles sample analysis should be process because it could represent the recovery of MPs extraction and detection

REFERENCES

[1] A.R. de Carvalho, F. Garcia, L. Riem-Galliano, L. Tudesque, M. Albignac, A. Ter Halle, J. Cucherousset, Urbanization and hydrological conditions drive the spatial and temporal variability of microplastic pollution in the Garonne River, Sci. Total Environ., 769 (2021) 144479.

[2] C. Loughlin, A.R. Marques Mendes, L. Morrison, A. Morley, The role of oceanographic processes and sedimentological settings on the deposition of microplastics in marine sediment: Icelandic waters, Mar. Pollut. Bull., 164 (2021) 111976.

[3] A.D. Gray, H. Wertz, R.R. Leads, J.E. Weinstein, Microplastic in two South Carolina Estuaries: Occurrence, distribution, and composition, Mar. Pollut. Bull., 128 (2018) 223-233.

[4] L. Frere, I. Paul-Pont, E. Rinnert, S. Petton, J. Jaffre, I. Bihannic, P. Soudant, C. Lambert, A. Huvet, Influence of environmental and anthropogenic factors on the composition, concentration and spatial distribution of microplastics: A case study of the Bay of Brest (Brittany, France), Environ. Pollut., 225 (2017) 211-222.

[5] L. Zhu, H. Bai, B. Chen, X. Sun, K. Qu, B. Xia, Microplastic pollution in North Yellow Sea, China: Observations on occurrence, distribution and identification, Sci. Total Environ., 636 (2018) 20-29.

[6] F.C. Alam, E. Sembiring, B.S. Muntalif, V. Suendo, Microplastic distribution in surface water and sediment river around slum and industrial area (case study: Ciwalengke River, Majalaya district, Indonesia), Chemosphere, 224 (2019) 637-645.

[7] Y. Jiang, F. Yang, Y. Zhao, J. Wang, Greenland Sea Gyre increases microplastic pollution in the surface waters of the Nordic Seas, Sci. Total Environ., 712 (2020) 1-9.

[8] D. Lithner, A. Larsson, G. Dave, Environmental and health hazard ranking and assessment of plastic polymers based on chemical composition, Sci. Total Environ., 409 (2011) 3309-3324.

[9] V.E.N. Alves, G.M. Figueiredo, Microplastic in the sediments of a highly eutrophic tropical estuary, Mar. Pollut. Bull., 146 (2019) 326-335.

[10] H. Nakano, H. Arakawa, T. Tokai, Microplastics on the sea surface of the semi-closed Tokyo Bay, Mar. Pollut. Bull., 162 (2021) 111887.

[11] M. Zobkov, E. Esiukova, Microplastics in Baltic bottom sediments: Quantification procedures and first results, Mar. Pollut. Bull., 114 (2017) 724-732.

[12] S. Zhao, L. Zhu, T. Wang, D. Li, Suspended microplastics in the surface water of the Yangtze Estuary System, China: first observations on occurrence, distribution, Mar. Pollut. Bull., 86 (2014) 562-568.

[13] Y. Jiang, Y. Zhao, X. Wang, F. Yang, M. Chen, J. Wang, Characterization of microplastics in the surface seawater of the South Yellow Sea as affected by season, Sci. Total Environ., 724 (2020) 138375.

[14] Z. Dai, H. Zhang, Q. Zhou, Y. Tian, T. Chen, C. Tu, C. Fu, Y. Luo, Occurrence of microplastics in the water column and sediment in an inland sea affected by intensive anthropogenic activities, Environ. Pollut., 242 (2018) 1557-1565.

[15] A. Isobe, K. Uchiyama-Matsumoto, K. Uchida, T. Tokai, Microplastics in the Southern Ocean, Mar. Pollut. Bull., 114 (2019) 623-626.

