

INFLUENCE OF SEASONAL VARIATIONS ON  
CONTAMINATION LEVEL AND ECOLOGICAL RISK OF  
HEAVY METALS IN THE SURFACE SEDIMENTS OF THE  
INNER GULF OF THAILAND

Mr. Phuttiaphat Lapat-atiwat



A Thesis Submitted in Partial Fulfillment of the Requirements  
for the Degree of Master of Science in Industrial Toxicology and Risk

Assessment

Department of Environmental Science

FACULTY OF SCIENCE

Chulalongkorn University

Academic Year 2021

Copyright of Chulalongkorn University

อิทธิพลของการเปลี่ยนแปลงฤดูกาลต่อระดับการปนเปื้อนและความเสี่ยงทางนิเวศของโลหะหนัก  
ในตะกอนดินชั้นผิวของอ่าวไทยตอนใน



วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต  
สาขาวิชาพิษวิทยาอุตสาหกรรมและการประเมินความเสี่ยง ภาควิชาวิทยาศาสตร์สิ่งแวดล้อม  
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย  
ปีการศึกษา 2564  
ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย





# # 6172164923 : MAJOR INDUSTRIAL TOXICOLOGY AND RISK ASSESSMENT

KEYWORD Heavy metal, Ecological risk assessment, The inner Gulf of Thailand, Seasonal variation

Phuttiaphat Lapat-atiwat : INFLUENCE OF SEASONAL VARIATIONS ON CONTAMINATION LEVEL AND ECOLOGICAL RISK OF HEAVY METALS IN THE SURFACE SEDIMENTS OF THE INNER GULF OF THAILAND. Advisor: Asst. Prof. SARAWUT SRITHONGOUTHAI, Ph.D.

The Inner Gulf of Thailand is a marine resource that provides ecological and economic value. Meanwhile, its can be acted like pollutions sink, especially heavy metals. After that, the extensions of industrialization, agriculturalization, and urbanization can degenerate to the inner Gulf environment quality. Therefore, this thesis was aimed to study the spatial distribution and seasonal variation of heavy metal concentration (Cd, Pb, Cu, Co, Ni, Mn and Zn) in surface sediment including the Mae Klong, the Tha Chin, the Chao Phraya and the Bangpakong River estuaries. Moreover, the contamination status and ecological risk were also evaluated. The results shown the seasonal mean values of Cd, Pb, Cu, Co, Ni, Mn, Zn are in a range of 0.13–0.19, 12.48–16.76, 7.40–15.49, 19.22–23.95, 47.64–73.03 mg/kg, respectively. The contamination status in this study, the comparison of heavy metals with Thailand's sediment quality guidelines (*SQG<sub>T</sub>*) and NOAA (*TEL-PEL*) shown that Pb, Cu, Co, Ni, Mn, and Zn were exceeded over guideline values. For enrichment factor (*EF*) and geo-accumulation index (*I<sub>geo</sub>*), the enrichment factor of Cd (0.05–10.03) and Zn (0.01–11.98) are considered as minor enrichment to severe enrichment level. And the enrichment factor of Cu (0.09–3.49) and Pb (0.19–5.18) are considered as minor enrichment to moderately severe enrichment. But the geo-accumulation index of all stations is considered as low contamination. The potential ecological risk (*E<sub>r</sub>*) and risk index (*RI*) are considered as low risk level. The result show that the influence of seasonal variation to heavy metal concentration of Cd and Zn in southwest monsoon season (Jul 2017 and Jul 2018) are not significantly different but higher than other seasons ( $p < 0.05$ ), Cu and Mn average concentration in both southwest monsoon season (Jul 2017 and Jul 2018) and northeast monsoon season (Dec 2017) are not significantly different but higher than dry season (May 2018) and Ni and Co in southwest monsoon season 2018 are the highest as significant ( $p < 0.05$ ) although contamination status and potential ecological risk following the heavy metals concentration distribution.

Field of Study:	Industrial Toxicology and Risk Assessment	Student's Signature .....
Academic Year:	2021	Advisor's Signature .....

## ACKNOWLEDGEMENTS

After I've finished this thesis, I already feel appreciate to many hands that toward me to help to support to push me forward even pull me back when I am too far. Even I've grateful when thesis done, I'm more grateful that I did not complete this work alone.

First, I'd like to thank Chulalongkorn University for financial, academic resources, and facilities to fully support this thesis.

Next, I'd like to deeply grateful to my research advisor, Assistant Professor Sarawut Srithongouthai, Ph.D. for push an effort on me. Not only support in knowledge, but also supports more by encouragement.

I'd also like to thank to the chairperson, Professor Orathai Chavalparit, Ph.D., Associate Professor Naiyanan Ariyakanon, Ph.D., Assistant Professor Vorapot Kanokkantapong, Ph.D., and Assistant Professor Marut Suksomjit, Ph.D. to make any clear guidance to make this straight through completeness.

I would like to recognize the invaluable assistance of this team, Ms. Patcha Leelakun, Ms. Anutsara Yottiam, and Mr. Pathompong Vibhatabandhu for sampling collected support, providing intimate information, even always helps in laboratory. I'm also would like to mention about laboratory assistant that always support.

For Science Program in Industrial Toxicology and Risk Assessment, Department Environmental Science, Faculty of Science, Chulalongkorn University and their staff for supporting everything that this work could needed.

And all classmate in this course (Science Program in Industrial Toxicology and Risk Assessment, Department Environmental Science, Faculty of Science, Chulalongkorn University), you're the one of amazing moments in my life, so thank you.

Finally, I would like to thank my family which they support me patiently.

Phuttiapat Lapat-atiwat

# TABLE OF CONTENTS

	<b>Page</b>
ABSTRACT (THAI) .....	iii
ABSTRACT (ENGLISH).....	iv
ACKNOWLEDGEMENTS.....	v
TABLE OF CONTENTS.....	vi
LIST OF TABLES.....	x
LIST OF FIGURES .....	xi
CHAPTER 1 INTRODUCTION.....	1
1.1 Significance of the Research.....	1
1.2 Research Objectives .....	3
1.3 Scope of the Research .....	3
1.4 Research Outcomes .....	5
CHAPTER 2 LITERATURE REVIEW.....	6
2.1 Heavy Metals.....	6
2.1.1 Cadmium (Cd).....	7
2.1.2 Lead (Pb).....	8
2.1.3 Copper (Cu).....	8
2.1.4 Cobalt (Co).....	9
2.1.5 Nickel (Ni).....	10
2.1.6 Manganese (Mn).....	11
2.1.7 Zinc (Zn).....	11
2.2 Cycle of Heavy Metals in Marine Environment.....	12
2.3 Contamination Status Assessment.....	15
2.3.1 Sediment quality guidelines .....	15
2.3.2 Enrichment factor .....	16
2.3.3 Geo-accumulation index.....	18

2.4 Ecological Risk Assessment.....	19
2.5 The Gulf of Thailand .....	21
2.5.1 The inner Gulf of Thailand.....	22
2.5.2 The Mae Klong River.....	25
2.5.3 The Tha Chin River .....	26
2.5.4 The Chao Phraya River .....	26
2.5.5 The Bangpakong River.....	26
2.6 Regulating Factors of Heavy Metal in the Inner Gulf of Thailand .....	27
CHAPTER 3 METHODOLOGY .....	31
3.1 Study Areas and Sampling Points .....	31
3.2 Research Materials .....	33
3.2.1 Sampling cruise .....	33
3.2.2 Sediment sampling .....	33
3.2.3 Laboratory instruments.....	33
3.2.4 Laboratory equipment .....	33
3.2.5 Chemical substances.....	34
3.3 Measurement Parameters.....	34
3.3.1 Total heavy metals.....	34
3.3.2 Physicochemical factors .....	35
3.4 Sampling and Sample Preparations .....	35
3.4.1 Sediment sampling .....	35
3.4.2 Sample preparations .....	36
3.5 Chemical Analysis.....	36
3.5.1 Total heavy metals analysis.....	36
3.5.2 Total organic matter analysis .....	36
3.5.3 Total organic carbon analysis.....	37
3.5.4 Total phosphorus analysis .....	37
3.5.5 Acid volatile sulfide analysis .....	37
3.5.6 Water content .....	38



3.6 Data Analysis.....	38
3.6.1 Spatial distributions .....	38
3.6.2 Contamination status of heavy metals.....	39
3.6.3 Potential ecological risk assessment.....	42
3.7 Quality Control.....	44
3.8 Statistical Analysis .....	44
CHAPTER 4 RESULTS AND DISCUSSION.....	45
4.1 Spatial distributions and seasonal variations .....	45
4.1.1 Cadmium (Cd).....	46
4.1.2 Lead (Pb) .....	50
4.1.3 Copper(Cu).....	54
4.1.4 Cobalt (Co).....	58
4.1.5 Nickel (Ni).....	62
4.1.6 Manganese (Mn).....	66
4.1.7 Zinc (Zn).....	70
4.1.8 Aluminum (Al).....	75
4.2 Physicochemical Characteristics of the Surface Sediment.....	80
4.2.1 Total organic matter .....	80
4.2.2 Total organic carbon.....	82
4.2.3 Total phosphorus .....	83
4.2.4 Acid volatile sulfide .....	85
4.3 Contamination Status of Heavy Metal Contaminations in the Surface Sediment.....	86
4.3.1 Sediment quality guideline .....	86
4.3.2 Enrichment factor .....	91
4.3.3 Geo–accumulation index.....	95
4.4 Risk of Heavy Metal Contaminations in the Surface Sediment .....	99
4.4.1 Potential ecological risk .....	99
4.4.2 Risk index.....	103

4.5 Regulating factors of Heavy Metal Concentration in the Surface Sediment...	104
CHAPTER 5 RESEARCH CONCLUSION.....	112
5.1 Spatiotemporal Heterogeneity Distributions and Regulating Factors .....	112
5.2 Contamination Status.....	113
5.3 Potential Ecological Risk .....	113
5.4 Future Research .....	113
REFERENCES .....	115
VITA.....	127



## LIST OF TABLES

	<b>Page</b>
Table 2.1	Characteristics of four major rivers and river runoff into the inner Gulf of Thailand. ....25
Table 3.1	Values of sediment quality guidelines (SQGs), the threshold effect levels (TELs), probable effect levels (PELs) and apparent effects threshold (AET) (in mg/kg) of each heavy metal. ....39
Table 3.2	Tiers of heavy metals contamination status in the surface sediment based on different the EF values. ....41
Table 3.3	Classes of heavy metals contamination status in the surface sediment based on different the $I_{geo}$ values. ....42
Table 3.4	Class of potential ecological risk ( $E_r$ ) and potential ecological risk index (RI) of heavy metal pollutions. ....43
Table 4.1	Comparison of mean value of heavy metal concentrations in the surface sediments. ....79
Table 4.2	Comparison of selected heavy metal concentration to sediment quality guidelines (SQGs) .....90
Table 4.3	Correlation among Heavy metal and Physicochemical Characteristics of the Surface Sediment ..... 107
Table 4.4	Principal component analysis of heavy metals and other environmental factors in the surface sediment of the inner Gulf of Thailand..... 110
Table 4.5	Principal component analysis of heavy metals and other environmental factors in all surface sediment during four different seasons of the inner Gulf of Thailand. .... 111

## LIST OF FIGURES

	<b>Page</b>
Figure 2.1	Causes, sources, uses, transports, fate, and cycle of heavy metals in the marine environment..... 14
Figure 2.2	Geological location of the Gulf of Thailand and the various depths of water.....22
Figure 2.3	Map of marine resources and various land uses around the inner Gulf of Thailand.....24
Figure 2.4	Various regulating factors that influence on heavy metal concentration in the inner Gulf of Thailand.....29
Figure 2.5	Current velocity and direction of surface water of the inner Gulf of Thailand in southwest monsoon season (Jul 2017), northeast monsoon season (Dec 2017), Dry season (Apr 2018) and southwest monsoon season (Jul 2018).....30
Figure 3.1	Sampling sites in the Mae Klong, the Tha Chin, the Chao Phraya, the Bangpakong River estuaries, and the inner Gulf of Thailand...32
Figure 4.1	Spatiotemporal heterogeneity distributions and seasonal variations of Cd concentration in the surface sediment of the inner Gulf of Thailand.....47
Figure 4.2	Seasonal comparisons of Cd contamination in the surface sediment of the Mae Klong (MK), the Tha Chin (TC), the Chao Phraya (CP), the Bangpakong (BK) river estuaries and the inner Gulf of Thailand (inner GoT).....50
Figure 4.3	Spatiotemporal heterogeneity distributions and seasonal variations of Pb concentration in the surface sediment of the inner Gulf of Thailand.....51
Figure 4.4	Seasonal comparisons of Pb contamination in the surface sediment of the Mae Klong (MK), the Tha Chin (TC), the Chao Phraya (CP), the Bangpakong (BK) river estuaries and the inner Gulf of Thailand (inner GoT).....54
Figure 4.5	Spatiotemporal heterogeneity distributions and seasonal variations of Cu concentration in the surface sediment of the inner Gulf of Thailand.....55

Figure 4.6	Seasonal comparisons of Cu contamination in the surface sediment of the Mae Klong (MK), the Tha Chin (TC), the Chao Phraya (CP), the Bangpakong (BK) river estuaries and the inner Gulf of Thailand (inner GoT).....	58
Figure 4.7	Spatial distributions and seasonal variations of Co concentration in the surface sediment of the inner Gulf of Thailand.....	59
Figure 4.8	Seasonal comparisons of Co contamination in the surface sediment of the Mae Klong (MK), the Tha Chin (TC), the Chao Phraya (CP), the Bangpakong (BK) river estuaries and the inner Gulf of Thailand (inner GoT).....	62
Figure 4.9	Spatial distributions and seasonal variations of Ni concentration in the surface sediment of the inner Gulf of Thailand.....	63
Figure 4.10	Seasonal comparisons of Ni contamination in the surface sediment of the Mae Klong (MK), the Tha Chin (TC), the Chao Phraya (CP), the Bangpakong (BK) river estuaries and the inner Gulf of Thailand (inner GoT).....	66
Figure 4.11	Spatiotemporal heterogeneity distributions and seasonal variations of Mn concentration in the surface sediment of the inner Gulf of Thailand.....	68
Figure 4.12	Seasonal comparisons of Mn contamination in the surface sediment of the Mae Klong (MK), the Tha Chin (TC), the Chao Phraya (CP), the Bangpakong (BK) river estuaries and the inner Gulf of Thailand (inner GoT).....	70
Figure 4.13	Spatial distributions and seasonal variations of Zn concentration in the surface sediment of the inner Gulf of Thailand.....	72
Figure 4.14	Seasonal comparisons of Zn contamination in the surface sediment of the Mae Klong (MK), the Tha Chin (TC), the Chao Phraya (CP), the Bangpakong (BK) river estuaries and the inner Gulf of Thailand (inner GoT).....	74
Figure 4.15	Spatiotemporal heterogeneity distributions and seasonal variations of Al concentration in the surface sediment of the inner Gulf of Thailand.....	76
Figure 4.16	Seasonal comparisons of Al contamination in the surface sediment of the Mae Klong (MK), the Tha Chin (TC), the Chao Phraya (CP), the Bangpakong (BK) river estuaries and the inner Gulf of Thailand (inner GoT).....	78

Figure 4.17	Spatial distributions and seasonal variations percentages of TOM in the surface sediment of the inner Gulf of Thailand.....	81
Figure 4.18	Spatial distributions and seasonal variations of TOC concentration in the surface sediment of the inner Gulf of Thailand. ....	83
Figure 4.19	Spatial distributions and seasonal variations of TP concentration in the surface sediment of the inner Gulf of Thailand.....	84
Figure 4.20	Spatial distributions and seasonal variations of AVS concentration in the surface sediment of the inner Gulf of Thailand. ....	86
Figure 4.21	Seasonal comparisons of enrichment factor (EF) of selected heavy metals in the surface sediment. ....	95
Figure 4.22	Seasonal comparisons of Geo-accumulation index ( $I_{geo}$ ) of selected heavy metals in the surface sediment.....	99
Figure 4.23	Seasonal comparisons of Potential ecological risk ( $E_r$ ) of selected heavy metals in the surface sediment.....	103
Figure 4.24	Seasonal comparisons of risk index (RI) in the surface sediment of selected heavy metals.....	104

# CHAPTER 1

## INTRODUCTION

---

### 1.1 Significance of the Research

**The inner Gulf of Thailand** is an important marine resource for economic and social developments. Moreover, the inner Gulf of Thailand is also an important ecological service, such as according to the diversity of marine organism habitats, breeding and nursery areas, and endangered species are found. And high values in economical services such as tourism, transportation, and logistics. According to industrial developments, agricultural expansions and urban extensions of Thailand have been significantly grown during the past century. These increasing of expansion activities and the developments causes release the various pollutants such as nutrients, organic matters, heavy metals, pesticides and/or toxic chemical compounds, particularly heavy metals were released into the environments.

Although the inner Gulf of Thailand takes a role as nutrition bank of Thailand by receiving runoff from major rivers including the Mae Klong, the Tha Chin, the Chao Phraya, and the Bangpakong Rivers, but it also is the pollutant sinks. Especially to the heavy metals, which are produced and utilized on land base, and subsequently will be runoff from land into rivers and finally contaminated into water and sediment of the inner Gulf of Thailand by 1. particulate heavy metals were suspended and deposited onto the surface sediments and make themselves as the source through benthic fauna and flora biochemical processes and 2. the dissolved heavy metals which are assimilated by primary producer organisms, subsequently absorbed in cell tissues (bioconcentration) and increasing concentration in organism (bioaccumulation) then transfer to upper-level food chain consumes contamination organisms (biomagnification).

Contamination of heavy metals in coastal sediment is the one of major worldwide environment issues. For instance, Jamapa area in the Gulf of Mexico found moderate severe enrichment of Arsenic (6.6–14.0 mg/kg) (Celis–Hernández et al.,

2013). In France, the north of Toulon Bay found extreme contamination of Hg (0.03–27.3 mg/kg), Cu (5.8–846 mg/kg), Pb (14.9–469 mg/kg) and Zn (24.3–1340 mg/kg) (Tessier et al., 2011) 0.41–1.09 mg/kg of Cd, 3.64–7.24 mg/kg of Pb and 11.57–24.75 mg/kg of Zn were found around Tupilipalem Coast, India (Ganugapenta et al., 2018). In Thailand, many studies showed the heavy metal contamination such as Cd concentration found greater 120 mg/kg in sediment at the Bangpakong River estuary (Qiao et al., 2015). At the Chao Phraya River estuary (Hungspreugs & Yuangthong, 1983) are found enriched of Cd (0.00–2.37 mg/kg) and Pb (14–42 mg/kg).

According to the heavy metals contamination can lead environmental to degradation, due to the one of heavy metal characteristic is toxicity. The effect of heavy metals toxic is depending on several factors, including dose, route of exposer, chemical species, target organisms and nutritional status of exposed individuals. The effects of heavy metals which be found in the inner Gulf of Thailand such as Mn which cause lung irritated and induced pneumonia in human (Howe et al., 2004), Co which is also known as radioactive isotopes is considered as carcinogen agent (Leyssens et al., 2017) when combined with tungsten carbide in cobalt dust form, Ni which is use for alloys production can cause nausea, vomiting, vertigo, irritation (Das et al., 2019), Cu is an abundant trace element found in rocks and minerals. And it is the one of essential element for organisms to use in metabolic processes but is extremely toxic to aquatic organisms (Flemming & Trevors, 1989), the adverse effect of Zn is found that cause fatality in two soldiers were dead after developed adult respiratory distress syndrome by accidently exposed by zinc chloride-containing smoke bomb in 25 and 32 days (Plum et al., 2010), Cd is a severe pulmonary and gastrointestinal irritant, which can be fatal if inhaled or ingested and Pb according to the Environmental Protection Agency (EPA), is considered a carcinogen (Jaishankar et al., 2014). The source of heavy metals is come from natural sources naturally enter to waters by chemical weathering of minerals in parent rocks and soil leaching (Gautam et al., 2016).

Although some heavy metals are essential element in marine organism, the high concentration of contamination the marine organisms which contact with heavy



metals can be affected in direct such as illness or fatality and indirect by accumulated in marine's organism tissues and passed into food web. Following the heavy metals contamination effect the higher concentration of heavy metals can cause relate to higher ecological risks in the inner Gulf of Thailand. Particularly, when the season changes, the currents in the inner Gulf of Thailand were changed and subsequently lead to different movements of both dissolved and particulate heavy metals in the seasonal variations. However, the effects of seasonal variations on heavy metal contamination in both water and sediment are not clear in the inner Gulf of Thailand.

As the consequence of sources, uses, fates, transports until contamination of heavy metals in the inner Gulf of Thailand, therefore the studies of contamination levels and ecological risk from heavy metal concentrations in the surface sediment during the different seasons were evaluated to meet the goal objectives.

## 1.2 Research Objectives

- 1.2.1 To determine total concentration of heavy metals including Cd, Pb, Cu, Co, Ni, Mn and Zn in the surface sediment of the Mae Klong, the Tha Chin, the Chao Phraya, the Bangpakong river estuaries and entire the inner Gulf of Thailand during four different seasons.
- 1.2.2 To evaluate contamination status of heavy metals in surface sediment of the study areas using sediment quality guidelines ( $SQG_s$ ), enrichment factors ( $EF$ ) and geo-accumulation index ( $I_{geo}$ ).
- 1.2.3 To assess ecological risk of heavy metals contaminations on surface sediment of the Mae Klong, the Tha Chin, the Chao Phraya, the Bangpakong river estuaries and the inner Gulf of Thailand using potential ecological risk ( $E_r$ ) and risk index ( $RI$ ).

## 1.3 Scope of the Research

- 1.3.1 **Study areas and sampling points:** the Mae Klong, the Tha Chin, the Chao Phraya, the Bangpakong River estuaries, and the inner Gulf of Thailand were chosen to study due to an area-specific quantity. Total 63

sampling points were established, including 35 stations were located in the four river estuarine areas and 28 stations entire the inner Gulf of Thailand.

**1.3.2 Samples:** the surface sediments (0–1 cm depth) were collected from all sampling points.

**1.3.3 Sampling periods:** the samplings were carried out four times in different seasons including in July 2017 (southwest monsoon season), December 2017 (northeast monsoon season), April 2018 (dry season) and July 2018 (southwest monsoon season).

**1.3.4 Parameters:** the sediment samples were analyzed for total concentration of selected heavy metals, including Cd, Pb, Cu, Co, Ni, Mn and Zn. Moreover, total organic matters (TOM), total organic carbon (TOC), total phosphorus (TP), acid volatile sulfide (AVS) were additionally analyzed.

**1.3.5 Laboratory analysis:** laboratory analysis was carried out during May 2020 to April 2021 at the Department of Environmental Science, Faculty of Science, Chulalongkorn University.

**1.3.6 Data analysis:** total concentrations of Cd, Pb, Cu, Co, Ni, Mn and Zn in the surface sediment were completed by deterministic interpolation technique using the ArcGIS™ program. Contamination status of total heavy metals were analyzed using the  $SQG_s$ ,  $EF$  and  $I_{geo}$ . While the  $E_r$  and  $RI$  were used to assess ecological risk.

## 1.4 Research Outcomes

- 1.4.1 The findings of the present work improve understanding of heterogeneity distributions, seasonal variations, contamination status and ecological risk of Cd, Pb, Cu, Co, Ni, Mn and Zn in the surface sediments of the inner Gulf of Thailand.
- 1.4.2 The findings of this study provide detailed information that could be used to evaluate the level of sediment qualities guideline for heavy metals pollution.