[16] C. Alomar, F. Estarellas, S. Deudero, Microplastics in the Mediterranean Sea: Deposition in coastal shallow sediments, spatial variation and preferential grain size, Marine Environmental Research, 115 (2016) 1-10.
[17] Y. Matsuguma, H. Takada, H. Kumata, H. Kanke, S. Sakurai, T. Suzuki, M. Itoh, Y. Okazaki, R. Boonyatumanond, M.P. Zakaria, S. Weerts, B. Newman, Microplastics in sediment cores from asia and africa as indicators of temporal trends in plastic pollution, Archives of Environmental Contamination and Toxicology, 73 (2017) 230-239.
[18] P. Xu, G. Peng, L. Su, Y. Gao, L. Gao, D. Li, Microplastic risk assessment in surface waters: A case study in the Changjiang Estuary, China, Mar. Pollut. Bull., 133 (2018) 647-654.
[19] L.J. Sánchez-Hernández, P. Ramírez-Romero, F. Rodríguez-González, V.H. Ramos-Sánchez, R.A. Márquez Montes, H. Romero-Paredes Rubio, S.B. Sujitha, M.P. Jonathan, Seasonal evidences of microplastics in environmental matrices of a tourist dominated urban estuary in Gulf of Mexico, Mexico, Chemosphere, 277 (2021) 130261.
[20] K. McEachern, H. Alegria, A.L. Kalagher, C. Hansen, S. Morrison, D. Hastings, Microplastics in Tampa Bay, Florida: Abundance and variability in estuarine waters and sediments, Mar. Pollut. Bull., 148 (2019) 97-106.
[21] J. Zhang, C. Zhang, Y. Deng, R. Wang, E. Ma, J. Wang, J. Bai, J. Wu, Y. Zhou, Microplastics in the surface water of small-scale estuaries in Shanghai, Mar. Pollut. Bull., 149 (2019) 1-6.
[22] N.H. Nor, J.P. Obbard, Microplastics in Singapore's coastal mangrove ecosystems, Mar. Pollut. Bull., 79 (2014) 278-283.
[23] M.R. Cordova, A.I.S. Purwiyanto, Y. Suteja, Abundance and characteristics of microplastics in the northern coastal waters of Surabaya, Indonesia, Mar. Pollut. Bull., 142 (2019) 183-188.
[24] N. Chinfak, P. Sompongchaiyakul, C. Charoenpong, H. Shi, T. Yeemin, J. Zhang, Abundance, composition, and fate of microplastics in water, sediment, and shellfish in the Tapi-Phumduang River system and Bandon Bay, Thailand, Sci. Total Environ., 781 (2021) 146700.
[25] A.T. Ta, S. Babel, Microplastic contamination on the lower Chao Phraya: Abundance, characteristic and interaction with heavy metals, Chemosphere, 257 (2020) 127234.
[26] G. Peng, B. Zhu, D. Yang, L. Su, H. Shi, D. Li, Microplastics in sediments of the Changjiang Estuary, China, Environ. Pollut., 225 (2017) 283-290.
[27] D. Rose, M. Webber, Characterization of microplastics in the surface waters of Kingston Harbour, Sci. Total Environ., 664 (2019) 753-760.
[28] W.M.A.W.M. Khalik, Y.S. Ibrahim, S.T. Anuar, S. Govindasamy, N.F. Baharuddin, Microplastics analysis in Malaysian marine waters: A field study of Kuala Nerus and Kuantan, Mar. Pollut. Bull., 135 (2018) 451-457.
[29] M. Claessens, S. De Meester, L. Van Landuyt, K. De Clerck, C.R. Janssen, Occurrence and distribution of microplastics in marine sediments along the Belgian coast, Mar. Pollut. Bull., 62 (2011) 2199-2204.
[30] C. Lorenz, L. Roscher, M.S. Meyer, L. Hildebrandt, J. Prume, M.G.J. Loder, S. Primpke, G. Gerdts, Spatial distribution of microplastics in sediments and surface waters of the southern North Sea, Environ. Pollut., 252 (2019) 1719-1729.

[31] M. Bergmann, V. Wirzberger, T. Krumpen, C. Lorenz, S. Primpke, M.B. Tekman, G. Gerdts, High Quantities of Microplastic in Arctic Deep-Sea Sediments from the HAUSGARTEN Observatory, Environmental Science & Technology, 51 (2017) 11000-11010.

[32] G. Peng, P. Xu, B. Zhu, M. Bai, D. Li, Microplastics in freshwater river sediments in Shanghai, China: A case study of risk assessment in mega-cities, Environ. Pollut., 234 (2018) 448-456.

[33] H.A. Nel, T. Dalu, R.J. Wasserman, Sinks and sources: Assessing microplastic abundance in river sediment and deposit feeders in an Austral temperate urban river system, Sci. Total Environ., 612 (2018) 950-956.

[34] H.A. Leslie, S.H. Brandsma, M.J. van Velzen, A.D. Vethaak, Microplastics en route: Field measurements in the Dutch river delta and Amsterdam canals, wastewater treatment plants, North Sea sediments and biota, Environment International, 101 (2017) 133-142.

[35] T. Jiwarungrueangkul, J. Phaksopa, P. Sompongchaiyakul, D. Tipmanee, Seasonal microplastic variations in estuarine sediments from urban canal on the west coast of Thailand: A case study in Phuket province, Mar. Pollut. Bull., 168 (2021) 112452.

[36] S. Eo, S.H. Hong, Y.K. Song, G.M. Han, W.J. Shim, Spatiotemporal distribution and annual load of microplastics in the Nakdong River, South Korea, Water Res., 160 (2019) 228-237.

[37] G. Wang, J. Lu, W. Li, J. Ning, L. Zhou, Y. Tong, Z. Liu, H. Zhou, N. Xiayihazi, Seasonal variation and risk assessment of microplastics in surface water of the Manas River Basin, China, Ecotoxicology and Environmental Safety, 208 (2021) 111477.

[38] M.K. Aliabad, M. Nassiri, K. Kor, Microplastics in the surface seawaters of Chabahar Bay, Gulf of Oman (Makran Coasts), Mar. Pollut. Bull., 143 (2019) 125-133.

[39] J.H. Kang, O.Y. Kwon, K.W. Lee, Y.K. Song, W.J. Shim, Marine neustonic microplastics around the southeastern coast of Korea, Mar. Pollut. Bull., 96 (2015) 304-312.

[40] L.F. Ruiz-Orejon, R. Sarda, J. Ramis-Pujol, Now, you see me: High concentrations of floating plastic debris in the coastal waters of the Balearic Islands (Spain), Mar. Pollut. Bull., 133 (2018) 636-646.

[41] Y. Wang, X. Zou, C. Peng, S. Qiao, T. Wang, W. Yu, S. Khokiattiwong, N. Kornkanitnan, Occurrence and distribution of microplastics in surface sediments from the Gulf of Thailand, Mar. Pollut. Bull., 152 (2020) 110916.

[42] W. Zhang, S. Zhang, Q. Zhao, L. Qu, D. Ma, J. Wang, Spatio-temporal distribution of plastic and microplastic debris in the surface water of the Bohai Sea, China, Mar. Pollut. Bull., 158 (2020) 111343.

[43] Y. Suteja, A.S. Atmadipoera, E. Riani, I.W. Nurjaya, D. Nugroho, M.R. Cordova, Spatial and temporal distribution of microplastic in surface water of tropical estuary: Case study in Benoa Bay, Bali, Indonesia, Mar. Pollut. Bull., 163 (2021) 111979.

[44] G.P. Olivatto, M.C.T. Martins, C.C. Montagner, T.B. Henry, R.S. Carreira, Microplastic contamination in surface waters in Guanabara Bay, Rio de Janeiro, Brazil, Mar. Pollut. Bull., 139 (2019) 157-162.

[45] T.S. Galloway, M. Cole, C. Lewis, Interactions of microplastic debris throughout the marine ecosystem, Nature Ecology & Evolution, 1 (2017) 108.

[46] M. Kooi, E.H.V. Nes, M. Scheffer, A.A. Koelmans, Ups and downs in the ocean: effects of biofouling on vertical transport of microplastics, Environmental Science & Technology, 51 (2017) 7963-7971.

[47] A.L. Andrady, Microplastics in the marine environment, Mar. Pollut. Bull., 62 (2011) 1596-1605.

[48] Y. Chae, Y.J. An, Effects of micro- and nanoplastics on aquatic ecosystems: Current research trends and perspectives, Mar. Pollut. Bull., 124 (2017) 624-632.

[49] M. Cole, P. Lindeque, C. Halsband, T.S. Galloway, Microplastics as contaminants in the marine environment: a review, Mar. Pollut. Bull., 62 (2011) 2588-2597.

[50] S. Anbumani, P. Kakkar, Ecotoxicological effects of microplastics on biota: a review, Environmental Science and Pollution Reseach, 25 (2018) 14373-14396.

[51] J.R. Jambeck, R. Geyer, C. Wilcox, T.R. Siegler, M. Perryman, A. Andrady, R. Narayan, K.L. Law, Plastic waste inputs from land into the ocean, Science, 347 (2015) 768-771.

[52] A.T. Ta, S. Babel, Microplastics pollution with heavy metals in the aquaculture zone of the Chao Phraya River Estuary, Thailand, Mar. Pollut. Bull., 161 (2020) 111747.

[53] R. Sukhsangchan, R. Keawsang, S. Worachananant, T. Thamrongnawasawat, J. Phaksopa, Suspended microplastics during a tidal cycle in sea-surface waters around Chao Phraya River mouth, Thailand, ScienceAsia, 46 (2020) 724-733.