# CHAPTER 2

## LITERATURE REVIEW

---

**Heavy metals** in the surface sediment of the inner Gulf of Thailand, which is complex ecosystems and valuable human resources, as they provide species habitats, ecological services, recreational opportunities, transportation links, and economic benefits. Sediments are major sinks of heavy metals, and changes in environmental conditions (e.g., pH, oxidation–reduction potential, and organic matter) and subsequent resuspension processes may release sediment–bound heavy metals back into the overlying water; this can lead to secondary contamination and threaten the local biota and ecosystems through bioaccumulation and bio–amplification in the food web. As a result, the inner Gulf of Thailand is the dynamic system, therefore, the fundamental knowledges of coastal ecosystem and their regulating factors, which make the extremely dynamics of pollution in particular area are needed to review as follows:

### 2.1 Heavy Metals

Heavy metals are a natural element that relatively high density compared to water, high atomic weight, or high atomic number. Heavy metals are natural components of the Earth’s crust, non-degradable and persistent in environment. The one of heavy metals characteristic is toxicity. The effect of heavy metals toxic is depending on several factors, including dose, route of exposer, chemical species, target organisms and nutritional status of exposed individuals. However, at a low concentration, some heavy metals are essential elements for living organism. The source of heavy metals can be from industrial, domestic, agricultural, or medical. Irrigation by effluents which adding various alkalies ammonia, cyanides and heavy metals were released from paper mills and fertilizer factories into the water resources. The wastewater from dyes and pigments factories, film and photography plants, metal cleaning, electroplating, leather, and mining industries contains significantly amount of heavy metal ions (Gautam et al., 2016). In contrast to other pollutants, heavy

metals cannot be removed from waterbody and will be persisted in sediment where they slowly released back to water. Moreover, the source of heavy metals which from industrial effluent, they can be transport by water that runoff from contaminated area.

### **2.1.1 Cadmium (Cd)**

Cadmium (Cd), average concentration is about 0.1–0.2 mg/kg and commonly found in association with zinc (Gautam et al., 2016). Cadmium is common available in oxide, chloride, or sulfide form. Cadmium is odorless, resistant to corrosion, when cadmium is in metal and oxide form its insoluble in water but in some form of cadmium such as cadmium chloride, cadmium sulfate and cadmium nitrate are more soluble from other forms.

Cadmium is frequently used in various industrial activities. The major industrial applications of cadmium include the production of alloys, pigments, and batteries. But now the commercial use of cadmium has declined in developed countries in response of environmental and health concerns (Tchounwou et al., 2012).

Cadmium is a severe pulmonary and gastrointestinal irritant, which can be fatal if inhaled or ingested. After acute ingestion, the symptoms such as abdominal pain, burning sensation, nausea, vomiting, salivation, muscle cramps, vertigo, shock, loss of consciousness and convulsions usually appear within 15 to 30 min. Acute effect from cadmium ingestion can cause gastrointestinal erosion, pulmonary, hepatic, or renal damaged then coma, depending on route of exposer. Chronic effect from cadmium is depressive effect on levels of norepinephrine, serotonin, and acetylcholine. And can also cause to single-strand DNA damage and disrupts the synthesis of nucleic acids and proteins.

Cadmium compounds are classified as human carcinogens by several regulatory agencies. The International Agency for Research on Cancer and the U.S. National Toxicology Program have concluded that there is adequate evidence that cadmium is a human carcinogen. This designation as a human carcinogen is based primarily on repeated findings of an association between occupational cadmium exposure and lung cancer, as well as on very strong rodent data showing the pulmonary system as a target site. Thus, the lung is the most

definitively established site of human carcinogenesis from cadmium exposure. In some studies, occupational or environmental cadmium exposure has also been associated with development of cancers of the prostate, kidney, liver, hematopoietic system, and stomach.

### **2.1.2 Lead (Pb)**

Lead is a naturally occurring element is a member of Group 14 (IVA) of the periodic table. Lead is not an abundant element, but its ore deposits are widely distributed on Earth. Lead also persistent to corrosion, low melting point. So, it's made easily to use for human activities.

Source of lead utilization is paints and ceramic products, caulking, and pipe solder. But in the recent years the amount of lead using in these industrials is reduced because they replace with less toxicity compound. Lead is also use in production of batteries, cosmetic, metal products such as ammunitions.

The largest source of lead poisoning in children come from dust and chips from deteriorating lead paint on interior surfaces. Children who live in homes with deteriorating lead paint can achieve blood lead concentrations of 20  $\mu\text{g}/\text{dL}$  or greater (Tchounwou et al., 2012). According to activities such as mining, manufacturing and fossil fuel burning are cause the accumulation of lead in environment. Lead poisoning was considered as classic disease that effect with central nervous system and gastrointestinal tract in children and adult (Jaishankar et al., 2014).

According to the Environmental Protection Agency (EPA), lead is considered a carcinogen (Jaishankar et al., 2014). Lead has critical effect on different parts of the body, and distribution in the body initially depend on blood flow which can transport lead into various tissues such as skeleton bones at 95% of body lead deposited.

### **2.1.3 Copper (Cu)**

Copper (Cu) is an abundant trace element found in rocks and minerals. And it is the one of essential element for organisms to use in metabolic processes. For oxidation property the copper metal can transition into 3 forms of ions: Cu, Cu(I)

and Cu(II). As copper is classified as heavy metals because of the density of copper are greater than 5 g/cm (Flemming & Trevors, 1989).

Copper can be found in electroplating industry, plastic industry, metal refining and industrial emissions. According to these activities, its cause copper contamination from world production increasing. In Flemming & Trevors (1989) study said the major problem of copper contamination was found in estuarine environment.

According to copper is essential element, clinical studies and domestic laboratory animals shown that for mammals the copper is non-toxic. However, copper is extremely toxic to aquatic organisms. The copper tolerance in mammals is 10 to 100 greater than fish or crustaceans, and 1000 greater than algae (Flemming & Trevors, 1989). According to the Integrated Risk Information System (IRIS), copper is classified as non-carcinogen.

#### **2.1.4 Cobalt (Co)**

Cobalt (Co) can be found in natural source in environment include volcanic eruption, seawater spray and forest fires. The chemical properties are highly like iron and nickel. The only one stable isotope of cobalt is  $^{59}\text{Co}$ . Cobalt also have 26 known radioactive isotopes, of which only two are common in commercial are  $^{60}\text{Co}$  and  $^{57}\text{Co}$ ,  $^{60}\text{Co}$  is used for gamma radiation source. Cobalt is more stable in Co (II) than Co (III), and  $\text{Co}^{3+}$  is a powerful oxidizing agent for oxidize water. And a biochemically important cobalt compound is vitamin B12 also known as cyanocobalamin (Leyssens et al., 2017).

Anthropogenic sources of cobalt which be found in atmosphere can come from the coal-fired power plant, incinerators, and vehicle's exhaust. As of the widespread occurrence of cobalt, humans are frequently exposed to various cobalt compound in daily life. Major source of exposure is inhalation from ambient air, food ingestion and cobalt contaminated water drinking.

The relation between risk of lung cancer and the inhalation of cobalt containing dust has been considered in occupational exposure setting. However, cobalt is certainly not the main causation of this negative effects because it is found cobalt dust was combined with tungsten carbide which is considered as carcinogen agent (Leyssens et al., 2017). Somehow the mixture of cobalt and

tungsten carbide is classified by International Agency for Research on Cancer (IARC) as probably carcinogenic to human (group 2A).

### **2.1.5 Nickel (Ni)**

Pure nickel (Ni) is a hard, silvery-white metal, which has properties that make very desirable for combining with other metals to form mixtures called alloys. Nickel mineral can be found from extraction of iron/nickel sulfides such as pentlandite and the other mineral including garnierite. For anthropogenic source of nickel is from metallurgical processes and electrical components, such as batteries production industrial which can be exposed by humans and animals in many pathways.

Human can be exposed to nickel from inhalation, drinking contaminated water and foods. Pollution of nickel in environment from nickel-manufacturing industries and airborne particles from combustion of fossil fuel is least concerned. However, nickel more likely found in food and in vegetables usually contains more nickel than the other food such as legumes, spinach, lettuce, and nuts and can be found in excessive amount of nickel in food product such as baking powder and cocoa power. Some soft drink and acid beverages can find nickel for container erosion too.

Toxicities of nickel, in human the acute effect of nickel absorption through the gastrointestinal tract or inhalation through lungs were reported. The inhalation of carbonyl cause two kinds of acute effect: instant and delayed. The acute effect symptoms are nausea, vomiting, vertigo, irritation, etc. And the delayed symptoms which occurred after instant effect in a few hours or days are stiffness of the chest, constant cough, dyspnea, cyanosis, tachycardia, palpitations, sweating, visual disturbances, and weakness etc. (Das et al., 2019).

In human, various studies have reported that divalent nickel is a potent carcinogen that can induce malignancy in both humans and rodents. Humans which exposure of nickel through refinery, mining and smelting, stainless steel industries and battery manufacturing facilities were found cancer, but it's difficult to identify the speciation of nickel compound. Then the International Committee on nickel carcinogenesis is currently working on identifying the specific nickel carcinogen (Das et al., 2019).



### **2.1.6 Manganese (Mn)**

Manganese (Mn) is a pinkish-gray metal, chemically active element, high melting point but easily to oxidized. It is found on rock, soil, and water. Crustal rock is a major source of manganese which be found in atmosphere. And the other sources of manganese are ocean spray, forest fires, vegetation, and volcanic activity. Manganese can be released to air mainly as particulate matter, and some manganese compounds are readily soluble in water as two dominant forms: Mn(II) and Mn(IV).

Manganese can also find in environment from human activities such as municipal wastewater discharges, sewage sludge, mining and mineral processing, emissions from alloy, steel, and iron production, combustion of fossil fuels (Howe et al., 2004). And manganese can be found in most foods as food additive for nutritional supplements also found in fireworks, dry-cell batteries, fertilizer, paints, a medical imaging agent and cosmetics.

The most common health adverse effect was found in workers who exposed to high levels of manganese in nervous system such as human movements: slow and clumsy. And the inhalation of large amount of manganese fume may cause lung irritated then induced pneumonia. Reproductive systems can be effect from high levels manganese in air exposed such as the decrease of sex drive and damaged sperms. But the EPA concluded that existing scientific information cannot determine whether or not excess manganese can cause cancer.

### **2.1.7 Zinc (Zn)**

Zinc (Zn) is found in group IIb in periodic table of the elements, together with two toxic metals cadmium and mercury. But zinc is considered to be non-toxic to human (Plum et al., 2010). According to TOXNET database of the U.S. National Library of Medicine, the oral LD50 for zinc is about to 3 g/kg body weight. Because of zinc homeostasis which allows handling of an excess of oral zinc ingestion. Zinc is known as essential trace element for all organisms, it is component of more than 300 enzymes.

Plum et al. (2010) said according to zinc is essential elements for organisms, the adverse effect of zinc can be from zinc deficiency and zinc excess.

For zinc deficiency, brain, thymus, skin, reproductive system, and systemic symptom will be effect including decrease nerve conduction, neuropsychiatric disorders, neurosensory disorders, and metal lethargy. Exposure to zinc can be in three major routes of entry into human body: inhalation, dermal or ingestion. For inhalation, fatality cases were reported as two soldiers were dead after developed adult respiratory distress syndrome (ARDS) by accidently exposed by zinc chloride-containing smoke bomb in 25 and 32 days, respectively. Dermal exposure, in a study the 25% zinc oxide patch (2.9 mg/cm<sup>2</sup>) was placed on human skin for 48 hours, there was no evidence of adverse effect such as dermal irritation. However, zinc chloride was found irritate to dermal in humans, mice, rabbits, and guinea pigs. Zinc ingestion, according to zinc is essential element the LD<sub>50</sub> of zinc consumption approximately 225–400 mg, but there is a fatality case of woman who died after oral intake 28 g of zinc sulfate. And zinc is not defined as carcinogen.

## **2.2 Cycle of Heavy Metals in Marine Environment**

Heavy metals that come from natural sources naturally enter to waters by chemical weathering of minerals in parent rocks and soil leaching (Gautam et al., 2016), while metals from the anthropogenic sources (industrial, agricultural, and urban sources) enter coastal and marine environments by rivers, atmospheric deposition, dumping, marine mining, and from ships (Figure 2.1).

The fates and behaviors of heavy metals that enter the compartments are changed and transferred among conditions where they are. After the metals enter marine environments, the dissolved heavy metals are transported into water bodies and move downstream, while others settle in sediments. Released heavy metals will rapidly bind to particulates, and then sink down to the bottom. Sediments have been identified as the main sink for heavy metals. Nevertheless, heavy metals are not permanently bound to sediments. When the surrounding conditions (e.g. temperature and pH) change or there are some disturbances, the heavy metals may be released into the water column by remobilization process.

Heavy metals are sunk and mobilized by various physical, chemical, and biological vectors. Processes of sinking and remobilization control fates and

behaviors of heavy metals. The processes of sinking consist of adsorption and co-precipitation, precipitation, and incorporation in biological activity, and the remobilization processes include salinity concentration, change in redox condition, lowering of pH, increasing use of organic complexing agents, and biochemical process.

Normally, heavy metals act as positive ions in chemical reactions. Sorption properties of particles that have negative charges are keys of the adsorption mechanism. In oxidizing conditions, Fe- and Mn-hydroxides and oxides are significant sinks of heavy metals in water systems. Also, adsorbed heavy metals are ready to be mobilized in reducing conditions; therefore, accumulations of hydrous Fe/Mn oxides can act as major sources of dissolved metals in water systems.

Furthermore, heavy metals can incorporate in a biological activity, which are detoxification by organisms. It can hide active metals ions within a protein or store them in insoluble form in intracellular granules or excrete them. Some metals are essentially used for ionic balances and are as integral parts of amino acids; while, some metals, which exceed threshold values, are dangerous for organisms. They compete with essential metals at active sites, resulted in deficiencies of the essential metals.

Remobilization is mainly caused by changes of chemicals in water. Increased salt contents relate to deposition of heavy metals. Metals' cations such as sodium, magnesium, and calcium in water can compete with adsorbed metal ions onto solid particles or sediments. As a result, the metal ions might be released to water.

Nutritious substances from fertilizers and feces such as N and P have decreased oxygen in water which is required for biodegrading organic substances. Therefore, sediments can supply oxygen for them through the surface sediments at a rated govern by biological respiration and metabolic activities, and diffusion which controls transportation. Moreover, organic complexing agents from sewage treatment effluents promote metal remobilization from aquatic sediments.

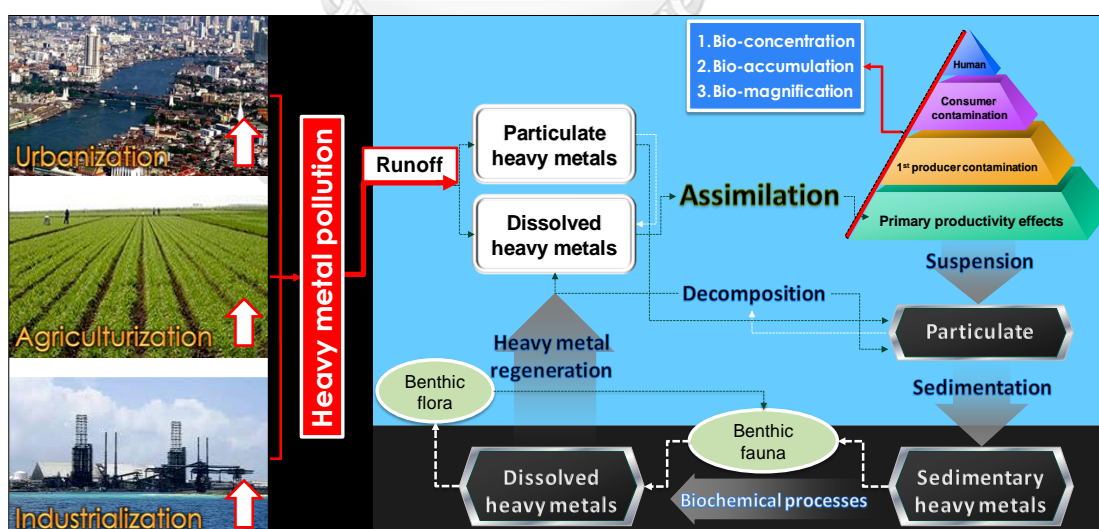
Organic matter, Fe, and Mn are major components which affect the rate of transported metals. Redox potential is used to define the tendency of an environment

to receive or supply electrons. It would have high redox potential in an oxidizing environment, while a reducing environment would have low redox potential. In reducing environment, heavy metals are ready to be remobilized through the water when there are strong enrichments of Fe and Mn in sediments between 15 and 10 cm depth, and redox potential value decreases sharply at 20 cm sediment depth.

Conditions that have low pH generally increase solubility of heavy metals. This is because of competing between hydronium ions ( $H^+$ ) and metal ions in adsorbing with particles; then, the metal ions are release.

In general, biodegradation affect remobilization of heavy metals adsorbed on to particulate organic matters or sediments. In biodegradation process, organic matter is destructed to molecular weight compartments that can compete with other metals. As a result, the adsorbed metals are released.

In contrast, Fe and Mn sulfides can be importance part of AVS-metal precipitations in the sediment. According to the reliable Fe and Mn concentrations are found likely in the oxic sediment surface layers and may lead to cause Fe and Mn oxide precipitation near the sediment-water interface, which can reduce the heavy metal mobility (Zhang et al., 2014).



**Figure 2.1** Causes, sources, uses, transports, fate, and cycle of heavy metals in the marine environment.

## 2.3 Contamination Status Assessment

### 2.3.1 Sediment quality guidelines

Sediment quality guidelines (*SQG<sub>s</sub>*) are tools for evaluate sediment contamination by comparing the sediment concentration with the corresponding quality guidelines (MacDonald et al., 2000). These guidelines evaluate the how much the sediment-associated chemical status that have adverse effect on marine organisms and was designed to assist the sediment qualities interpretation.

Two values were obtained from each chemical or chemical group. The lower 10<sup>th</sup> percentile of the effects data of each chemical that were identified and referred to the effect range–low (*ERL*). And the median or 50<sup>th</sup> percentile of the effects data were identified and referred to the effect range–median (*ERM*). The percentile of aquatic toxicity will be used following Klapow Lawrence A. & Lewis Robert H., (1979) to calculate marine water quality standards. The concentration which below the *ERL* value is represented a minimal–effects range; a range that estimate conditions that effect would be rarely detected. And the concentration which equal to or greater than *ERL*, but not over the *ERM* value, is represented a possible-effects range which effects would be occasionally appeared. The concentrations which equal or greater that *ERM* value is represented a probable–effect range which effects would be frequently appeared.

Two *SQG<sub>s</sub>* were obtained from each analyze that using the information both in the effects and the no effects data sets and using percentile for determine the distributions of these data sets. For each analyze, a *TEL* was found by calculate the geometric mean of the 15th percentile of the effects data sets and the 50th percentile of the no effects data sets. In addition, a *PEL* was developed for each chemical from determine the geometric mean of the 50th percentile of the effects data sets and 85th percentile of the no effects data sets. The *TEL* will show that the concentration of chemical which less the adverse effects are rarely appeared. Then the concentration which is greater than *PEL* value show that adverse effects is occasionally appeared. Then, the *TEL* and *PEL* were designed to define chemical concentration ranges in three range such as rarely, occasionally, and frequently associated with adverse effects (Macdonald et al., 1996).

### 2.3.2 Enrichment factor

The assessment of metal contamination is most important for the human survival. The only determination of the rates of metals in the surface horizons of the sediment cannot provide extensive indications about the state of contamination of sediments. This kind of information does not allow for the distinction between natural background and anthropogenic enrichment. Furthermore, it must be evaluated the possible relationship with the characteristics of the substrate (parental material), and the use of the sediment. The natural content of heavy metals can vary in a large range depending on the material of which the sediment has made of. Very important is the difference between background values and baseline values:

Background values: Natural contents of substance in the soil completely dependent on the compositional and mineralogical characteristic of the parent/source geological material.

Baseline values: Actual mostly diffuse range of concentration of an element in a specific area dependent both on the nature of the parent geological/source material and on the historic diffuse release into the environment of contaminants from anthropogenic sources.

There are different indexes generally used to identify metal concentrations of environmental concern like: the metal enrichment factor (*EF*) and geo-accumulation index ( $I_{geo}$ ). These indexes identify, numerically, pollution level soils and normally they are calculated on the sediment exchangeable fraction because it represents the real bio-available fraction. This fraction is obtained by applying the first step of (A. Tessier et al., 1979). The bio-available metal content in soil exerts a decisive impact on soil quality and it's used in food production. Hence, the assessment of metal contamination is of vital importance in farming areas.

The *EF* in metals and the  $I_{geo}$  are indicators used to assess the presence and intensity of anthropogenic contaminant deposition on surface sediment (Dash et al., 2021) These indexes of potential contamination are calculated by the normalization of one metal concentration in the topsoil with respect to the concentration of a reference element. A reference element is an element

particularly stable in the sediment, which is characterized by an absence of vertical mobility and/or degradation phenomena. The constituent chosen should also be associated with finer particles (related to grain size), and its concentration should not be anthropogenically altered (Frankowski et al., 2010). Typical elements used in many studies are Al, Fe, Mn and Rb, and also total organic carbon and grain size are among those most used (Frankowski et al., 2010). Aluminum is a conservative element and a major constituent of clay minerals, and it has been used successfully by several scientists (Sinex & Wright, 1988).

The Fe has been used by many authors working on marine and estuarine sediments (Dash et al., 2021; Usese et al., 2017). But Iron is not a matrix element, and its geochemistry is similar to that of many trace elements in oxic and anoxic environment. For many years, the background values used were Earth crust and soil values (Sutherland et al., 2000). Some authors suggest that element concentrations measured in a deeper soil horizon (subsoil) can be considered a “local background” for the upper soil horizons (Sutherland et al., 2000).

The enrichment factor (*EF*) is an indicator used to assess the presence of anthropogenic contaminant deposition in sediment. The *EF* is calculated based on reference element concentration and the presence of other metal which were normalized by comparing to the reference element. The reference element which suitable to calculation should be stable in soil and classified as low mobility and degradation. As usually the reference elements are Al, Fe, and Rb (Loring, 1990). Several scientists were used aluminum (Ryan J.D. & Windom H.L., 1988) as reference element because of Aluminum is a conservative element. Fe usually has been used in marine and estuarine sediments studies or working (Emmerson R.H.C. et al., 1997; Lee et al., 1998). So that as Earth crust and soil values were used as the background values for many years (Taylor & McLennan, 1995). The *EF* can calculate using based on equation 2.1

$$EF = \frac{\left(\frac{M}{X}\right)_{\text{sample}}}{\left(\frac{M}{X}\right)_{\text{background}}} \quad (2.1)$$

where  $EF$  is metal enrichment factor for sediment

$\left(\frac{M}{X}\right)_{\text{sample}}$  is metal and background concentration ratio observed for sediment sample.

$\left(\frac{M}{X}\right)_{\text{background}}$  is natural metal and background concentration ratio for reference sediment.

### 2.3.3 Geo-accumulation index

The geo-accumulation index ( $I_{\text{geo}}$ ) was proposed by Müller (1979) to assess heavy metal contamination of sediments and it builds on the background level of natural fluctuations including very low anthropogenic input. The respective background concentration is multiplied by a factor of 1.5 to get the upper limit of the lowest load class 0. The doubling of this value provides the upper limit of the next higher class and each subsequent doubling leads to upper limit of a higher class.

The  $I_{\text{geo}}$  calculation was done using based on the following equation 2.2:

$$I_{\text{geo}} = \log_2 \left( \frac{C_n}{1.5 B_n} \right) \quad (2.2)$$

Where  $C_n$  is the measured concentration of metal  $n$  in the sediment.

$B_n$  is the geochemical background value of element  $n$  in the background sample

1.5 is the factor of used to account for possible variations of background values because of lithogenic effects.



## 2.4 Ecological Risk Assessment

Ecological risk assessment is a process that evaluates the likelihood that adverse ecological effects may occur or are occurring as a result of exposure to one or more stressors (US EPA, 1992). The process is used to systematically evaluate and organize data, information, assumptions, and uncertainties in order to help understand and predict the relationships between stressors and ecological effects in a way that is useful for environmental decision making. An assessment may involve chemical, physical, or biological stressors, and one stressor or many stressors may be considered (Norton et al., 1992).

Ecological risk assessments can be used to predict the likelihood of future adverse effects (prospective) or evaluate the likelihood that effects are caused by past exposure to stressors (retrospective). In many cases, both approaches are included in a single risk assessment. For example, a retrospective risk assessment designed to evaluate the cause for amphibian population declines may also be used to predict the effects of future management actions. Combined retrospective and prospective risk assessments are typical in situations where ecosystems have a history of previous impacts and the potential for future effects from multiple chemical, physical, or biological stressors.

The following terms overlap to varying degrees with the concept of ecological risk assessment used according to (Norton et al., 1992).