[54] Department of marine and coastal resources, Burapha University, Investigation and identification of marine microplastic debris (in Thai), in, 2014.

[55] P. Tharamon, S. Praisanklul, N. Leadpathom, Contamination of microplastic in bivalve at Chaolao and Kungwiman beach Chanthaburi province (in Thai), Khon Kaen Agriculture Journal, 44 (2016) 738-744.

[56] G.G.N. Thushari, J.D.M. Senevirathna, A. Yakupitiyage, S. Chavanich, Effects of microplastics on sessile invertebrates in the eastern coast of Thailand: An approach to coastal zone conservation, Mar. Pollut. Bull., 124 (2017) 349-355.

[57] A. Buranapratheprat, Circulation in the upper gulf of Thailand: A review, Burapha Science Journal, 13 (2008) 75-83.

[58] S. Maksumpun, J. Phaksopa, P. Thaipichitburapa, S. Srithongouthai, W. Sirinawin, T. Pokavanich, N. Thawonsode, M. Suksomjit, M. Srisomwong, O. Veschasit, R. Mengchouy, Development of Socio-Ecological Based Effective Fishery Management Policy for Good Governance in Sustainable Fishery of the Inner Gulf of Thailand, in: Assessments of Impacts from Climate Changes and Specific Hydro-ecological Characteristics of surrounded Estuaries on the Water Quality and Pollution Status of the Inner Gulf of Thailand, 2019.

[59] J. Masura, J. Baker, G. Foster, C. Arthur, Laboratory method for the analysis of microplastics in the marine environment: recommendations for quantifying synthetic particles in waters and sediments, in, National Oceanic and Atmospheric Administration, NOAA Technical Memorandum NOS-OR&R-48, 2015.

[60] C.B. Crawford, B. Quinn, Microplastic Pollutants, Candice G.Janco, 2017.

[61] V. Hidalgo-Ruz, L. Gutow, R.C. Thompson, M. Thiel, Microplastics in the marine environment: a review of the methods used for identification and quantification, Environmental Science & Technology, 46 (2012) 3060-3075.

[62] A.A. Shah, F. Hasan, A. Hameed, S. Ahmed, Biological degradation of plastics: a comprehensive review, Biotechnol. Adv., 26 (2008) 246-265.

[63] D. Lobelle, M. Cunliffe, Early microbial biofilm formation on marine plastic debris, Mar. Pollut. Bull., 62 (2011) 197-200.

[64] B.J.L. Laglbauer, R.M. Franco-Santos, M. Andreu-Cazenave, L. Brunelli, M. Papadatou, A. Palatinus, M. Grego, T. Deprez, Macrodebris and microplastics from beaches in Slovenia, Mar. Pollut. Bull., 89 (2014) 356-366.

[65] A. Massos, A. Turner, Cadmium, lead and bromine in beached microplastics, Environ. Pollut., 227 (2017) 139-145.

[66] A. Turner, Heavy metals, metalloids and other hazardous elements in marine plastic litter, Mar. Pollut. Bull., 111 (2016) 136-142.

[67] A. Turner, K.S. Lau, Elemental concentrations and bioaccessibilities in beached plastic foam litter, with particular reference to lead in polyurethane, Mar. Pollut. Bull., 112 (2016) 265-270.

[68] A. Turner, Trace elements in fragments of fishing net and other filamentous plastic litter from two beaches in SW England, Environ. Pollut., 224 (2017) 722-728.

[69] L.A. Holmes, A. Turner, R.C. Thompson, Adsorption of trace metals to plastic resin pellets in the marine environment, Environ. Pollut., 160 (2012) 42-48.

[70] K. Ashton, L. Holmes, A. Turner, Association of metals with plastic production pellets in the marine environment, Mar. Pollut. Bull., 60 (2010) 2050-2055.

[71] B. Munier, L.I. Bendell, Macro and micro plastics sorb and desorb metals and act as a point source of trace metals to coastal ecosystems, PLoS One, 13 (2018) 1-13.

[72] L.A. Holmes, A. Turner, R.C. Thompson, Interactions between trace metals and plastic production pellets under estuarine conditions, Mar. Chem., 167 (2014) 25-32.

[73] J. Wang, J. Peng, Z. Tan, Y. Gao, Z. Zhan, Q. Chen, L. Cai, Microplastics in the surface sediments from the Beijiang River littoral zone: Composition, abundance, surface textures and interaction with heavy metals, Chemosphere, 171 (2017) 248-258.

[74] T.M. Karlsson, A.D. Vethaak, B.C. Almroth, F. Ariese, M. van Velzen, M. Hassellov, H.A. Leslie, Screening for microplastics in sediment, water, marine invertebrates and fish: Method development and microplastic accumulation, Mar. Pollut. Bull., 122 (2017) 403-408.

[75] S. Zhao, L. Zhu, D. Li, Microplastic in three urban estuaries, China, Environ. Pollut., 206 (2015) 597-604.

[76] M.T. Nuelle, J.H. Dekiff, D. Remy, E. Fries, A new analytical approach for monitoring microplastics in marine sediments, Environ. Pollut., 184 (2014) 161-169.

[77] L. Fok, P.K. Cheung, G. Tang, W.C. Li, Size distribution of stranded small plastic debris on the coast of Guangdong, South China, Environ. Pollut., 220 (2017) 407-412.

[78] M. Fischer, B.M. Scholz-Bottcher, Simultaneous trace identification and quantification of common types of microplastics in environmental samples by Pyrolysis-Gas Chromatography-Mass Spectrometry, Environmental Science & Technology, 51 (2017) 5052-5060.

[79] D.A. Miranda, G.F. de Carvalho-Souza, Are we eating plastic-ingesting fish?, Mar. Pollut. Bull., 103 (2016) 109-114.

[80] F.M. Fazey, P.G. Ryan, Biofouling on buoyant marine plastics: An experimental study into the effect of size on surface longevity, Environ. Pollut., 210 (2016) 354-360.

[81] M. Long, B. Moriceau, M. Gallinari, C. Lambert, A. Huvet, J. Raffray, P. Soudant, Interactions between microplastics and phytoplankton aggregates: Impact on their respective fates, Mar. Chem., 175 (2015) 39-46.

[82] M. Long, I. Paul-Pont, H. Hegaret, B. Moriceau, C. Lambert, A. Huvet, P. Soudant, Interactions between polystyrene microplastics and marine phytoplankton lead to species-specific hetero-aggregation, Environ. Pollut., 228 (2017) 454-463.

[83] T. Huffer, A.K. Weniger, T. Hofmann, Sorption of organic compounds by aged polystyrene microplastic particles, Environ. Pollut., 236 (2018) 218-225.

[84] H. Zhang, Transport of microplastics in coastal seas, Estuarine, Coastal and Shelf Science, 199 (2017) 74-86.

[85] I. Chubarenko, A. Bagaev, M. Zobkov, E. Esiukova, On some physical and dynamical properties of microplastic particles in marine environment, Mar. Pollut. Bull., 108 (2016) 105-112.

[86] A. Van, C.M. Rochman, E.M. Flores, K.L. Hill, E. Vargas, S.A. Vargas, E. Hoh, Persistent organic pollutants in plastic marine debris found on beaches in San Diego, California, Chemosphere, 86 (2012) 258-263.

[87] W. Zhang, X. Ma, Z. Zhang, Y. Wang, J. Wang, J. Wang, D. Ma, Persistent organic pollutants carried on plastic resin pellets from two beaches in China, Mar. Pollut. Bull., 99 (2015) 28-34.

[88] M. Heskett, H. Takada, R. Yamashita, M. Yuyama, M. Ito, Y.B. Geok, Y. Ogata, C. Kwan, A. Heckhausen, H. Taylor, T. Powell, C. Morishige, D. Young, H. Patterson, B. Robertson, E. Bailey, J. Mermoz, Measurement of persistent organic pollutants (POPs) in plastic resin pellets from remote islands: toward establishment of background concentrations for International Pellet Watch, Mar. Pollut. Bull., 64 (2012) 445-448.

[89] J.C. Antunes, J.G.L. Frias, A.C. Micaelo, P. Sobral, Resin pellets from beaches of the Portuguese coast and adsorbed persistent organic pollutants, Estuarine, Coastal and Shelf Science, 130 (2013) 62-69.

[90] W. Wang, J. Wang, Different partition of polycyclic aromatic hydrocarbon on environmental particulates in freshwater: Microplastics in comparison to natural sediment, Ecotoxicology and Environmental Safety, 147 (2018) 648-655.

[91] J. Li, K. Zhang, H. Zhang, Adsorption of antibiotics on microplastics, Environ. Pollut., 237 (2018) 460-467.