- 1) Hazard assessment
- 2) Comparative risk assessment
- 3) Cumulative ecological risk assessment
- 4) Environmental impact statement

Ecological risk assessment provides a critical element for environmental decision making by giving risk managers an approach for considering available scientific information along with the other factors they need to consider (e.g., social, legal, political, or economic) in selecting a course of action.

Håkanson, (1980) aims to achieve one of many possible ways towards a potential ecological risk index to be used as a diagnostic tool for water pollution control purposes and sedimentary risk index for toxic substances in limnic systems i.e., estuary, lagoon.

Potential ecological risk index, which was developed by Håkanson, (1980), is a popular methodology used to assess ecological risks of aquatic pollution control. The methodology is based on the assumption that the sensitivity of the aquatic system depends on its productivity. The purpose of creating ecological risk index is to be used in aquatic environmental pollution control. Håkanson also provided simple values on ecological risk for using in a given contamination situation in lake or basin water systems. For an effective use, there are four requirements for implementing the index as follow:

1. The concentration requirement.
2. The number requirement, which is built on the following ideas.

$$C_d = \sum_{i=1}^n C_f^i = \sum_{i=1}^n \frac{C_{0-1}^i}{C_n^i} \quad (2.3)$$

where

$C_d$  =the degree of contamination.

$C_f^i$  =the contamination factor.

$C_{0-1}^i$  =the mean content of the substance in question (i) from superficial sediment (0-1 cm) from accumulation areas. At least 5 samples, which provide an even area cover of the lake/basin should be taken.

$C_n^i$  =the standard preindustrial reference level determined from various European and American lakes to be (in ppm): PCB=0.01, Hg=0.25, Cd=1.0, As=15, Cu=50, Pb=70, Cr=90 and Zn=175. These are the substances discussed in this approach.

3. The toxic factor requirement should account for the fact that various substances have different toxic effects (compare e.g., LC<sub>50</sub>-values) in aquatic systems. The following principles have been discussed.
4. The sensitivity requirement, saying that different lakes/basins have different sensitivity to different toxic substances.
5. The potential ecological risk factor for any given substance has been defined as:

$$Er^i = Tr^i \cdot C_f^i \quad (2.4)$$

6. The potential ecological risk index for any given lake or basin has been defined as:

$$RI = \sum_{i=1}^n Er^i \quad (2.5)$$

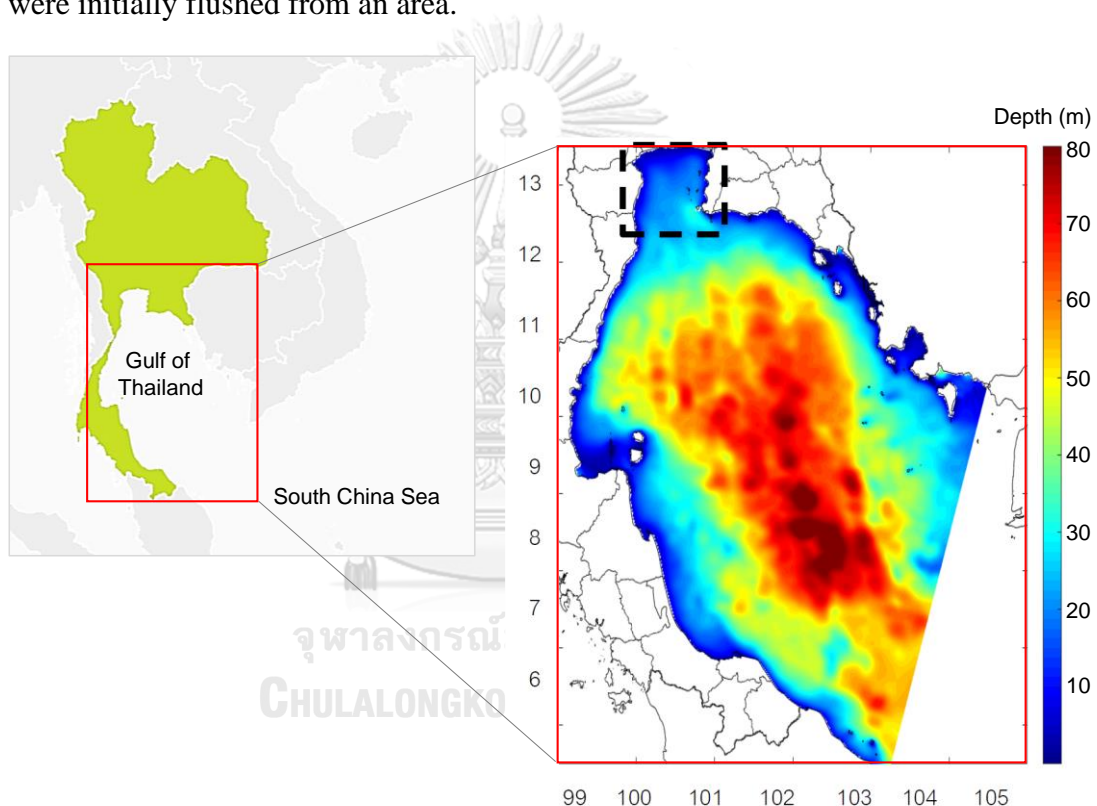
The use of the risk factors and the risk index means that a second step towards a diagnostic tool to establish ecological effects has been taken. The main advantages with these two steps, first the contamination factor and the degree of contamination and then the risk factors and the risk index, are that they may be used to optimize resources in very complicated economic and ecological issues, so that efforts are focused on substances that show high risk factors.

## 2.5 The Gulf of Thailand

The Gulf of Thailand is an enclosed body of water in the southwestern part of the South China Sea that is situated between latitudes 5°000 and 13°300 N and longitudes 99°000 and 106°000 E. The maximum depth of the Gulf of Thailand is 80 m and at the center of the Gulf has average depth is 45 m. The Gulf also be divided into two parts: the upper Gulf and the lower Gulf. The upper Gulf is an inverted U-shape (also call the inner Gulf of Thailand) that is characterized as a pollution accumulation from four major rivers, including the Mae Klong, the Tha Chin, the Chao Phraya, the Bangpakong rivers. The inner Gulf, also known as a major source of fisheries resource, such as fishes, crabs, and mollusks. The average runoff per year of the Chao Phraya is  $13.22 \times 10^3 \text{ km}^3$  and at Mekong is  $326 \times 10^3 \text{ km}^3$ . It shown that the amount nutrients which runoff and sink in the Gulf of Thailand (Wattayakorn, 2006).

Seasonal circulation in the Gulf of Thailand, deduced from oceanographic data, suggested that circulation in the Gulf is generally weak and variable. The mean circulation in the Gulf is forced by the South China Sea and not by the local wind as previously suspected, a phenomenon particularly marked during the Northeast monsoon when Mekong River water enters the lower Gulf (Wattayakorn et al., 1998). During January to February, currents throughout the Gulf are at their weakest, with little mixing of Upper and Lower Gulf water masses.

From March to August, anticyclonic (clockwise) circulation predominates in the lower Gulf and penetrates into the upper Gulf. In September, the circulation direction reverses to cyclonic in the lower Gulf, initially producing cyclonic current in the upper Gulf; by November the flow in the upper Gulf becomes anticyclonic (Figure 2.2). Overall, the Gulf of Thailand is poorly flushed. In the upper Gulf, little mixing occurs between coastal and offshore waters. As a consequence of these comparatively static conditions, contaminants discharged into the upper Gulf may accumulate. Variability in current directions may also result in the return of contaminants that were initially flushed from an area.



Source: applied from Maksumpun et al. (2019)

**Figure 2.2** Geological location of the Gulf of Thailand and the various depths of water.

### 2.5.1 The inner Gulf of Thailand

#### 1) Geological and hydrological characterizations

The inner Gulf of Thailand is a semi-enclosed square bay, which is located between  $12^{\circ}30'$  N and  $13^{\circ}30'$  N and with a total area of

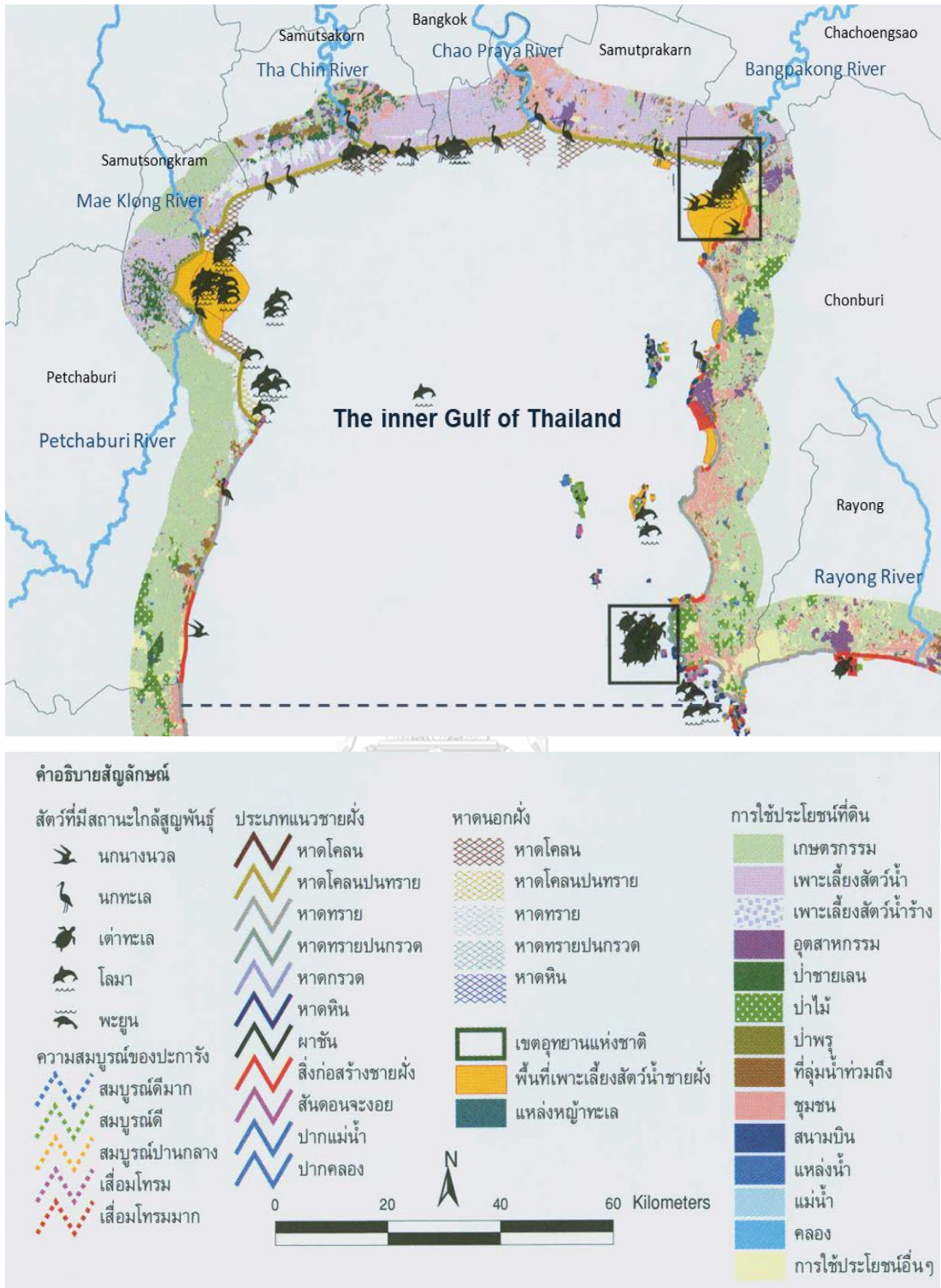
approximately 90×90 km<sup>2</sup> (Hungspreugs & Yuangthong, 1983). Not only the inner Gulf of Thailand is runoff collected area from four major estuaries (the Mae Klong, the Tha Chin, the Chao Phraya and the Bangpakong Rivers) about 50% but this also populated for industrial site, agricultural and residential areas. All that runoff can cause the inner Gulf of Thailand contaminated by surrounding land such as heavily polluting industries, domestic wastewaters which are runoff from residential areas. Then the inner Gulf have been collected the contaminants and nutrients from the four major rivers. Thus, frequent algae blooms have become common in the Gulf (Wattayakorn & Jaiboon, 2014). Additionally, the inner Gulf of Thailand tide and wind flow are under the influence of 2 seasonal monsoon: firstly, southwest monsoon during May–September and secondary northeast monsoon during November–February, additionally dry season is during March–April.

## **2) Ecological and economic services**

According to the inner Gulf of Thailand is use for fisheries and marine organism nurseries (Figure 2.3). Moreover, the inner Gulf of Thailand is not only important as ecological services in this area is used for transportation, traveling, cargo shipment. As economic services are important in the inner Gulf of Thailand. And this area is received 4 major rivers discharge which from industrial effluent, agricultural runoff, and domestic wastewater (Wattayakorn & Jaiboon, 2014).

## **3) Sink and source of pollutions**

As the inner Gulf of Thailand is collection of runoff water, effluent discharge from pollution plant including river, effluent discharge from industrial areas, domestic waste from residential areas, surface off and drainage from port areas and spillage pollutants from ships (Figure 2.3). According to nearby areas of the Mae Klong River, the Tha Chin River, the Chao Phraya River and the Bangpakong river are urban and intensive utilize for living, then domestic wastes can dump directly into the river and contaminated (Wattayakorn, 2006).



Source: applied from Pollution Control Department (2012)

**Figure 2.3** Map of marine resources and various land uses around the inner Gulf of Thailand.

**Table 2.1** Characteristics of four major rivers and river runoff into the inner Gulf of Thailand.

Characteristic	River				
	Mae Klong	Tha Chin	Chao Phraya	Bangpakong	
Drainage area (km <sup>2</sup> ) <sup>a</sup>	30,837	14,199	160,000	8,706	
Length (km) <sup>a</sup>	520	325	1,352	434	
Annual rainfall (mm) <sup>a</sup>	1,147	1,391	1,487	1,895	
Runoff (m <sup>3</sup> /s)	July 2017	370	174	417	222
	December 2017	290	9	185	43
	April 2018	753	180	160	80
	July 2018	370	174	417	222

Source: applied from Maksumpun et al. (2019)

### 2.5.2 The Mae Klong River

The geological features of the Mae Klong River, this river hydrographical basin is greatly influence by chemistry of river waters and the chemical fluxes of trace elements from the central part of coastal region. Especially, the Mae Klong River is lies western part of the upper Gulf of Thailand. The river length is 138 km, start from confluence of Kwai Noi and Kwai Yai in Kanchanaburi Province and flow into Ratchaburi and Samut Songkhram Province then discharge to the Gulf of Thailand, where of the one of the most important areas of tin production in Southeast Asia is located. (Censi et al., 2006).

Surface water from Mar Klong River is use for irrigation and aquaculture industries including fish culture ponds and shrimp farms. And the Mae Klong tributaries are used for agriculture such as rice crops, vegetable crops, fruit orchard farms and several industrial plants including chemical industries, paper manufacturing plants and battery storage plants. All of discharge and runoff from agriculture areas, industrials plants and residential areas will be released into The Mae Klong River. Especially heavy metal from these plants is the one of major pollutant that causing aquatic environment degradation.

### **2.5.3 The Tha Chin River**

The Tha Chin River is the one of major river in the central basin of Thailand. Total length of river which starts from Chainat Province then end at Samut Prakan Province is 325 km. 76% of the Tha Chin water supplies are uses for agriculture, 13% will be used for support residential areas and the 0.1% of area will be used for industrial. Moreover, the agriculture, residential and industrial areas which can discharge effluent into the Tha Chin River. This river was received pollutions from 3 tributaries including Mahasawat canal, Phasicharoen canal and Mahachai canal.

### **2.5.4 The Chao Phraya River**

Chao Phraya river is the largest river which located in the northern and central parts of Thailand. The 49% of fresh water which discharge into the Gulf of Thailand is from the Chao Phraya River. Then this river is the major load of pollutants in the Gulf of Thailand. And the river and estuary are the main transportation to sea near Bangkok. Moreover, following the important of this river having intensive of domestic and industrial activities along river.

According to major river of Thailand and it's formed from 4 major rivers in the northern of Thailand. That cause intensive domestic, transportation and industrial activities including industrial plants, fisheries, agriculture, transportation, domestic consumption, etc. especially the most of communities and consumers in Bangkok. Extremely load of fresh water in Chao Phraya River can cause the largest of runoff pollutants from industrial plants, fisheries, agriculture, transportation, domestic consumption such as the heavy metals pollutants discharge into water and sediment in the Gulf of Thailand (Sirirattanachai & Utoomprurkporn, 2005)

### **2.5.5 The Bangpakong River**

A hydro-geological map of the Bangpakong River basin was constructed by the Department of Geological Resources in 2001. Based on this map, the basin's geological structure consists of porous layers with gravel sediments,



semi-hardened sediments, and hardened rocks; about half (3,341,072 rai or 534,572 ha) of the geological structure of the basin consists of different porous layers with sediments, which makes the soil fertile and suitable for cultivation. Most of most of the Bangpakong River basin (about 70%) has been used for agricultural purposes, including the cultivation of rice, field crops, fruit trees and perennials and other farming activities. Urban and built-up land are expanding throughout the area, but especially in the estuary. The estuary area of the Bangpakong River in the four sub-districts totals 77,388 rai (12,382 ha). Most of the land (49.6%) is used for farming (aquaculture, salt farms), followed by community area, urban and building area (28.6%), forest area (11.7%), water bodies (8.4%) and miscellaneous (1.7%). Since 2002, there has been a notable change in demand and expansion of urban and industrial areas. (Chaiyarak et al., 2019).

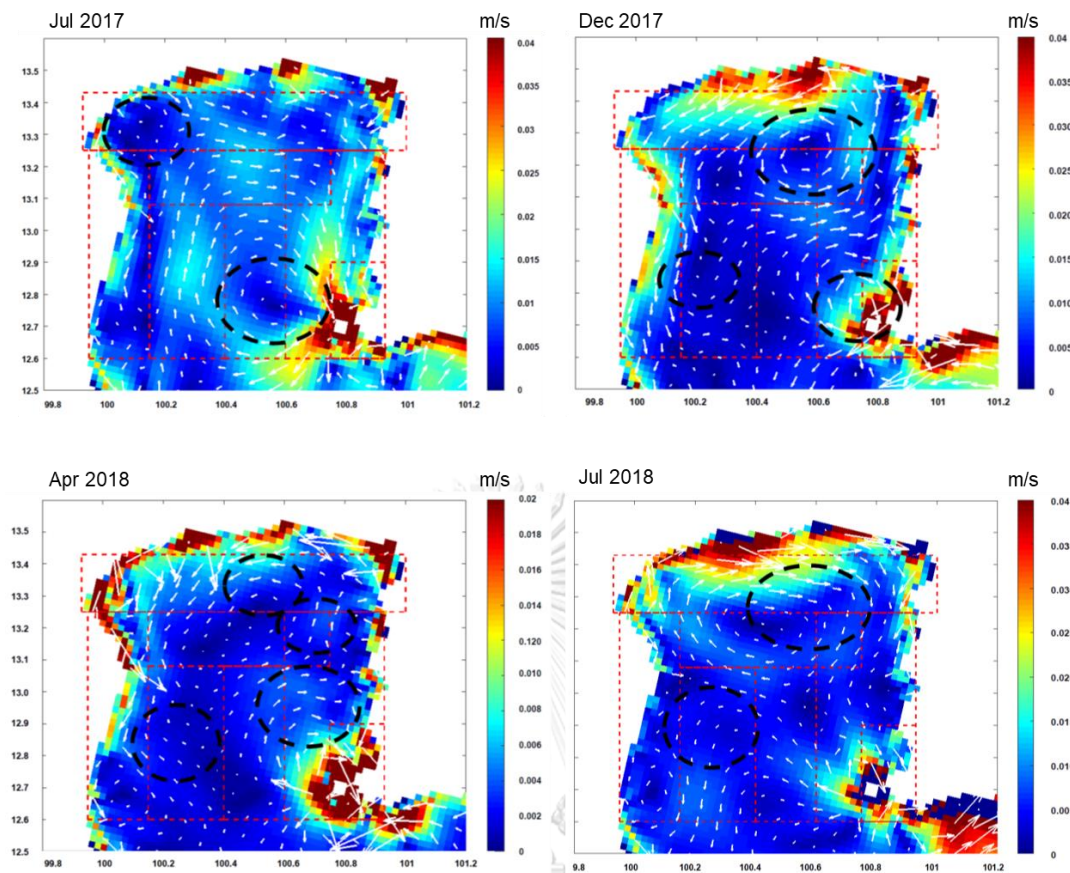
The Bangpakong River is considered as a significant source of nutrient loading because it carries a great amount of contaminant from urban, rural area, pig farms, rice farms, and fish and shrimp ponds. Thus, plankton bloom can be occurred frequently in the eastern part of the inner Gulf of Thailand (Bordalo et al., 2001).

## **2.6 Regulating Factors of Heavy Metal in the Inner Gulf of Thailand**

Due to high population-growth rates and development around the inner Gulf of Thailand during the last three decades has caused land contamination. There is various land used activities that affected soil and water quality such as mining, unplanned urban growth, industrial development, and chemical use in agriculture, solid waste from tourism, road transportation etc. (Figure 2.3). Moreover, the inner Gulf of Thailand was utilized for mariculture and marine transportation, marine transshipment etc. therefore the inner Gulf of Thailand is risk to contaminate with various pollutants, particularly heavy metals which were heterogeneously contaminated in the water, sediment, and organism. As a result, the inner Gulf of Thailand is a very dynamic coastal ecosystem, which has various regulating factors that effect on both quantity and quality of heavy metal changes in the water, sediment, and organism (Figure 2.4). Heavy metals from ❶ anthropogenic activities, particularly industrial, agricultural, urban pollutants were major sources due to ❷

river runoff from the Mae Klong, the Tha Chin, the Chao Phraya, and the Bangpakong Rivers. Due to different characteristic of 4 major river (Table 2.1), therefore the river runoff was loaded differently both in quantity and quality of heavy metals into the inner Gulf of Thailand. Additionally, ⑥ coastal erosion and runoff from various activities along the coastal line. Importantly, erosion includes not only the transport of sediment particles but also the transport of heavy metals and pollutants. Moreover, ② marine utilizations were also a major source of heavy metal due to mari–culture, fisheries, and longline cable on the seafloor etc. On the other hand, ③ tidal current was affected both sink and source of heavy metals of the inner Gulf of Thailand. While ④ density of marine transportation was another cause of heavy metal loading into this area. ⑦ Water circulation is the factor that moves heavy metals, which heterogeneously distributed entire the inner Gulf of Thailand. Moreover, velocities and directions of water were different patterns during the season changes (Figure 2.5). In addition, ⑧ southwest monsoon season and ⑨ northeast monsoon season were regulated runoff and water circulation, particularly the different concentration of heavy metal loading into the inner Gulf of Thailand.





Source: applied from Maksumpun et al. (2019)

**Figure 2.5** Current velocity and direction of surface water of the inner Gulf of Thailand in southwest monsoon season (Jul 2017), northeast monsoon season (Dec 2017), Dry season (Apr 2018) and southwest monsoon season (Jul 2018).

# CHAPTER 3

## METHODOLOGY

---

To meet the objectives of the present study, the methodologies including appropriate materials and standard methods were used to evaluate the influence of seasonal variations on contamination level and ecological risk of heavy metals in the surface sediments as follow:

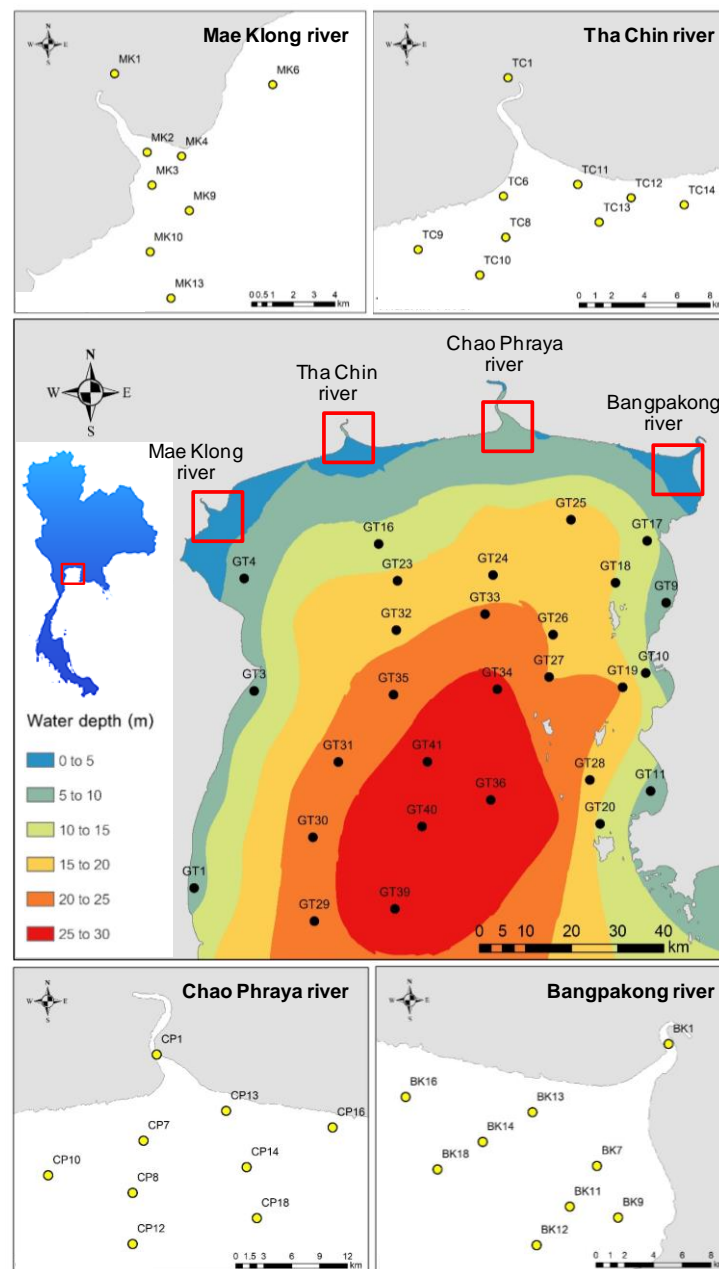
### 3.1 Study Areas and Sampling Points

The inner Gulf of Thailand, including the Mae Klong, the Tha Chin, the Chao Phraya, the Bangpakong River estuaries are chosen for the present study. The inner Gulf of Thailand is a semi-enclosed bay that located  $13^{\circ}2'44.43''\text{N}$  and  $100^{\circ}29'20.43''\text{E}$ . The climate in this region is influenced by the tidal current from the lower Gulf, South China Sea (Figure 3.1). The Gulf is about 90 km in length and widens from approximately 90 km at the mouth of the Gulf with a surface area of approximately  $8100 \text{ km}^2$  and an average depth of 15 m, the total water volume is ca.  $121.5 \text{ km}^3$ . Total 63 sampling sites are established in the inner Gulf of Thailand and four river estuaries in order to analyze total concentration of heavy metals in the surface sediment.

Sampling sites of river estuaries are established 8 stations for the Mae Klong river estuary (MK1, 2, 3, 4, 6, 9, 10 and 13), 9 stations for the Tha Chin river estuary (TC1, 6, 8, 9, 10, 11, 12, 13 and 14), 9 stations for Chao Phraya river estuary (CP1, 7, 8, 10, 12, 13, 14, 16 and 18) and 9 stations for the Bangpakong River estuary (BK1, 7, 9, 11, 12, 13, 14, 16 and 18) (Figure 3.1). Station MK1, TC1, CP1 and BK1 are located in the rivers influences zone for source pollutants river runoff (Figure 2). While, the other stations are located in eastern and western areas, where are in sedimentation zone of river estuaries (Figure 3.1), in order to characterize the accumulation of heavy metal in the surface sediments.

Total 28 sampling sites are established entire the inner Gulf of Thailand (Figure 3.1). Station GT1, GT3, GT4, GT9, GT10 and GT11 were in the range of 0–10 m

water depth. While maximum water depth of station GT16, GT17, GT18 and GT20 was in the range of 10–15 m. Maximum water depth of station GT23, GT24, GT25, GT26, GT27, GT28 and GT32 was in the range of 15–20 m. Maximum water depth of GT19, GT29, GT30, GT31, GT33, GT35 and GT36 was in the range of 20–25 m. Finally, maximum water depth of GT34, GT39, GT40 and GT41 was in the range of 25–30 m (Figure 3.1).



**Figure 3.1** Sampling sites in the Mae Klong, the Tha Chin, the Chao Phraya, the Bangpakong River estuaries, and the inner Gulf of Thailand.

## 3.2 Research Materials

### 3.2.1 Sampling cruise

- 1) Research vessel (Kasetsart Research Ship I)
- 2) Global positioning system (GPS)
- 3) Depth meter (Sonar sensor)

### 3.2.2 Sediment sampling

- 1) Ekman grab sampler
- 2) Smith-McIntyre grab sampler
- 3) Measuring scale
- 4) Polyethylene spatula
- 5) Polyethylene zip bag
- 6) Waterproof labeling pen
- 7) Cooling container

### 3.2.3 Laboratory instruments

- 1) Freeze dryer (LABCONCO freeze zone 6, USA)
- 2) Digital balance four digits (Mettler Toledo, MS204S, Switzerland)
- 3) High performance microwave digester (Milestone Series 135931, Italy)
- 4) ICP-OES (Analtik Jena, PlasmaQuant 9100 Elite, Germany)
- 5) TOC analyzer (Analtik Jena Multi N/C® 3100, Germany)
- 6) Muffle furnace (Nabertherm LT5/12, Germany)
- 7) Spectrophotometer (UNICO Spectrophotometers 1200)

### 3.2.4 Laboratory equipment

- 1) Filter paper (Whatman, No.42, UK)
- 2) Acid washed glassware

- 3) ASTM sieve 1 mm
- 4) Agate mortar
- 5) Acid washed polypropylene tube
- 6) Desiccator

### 3.2.5 Chemical substances

- 1) HNO<sub>3</sub> (QReC, AR, New Zealand)
- 2) HCl (QReC, AR, New Zealand)
- 3) HF (MERCK, AR, Germany)
- 4) H<sub>2</sub>BO<sub>3</sub> (QReC, AR, New Zealand)
- 5) HClO<sub>4</sub> (Sigma-Aldrich, AR, USA)
- 6) H<sub>2</sub>O<sub>2</sub>
- 7) NaOAc
- 8) NH<sub>2</sub>OH.HCl
- 9) MgCl<sub>2</sub>
- 10) Mg(NO<sub>3</sub>)<sub>2</sub>
- 11) Ammonium acetate
- 12) ICP multi-element standard (18 Elements) in 2% Nitric Acid (HNO<sub>3</sub>)  
(Reagecon, Ultrapure, Ireland)

## 3.3 Measurement Parameters

### 3.3.1 Total heavy metals

- 1) Cadmium (Cd)
- 2) Lead (Pb)
- 3) Copper (Cu)
- 4) Cobalt (Co)



- 5) Nickel (Ni)
- 6) Manganese (Mn)
- 7) Zinc (Zn)
- 8) Aluminum (Al)

### **3.3.2 Physicochemical factors**

- 1) Total organic matter (TOM)
- 2) Total organic carbon (TOC)
- 3) Total phosphorus (TP)
- 4) Acid volatile sulfide (AVS)
- 5) Water content

## **3.4 Sampling and Sample Preparations**

### **3.4.1 Sediment sampling**

All sediment samplings were carried out four times in different seasons by Faculty of Fisheries (2019) and Yottiam, (2019), including July 2017, which was represented southwest monsoon season, in December 2017, which was represented northeast monsoon season, in April 2018, which was represented dry season and finally in July 2018, which was southwest monsoon season.

Surface sediment sample (0–1 cm) were collected from all stations of river estuaries and 12 stations (GT1, GT3, GT4, GT9, GT10, GT11, GT16, GT17, GT18, GT19, GT20 and GT25) of the inner Gulf of Thailand using the Ekman grab sampler, while, station GT23, GT24, GT26, GT27, GT28, GT29, GT30, GT31, GT32, GT33, GT34, GT35, GT36, GT39, GT40 and GT41 were collected using the Smith-McIntyre grab sampler. All surface sediment samples were transported into cleaned polyethylene zip bag and stored in a cooling container (4 °C) for later analysis in a laboratory.

### 3.4.2 Sample preparations

At laboratory, the wet sediment samples were divided into two sub-samples. The first sub-sample was used to determine the AVS and water content. The others sub-sample was dried at  $-40\text{ }^{\circ}\text{C}$  for 72 hours using freeze-dryer (LABCONCO, Freezone 6, USA). Then, dried sediment samples were sieved through a 1 mm of standard test sieve series (ASTM, E11, USA) for removed coarse debris and shells fragments. After sediment samples were sieved, the sediment samples were grounded into powder homogenous texture by agate mortar. Finally, sediment samples were stored in acid-washed polyethylene tube and kept in desiccators for later analysis of heavy metals, TOM, TOC, and TP.

## 3.5 Chemical Analysis

### 3.5.1 Total heavy metals analysis

Homogenized sediment (0.5 g) of each sediment sample was transferred to a Teflon vessel. The sample was added by 4 mL of HF (overnight) and 2 mL of aqua regia (1  $\text{HNO}_3$ : 3  $\text{HCl}$ ) was subsequently added (Loring & Rantala, 1992; Yottiam et al., 2019) The vessel was closed tightly and placed in the microwave digester (Milestone Series 135931, Ethos one, Italy) and heat to  $175\text{ }^{\circ}\text{C}$  for 30 minutes. After cooling, HF residues have been eliminated by preparing of 4 g boric acid with 20 mL MilliQ water in 50 mL polyethylene volume metric flask. The extracted sample was transferred to the 50 mL flask, shook briefly, and make up to 50 mL with MilliQ water. The samples were filtered using paper filter (Whatman No.42, UK). The filtrate samples were stored in acid-washed polyethylene bottle until analysis. The selected heavy metals were determined by ICP-OES (Analtik Jena Plasma Quant 9100 Elite, Germany).

### 3.5.2 Total organic matter analysis

Total organic matter was measured weight loss after heating the samples for overnight at  $100\text{ }^{\circ}\text{C}$  to remove water and at  $550\text{ }^{\circ}\text{C}$  for 4 hours to remove organic

matter. The difference of mass between before and after the ignition process was used to calculate the TOM as follow:

$$\%LOI = \frac{(W_a - W_b) \times 100}{W_s} \quad (3.1)$$

where  $W_a$  is the weight of crucible with sample after heated at 550 °C (g)

$W_b$  is the weight of crucible with sample before heated at 550 °C (g)

$W_s$  is the dried weight of surface sediment sample (g)

### 3.5.3 Total organic carbon analysis

Total organic carbon in the surface sediment was determined in part of the samples after removal of carbonate with 1.2 N HCl (at room temperature, 24 hrs) using the TOC Analyzer (Analytik Jena, multi N/C® 3100, Germany). All samples were analyzed via catalytic oxidation combustion technique at high temperature (1,200 °C), to convert organic carbon into CO<sub>2</sub>. The CO<sub>2</sub> generated by oxidation is measured with the high-power long-life UV reactor uses two wavelengths (185/254 nm) for complete oxidation.

### 3.5.4 Total phosphorus analysis

Total phosphorus (TP) determination is consisted of initial ashing of dry samples with 5% (w/v) Mg(NO<sub>3</sub>)<sub>2</sub> as an oxidant (Krom & Berner, 1981) at 550 °C for 2 h followed by extracted with 1 N HCl for 16 h at room temperature (Aspila et al., 1976). The resulting solution was then analyzed for orthophosphate, using the acid molybdate–ascorbic method (Parsons et al., 1984).

### 3.5.5 Acid volatile sulfide analysis

Data of AVS in surface sediment were taken from previous study (Faculty of Fisheries, 2019; Yottiam, 2019). Analysis was as following: wet sediment sample (0.5–1.0 g) has been reacted with 18 N H<sub>2</sub>SO<sub>4</sub> in colorimetric gas

detection tubes (Gastec, 201LH, Japan) in order to liberate hydrogen sulfide (H<sub>2</sub>S) from the solid-phase sulfide in sediment. Generated gas was accumulated on the scale in mg unit of gas detector tube.

### 3.5.6 Water content

Water content analysis was determined by removed of the water from wet sediment sample. A wet sediment sample with container was dried at 105 °C by hot air oven for 24 hrs. The weight of sediment sample after oven was assessed as the dry sample weight. Then water content (%) was calculated by determine mass ratio of difference the weight of after–before oven and the weight dry sediment sample.

$$\text{Water content (\%)} = 100 \times \frac{(W_w - W_d)}{(W_d - W_c)} \quad (3.2)$$

Where  $W_w$  is the weight of wet sediment with container

$W_d$  is the weight of dry sediment with container

$W_d$  is the weight of dry sediment with container

$W_c$  is the weight of blank container

## 3.6 Data Analysis

### 3.6.1 Spatial distributions

Spatial heterogeneity distributions of total heavy metals (Cd, Pb, Cu, Co, Ni, Mn and Zn) concentrations and related parameters in the surface sediment were performed by deterministic interpolation technique using an inverse distance weighting (IDW) of ArcGIS<sup>TM</sup> v.10.7.1 software. IDW interpolation is the one of accurate interpolation method which commonly used for determine concentration by distance weighting.

### 3.6.2 Contamination status of heavy metals

#### 1) Sediment quality guidelines

**Sediment quality guideline of Thailand ( $SQG_T$ )** is established as the acceptable level of pollution in sediments that will not pose any effect on benthic fauna and quality of an environment (Pollution Control Department, 2015). Each total heavy metal concentration of each sample were compared to the guideline. The guideline values of coastal sediment are listed in Table 3.1.

**Sediment quality guidelines ( $SQGs$ )** are developed as interpretive tools for assessing the quality of sediments. The threshold effect levels ( $TELs$ ) and probable effect levels ( $PELs$ ) are the main parameters for defining three ranges of chemical concentrations, including those that were (1) rarely, (2) occasionally or (3) frequently associated with adverse effects of metals in marine sediment (Long & MacDonald, 1998; Macdonald et al., 1996). The values of  $TELs$  and  $PELs$  are listed in Table 3.1.

**Table 3.1** Values of sediment quality guidelines ( $SQGs$ ), the threshold effect levels ( $TELs$ ), probable effect levels ( $PELs$ ) and apparent effects threshold ( $AET$ ) (in mg/kg) of each heavy metal.

Metals	$SQG_T^a$	$TEL^b$	$PEL^b$	$AET^c$
Cadmium	2.0	0.68	4.21	3.0
Lead	52.0	30.20	112.0	400.0
Copper	25.0	18.70	108.0	390.0
Cobalt	NA	NA	NA	10.0
Nickel	NA	15.90	42.8	110.0
Manganese	NA	NA	NA	260.0
Zinc	102.0	124.00	271.0	410.0

**Remarks:** NA means not available.

<sup>a</sup> Coastal sediment quality standard of Thailand (Pollution Control Department, 2015)

<sup>b</sup> Macdonald et al., (1996)

<sup>c</sup> Buchman (2008)

## 2) Enrichment factor

Enrichment factor ( $EF$ ) is a useful tool to assess the extent of sediment contamination by metals, calculating their naturally occurring and anthropogenic concentrations. To calculate the  $EF$  values for a given heavy metal, the concentration was normalized with basal samples of station. This study used Aluminum (Al) as normalizer because it is one of the main components of the Earth's crust and alumina-silicate is generally the predominant carrier phase for metals in coastal sediments, together with that the natural concentration of Al in marine sediments tends to be uniform (Wang et al., 2015). The  $EF$  was calculated using eq 3.3.

$$EF = \frac{\left(\frac{C_n}{Al}\right)_{sample}}{\left(\frac{C_n}{Al}\right)_{background}} \quad (3.3)$$

where  $C_n$  is the concentration of heavy metal in sediment sample and background value.

$\left(\frac{C_n}{Al}\right)_{sample}$  is heavy metal and aluminum ratio observed for sediment sample.

$\left(\frac{C_n}{Al}\right)_{background}$  is natural heavy metal and aluminum ratio for reference sediment (Cd = 0.42, Pb = 80, Cu = 250, Co = 74, Ni = 225, Mn = 6700, Zn = 165 and Al = 84,000 mg/kg). The baseline values obtained from Turekian & Wedepohl (1961).

The degrees of heavy metals pollution are classified as seven tiers of  $EF$  indices are defined in Table 3.2.

**Table 3.2** Tiers of heavy metals contamination status in the surface sediment based on different the EF values.

Tier	EF values	Level of enrichment
1	<1	no enrichment
2	1–3	minor enrichment
3	3–5	moderate enrichment
4	5–10	moderately severe enrichment
5	10–25	severe enrichment
6	25–50	very severe enrichment
7	> 50	extremely severe enrichment

Source: Jamshidi-Zanjani & Saeedi, (2013)

### 3) Geo-accumulation index

The index of geo-accumulation ( $I_{geo}$ ) was employed to separate the anthropogenic influences on the sediment from the natural influences (Li et al., 2016). The  $I_{geo}$  calculation was done using the following equation:

$$I_{geo} = \log_2 \left( \frac{C_n}{1.5 B_n} \right) \quad (3.4)$$

where  $C_n$  is heavy metals concentration in the surface sediment (mg/kg).

$B_n$  is the geochemical background value of heavy metals (Cd = 0.42, Pb = 80, Cu = 250, Co = 74, Ni = 225, Mn = 6700, Zn = 165 and Al = 84,000 mg/kg). In this study, the value of heavy metals was used according to Turekian & Wedepohl (1961).

1.5 is the factor of used to account for possible variations of background values because of lithogenic effects.

The degrees of heavy metals contamination are classified as seven classes of the  $I_{geo}$  values, which were defined in Table 3.3.

**Table 3.3** Classes of heavy metals contamination status in the surface sediment based on different the  $I_{geo}$  values.

Class	Values	Level of contaminations
0	$I_{geo} < 0$	practically uncontaminated
1	$0 < I_{geo} < 1$	uncontaminated to moderately
2	$1 < I_{geo} < 2$	moderately contaminated
3	$2 < I_{geo} < 3$	moderately to heavily contaminated
4	$3 < I_{geo} < 4$	heavily contaminated
5	$4 < I_{geo} < 5$	heavily to extremely contaminated
6	$I_{geo} > 5$	extremely contaminated

Source: Müller (1969)

### 3.6.3 Potential ecological risk assessment

Potential ecological risk ( $E_r$ ) is an index of ecological risk assessment proposed by Hakanson (1980) and widely used to evaluate the degree of pollution of element in the sediment.

Potential ecological risk ( $E_r$ ) is an index of ecological risk assessment developed by Hakanson (1980) and widely used to evaluate the degree of pollution of element in the sediments.  $E_r$  led to finding potential ecological risk index ( $RI$ ). The equations for calculating the  $E_r$  and  $RI$  are as follows:

$$E_r = T_r^i \times C_f^i \quad (3.5)$$

where  $E_r$  is the potential risk of heavy metals.

$T_r^i$  is the toxic response factor (TRF) value of each heavy metals are Cd = 30, Pb = 5, Cu = 5, Co = 5, Ni = 5, Mn = 1 and Zn = 1 Hakanson (1980) and Kolawole et al. (2018).



$$C_f^i = \frac{C_D^i}{C_r^i} \quad (3.6)$$

$$RI = \sum_{i=1}^n E_r^i \quad (3.7)$$

Where  $C_f^i$  is the contamination factor.

$C_D^i$  is the mean concentration of each heavy metals for present study.

$C_r^i$  is the preindustrial reference value of heavy metals in the sediment. In this study, the value of Cd = 1, Pb = 70, Cu = 50, Co = 18.5, Ni = 49.7, Mn = 368 and Zn = 175 were used according to the suggestion of Hakanson (1980).

The  $E_r$  index consists of five classes for ecological risk level of chromium (Table 3.4).

**Table 3.4** Class of potential ecological risk ( $E_r$ ) and potential ecological risk index (RI) of heavy metal pollutions.

Class	$E_r$ values	Level of risk	RI values	Level of risk
1	$E_r < 40$	low potential ecological risk	$RI < 150$	Low ecological risk
2	$40 \leq E_r < 80$	moderate potential ecological risk	$150 \leq RI < 300$	moderate ecological risk
3	$80 \leq E_r < 160$	considerable potential ecological risk	$300 \leq RI < 600$	considerable ecological risk
4	$160 \leq E_r < 320$	high potential ecological risk	$RI \geq 600$	very high ecological risk
5	$E_r \geq 320$	very high potential ecological risk		

Source: Hakanson (1980); Wang et al. (2015)

### 3.7 Quality Control

Precision and accuracy of heavy metal analyses were checked against the certified reference materials (sediment reference material MESS-4), which is a polluted marine sediment standard prepared by the National Research Council Canada (NRCC).

### 3.8 Statistical Analysis

One-way ANOVA was applied to evaluate 1. The difference of each heavy metal concentrations between seasons and different areas (4 river estuaries and the inner Gulf of Thailand) 2. The difference of TOM, TOC, TP and AVS between seasons and study areas (4 river estuaries and the inner Gulf of Thailand). Pearson's correlation analysis was conducted to identify the relationships between the detected sediment properties and total heavy metals. Differences were considered to be significant if  $p$  value lower than 0.05. All statistical analysis was performed using SPSS v.28.0 for Windows software package.

# CHAPTER 4

## RESULTS AND DISCUSSION

---

The inner Gulf of Thailand is trend to be contaminated with heavy metals due to recent rapid industrialization, urbanization, agriculturization and economic growth in the surrounding area. The present study is focused on spatial distribution evaluation, seasonal variation of total concentration of Cd, Pb, Cu, Co, Ni, Mn and Zn and physiochemical factors in the surface sediment in the inner Gulf of Thailand and the concentration of selected heavy metals. The results of heavy metals in the surface sediment of the inner Gulf of Thailand are reported including the Mae klong, the Tha Chin, the Chao Phraya and the Bangpakong River estuaries, and then these results were evaluated the contamination status by using sediment quality guidelines, enrichment factor and geo-accumulation index. Also assessed the potential ecological risk and risk index for indicated the risk levels from heavy metals contamination in the inner Gulf of Thailand. Lastly, the relationship between the heavy metal concentration and physiochemical factors was conducted by using correlation coefficient. All result and discussion described as follow:

### **4.1 Spatial distributions and seasonal variations**

Data presented here provide, a bay-wide synaptic distribution of sediment characteristics of the inner Gulf of Thailand. Noticeable data on the surface sediment at the 52–60 frequently sampled sites over the study periods (229 sediment samples) showed spatial and seasonal variations (Figure 4.1–4.20). Heterogeneity distributions of heavy metal and physicochemical factors in the surface sediment were indicated entire the inner Gulf of Thailand. Moreover, heavy metals were differently accumulated in the Mae Klong, the Tha Chin, the Chao Phraya and the Bangpakong River estuaries. While southwest monsoon, northeast monsoon and dry season were also affected in the heavy metal concentrations. Data of the present study were much and complicated, however all data analysis were reported as follow:

#### 4.1.1 Cadmium (Cd)

Spatial heterogeneity distribution of Cd in the surface sediment in southwest monsoon season (July 2017) is demonstrated in Figure 4.1. The horizontal distribution was characterized by the highest concentration at the mouth of the Bangpakong River estuary (Stn.BK12: 0.36 mg/kg), while the lowest concentration was found at middle part of the Gulf (Stn. GT26: 0.02 mg/kg). As a result, Cd concentrations were decreased from the mouth of the Bangpakong, the Chao Phraya and the Tha Chin River estuaries to the middle Gulf, subsequently slightly increased at the lower Gulf.