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

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

[94] C.M. Rochman, B.T. Hentschel, S.J. Teh, Long-term sorption of metals is similar among plastic types: implications for plastic debris in aquatic environments, PLoS One, 9 (2014) 1-10.

[95] A.A. Koelmans, A. Bakir, G.A. Burton, C.R. Janssen, Microplastic as a vector for

chemicals in the aquatic environment: Critical review and model-supported reinterpretation of empirical studies, Environmental Science & Technology, 50 (2016) 3315-3326.

[96] L. Hakanson, An ecological risk index for aquatic pollution control.a sedimentological approach, Water Res., 14 (1980) 975-1001.

[97] Z. Xu, S. Ni, X. Tuo, C. Zhang, Calculation of Heavy Metals'Toxicity Coefficient in the Evaluation of Potential Ecological Risk Index, Environmental Science & Technology, 31 (2008) 112-115.

[98] L. Hakanson, The quantitative impact of pH, bioproduction and Hg-contamination on the Hg-content of fish (pike), Environmental Pollution Series B, Chemical and Physical, 1 (1980) 285-304.

[99] D.L. Tomlinson, J.G. Wilson, C.R. Harris, D.W. Jeffrey, Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index, Helgoländer Meeresuntersuchungen, 33 (1980) 566-575.

[100] J.N. Hahladakis, C.A. Velis, R. Weber, E. Iacovidou, P. Purnell, An overview of chemical additives present in plastics: Migration, release, fate and environmental impact during their use, disposal and recycling, J. Hazard. Mater., 344 (2018) 179-199.

[101] S. Maksumpun, J. Phaksopa, P. Thaipichitburapa, S. Srithongouthai, W. Sirinawin, T. Pokavanich, N. Thawonsode, M. Suksomjit, M. Srisomwong, O. Veschasit, R. Mengchouy, Assessments of Impacts from Climate Changes and Specific Hydro-ecological Characteristics of surrounded Estuaries on the Water Quality and Pollution Status of the Inner Gulf of Thailand, in, 2019.

[102] J.P. Da Costa, A.R. Nunes, P.S.M. Santos, A.V. Girao, A.C. Duarte, T. Rocha-Santos, Degradation of polyethylene microplastics in seawater: Insights into the environmental degradation of polymers, Journal of Environmental Science and Health, part A Toxic/Hazardous Substances and Environmental Engineering, 53 (2018) 866-875.

[103] F. Julienne, N. Delorme, F. Lagarde, From macroplastics to microplastics: Role of water in the fragmentation of polyethylene, Chemosphere, 236 (2019) 1-8.

[104] Y. Mao, H. Ai, Y. Chen, Z. Zhang, P. Zeng, L. Kang, W. Li, W. Gu, Q. He, H. Li, Phytoplankton response to polystyrene microplastics: Perspective from an entire growth period, Chemosphere, 208 (2018) 59-68.

[105] F. Gao, J. Li, C. Sun, L. Zhang, F. Jiang, W. Cao, L. Zheng, Study on the capability and characteristics of heavy metals enriched on microplastics in marine environment, Mar. Pollut. Bull., 144 (2019) 61-67.

[106] S. Veerasingam, M. Saha, V. Suneel, P. Vethamony, A.C. Rodrigues, S. Bhattacharyya, B.G. Naik, Characteristics, seasonal distribution and surface degradation features of microplastic pellets along the Goa coast, India, Chemosphere, 159 (2016) 496-505.

[107] A.R. Lima, M.F. Costa, M. Barletta, Distribution patterns of microplastics within the plankton of a tropical estuary, Environ. Res., 132 (2014) 146-155.

[108] A.R.A. Lima, M. Barletta, M.F. Costa, Seasonal distribution and interactions between plankton and microplastics in a tropical estuary, Estuarine, Coastal and Shelf Science, 165 (2015) 213-225.

[109] W. Luo, L. Su, N.J. Craig, F. Du, C. Wu, H. Shi, Comparison of microplastic pollution in different water bodies from urban creeks to coastal waters, Environ.

Pollut., 246 (2019) 174-182.

[110] C. Dussud, C. Hudec, M. George, P. Fabre, P. Higgs, S. Bruzaud, A.M. Delort, B. Eyheraguibel, A.L. Meistertzheim, J. Jacquin, J. Cheng, N. Callac, C. Odobel, S. Rabouille, J.F. Ghiglione, Colonization of Non-biodegradable and Biodegradable Plastics by Marine Microorganisms, Frontier in Microbiology, 9 (2018) 1-13.