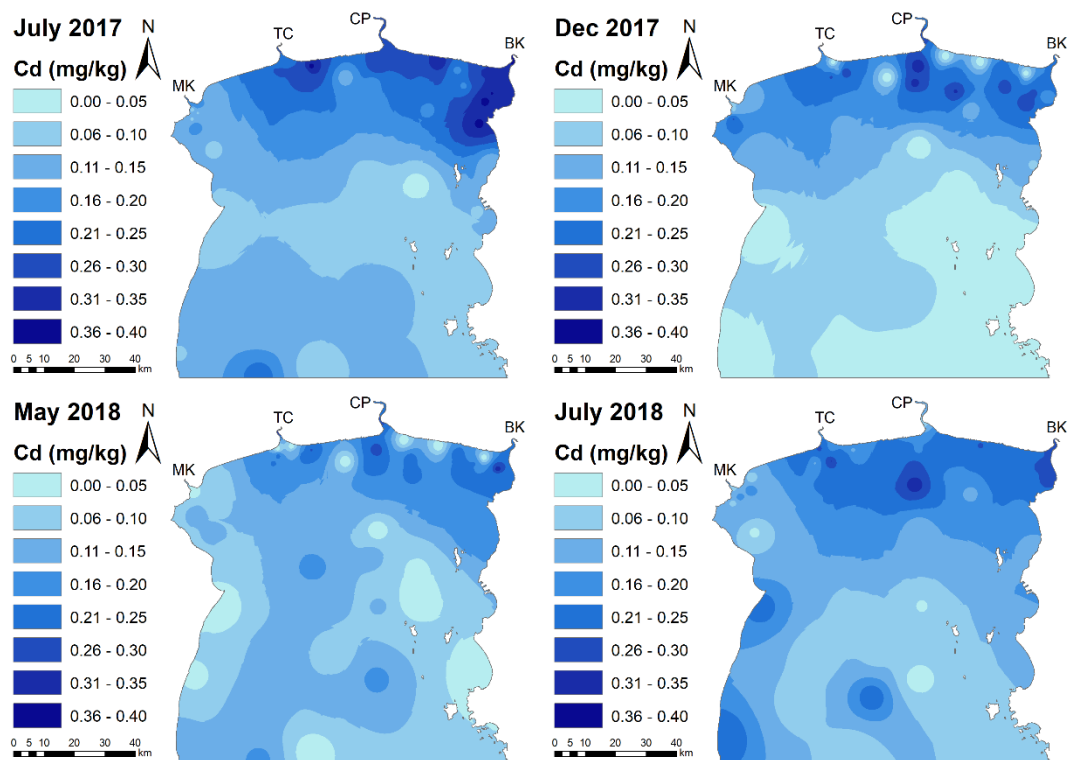
In northeast monsoon season (December 2017), Cd was spatially distributed in the range of 0.003–0.33 mg/kg, which was characterized high concentration at the mouth of the Chao Phraya River (Stn.CP7), while the lowest one was observed at the lower Gulf (Stn.GT37). As a result, decreasing concentration trend was occurred from the upper to lower areas of the inner Gulf of Thailand (Figure 4.1).

In dry season (May 2018), Cd in the surface sediment was varied between 0.005–0.35 mg/kg, the lowest concentration was found at the western area of the Mae Klong River mouth, while the highest value was occurred at the eastern area of the Tha Chin River mouth (Figure 4.1). In this season, Cd distribution in the surface sediment entire the Gulf was not clear pattern. However, Cd concentrations were slightly decreased from the river mouths to the lower area of the inner Gulf of Thailand.

In southwest monsoon season (July 2018), the horizontal distribution was characterized by the highest concentration at the outer part of the Chao Phraya River estuary (Stn.CP12: 0.33 mg/kg), while the lowest concentration was found at lower part of the Gulf (Stn. GT36: 0.03 mg/kg). As a result, Cd concentrations were decreased from the mouth of the four main rivers to the middle Gulf.

In both southwest monsoon seasons were significantly higher in the upper Gulf than in the lower Gulf, particularly eastern area ( $p < 0.05$ ) (Figure 4.1). These comparisons suggest that anthropogenically sources of Cd were largely diluted in the lower Gulf. Although the inner Gulf of Thailand is semi-enclosed bay, the

strong hydrodynamic conditions and flat geomorphic characteristics allow for the sufficient exchange of water and sediment between the inner and lower Gulf, which prevents heavy metal accumulation in the bay (X. Yang et al., 2017; Yao et al., 2021). For the mean concentrations across the entire the inner Gulf of Thailand (Table 4.1), both southwest monsoon seasons in 2017 ( $0.19\pm 0.10$  mg/kg) and 2018 ( $0.18\pm 0.08$  mg/kg) were significantly higher than northeast monsoon season ( $0.14\pm 0.11$  mg/kg) and dry season ( $0.13\pm 0.09$  mg/kg) ( $p < 0.05$ ).



**Figure 4.1** Spatiotemporal heterogeneity distributions and seasonal variations of Cd concentration in the surface sediment of the inner Gulf of Thailand.

According to the distribution pattern of Cd in the surface sediment entire the inner Gulf of Thailand (Figure 4.1), the results indicated that the four major rivers, particularly the Bangpakong, the Chao Phraya and the Tha Chin Rivers, are sources of Cd. Therefore, analysis of individual areas and comparison were necessary to identify the effects of rivers on the Cd distributions in the inner Gulf of Thailand.

The Mae Klong River estuary, Cd concentration was found in the range of 0.08–0.33 ( $0.16\pm 0.08$ ) mg/kg for southwest monsoon season (July 2017),

0.07–0.28 (0.17±0.08) mg/kg for northeast monsoon season (December 2017), 0.005–0.14 (0.08±0.05) mg/kg for the dry season (May 2018), and 0.06–0.32 (0.14±0.08) mg/kg for southwest monsoon season (July 2018). According to Cd distributions, the relative high concentrations were found at the inner zone of the river (Stn.MK1). The mean values are compared in order to evaluate seasonal variations. Results indicated that the Cd concentration in four seasons were not significant differences (Figure 4.2).

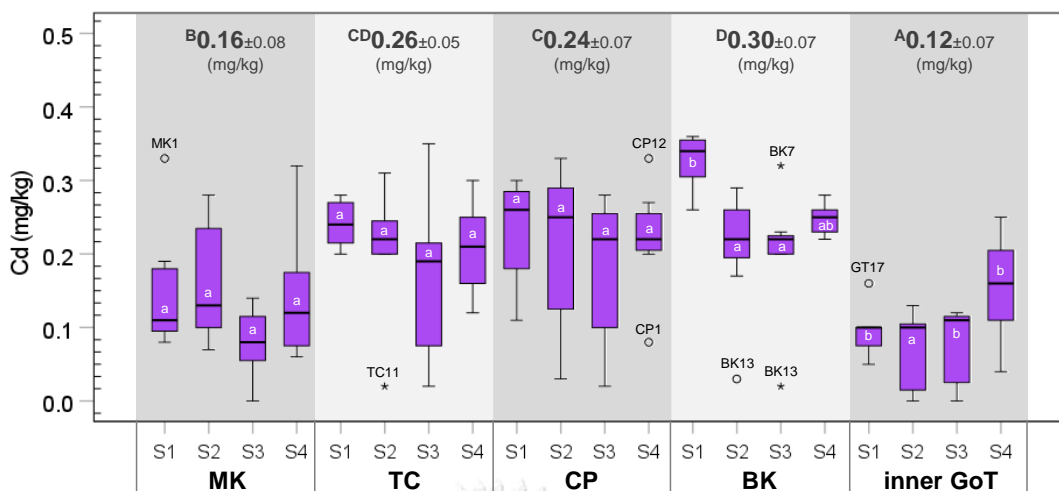
The Tha Chin River estuary, Cd concentration was found in the range of 0.20–0.36 (0.26±0.05) mg/kg for southwest monsoon season (July 2017), 0.02–0.31 (0.21±0.08) mg/kg for northeast monsoon season (December 2017), 0.02–0.35 (0.18±0.10) mg/kg dry season (May 2018), and 0.12–0.20 (0.20±0.06) mg/kg for southwest monsoon season (July 2018). The spatial distribution was characterized by the highest concentration at the inner part of river in northeast monsoon and dry seasons, while both southwest monsoon seasons were relative high concentrations in mouth of the river. As a result, Cd concentrations were decreased from southwest monsoon season to dry season, subsequently increased again in southwest monsoon season. However, mean comparison indicated that the Cd concentration in four seasons were not significant differences (Figure 4.2).

The Chao Phraya River estuary, Cd concentration was found in the range of 0.11–0.24 (0.24±0.07) mg/kg for southwest monsoon season (July 2017), 0.03–0.33 (0.20±0.12) mg/kg for northeast monsoon season (December 2017), 0.02–0.28 (0.16±0.10) mg/kg dry season (May 2018), and 0.08–0.33 (0.22±0.07) mg/kg for southwest monsoon season (July 2018). The spatial distribution was characterized by the highest concentration at Stn.CP7, where is located in the mouth of river both in northeast monsoon and dry seasons, while southwest monsoon seasons were relative high concentrations in eastern direction and the outer part of the river estuary for 2017 and 2018, respectively. As a result, Cd concentrations were decreased from southwest monsoon season to dry season, subsequently increased again in southwest monsoon season. However, mean comparison indicated that the Cd concentration in four seasons were not significant differences (Figure 4.2).

The Bangpakong River estuary, Cd concentration was found in the range of 0.19–0.36 (0.30±0.07) mg/kg for southwest monsoon season (July 2017), 0.03–0.29 (0.22±0.08) mg/kg for northeast monsoon season (December 2017), 0.02–0.32 (0.16±0.10) mg/kg dry season (May 2018), and 0.22–0.28 (0.24±0.02) mg/kg for southwest monsoon season (July 2018). The spatial distribution was characterized by relatively high concentrations in the eastern part (Stn.BK12 for southwest and northeast monsoon seasons of 2017, BK7 for dry season and BK8 for southwest monsoon season of 2018). Mean comparisons indicated that the Cd concentration in southwest and northeast monsoon seasons of 2017 were significant highest, while mean Cd concentrations of northeast monsoon and dry seasons were not differences (Figure 4.2).

The inner Gulf of Thailand excludes river estuaries, Cd concentration was found in the range of 0.02–0.36 (0.12±0.07) mg/kg for southwest monsoon season (July 2017), 0.003–0.13 (0.05±0.04) mg/kg for northeast monsoon season (December 2017), 0.005–0.18 (0.09±0.06) mg/kg dry season (May 2018), and 0.03–0.25 (0.12±0.07) mg/kg for southwest monsoon season (July 2018). Mean comparisons indicated that the Cd concentration in northeast monsoon seasons of 2017 was significantly lower than southwest monsoon season 2017 and dry season 2018. While mean concentration of southwest monsoon season 2018 was significant highest (Figure 4.2).

The mean value of Cd concentrations in the study area follows a descending order of the Bangpakong (0.30±0.17 mg/kg) > Tha Chin (0.26±0.05 mg/kg) > Chao Phraya (0.24±0.07 mg/kg) > Mae Klong (0.16±0.05 mg/kg) > the inner Gulf (0.12±0.07 mg/kg). According to comparison of mean values in different areas (Figure 4.2), Cd concentration in the Bangpakong River estuary was significantly highest ( $p<0.05$ ). On the other hand, the inner Gulf was significantly lowest concentration ( $p<0.05$ ). While mean concentration of the Tha Chin River was relative similarly to the Chao Phraya River (Figure 4.2). However, Cd concentrations in all seasons and areas based on the inner Gulf of Thailand are relatively lower than in other areas (Table 4.1).



Remark: S1 is July 2017, S2 is December 2017, S3 is May 2018 and July 2018

Alphabet indicated the significant differences between seasons and areas

**Figure 4.2** Seasonal comparisons of Cd contamination in the surface sediment of the Mae Klong (MK), the Tha Chin (TC), the Chao Phraya (CP), the Bangpakong (BK) river estuaries and the inner Gulf of Thailand (inner GoT).

#### 4.1.2 Lead (Pb)

Spatial distribution of Pb in the surface sediment in southwest monsoon season (July 2017) is displayed as Figure 4.3. The highest Pb concentration was found at the Mae Klong River estuary (Stn.MK1; 36.42 mg/kg), while the lowest Pb concentration was found in the inner Gulf of Thailand (Stn.GT1; 1.87 mg/mg). The greater amount of Pb concentration likely to found in the upper area of Gulf more than the concentration which were found in the low of Gulf area.

In northeast monsoon season (December 2017), the average concentration of Pb in the Mae Klong, the Tha Chin, and the Chao Phraya River estuaries was higher than the average in all study areas. Especially, in the Tha Chin River estuary has the highest concentration at station TC1 (33.40 mg/kg) and the lowest concentration found in the inner Gulf of Thailand (Stn.GT39; 3.59 mg/kg). In this season, the horizontal distribution of Pb concentration seems to be separated by the upper and the lower Gulf.

Spatial distribution of Pb in the dry season (May 2018) was in the range of 1.82–24.82 mg/kg. As Figure 4.3 the concentration of Pb likely to distribute all over the inner Gulf of Thailand, but the highest concentration found at the Tha



Chin River Estuary (Stn.TC2) and the lowest concentration was found in the inner Gulf of Thailand (Stn.GT2).

In southwest monsoon season (July 2018), the horizontal distribution was characterized by the highest concentration at the inner The Mae klong River estuary (Stn.MK1; 44.86 mg/kg) and the lowest concentration at the middle of the Gulf (Stn.GT36; 7.86 mg/kg). As Figure 4.3 the concentration which that lower than 15 mg/kg was found at the lower Gulf area.

In both southwest monsoon and dry season, the Pb concentration was widespread all over the Gulf, but in dry season the distribution seems to be influenced from circulated tidal in the inner Gulf of Thailand. And the upper of Gulf in northeast monsoon season was found higher than the lower area. As Table 4.1 the mean concentration across entire the inner Gulf of Thailand, in 2018 southwest monsoon seasons ( $16.76 \pm 6.11$  mg/kg) was significantly higher than 2017 southwest monsoon ( $15.69 \pm 6.39$  mg/kg) and northeast monsoon season ( $14.05 \pm 7.74$  mg/kg) and the lowest mean concentration was in dry season ( $12.48 \pm 4.36$  mg/kg) ( $p < 0.05$ ).



**Figure 4.3** Spatiotemporal heterogeneity distributions and seasonal variations of Pb concentration in the surface sediment of the inner Gulf of Thailand.

According to the horizontal distribution pattern of Pb in the surface sediment entire the inner Gulf of Thailand as shown as Figure 4.3, the results displayed that the four major rivers, especially the Mae Klong, the Tha Chin and the Chao Phraya Rivers are source of Pb, which was affected relatively the high concentration in the estuarine areas. Therefore, analysis of individual areas and comparison were necessary to identify the effect of rivers on Pb distributions in the inner Gulf of Thailand.

The Mae Klong River estuary, Pb concentration was found in the range of 16.33–36.42 ( $23.17\pm 6.61$ ) mg/kg for the southwest monsoon season (July 2017), 17.67–30.20 ( $23.18\pm 4.27$ ) mg/kg for northeast monsoon season (December 2017), 7.84–21.77 ( $13.69\pm 4.17$ ) mg/kg for the dry season (May 2018), and 16.20–44.86 ( $23.37\pm 9.17$ ) mg/kg for southwest monsoon season (July 2018). According to Pb distribution, the relatively high concentrations were found at the inner zone of the river (Stn.MK1) but in the dry season Pb's concentration was decreased from the northeast monsoon. The mean values are compared in order to evaluate seasonal variations, the result shown that the Pb concentrations in the southwest monsoon (July 2017), the northeast monsoon (December 2017), and the southwest monsoon (July 2018) were significantly higher than the concentration in dry season (May 2018) ( $p < 0.05$ ) (Figure 4.4).

The Tha Chin River estuary, Pb concentration was found in the range of 13.68–25.70 ( $18.58\pm 4.11$ ) mg/kg for the southwest monsoon season (July 2017), 14.24–43.35 ( $20.99\pm 5.52$ ) mg/kg for the northeast monsoon season (December 2017), 8.36–24.82 ( $16.93\pm 4.15$ ) mg/kg for the dry season (May 2018), and 8.46–27.83 ( $16.53\pm 5.61$ ) mg/kg for southwest monsoon season (July 2018). The spatial distribution was characterized by the highest concentration at inner part of rivers (Stn.TC1) in northeast monsoon season (December 2017). As a result, the mean comparison of four seasons displayed no significant difference (Figure 4.4).

The Chao Phraya River estuary, Pb concentration was found in the range of 3.33–26.43 ( $15.86\pm 7.35$ ) mg/kg for southwest monsoon season (July 2017), 17.66–24.44 ( $21.13\pm 2.56$ ) mg/kg for northeast monsoon season (December 2017), 12.21–18.48 ( $14.39\pm 1.88$ ) mg/kg for the dry season (May 2018), and

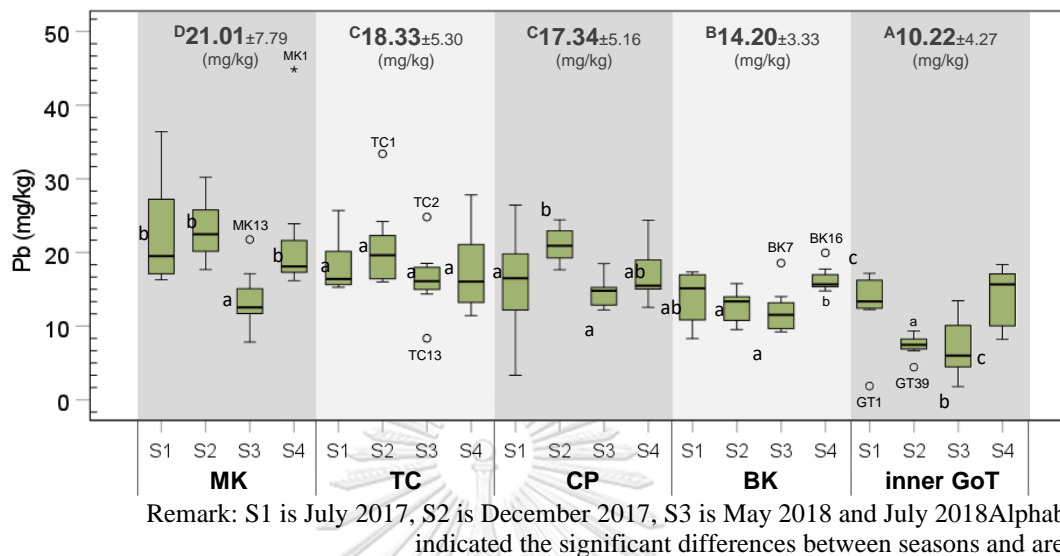
12.57–24.40 (17.98±3.73) mg/kg for southwest monsoon season (July 2018). The spatial distribution was characterized by the highest concentration at inner of river area in four seasons. As a result, concentration of Pb was increased from the southwest monsoon season to the northeast monsoon season, later was decreased again in the dry season. For mean comparison evaluation, in northeast monsoon season was the significantly highest mean ( $p<0.05$ ) (Figure 4.4).

The Bangpakong River estuary, Pb concentration was found in the range of 1.87–19.28 (12.43±4.35) mg/kg for southwest monsoon season (July 2017), 9.54–15.78 (13.07±2.09) mg/kg for northeast monsoon season (December 2017), 9.23–18.57 (12.25±2.74) mg/kg for the dry season (May 2018), and 14.79–20.61 (16.83±2.01) mg/kg for southwest monsoon season (July 2018). The spatial distribution was characterized by highest concentration at the inner part of the river in the dry season (May 2018) and highest concentration in the river mouth in both southwest monsoon and northwest monsoon seasons. Mean comparison indicated that the Pb concentration in the southwest monsoon season 2018 was significantly highest (Figure 4.4).

The inner Gulf of Thailand excludes river estuaries, Pb concentration was found in a range of 1.87–19.28 (12.43±4.35) mg/kg for southwest monsoon season (July 2017), 3.59–9.36 (6.51±1.50) mg/kg for northeast monsoon season (December 2017), 1.82–15.95 (9.84±3.63) mg/kg for the dry season (May 2018), and 7.86–18.35 (13.09±3.37) mg/kg for southwest monsoon season (July 2018). Mean comparison as seen Figure 4.4 shown that both southwest monsoon season was significantly higher than dry season 2018, and the lowest Pb concentration was northeast monsoon season.

The mean value of Pb concentration in the study area follows a descending order of Mae Klong (21.01±7.79 mg/kg) > Tha Chin (18.33±5.30 mg/kg) > Chao Phraya (17.34±5.16 mg/kg) > Bangpakong (14.20±3.33 mg/kg) > the inner Gulf of Thailand (10.22±4.27 mg/kg). As the mean comparison between all area results in Figure 4.4, the Pb concentration in The Mae Klong River estuary was significantly highest ( $p<0.05$ ), whereas the lowest concentration was in the inner

Gulf of Thailand ( $p < 0.05$ ). While the concentration of the Tha Chin and the Chao Phraya River estuaries were not significantly difference.



**Figure 4.4** Seasonal comparisons of Pb contamination in the surface sediment of the Mae Klong (MK), the Tha Chin (TC), the Chao Phraya (CP), the Bangpakong (BK) river estuaries and the inner Gulf of Thailand (inner GoT).

#### 4.1.3 Copper(Cu)

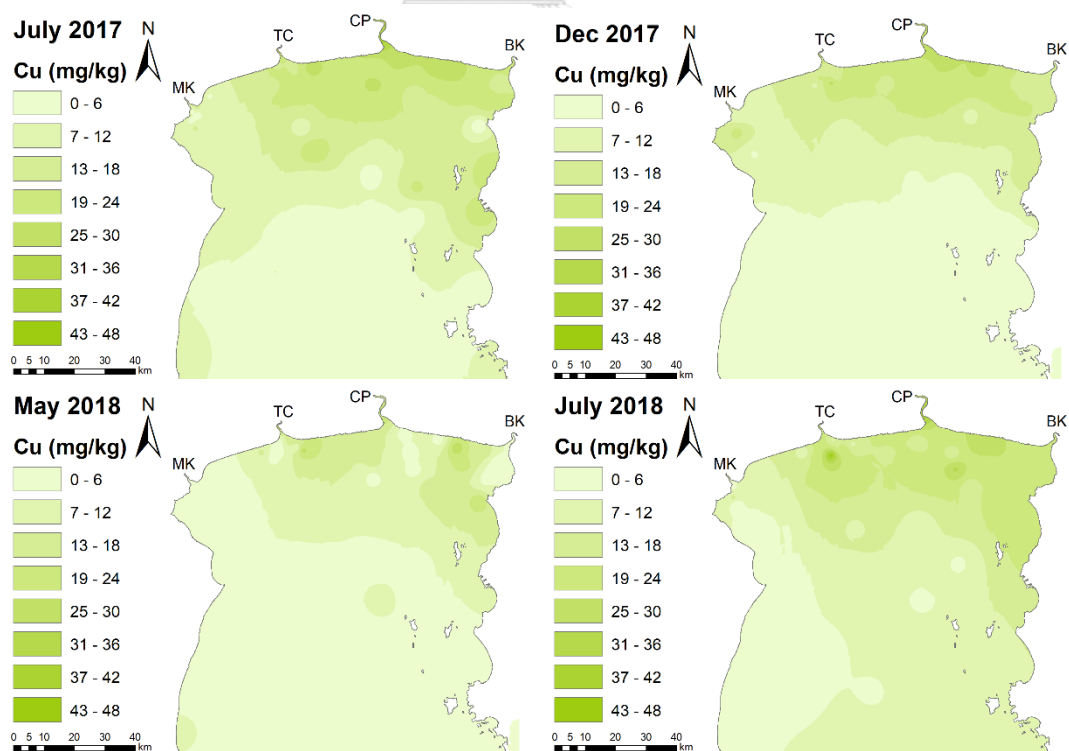
Spatial heterogeneity distribution of Cu in surface sediment in southwest monsoon season (July 2017) is demonstrated in Figure 4.5. The horizontal distribution was characterized by highest concentration at the Tha Chin River estuary (Stn.TC1; 48.54 mg/kg). By contrast, the lowest concentration of Cu was found in the eastern part of Gulf (Stn.17; 1.20 mg/kg). And the result shown that the concentration of Cu in southwest monsoon season (2017) was high around rivers and estuaries part then also found decreasing of the concentration toward the middle part of the Gulf.

In northeast monsoon season (December 2017), Cu in the surface sediment was varied between 0.74–43.35 mg/kg. The lowest concentration was found lower part of the Gulf at Stn.GT20 and the highest was found at Stn.TC1 in the Tha Chin River estuaries. Spatial distribution as Figure 4.5, shown that the upper Gulf mostly found the Cu higher than 6 mg/kg.

In dry season (May 2018), the Cu concentration was lowest in the Mae Klong River estuary by 0.25–1.21 ( $0.74\pm 0.38$ ) mg/kg. The great amount of Cu concentration was found in the Tha Chin, the Chao Phraya, and the Bangpakong River estuaries, but the highest was at the Tha Chin River estuary (Stn.TC2; 35.02 mg/kg).

In southwest monsoon season (July 2018), the highest Cu concentration was found in the Tha Chin River estuary (Stn.TC5; 43.04 mg/kg). The lowest concentration was found in the inner Gulf of (Stn.GT4; 0.49 mg/kg). As spatial distribution pattern shown that the decreasing of Cu concentration was start from four main estuaries to the western part of the Gulf.

For all seasons, the southwest season (July 2018) has least influence from exchange of water and sediment. While mean comparison in entire the inner Gulf of Thailand, (Table 4.1), both southwest monsoon seasons in 2017 ( $14.80\pm 10.04$  mg/kg) and 2018 ( $15.49\pm 10.07$  mg/kg) and northeast monsoon season in 2017 ( $12.51\pm 9.02$  mg/kg) were significantly higher than the dry season ( $7.40\pm 8.42$  mg/kg) ( $p < 0.05$ ).



**Figure 4.5** Spatiotemporal heterogeneity distributions and seasonal variations of Cu concentration in the surface sediment of the inner Gulf of Thailand.

According to the result which can be seen from horizontal distribution of Cu in the surface sediment entire in the inner Gulf of Thailand (Figure 4.5), the four major rivers which considerably the Tha Chin, the Chao Phraya and the Bangpakong River estuaries are the source of Cu. Then analysis of each part of areas and comparison were conducted to identify the effects of rivers on the Cu distribution in the inner Gulf of Thailand.

The Mae Klong River estuary, Cu concentration was found in the range of 3.00–26.71 (10.45±7.54) mg/kg for southwest monsoon season in July 2017, 6.10–22.42 (11.46±5.56) mg/kg for northeast monsoon season (December 2017), 0.25–1.21 (0.74±0.38) mg/kg for a dry season in May 2018, and 1.24–34.29 (10.22±9.76) mg/kg for southwest monsoon season (July 2018). According to Cu distribution, the relatively high concentration also found at the inner part of the river (Stn.MK1) and river estuary (Stn.MK13). The result of a mean comparison between seasonal shown that the dry monsoon season (May 2018) was significantly lower than others season ( $p<0.05$ ) (Figure 4.6).

The Tha Chin River estuary, Cu concentration was found in the range of 14.18–48.54 (22.25±10.33) mg/kg for southwest monsoon season (July 2017), 10.71–43.35 (19.67±9.17) mg/kg for northeast monsoon season (December 2017), 0.35–35.02 (13.83±11.12) mg/kg for the dry season (May 2018), and 7.79–43.04 (20.66±11.41) mg/kg for southwest monsoon season (July 2018). According to the Cu distribution, the relatively high concentration was found in the inner part of the river (Stn.TC1&2). The result of mean value comparison spoke that in the Tha Chin River estuary has no significant difference concentration between seasons.

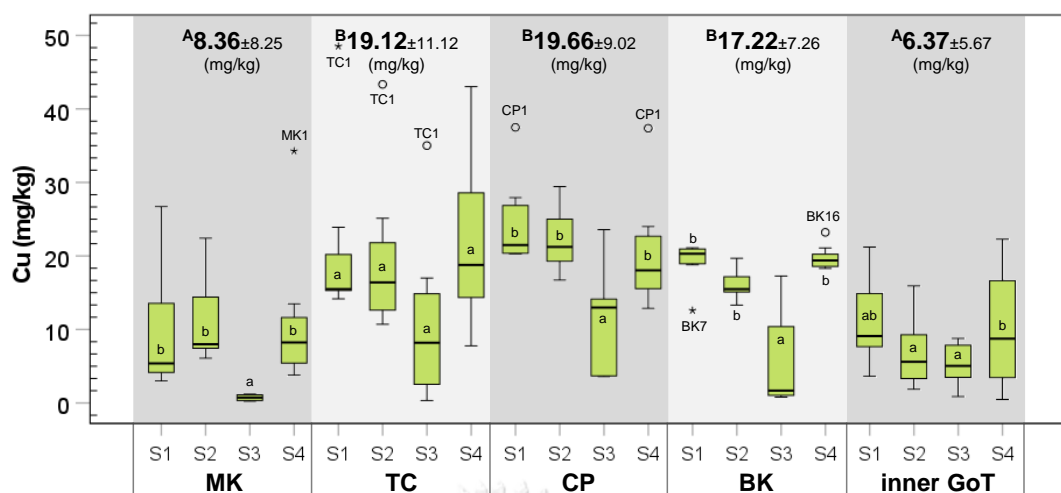
The Chao Phraya River estuary, Cu concentration was found in the range of 13.81–37.50 (24.16±6.54) mg/kg for southwest monsoon season (July 2017), 10.71–43.35 (19.67±9.17) mg/kg for northeast monsoon season (December 2017), 3.60–23.60 (9.27±6.85) mg/kg for the dry season (May 2018), and 12.88–37.38 (22.79±7.84) mg/kg for southwest monsoon season (July 2018). The spatial distribution was characterized by highest concentration at inside river zone (Stn.CP1). As seen in Figure 4.6, the mean values comparison result indicated

that the mean concentration of dry season (May 2018) was significantly lowest ( $p<0.05$ ).

The Bangpakong River estuary, Cu concentration was found in the range of 12.60–29.05 ( $20.36\pm 3.96$ ) mg/kg for southwest monsoon season (July 2017), 13.32–22.90 ( $17.39\pm 2.93$ ) mg/kg for northeast monsoon season (December 2017), 0.80–28.43 ( $10.39\pm 10.22$ ) for dry season (May 2018), and 18.30–27.16 ( $36.67\pm 2.92$ ) mg/kg for southwest monsoon season (July 2018). The spatial distribution was characterized by relative high concentration was found at the western part of river estuary (Stn.BK16) in both southwest monsoon season (2017 and 2018) and dry season, while in northeast monsoon season the high relative concentration was found in the river mouth (Stn.BK18). The mean values comparison evaluation, which was shown in Figure 4.6, displayed the Cu concentration in the dry season was significantly lower from the others ( $p<0.05$ ).

The inner Gulf of Thailand exclude river estuaries, Cu concentration was found in the range of 1.20–23.11 ( $7.87\pm 6.56$ ) mg/kg for southwest monsoon season (July 2017), 0.74–15.93 ( $4.62\pm 3.57$ ) mg/kg for northeast monsoon season (December 2017), 0.34–22.29 ( $5.11\pm 5.16$ ) mg/kg for the dry season, and 0.49–22.29 ( $8.61\pm 6.04$ ) mg/kg for southwest monsoon season. Then the mean values comparison evaluated which was given in Figure 4.6 shows the mean Cu concentration in southwest monsoon season in 2018 was significantly higher than northeast monsoon season in 2017 and dry season 2018 ( $p<0.05$ ).

The mean value of Cu concentration in the study area follows a descending order of Chao Phraya ( $19.66\pm 9.02$  mg/kg) > Tha Chin ( $19.12\pm 11.12$  mg/kg) > Bangpakong ( $17.22\pm 7.26$  mg/kg) > Mae Klong ( $8.36\pm 8.25$  mg/kg) > the inner Gulf ( $6.37\pm 5.67$  mg/kg). Although the highest concentration of Cu concentration was found in the Chao Phraya but the significant differences between the Chao Phraya, the Tha Chin, and the Bangpakong River estuaries was not observed. And the lowest mean value was in inner Gulf ( $p<0.05$ ) (Figure 4.6).



Remark: S1 is July 2017, S2 is December 2017, S3 is May 2018 and July 2018  
Alphabet indicated the significant differences between seasons and areas

**Figure 4.6** Seasonal comparisons of Cu contamination in the surface sediment of the Mae Klong (MK), the Tha Chin (TC), the Chao Phraya (CP), the Bangpakong (BK) river estuaries and the inner Gulf of Thailand (inner GoT).

#### 4.1.4 Cobalt (Co)

Spatial heterogeneity distribution of Co in the surface sediment in the southwest monsoon season (July 2017) is illustrated in Figure 4.7. The horizontal distribution was characterized by the highest concentration at the mouth of the Bangpakong River estuary (Stn.BK7; 41.71 mg/kg), while the lowest concentration was found at the middle zone of the Gulf (Stn.GT26; 6.70 mg/kg). As a result, the pattern of Co distribution show that the high relative concentrations were found both upper Gulf and lower Gulf area.

In northeast monsoon season (December 2017), Co in the surface sediment was varied between 2.58–35.75 mg/kg. As Figure 4.7, the highest concentration of Co was found the Chao Phraya River estuary (Stn.CP8; 35.75 mg/kg) and the lowest concentration was found at the inner Gulf (Stn.GT20; 2.58 mg/kg). According to Co distribution pattern, the hotspot of exorbitant amount was found in upper Gulf and the concentration was descended toward to the lower area of the Gulf.

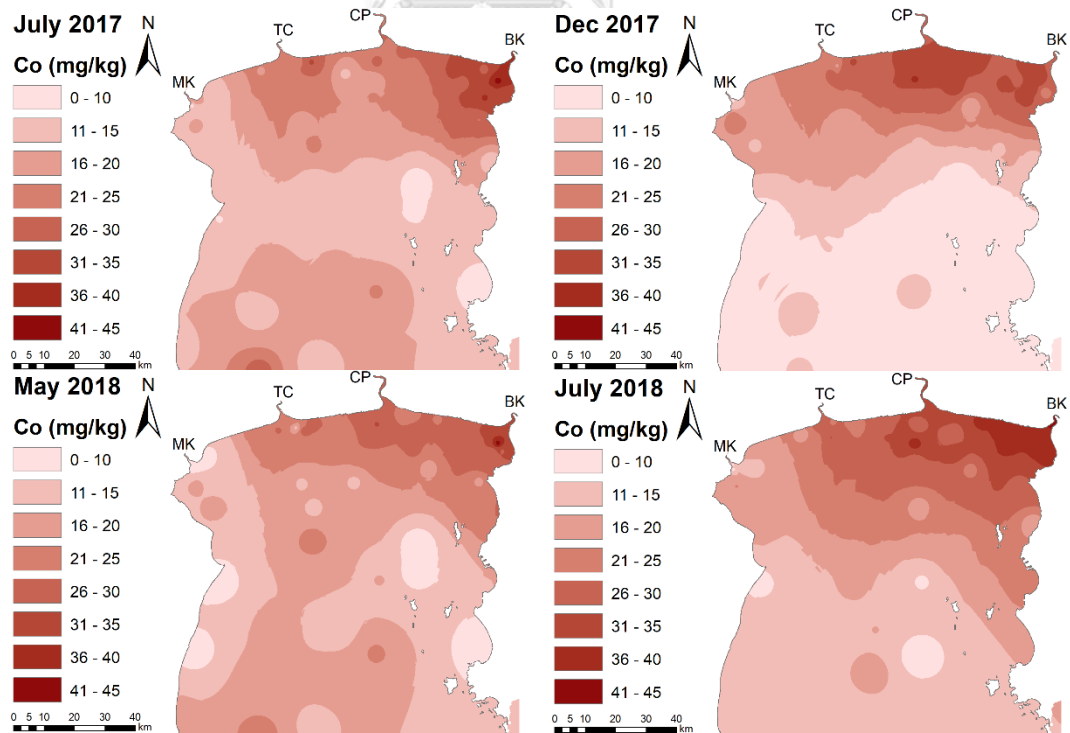
In the dry season (May 2018), Co was spatially distribution in the range of 5.51–41.69 mg/kg. The lowest concentration was found at the inner Gulf



(Stn.GT26; 5.51 mg/kg) on the other hand, the highest concentration of Co was found at the Bangpakong River estuary (Stn.BK7; 41.69 mg/kg).

In southwest monsoon season (July 2018), the horizontal distribution was represented by the highest concentration was found in the inner zone the Bangpakong River (Stn.BK1; 44.00 mg/kg). While the lowest concentration was found at the middle area of the Gulf (Stn.GT36; 6.53 mg/kg). According to Figure 4.7, the concentration of Co has a particular number around the mouth of the Bangpakong River. On the other hand, the concentration was decreased to the lower Gulf.

Following to Table 4.1, the mean concentration across entire the inner Gulf of Thailand in southwest monsoon season in 2018 ( $23.95 \pm 9.90$  mg/kg) was the significantly higher than the southwest monsoon season in 2017 ( $20.44 \pm 8.35$  mg/kg), northeast monsoon season in 2017 ( $19.22 \pm 10.24$  mg/kg), and dry season in 2018 ( $19.66 \pm 7.90$  mg/kg). And the concentration of all areas in this study was higher than Hainan Island, China (Cai et al., 2021).



**Figure 4.7** Spatial distributions and seasonal variations of Co concentration in the surface sediment of the inner Gulf of Thailand.

According to the distribution pattern of Co in the surface sediment entire the inner Gulf of Thailand (Figure 4.7), the results demonstrated that the source of Co were from river estuaries, especially the Bangpakong and the Chao Phraya River estuaries. Analysis the Co distribution of river mouth areas and the inner Gulf of Thailand were conducted to identify the effect of Co source on individual areas.

The Mae Klong River estuary, Co concentration was found in the range of 8.43–28.36 ( $15.17 \pm 6.10$ ) mg/kg for southwest monsoon season (July 2017), 8.78–24.07 ( $17.04 \pm 5.25$ ) mg/kg for northeast monsoon season (December 2017), 6.48–19.13 ( $11.37 \pm 4.70$ ) mg/kg for the dry season (May 2018), and 9.13–37.07 ( $17.17 \pm 8.54$ ) mg/kg for southwest monsoon season (July 2018). In both southwest monsoon season (2017 and 2018), the relatively high concentrations were found inner part of the river (Stn.MK1). On the other hand, the relative high concentrations in northeast monsoon and dry seasons were found at the river mouth (Stn.MK13). For mean comparison analysis between seasons of the Co concentration, the significant difference was not observed.

Spatial distribution in the Tha Chin River estuary was in the range of 19.43–30.78 ( $23.69 \pm 3.36$ ) mg/kg for southwest monsoon season (July 2017), 19.13–31.62 ( $25.69 \pm 3.76$ ) mg/kg for northeast monsoon season (December 2017), 14.06–27.11 ( $23.16 \pm 3.71$ ) mg/kg for the dry season (May 2018), and 16.71–33.33 ( $25.41 \pm 4.69$ ) mg/kg for southwest monsoon season (July 2018). According to Figure 4.7, the hotspot of high Co concentration was found both of inner river zone and river mouth area. As the result of mean comparison as Figure 4.8, there is no significant difference mean values of Co concentration between seasons.

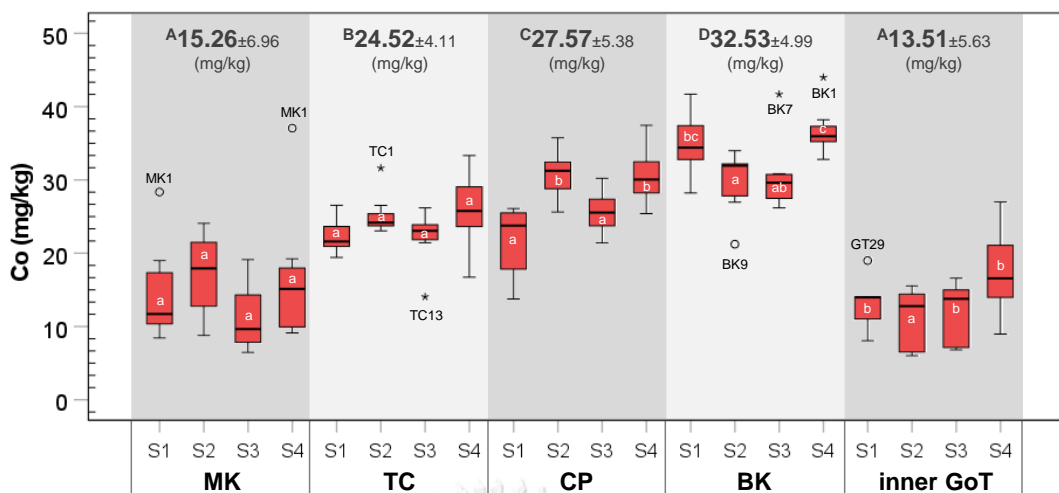
The Chao Phraya River estuary, Co concentration was found in range of 13.76–28.04 ( $22.05 \pm 4.69$ ) mg/kg for southwest monsoon season (July 2017), 25.63–35.75 ( $31.16 \pm 2.83$ ) mg/kg for northeast monsoon season (December 2017), 21.41–30.24 ( $25.57 \pm 2.44$ ) mg/kg for the dry season (May 2018), and 25.42–37.46 ( $31.50 \pm 3.71$ ) mg/kg for southwest monsoon season (July 2018). The spatial distribution was characterized by highest concentration was found at the

middle part of river estuary (Stn.CP8) in southwest monsoon season (July 2018). As figure 4.8, the mean values of southwest monsoon season (July 2018) and northeast monsoon season (December 2017) significantly higher than southwest monsoon season (July 2017) and dry season (May 2018).

The Bangpakong River estuary, Co concentration was found in the range of 27.72–41.71 (33.96±4.32) mg/kg for southwest monsoon season (July 2017), 21.24–34.00 (39.49±3.87) for northeast monsoon season (December 2017), 26.19–41.69 (31.63±4.54) mg/kg for the dry season (May 2018), and 32.82–44.00 (36.67±2.92) mg/kg for southwest monsoon season (July 2018). The spatial distribution was characterized by relative high concentration was found in inner river area (Stn.BK1). While the mean comparison between seasons show that the southwest monsoon season (July 2018) was significantly higher than the northeast monsoon (December 2017) and dry (May 2018) seasons ( $p<0.05$ ).

The inner Gulf of Thailand exclude river estuaries, Co concentration was found in the range of 6.70–27.54 (15.29±5.23) mg/kg for southwest monsoon season (July 2017), 2.58–16.86 (9.25±4.29) mg/kg for northeast monsoon season (December 2017), 5.51–23.14 (14.66±4.90) mg/kg for the dry season (May 2018), and 6.53–26.99 (15.64±5.38) mg/kg for southwest monsoon season (July 2018). The mean comparisons displayed that the Co concentration of northeast monsoon season (December 2017) was found significant lowest ( $p<0.05$ ).

The mean value of Co concentrations in the study area follows a descending order of Bangpakong (32.53±4.99 mg/kg) > Chao Phraya (27.57±5.38 mg/kg) > Tha Chin (24.52±4.11 mg/kg) > Mae Klong (15.26±6.96 mg/kg) > inner Gulf of Thailand (13.51±5.63 mg/kg). As the results of mean value comparison in Figure 4.8, indicated that the highest concentration of Co in the Bangpakong was significantly highest ( $p<0.05$ ). By contrast, the significant lowest were the Mae Klong and the inner Gulf of Thailand ( $p<0.05$ ).



Remark: S1 is July 2017, S2 is December 2017, S3 is May 2018 and July 2018  
Alphabet indicated the significant differences between seasons and areas

**Figure 4.8** Seasonal comparisons of Co contamination in the surface sediment of the Mae Klong (MK), the Tha Chin (TC), the Chao Phraya (CP), the Bangpakong (BK) river estuaries and the inner Gulf of Thailand (inner GoT).

#### 4.1.5 Nickel (Ni)

Spatial heterogeneity distribution of Ni in the surface sediment in southwest monsoon season (July 2017) is demonstrated in Figure 4.9. The horizontal distribution was characterized by the highest concentration at the river mouth of the Tha Chin (Stn.TC14; 44.35 mg/kg), by the contrast, the lowest concentration was found in the middle part of Gulf (Stn.GT27; 7.95 mg/kg). As a result, Ni concentration were decreased from the Tha Chin and the Bangpakong River estuaries to the middle part of Gulf.

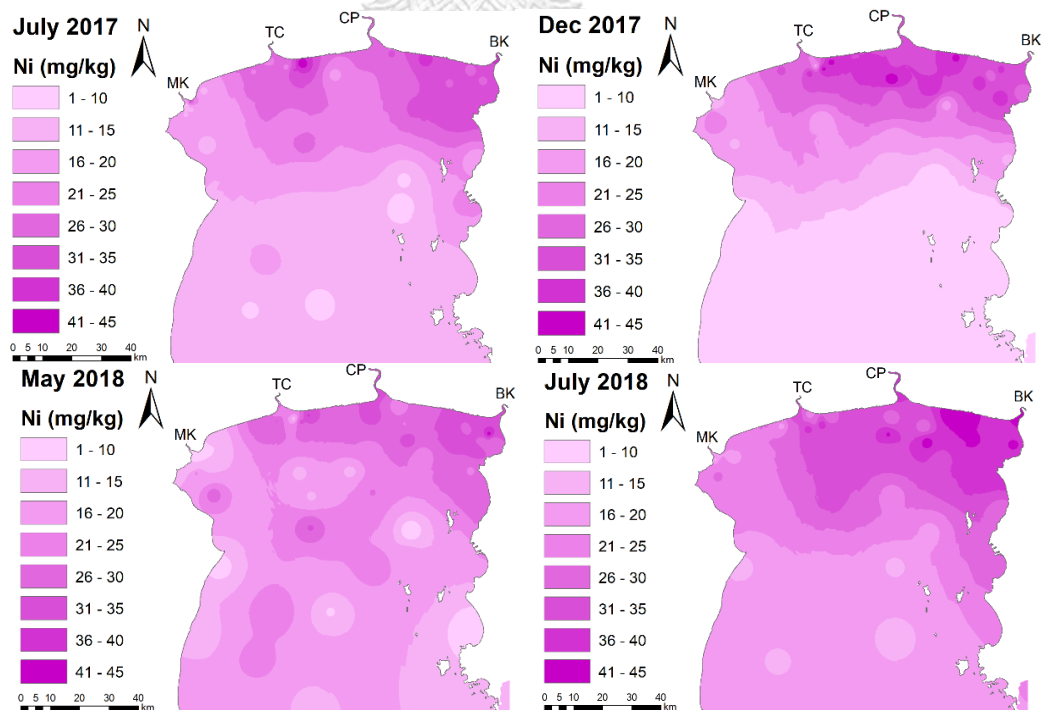
In northeast monsoon season (December 2017), Ni was spatially distributed in the range of 1.48–43.33 mg/kg. The highest concentration was found in the middle area of the Chao Phraya River estuary (Stn.CP8) and for the lowest concentration was found in the Gulf near eastern part of coastal (Stn.GT20). As figure 4.9, Ni distribution in the surface sediment showed that the numerous portion concentrations were found in the upper Gulf.

In the dry season (May 2018), Ni in the surface sediment was varied between 5.41–41.18 mg/kg. The lowest concentration was found in the Mae

Kling River estuary (Stn.MK4) and the highest concentration was found in the Bangpakong River estuary (Stn.BK7). While the Ni distribution pattern was not cleared.

In southwest monsoon season (July 2018), the Ni concentration was found in range of 12.66–47.57 mg/kg. The highest concentration was found in the inner zone of the Bangpakong river (Stn.BK1) and the lowest concentration which was found at lower part of the inner Gulf of Thailand (Stn.GT36). As Figure 4.9, the decreased of concentration was start from middle part to lower part of Gulf.

In both southwest monsoon seasons (2017 and 2018) and northeast monsoon season (December 2017), the Ni concentration in the lower part of Gulf was found serious diluted. And mean concentration across the entire the Gulf (Table 4.1), the southwest monsoon season in July 2018 ( $28.78 \pm 10.20$  mg/kg) was significantly higher than southwest monsoon season in July 2017, dry season in May 2018 ( $22.01 \pm 8.98$  mg/kg), northeast monsoon season in December 2017 ( $21.09 \pm 12.74$  mg/kg) ( $p < 0.05$ ) and the others study such as 1. Galveston Bay, USA (Lopez, Brandon, et al., 2021) 2. Hainan Island, China (Cai et al., 2021) 3. Yellow Sea, China (Zu et al., 2016).



**Figure 4.9** Spatial distributions and seasonal variations of Ni concentration in the surface sediment of the inner Gulf of Thailand.

According to the Ni distribution pattern in the surface sediment entire the inner Gulf of Thailand (Figure 4.9), the results shown that the source of Ni concentration which found in this study were from the four main rivers, especially the Bangpakong, the Chao Phraya and the Tha Chin River. After that, this study investigated the individual area to identify the river effects on Ni distributions in the inner Gulf of Thailand.