[111] Y. Li, X. Wang, W. Fu, X. Xia, C. Liu, J. Min, W. Zhang, J.C. Crittenden, Interactions between nano/micro plastics and suspended sediment in water: Implications on aggregation and settling, Water Res., 161 (2019) 486-495.

[112] A. Porter, B.P. Lyons, T.S. Galloway, C. Lewis, Role of Marine Snows in Microplastic Fate and Bioavailability, Environmental Science & Technology, 52 (2018) 7111-7119.

[113] L. Khatmullina, I. Isachenko, Settling velocity of microplastic particles of regular shapes, Mar. Pollut. Bull., 114 (2017) 871-880.

[114] N. Kowalski, A.M. Reichardt, J.J. Waniek, Sinking rates of microplastics and potential implications of their alteration by physical, biological, and chemical factors, Mar. Pollut. Bull., 109 (2016) 310-319.

[115] H. Takeoka, Fundamental concepts of exchange and transport time scales in a coastal sea, Continental Shelf Research, 3 (1984) 311-326.

[116] D. Li, K. Liu, C. Li, G. Peng, A.L. Andrady, T. Wu, Z. Zhang, X. Wang, Z. Song, C. Zong, F. Zhang, N. Wei, M. Bai, L. Zhu, J. Xu, H. Wu, L. Wang, S. Chang, W. Zhu, Profiling the Vertical Transport of Microplastics in the West Pacific Ocean and the East Indian Ocean with a Novel in Situ Filtration Technique, Environmental Science & Technology, 54 (2020) 12979-12988.

[117] X. Liu, X.-P. Ren, R. Yang, Infectious Behavior in Photo-oxidation of Polymers, Chin. J. Polym. Sci., 38 (2019) 248-256.

[118] D. Feldman, Polymer Weathering: Photo-Oxidation, Journal of Polymer and the Environmnet, 10 (2002) 163-173.

[119] Y.K. Song, S.H. Hong, M. Jang, G.M. Han, S.W. Jung, W.J. Shim, Combined Effects of UV Exposure Duration and Mechanical Abrasion on Microplastic Fragmentation by Polymer Type, Environmental Science & Technology, 51 (2017) 4368-4376.

[120] L. Canopoli, F. Coulon, S.T. Wagland, Degradation of excavated polyethylene and polypropylene waste from landfill, Sci. Total Environ., 698 (2020) 134125.

[121] A. Ter Halle, L. Ladirat, X. Gendre, D. Goudouneche, C. Pusineri, C. Routaboul, C. Tenailleau, B. Duployer, E. Perez, Understanding the Fragmentation Pattern of Marine Plastic Debris, Environmental Science & Technology, 50 (2016) 5668-5675.

[122] T. Liu, Y. Zhao, M. Zhu, J. Liang, S. Zheng, X. Sun, Seasonal variation of micro- and meso-plastics in the seawater of Jiaozhou Bay, the Yellow Sea, Mar. Pollut. Bull., 152 (2020) 110922.

[123] C. Li, X. Wang, K. Liu, L. Zhu, N. Wei, C. Zong, D. Li, Pelagic microplastics in surface water of the Eastern Indian Ocean during monsoon transition period: Abundance, distribution, and characteristics, Sci. Total Environ., 755 (2021) 142629.

[124] L. Zhu, S. Zhao, T.B. Bittar, A. Stubbins, D. Li, Photochemical dissolution of buoyant microplastics to dissolved organic carbon: Rates and microbial impacts, J. Hazard. Mater., 383 (2020) 121065.

[125] X. Chen, X. Chen, Y. Zhao, H. Zhou, X. Xiong, C. Wu, Effects of microplastic biofilms on nutrient cycling in simulated freshwater systems, Sci. Total Environ., 719 (2020) 137276.

[126] C. Martin, E. Corona, G.A. Mahadik, C.M. Duarte, Adhesion to coral surface as a potential sink for marine microplastics, Environ. Pollut., 255 (2019) 113281.

[127] F. Wang, W. Yang, P. Cheng, S. Zhang, S. Zhang, W. Jiao, Y. Sun, Adsorption characteristics of cadmium onto microplastics from aqueous solutions, Chemosphere, 235 (2019) 1073-1080.

[128] G. Liu, Z. Zhu, Y. Yang, Y. Sun, F. Yu, J. Ma, Sorption behavior and mechanism of hydrophilic organic chemicals to virgin and aged microplastics in freshwater and seawater, Environ. Pollut., 246 (2019) 26-33.