The Mae Klong River estuary, Ni concentration was found in the range of 9.56–31.41 ( $18.67 \pm 7.63$ ) mg/kg for southwest monsoon season (July 2017), 9.40–24.30 ( $17.09 \pm 5.25$ ) mg/kg for northeast monsoon season (December 2017), 5.41–20.49 ( $11.36 \pm 4.80$ ) mg/kg for the dry season (May 2018), and 14.29–40.66 ( $23.01 \pm 7.77$ ) mg/kg for southwest monsoon season (July 2018). According to Ni distribution, the inner river area was the relatively high concentration (Stn.MK1 and MK4) in both southwest monsoon seasons (2017 and 2018). The mean comparison in Figure 4.10 show that the southwest monsoon season (July 2018) was significantly highest, and the lowest was the dry season (May 2018) ( $p < 0.05$ ).

The Tha Chin River estuary, Ni concentration was found in the range of 22.10–44.35 ( $29.74 \pm 7.21$ ) mg/kg for southwest monsoon season (July 2017), 18.15–41.26 ( $31.00 \pm 7.62$ ) mg/kg for northeast monsoon season (December 2017), 12.29–35.23 ( $26.53 \pm 6.32$ ) mg/kg for the dry season (May 2018), and 18.68–44.97 ( $30.58 \pm 8.08$ ) mg/kg for southwest monsoon season (July 2018). Following the Ni distribution, the relatively high concentration in both southwest monsoon (2017 and 2018) seasons were found in the river mouth, while the relatively high concentration in southwest monsoon season (July 2018) and dry season (May 2018) were found at inner river. As in mean comparison results (Figure 4.10), the significantly difference between seasonal was not observed ( $p < 0.05$ ).

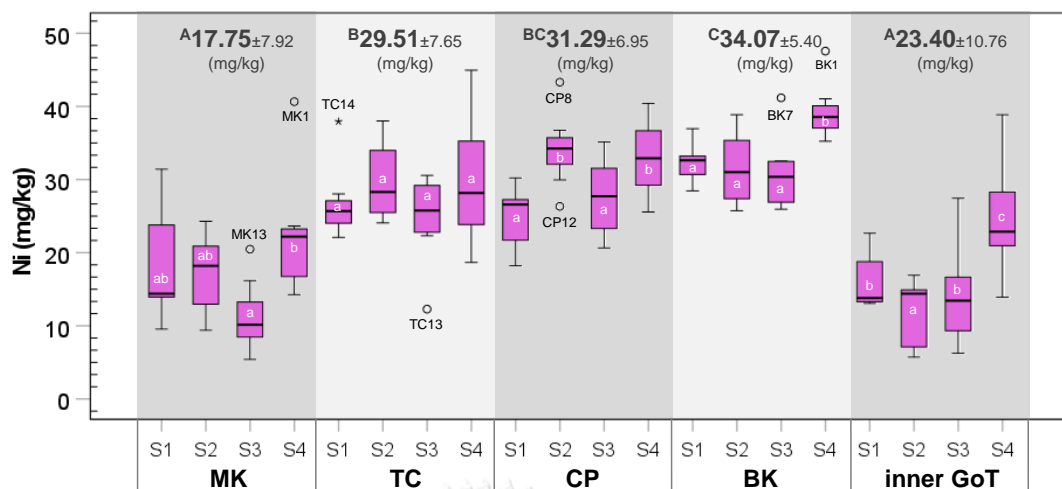
The Chao Phraya River estuary, Ni concentration was found in the range of 18.22–36.90 ( $26.13 \pm 5.16$ ) mg/kg for southwest monsoon season (July 2017), 26.34–43.33 ( $35.49 \pm 4.97$ ) mg/kg for northeast monsoon season (December 2017), 20.67–35.17 ( $25.57 \pm 2.44$ ) mg/kg for dry season monsoon season (May

2018), and 25.57–45.37 (35.36±6.58) mg/kg for southwest monsoon season (July 2018). The relatively high concentration in both southwest monsoon seasons (2017 and 2018) were found in river mouth (Stn.CP16). According to mean comparison (Figure 4.10), the mean values of Ni in the southwest monsoon (July 2017) and the dry (May 2018) seasons were significantly lower than the others ( $p<0.05$ ).

The Bangpakong River estuary, Ni concentration was varied in the range of 28.46–36.97 (32.14±2.70) mg/kg for southwest monsoon season (July 2017), 25.76–38.87 (32.32±4.66) mg/kg for northeast monsoon season (December 2017), 25.96–41.18 (31.63±4.54) mg/kg for the dry season (May 2018), and 35.25–47.57 (40.20±3.71) mg/kg for southwest monsoon season (July 2018). As Figure 4.10, the significant highest mean value of Ni concentration was southwest monsoon season in July 2018 ( $p<0.05$ ).

The inner Gulf of Thailand exclude river estuaries, Ni concentration was found in the range of 7.95–31.54 (15.77±6.69) mg/kg for southwest monsoon season (July 2017), 1.48–18.73 (9.02±5.09) mg/kg for northeast monsoon season (December 2017), 6.21–30.34 (17.49±6.58) mg/kg for dry season (May 2018), and 12.66–38.88 (21.01±7.00) mg/kg for southwest monsoon season (July 2018). In both southwest monsoon seasons (2017 and 2018) the relative high concentration was found in the eastern part of the Gulf (Stn.GT17), while the lowest concentration was found in the lower Gulf. As a result of mean values comparison (Figure 4.10), southwest monsoon season in 2018 significantly higher than southwest monsoon season in 2017 and the dry season. And the lowest was in northeast monsoon season.

The mean values of Ni concentration in all season comparison between areas in this study shown that the concentration in the Bangpakong was highest (34.07±5.40 mg/kg) ( $p<0.05$ ), then the concentration in the Chao Phraya was slightly lower (31.29±6.95 mg/kg), and for the Tha Chin (29.51±7.65 mg/kg) was higher than the Mae Klong (17.75±7.92 mg/kg) and the inner Gulf of Thailand (23.40±10.76 mg/kg).



Remark: S1 is July 2017, S2 is December 2017, S3 is May 2018 and July 2018

Alphabet indicated the significant differences between seasons and areas

**Figure 4.10** Seasonal comparisons of Ni contamination in the surface sediment of the Mae Klong (MK), the Tha Chin (TC), the Chao Phraya (CP), the Bangpakong (BK) river estuaries and the inner Gulf of Thailand (inner GoT).

#### 4.1.6 Manganese (Mn)

Spatial heterogeneity distribution of Mn in the surface sediment in southwest monsoon season (July 2017) is represented in Figure 4.11. The horizontal distribution was characterized by the highest concentration at the mouth of the Mae Klong River estuary (Stn.MK4; 2127.73 mg/kg), while the lowest concentration was found at the middle of the Gulf (Stn.GT33; 27.81 mg/kg). As Mn distribution, the high concentration usually found near the river mouth and decreased toward to the Gulf area.

In northeast monsoon season (December 2017), the Mn concentration was varied in the range of 104.26–1548.30 mg/kg, which was characterized as highest concentration at the mouth of the Bangpakong (Stn.BK7), while the lowest concentration was found in lower eastern part of the Gulf (Stn.GT38). As Mn distribution (Figure 4.11), the Mn concentration were found high at the upper part of the Gulf then the lower area was reduced following north to south.

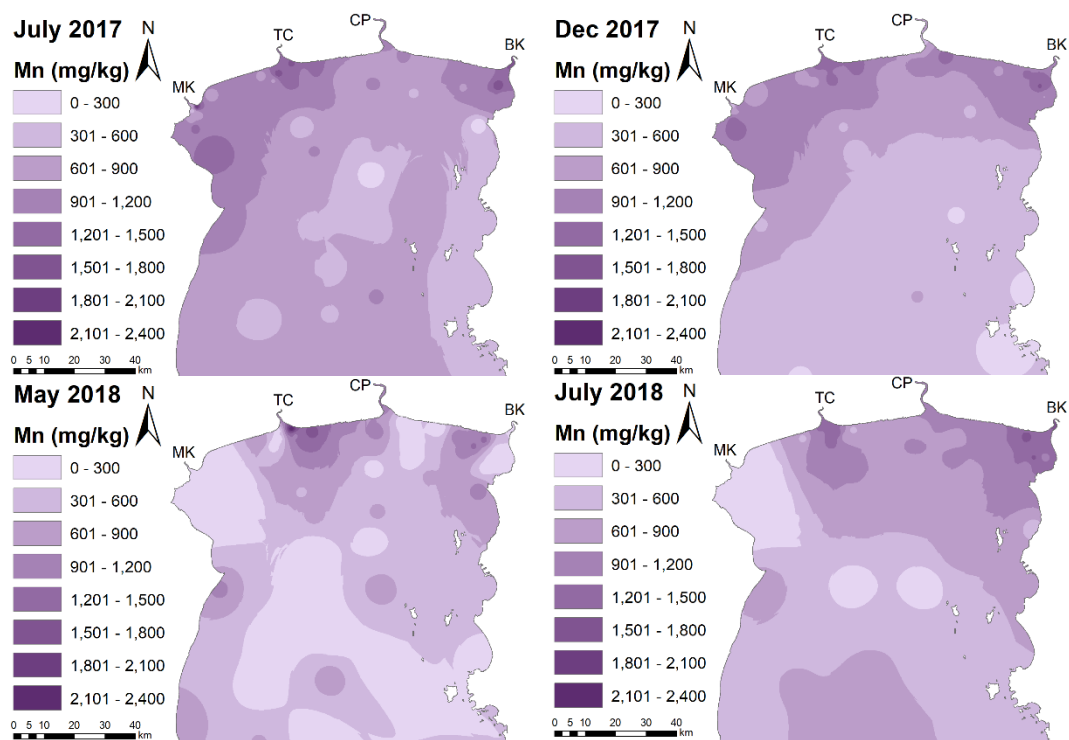
In dry season (May 2018), Mn was spatially distributed in the range of 3.77–2259.28 mg/kg. The lowest concentration of Mn was found in the mouth of



The Mae Klong River estuary (Stn.MK5) and the highest was found the mouth of the Tha Chin estuary (Stn.TC11). As Figure 4.11, the pattern of Mn distribution was scatter around the Gulf while the diluted concentration was seen from the Mae Klong River estuary to the lower part of eastern Gulf.

In southwest monsoon season (July 2018), Mn was found in the range of 36.78–1582.27 mg/kg. The highest concentration spot was in the Bangpakong River estuary (Stn.BK13) and the lowest was found in the mouth of the Mae Klong River estuary (Stn.MK3). In this season, the pattern of Mn distribution was likely to the dry season (May 2018).

According to the comparison of mean value of Mn concentration result (Table 4.1), the mean concentration in both southwest monsoon seasons in (July 2017 and 2018) ( $893.9 \pm 438.7$  and  $762.3 \pm 469.0$  mg/kg) and the northeast monsoon season in December 2017 ( $790.8 \pm 386.0$  mg/kg) were higher than the Mn in surface sediment in Thessaloniki Bay, Greece (Christophoridis et al., 2019), Southeast coast of India (Gropal et al., 2021), and Galveston Bay in USA (Lopez et al., 2021) except the mean concentration of dry season (May 2018) ( $504.7 \pm 525.6$  mg/kg) was lower than the Mn concentration in Southeast coast of India (Gropal et al., 2021). Following this result, the significantly lowest concentration between season was in the dry season (May 2018) ( $p < 0.05$ ).



**Figure 4.11** Spatiotemporal heterogeneity distributions and seasonal variations of Mn concentration in the surface sediment of the inner Gulf of Thailand.

For identify the effect of four major rivers on Mn distribution in surface sediment entire the inner Gulf of Thailand, its necessary to analyze in individual areas.

The Mae Klong River estuary, Mn concentration was found in the range of 361.9–2127.7 ( $1092.9 \pm 629.6$ ) mg/kg for southwest monsoon season (July 2017), 443.4–1414.8 ( $1017.7 \pm 375.9$ ) mg/kg for northeast monsoon season (December 2017), 3.77–162.8 ( $75.3 \pm 51.9$ ) mg/kg for the dry season (May 2018), and 36.8–266.5 ( $96.3 \pm 74.0$ ) mg/kg for southwest monsoon season (July 2018). The concentration in southwest monsoon season (July 2017) and northeast monsoon season (December 2017) was high and decreased was beginning with in the dry season (May 2018). According to seasonal mean comparison of the Mae Klong River estuary (Figure 4.12), in the dry season and southwest monsoon in 2018 were found significantly lower than the southwest monsoon season in 2017 and northeast monsoon season ( $p < 0.05$ ).

The Tha Chin River estuary, Mn concentration was found in the range of 785.3–1700.2 ( $1231.5 \pm 306.5$ ) mg/kg for southwest monsoon season (July 2017),

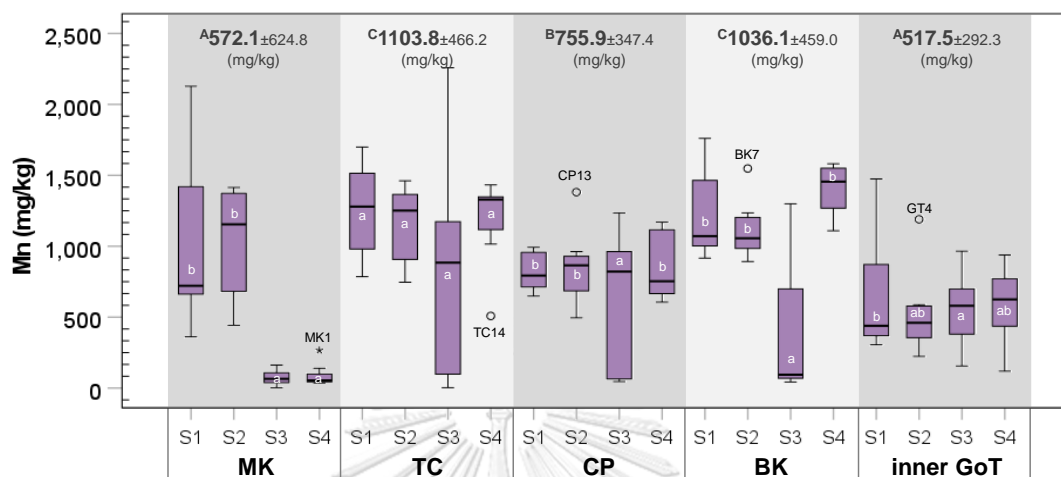
746.9–1461.8 (1152.2±238.4) mg/kg for northeast monsoon season (December 2017), 3.77–2259.3 (979.4±740.5) mg/kg for dry season, and 503.8–1432.8 (1046.9±355.4) mg/kg for southwest monsoon season (July 2018). The seasonal relatively high concentrations were found at the mouth of river estuary (Stn.TC8 and TC11). According to seasonal comparison which show in Figure 4.11, the difference of mean value between season was not observed.

The Chao Phraya River estuary, Mn concentration was found in the range of 549.4–992.9 (790.2±146.7) mg/kg for southwest monsoon season (July 2017), 495.9–1381.7 (851.2±243.9) mg/kg for northeast monsoon season (December 2017), 46.20–1236.3 (475.8±479.2) mg/kg for dry season (May 2018), and 606.7–1169.5 (906.6±217.1) mg/kg for southwest monsoon season (July 2018). While the relatively high concentration in northeast monsoon season (December 2017) was found at the mouth of river estuary (Stn.CP13) but the relatively high concentration in the dry season was found in the inner river zone (Stn.CP1). As seen in Figure 4.11, the concentration in the dry season (May 2018) was significantly lowest ( $p<0.05$ ).

The Bangpakong River estuary, Mn concentration was found in the range of 864.1–1761.1 (1179.7±318.9) mg/kg for southwest monsoon season (July 2017), 851.5–1548.3 (1091.7±199.2) mg/kg for northeast monsoon season (December 2017), 43.0–1299.5 (559.8±543.9) mg/kg for the dry season (May 2018), and 919.6–1582.3 (1313.3±233.9) mg/kg for southwest monsoon season (July 2018). The relative high concentration in southwest monsoon season in July 2017 and northeast monsoon season in December 2017 were found at the mouth of river estuary (Stn.BK7) and the relatively high concentration in dry season (May 2018) and southwest monsoon season in July 2018 were found at Stn.BK13. Mean comparisons indicated that the significant lowest concentration was in the dry season (May 2018) ( $p<0.05$ ).

The mean value of Mn concentrations in the study area follow a descending order of Tha Chin (1103.8±466.2 mg/kg) > Bangpakong (1036.1±459.0 mg/kg) > Chao Phraya (755.9±347.4 mg/kg) > Mae Klong (572.1±624.8 mg/kg) > the inner Gulf of Thailand (517.5±292.3 mg/kg). According to comparisons of mean

values in different areas (Figure 4.12), the Tha Chin River estuary was significantly highest ( $p<0.05$ ) while the significantly lowest were found in The Mae Klong River estuary and the inner Gulf of Thailand ( $p<0.05$ ).



Remark: S1 is July 2017, S2 is December 2017, S3 is May 2018 and July 2018  
Alphabet indicated the significant differences between seasons and areas

**Figure 4.12** Seasonal comparisons of Mn contamination in the surface sediment of the Mae Klong (MK), the Tha Chin (TC), the Chao Phraya (CP), the Bangpakong (BK) river estuaries and the inner Gulf of Thailand (inner GoT).

#### 4.1.7 Zinc (Zn)

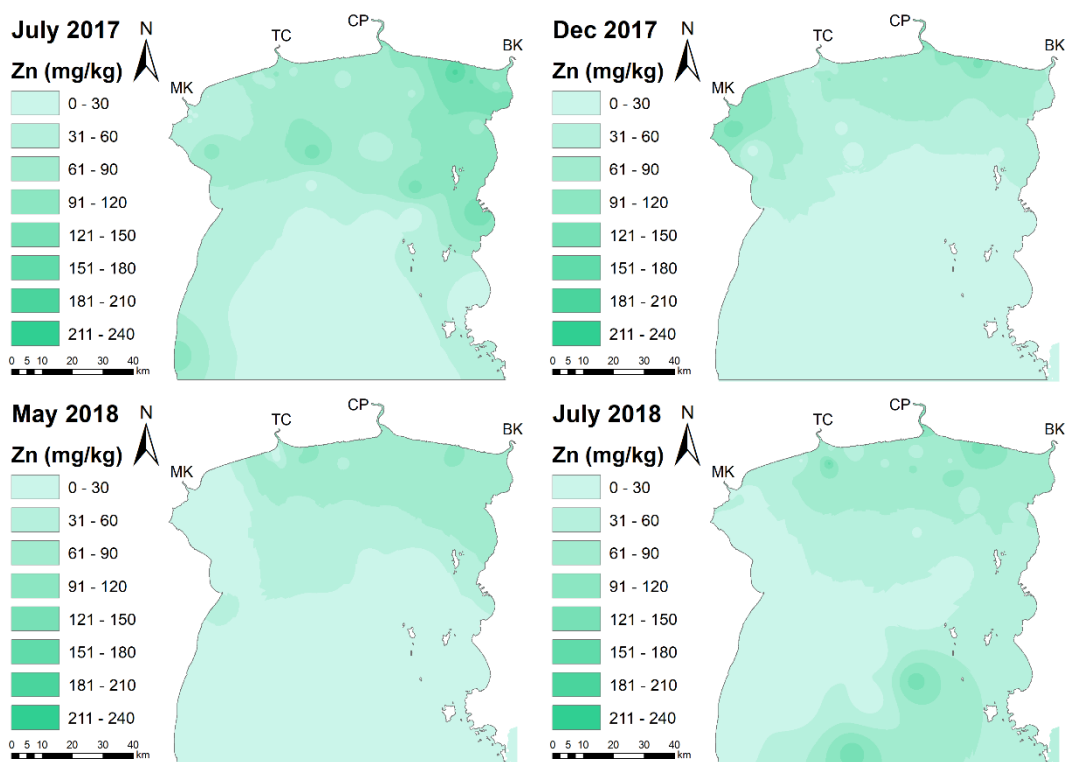
Spatial heterogeneity distribution of Zn in the surface sediment in southwest monsoon season (July 2017) is demonstrated in Figure 4.13. The horizontal distribution was characterized by the highest concentration at the mouth of the Tha Chin River estuary (Stn.TC1; 203.46 mg/kg), while the lowest concentration was found in the middle part of inner Gulf (Stn.GT34; 10.81 mg/kg). In this season, the high Zn concentrations were found in the upper part of Gulf then the lower part concentration was lower according to the influenced diluted.

In northeast monsoon season (December 2017), Zn in the surface sediment was varied between 0.10–223.37 mg/kg. The highest concentration was found at the inner part of the Tha Chin River (Stn.TC1) and the lowest concentration was found lower eastern part of the Gulf (Stn.GT28). As Figure 4.13, the high concentration areas were found in the upper Gulf.

In dry season (May 2018), Zn was spatially distributed in the range of 2.60–146.96 mg/kg. While the highest concentration has shown at the mouth of the Tha Chin River estuary (Stn.TC2), but the lowest concentration was found in the middle part of the Gulf (Stn.GT26). According to Zn distribution (Figure 4.13), the area from the Mae Klong River estuary to the lower Gulf were shown the concentration that below 30 mg/kg.

In southwest monsoon season (July 2018), Zn in the surface sediment was varied between 2.10–153.58 mg/kg. The lowest concentration was at the upper Gulf near The Mae Klong River estuary (Stn.GT4) and the highest concentration was shown at the mouth of the Tha Chin River estuary (Stn.TC5). In this season, the low concentration zone was found around The Mae Klong River estuary, the western and the middle of the Gulf.

In both southwest monsoon season, the high concentration zone was in upper area of the Gulf, but in the lower part of the Gulf also found some areas which have high concentration (Figure 4.13). For mean concentrations across the entire the inner Gulf of Thailand (Table 4.1), southwest monsoon season in 2017 ( $73.03 \pm 47.11$  mg/kg) was significantly higher than the northeast monsoon season ( $53.76 \pm 44.79$  mg/kg) and dry season ( $47.64 \pm 34.12$  mg/kg) ( $p < 0.05$ ). And the southwest monsoon season in 2017 was higher than Zn concentration which were found in 1. Hainan Island, China (Cai et al., 2021) 2. Yellow Sea, China (Xu et al., 2016) 3. Bizerte Lagoon, Tunisia (El Zrelli et al., 2021) 4. Galveston Bay, USA (Lopex et al., 2021) 5. Bohai Sea, China (Ding et al., 2018) 6. The Bay of Bengal, Bangladesh (Rami et al., 2021).



**Figure 4.13** Spatial distributions and seasonal variations of Zn concentration in the surface sediment of the inner Gulf of Thailand.

According to the distribution pattern of Zn in the surface sediment entire the inner Gulf of Thailand (Figure 4.13) the results indicated that the four major rivers, especially the Tha Chin Rivers are the source of Zn. Therefore, analysis of individual areas and comparison were necessary to identify the effects of rivers on the Zn distributions in the inner Gulf of Thailand.

The Mae Klong River estuary, Zn concentration was found in the range of 22.52–72.23 ( $41.28 \pm 17.09$ ) mg/kg for southwest monsoon season (July 2017), 100.12–143.64 ( $114.50 \pm 14.10$ ) mg/kg for northeast monsoon season (December 2017), 2.90–9.90 ( $6.10 \pm 2.66$ ) mg/kg for the dry season (May 2018), and 6.31–102.51 ( $35.65 \pm 27.97$ ) mg/kg for southwest monsoon season (July 2018). As Figure 4.13, at first the Zn concentration start increased from southwest monsoon season in July 2017 to northeast monsoon season, after that the concentration was decreased to dry season and raised after starting the southwest monsoon season in 2018. For mean comparison indicated that the Zn concentration in northeast

monsoon season was significantly highest ( $p<0.05$ ) and the significantly lowest concentration was found in the dry season ( $p<0.05$ ).

The Tha Chin River estuary, Zn concentration was found in the range of 47.38–203.46 ( $81.13\pm45.88$ ) mg/kg for southwest monsoon season (July 2017), 20.39–223.37 ( $74.33\pm55.32$ ) mg/kg for northeast monsoon season (December 2017), 7.42 – 146.96 ( $75.32\pm42.21$ ) mg/kg for the dry season (May 2018), and 27.66–153.58 ( $76.33\pm38.15$ ) mg/kg for southwest monsoon season. The relative high concentration was found at the inner river of the Tha Chin River estuary in both southwest monsoon seasons and northeast monsoon season (Stn.TC1) and in dry season (Stn.TC2). According to mean comparison in Figure 4.14, the significant different between season was not found.