[129] K. Martin, A. Turner, Mobilization and bioaccessibility of cadmium in coastal sediment contaminated by microplastics, Mar. Pollut. Bull., 146 (2019) 940-944.

[130] P. Lapat-Atiwat, Influence of seasonal variations on contamination level and ecological risk of heavy metals in surface sediments of the inner Gulf of Thailand, in: Department of Environmental Science, Chulalongkorn University, 2021, pp. 114.

[131] P. Leelakun, Assessments of chromium pollution in surface sediment of the inner Gulf of Thailand, in: Department of Environmental Science, Chulalongkorn University, 2021, pp. 180.

[132] F.G. O'Neill, A. Ivanović, The physical impact of towed demersal fishing gears on soft sediments, ICES Journal of Marine Science, 73 (2016) i5-i14.

[133] J. Gao, S. Pan, P. Li, L. Wang, R. Hou, W.M. Wu, J. Luo, D. Hou, Vertical migration of microplastics in porous media: Multiple controlling factors under wet-dry cycling, J. Hazard. Mater., 419 (2021) 126413.

[134] D. O'Connor, S. Pan, Z. Shen, Y. Song, Y. Jin, W.M. Wu, D. Hou, Microplastics undergo accelerated vertical migration in sand soil due to small size and wet-dry cycles, Environ. Pollut., 249 (2019) 527-534.

[135] L. Cai, L. He, S. Peng, M. Li, M. Tong, Influence of titanium dioxide nanoparticles on the transport and deposition of microplastics in quartz sand, Environ. Pollut., 253 (2019) 351-357.

[136] R. Boonyatumanond, G. Wattayakorn, A. Amano, Y. Inouchi, H. Takada, Reconstruction of pollution history of organic contaminants in the upper Gulf of Thailand by using sediment cores: first report from Tropical Asia Core (TACO) project, Mar. Pollut. Bull., 54 (2007) 554-565.

[137] V. Kumar, S. Pandita, R. Setia, A meta-analysis of potential ecological risk evaluation of heavy metals in sediments and soils, Gondwana Research, 103 (2022) 487-501.

[138] V. Kumar, A. Sharma, S. Pandita, R. Bhardwaj, A.K. Thukral, A. Cerda, A review of ecological risk assessment and associated health risks with heavy metals in sediment from India, International Journal of Sediment Research, 35 (2020) 516-526.

[139] J.B. Kowalska, R. Mazurek, M. Gasiorek, T. Zaleski, Pollution indices as useful tools for the comprehensive evaluation of the degree of soil contamination-A review, Environ. Geochem. Health, 40 (2018) 2395-2420.

[140] P. Prarat, P. Hongsawat, Microplastic pollution in surface seawater and beach sand from the shore of Rayong province, Thailand: Distribution, characterization,

and ecological risk assessment, Mar. Pollut. Bull., 174 (2022) 113200.

[141] G. Everaert, L. Van Cauwenberghe, M. De Rijcke, A.A. Koelmans, J. Mees, M. Vandegehuchte, C.R. Janssen, Risk assessment of microplastics in the ocean: Modelling approach and first conclusions, Environ. Pollut., 242 (2018) 1930-1938.

VITA

NAME	Pathompong Vibhatabandhu
DATE OF BIRTH	31 January 1992
INSTITUTIONS ATTENDED	2010-2014 Department of Environmental Science, Faculty of Science, Chulalongkorn University 2014-2016 Program in Biotechnology, Faculty of Science, Chulalongkorn University 2017 International Program in Hazardous Substance and Environmental Management, Graduate School, Chulalongkorn University,
PUBLICATION	2022. Influence of seasonal variations on the distribution characteristics of microplastics in the surface water of the Inner Gulf of Thailand. Marine Pollution Bulletin. vol.180, 113747 2022. Abundance and characteristics of microplastics contaminating the surface water of the Inner Gulf of Thailand. Water, Air, & Soil Pollution. vol.233, 50 2020. CU Zero Waste case study of waste management in canteens of Chulalongkorn University (in Thai). Environmental Journal. vol.3, 1-9 2018. Biosorption of Cr (III) and Ni (II) from an aqueous solution using cuttlebone and application for battery manufacturing wastewater treatment. EnvironmentAsia. vol.11, 1-14 2017. Removal of Pb (II) from an aqueous solution using modified cuttlebone as a biosorbent. EnvironmentAsia. vol. 10, 34-43 2016. Removal of copper (II) from aqueous solutions using cuttlebone as bio-adsorbent. Applied Environmental Research. vol.38, 39-47