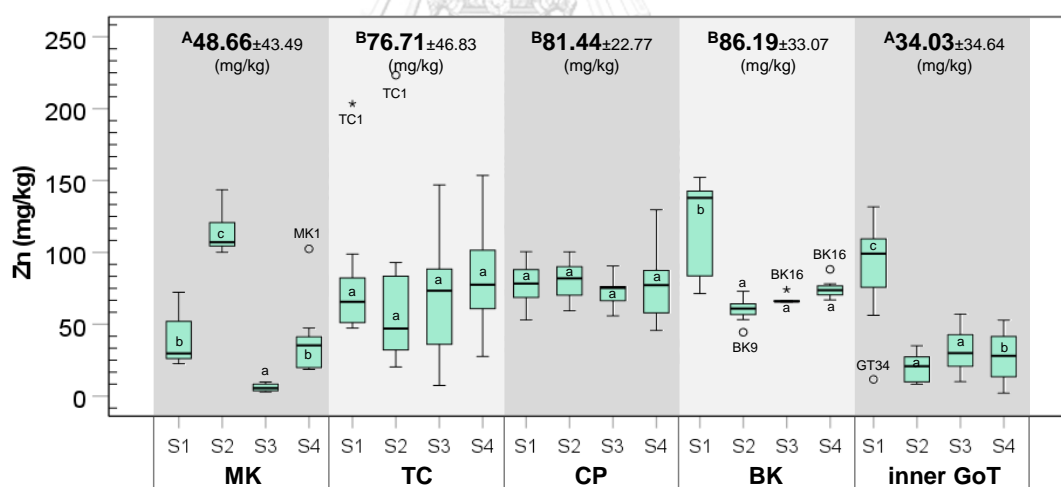
The Chao Phraya River estuary, Zn concentration was found in the range of 52.99–128.40 ( $80.89\pm22.85$ ) mg/kg for southwest monsoon season (July 2017), 59.34–128.22 ( $84.48\pm20.15$ ) mg/kg for northeast monsoon season (December 2017), 55.88–90.52 ( $73.02\pm9.17$ ) mg/kg for the dry season (May 2018), and 45.66–132.43 ( $87.36\pm29.81$ ) mg/kg for southwest monsoon season (July 2018). The relatively high concentration was found at nearly coast river mouth in southwest monsoon season in 2018 (Stn.CP16). As Figure 4.14, the mean comparisons show that the significantly different between seasons was not shown.

The Bangpakong River estuary, Zn concentration was found in the range of 71.37–184.73 ( $127.24\pm36.58$ ) mg/kg for southwest monsoon (July 2017), 44.47–85.97 ( $63.79\pm11.08$ ) mg/kg for northeast monsoon (December 2017), 65.60–115.42 ( $74.63\pm15.81$ ) mg/kg for the dry season (May 2018), and 66.93–112.05 ( $79.08\pm13.01$ ) mg/kg for southwest monsoon (July 2018). The high relative concentration in all seasons was found at the mouth near coastal (Stn.BK16). As seen in Figure, the mean comparisons result between seasonal show that the southwest monsoon season in 2017 was significantly highest concentration ( $p<0.05$ ).

The inner Gulf of Thailand excludes river estuaries, Zn concentration was found in the range of 10.81–131.78 ( $57.30\pm45.23$ ) mg/kg for southwest monsoon

season (July 2017), 0.10–35.06 (13.86±9.72) mg/kg for northeast monsoon season (December 2017), 2.60–79.07 (29.73±18.52) mg/kg for the dry season (May 2018), and 2.10–133.18 (36.92±37.05) mg/kg for southwest monsoon season (July 2018). Mean comparisons indicated that the Zn concentration in southwest monsoon season (July 2017) was significantly higher than the northeast monsoon season, dry season, and southwest monsoon season in 2018 ( $p<0.05$ ).

The mean value of Zn concentration in the study area follows a descending order of Bangpakong (34.03±34.64 mg/kg) > Chao Phraya (81.44±22.77 mg/kg) > Tha Chin (76.71±46.83 mg/kg) > Mae Klong (48.66±43.49 mg/kg) > the inner Gulf of Thailand (34.03±34.64 mg/kg). As a result, mean concentrations of Zn in the Tha Chin, the Chao Phraya, and the Bangpakong River estuaries were significantly higher than the Mae Klong and the inner Gulf of Thailand ( $p<0.05$ ).



Remark: S1 is July 2017, S2 is December 2017, S3 is May 2018 and July 2018  
Alphabet indicated the significant differences between seasons and areas

**Figure 4.14** Seasonal comparisons of Zn contamination in the surface sediment of the Mae Klong (MK), the Tha Chin (TC), the Chao Phraya (CP), the Bangpakong (BK) river estuaries and the inner Gulf of Thailand (inner GoT).



#### 4.1.8 Aluminum (Al)

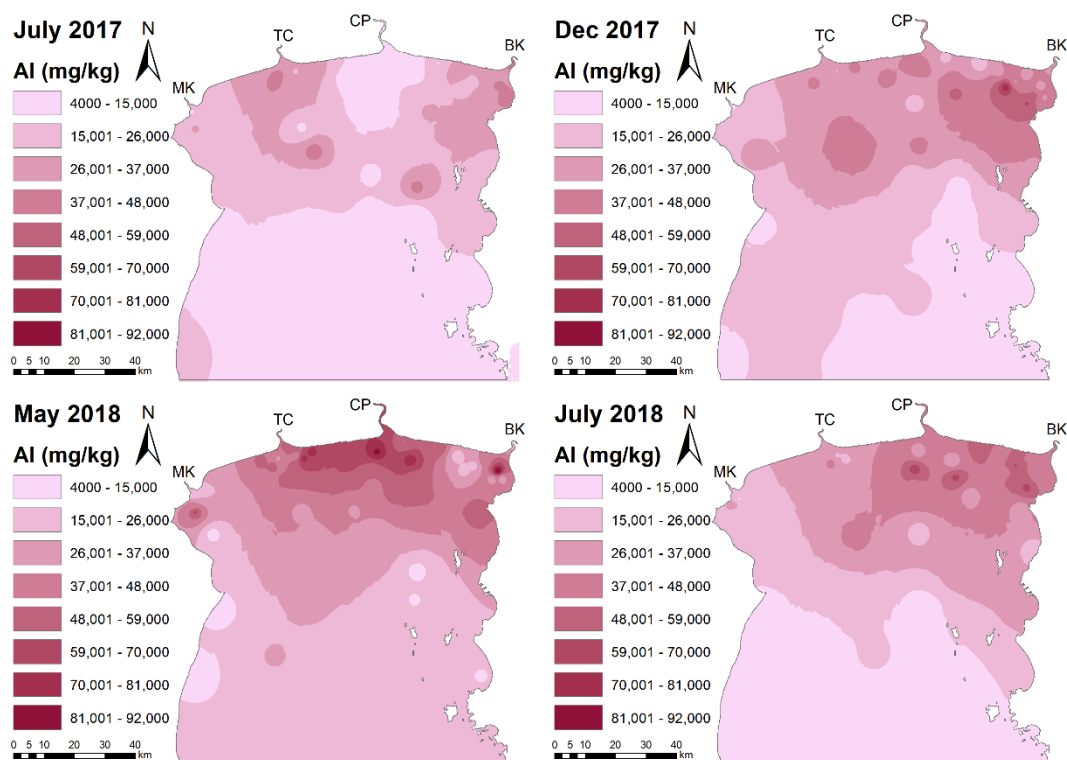
Spatial heterogeneity distribution of Al in the surface sediment in southwest monsoon season (July 2017) is displayed in Figure 4.15. As a result, the highest concentration was found in the Bangpakong River estuary (Stn.BK9; 43.63 g/kg), while the lowest concentration was found in the mouth of the Chao Phraya River (Stn.CP7; 5.72 g/kg). As a result, Al concentration were found high in the Tha Chin and the Bangpakong River estuarine areas.

In northeast monsoon season (December 2017), the horizontal distribution was characterized by the highest concentration at the outer of the Bangpakong River estuary (Stn.BK18; 76.08 g/kg), by contrast the lowest concentration was found in the lower eastern part of the Gulf (Stn.GT20; 4.47 g/kg). As Al distribution, the decreasing concentration from Bangpakong River estuary toward to the middle part of the Gulf.

In the dry season (May 2018), Al was spatially distribution in the range of 8.15–91.32 g/kg. The lowest concentration was found at the western part of the Gulf (Stn.GT2), while the highest concentration was found at the Bangpakong River estuary (Stn.BK7). As a result, Al concentrations were decreased from the mouth of major rivers to the middle of the Gulf.

In southwest monsoon (July 2018), Al in the surface sediment was varied between 5.54–64.46 g/kg. The highest concentration was found at the middle of Chao Phraya River estuary (Stn.CP8), while the lowest concentration was found at the middle of the Gulf (Stn.GT36). As a result, decreasing concentration trend was occurred from the mouth of the Bangpakong River to lower areas of the inner Gulf of Thailand (Figure 4.15).

According to the distribution pattern of Al in the surface sediment entire the inner Gulf of Thailand (Figure 4.15), the result indicated that the four main rivers especially the Bangpakong River estuary is source of Al. And for mean comparison the highest concentration was in dry season (May 2018) ( $p < 0.05$ ).



**Figure 4.15** Spatiotemporal heterogeneity distributions and seasonal variations of Al concentration in the surface sediment of the inner Gulf of Thailand.

The Mae Klong River estuary, Al concentration was found in the range of 12.44–28.27 ( $21.37 \pm 4.95$ ) g/kg for southwest monsoon season (July 2017), 9.01–24.73 ( $17.44 \pm 4.92$ ) g/kg for northeast monsoon season (December 2017), 15.83–60.94 ( $30.95 \pm 15.09$ ) g/kg for dry season (May 2018), and 13.77–38.17 ( $24.43 \pm 6.89$ ) g/kg for southwest monsoon season (July 2018). The spatial distribution was characterized by highest concentration at the mouth of the river in southwest monsoon season in 2017, northwest monsoon season, and dry season. While the high relative concentration in southwest monsoon season in 2018 was found at inner river zone. As a mean comparisons result, the Al concentration in the dry season (May 2018) was significantly higher than the other seasons ( $p < 0.05$ ).

The Tha Chin River estuary, Al concentration was found in the range of 24.33–42.43 ( $32.83 \pm 5.56$ ) g/kg for southwest monsoon season (July 2017), 18.10–43.74 ( $31.35 \pm 7.28$ ) g/kg for northeast monsoon season (December 2017), 15.83–60.94 ( $30.95 \pm 15.09$ ) g/kg for dry season (May 2018), and 22.37–40.92

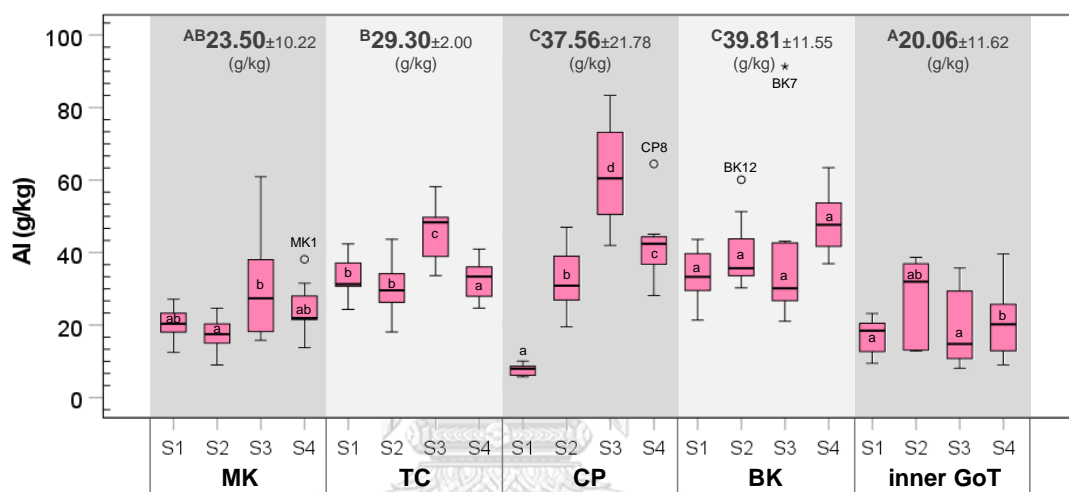
(30.90±5.74) g/kg for southwest monsoon season (July 2018). The relative high concentration was found at the western part of the river mouth in southwest monsoon season (July 2017) and northeast monsoon season (December 2017), found high concentration at eastern part of the river mouth and in the dry season (May 2018), and lastly the relative high concentration in southwest monsoon season (July 2018) was found in the inner zone of the river. As Figure 4.16, the Al concentration in the dry season (May 2018) was significantly highest ( $p<0.05$ ) while the significantly lowest was found in southwest monsoon season.

The Chao Phraya River estuary, Al concentration was found in the range of 5.72–22.10 (10.04±5.01) g/kg for southwest monsoon season (July 2017), 17.66–52.12 (33.25±11.35) g/kg for northeast monsoon season (December 2017), 42.01–83.36 (60.75±12.70) g/kg for dry season (May 2018), and 28.20–64.56 (46.21±11.85) g/kg for southwest monsoon season (July 2018). As a result, in Figure 4.16, the Al concentration of dry season (May 2018) was significantly highest ( $p<0.05$ ). While the lowest was in southwest monsoon season (July 2018) ( $p<0.05$ ).

Tha Bangpakong River estuary, Al concentration was found in the range of 19.87–43.63 (32.56±7.83) g/kg for southwest monsoon season (July 2017), 30.32–76.08 (43.45±14.79) g/kg for northeast monsoon season (December 2017), 19.43–91.32 (35.85±21.28) for dry season monsoon (May 2018), and 36.95–63.44 (47.39±8.26) g/kg for southwest monsoon season (July 2018). For mean comparison result in Figure 4.16, significant different concentrations in seasonal was not found.

The inner Gulf of Thailand excludes river estuaries, Al concentration was found in range 5.94 – 42.16 (16.70±9.78) g/kg for southwest monsoon season (July 2017), 4.47–42.78 (20.26±12.07) g/kg for northeast monsoon season (December 2017), 8.15–58.98 (24.98±12.11) g/kg for dry season (May 2018), and 5.54–39.68 (17.55±9.66) g/kg for southwest monsoon season (July 2018). Mean comparisons indicated that the Al concentration (Figure 4.16) in southwest monsoon season (July 2017) and dry season (May 2018) were significantly lower than southwest monsoon season (July 2018) ( $p<0.05$ ).

The mean value of Al concentrations in the study areas follows a descending order of the Bangpakong ( $39.81 \pm 11.55$  g/kg) > Chao Phraya ( $37.56 \pm 21.78$  g/kg) > Tha Chin ( $29.30 \pm 2.00$  g/kg) > Mae Klong ( $23.50 \pm 10.22$  g/kg) > inner Gulf of Thailand ( $20.06 \pm 11.62$  g/kg). According to mean comparison in different areas (Figure 4.16), Al concentration in the Bangpakong River and the Chao Phraya estuary were significantly higher than the Tha Chin River and the Mae Klong River estuaries while the lowest concentration was the inner Gulf of Thailand ( $p < 0.05$ ).



Remark: S1 is July 2017, S2 is December 2017, S3 is May 2018 and July 2018  
Alphabet indicated the significant differences between seasons and areas

**Figure 4.16** Seasonal comparisons of Al contamination in the surface sediment of the Mae Klong (MK), the Tha Chin (TC), the Chao Phraya (CP), the Bangpakong (BK) river estuaries and the inner Gulf of Thailand (inner GoT).

**Table 4.1** Comparison of mean value of heavy metal concentrations in the surface sediments.

Area	Heavy metals (mg/kg)							Reference
	Cd	Pb	Cu	Co	Ni	Mn	Zn	
The Mae Klong River estuary	0.14	21.0	8.4	15.3	17.8	572.1	48.7	The present study
The Tha Chin River estuary	0.21	18.3	19.1	24.5	29.5	1103.8	76.7	The present study
The Chao Phraya River estuary	0.20	17.3	19.7	27.6	31.3	756.0	81.4	The present study
The Bangpakong River estuary	0.24	14.2	17.2	32.5	34.1	1036.1	86.2	The present study
The inner GoT <sup>(ex)</sup>	0.09	10.2	6.4	13.5	15.3	517.6	34.0	The present study
The inner Gulf of Thailand	0.16	14.7	12.5	20.7	23.4	738.4	58.5	The present study
Yueqing Bay, China	0.12	28.4	34.2	–	–	–	107.3	Yao et al. (2021)
Thessaloniki Bay, Greece	2.51	84.2	77.2	–	82.4	314.2	218.0	Christophoridis et al. (2019)
Bohai Sea, China	0.10	19.4	16.1	–	–	–	50.0	Ding et al. (2018)
Yellow Sea, China	0.20	23.3	20.3	–	26.7	–	66.0	Xu et al. (2016)
Bizerte Lagoon, Tunisia	1.10	15.3	6.7	–	–	–	55.6	El Zrelli et al. (2021)
Hainan Island, China	–	26.8	15.0	13.2	25.3	–	70.5	Cai et al. (2021)
Southeast coast, India	–	–	71.6	60.6	88.8	584.2	246.2	Gopal et al. (2021)
Galveston Bay, USA	0.10	9.7	7.0	–	9.7	185.8	50.4	Lopez, Fitzsimmons, et al. (2021)
Bay of Bengal, Bangladesh	0.45	9.5	8.9	–	–	–	21.8	Rani et al. (2021)
Arabian Gulf, Saudi Arabia	0.57	39.0	118.0	9.1	282.2	233.8	79.2	Mahboob et al. (2022)
Galveston Bay estuary, Texas, USA (Estuary)	0.10	13.5	17.5	-	11.1	208.2	65.9	Lopez et al. (2022)
Galveston Bay estuary, Texas, USA (Shoreline)	0.07	8.3	7.2	-	13.6	209.7	31.4	Lopez et al., (2022)
Galveston Bay estuary, Texas, USA (Bay)	0.10	9.7	7.0	-	9.7	185.8	50.4	Lopez et al., (2022)

Remark: The inner GoT<sup>(ex)</sup> is heavy metal concentration in the inner Gulf of Thailand exclude estuaries.

## 4.2 Physicochemical Characteristics of the Surface Sediment

The important factors which could be considered to influence heavy metal distribution in surface sediment are chemical properties of the surface sediment including total organic matter (TOM), total organic carbon (TOC), total phosphorus (TP), and acid volatile sulfide (AVS). All results of chemical properties analysis as follow:

### 4.2.1 Total organic matter

In southwest monsoon season (July 2017), TOM in surface sediment was found in range of 1.86–15.44% (Figure 4.17). The lowest percentage of TOM was found at the mouth of The Mae Klong River (Stn.MK9) while the highest percentage of TOM was found at the upper part of the Gulf (Stn.GT23). The mean value of percentage of TOM across the entire of the inner Gulf of Thailand is  $8.87 \pm 2.95$ . The distribution pattern of TOM in this season was not clear but the upper of Gulf was found in a large number than lower part.

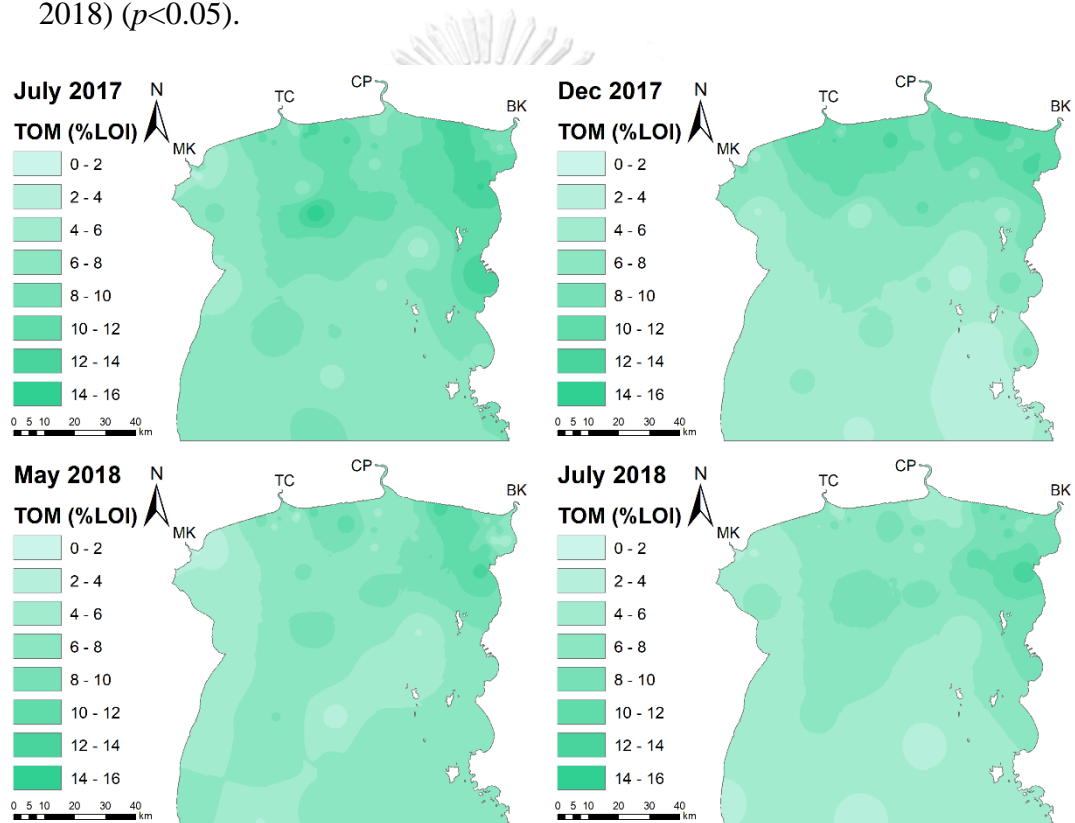
In northeast monsoon season (December 2017), TOM in surface sediment was found in the range of 2.28–13.69%. The highest percentage of TOM was found at the outer part of the Bangpakong River (Stn.BK16) while the lowest was found near lower part of the Gulf (Stn.GT28). The trend of TOM pattern was the high percentage in the upper part of Gulf and the decreasing was found along the southern part to eastern part.

In the dry season (May 2018), TOM in surface sediment was varied between 1.53–13.12%. The highest percentage of TOM was found at the Chao Phraya River estuary (Stn.CP16) while the lowest percentage of TOM was found at the mouth of The Mae Klong River (Stn.MK4).

In southwest monsoon season (July 2018), TOM in surface sediment was found in the range of 2.28–13.97%, The highest percentage of TOM was found at the inner Gulf of Thailand (Stn.GT17) on the other hand the lowest percentage of TOM in this season was found at the mouth of The Mae Klong River (Stn.MK3).

As Figure 4.17, the decreasing of TOM was to start from the Bangpakong River estuary into the lower southern part of Gulf.

For varied seasonal, the mean percentage of TOM in this study follow a descending order of southwest monsoon season in 2017 ( $8.87\pm 2.97\%$ ) > northeast monsoon season ( $8.27\pm 3.17\%$ ) > dry season ( $7.05\pm 2.70\%$ ) > southwest monsoon season ( $6.77\pm 2.54\%$ ). As mean comparisons, southwest monsoon season (July 2017) and northeast monsoon season were significantly higher than the mean percentage of TOM in dry season and southwest monsoon season (July 2018) ( $p < 0.05$ ).



**Figure 4.17** Spatial distributions and seasonal variations percentages of TOM in the surface sediment of the inner Gulf of Thailand.

#### 4.2.2 Total organic carbon

Total organic carbon (TOC) concentration was found in the range of 2.79–43.17 mgC/g for southwest monsoon season (July 2017). The lowest TOC concentration was found at the mouth of The Mae Klong River (Stn.MK9) while the highest TOC concentration was found at the middle of the Gulf (Stn.GT35). As Figure 4.18, the relatively high concentration commonly found in the Gulf area by contrast the lower spot were found rarely in river estuaries.

In northeast monsoon season (December 2017), TOC concentration was varied between 3.44–30.22 mgC/g. As Figure 4.18, the lowest concentration was found at the lower part of the Gulf (Stn.GT28), while the highest concentration was found at Station GT19. The relative high concentration was rarely found in river mouth estuaries and the inner Gulf of Thailand, but some areas of the lower part of the Gulf seem to be diluted from others influenced.

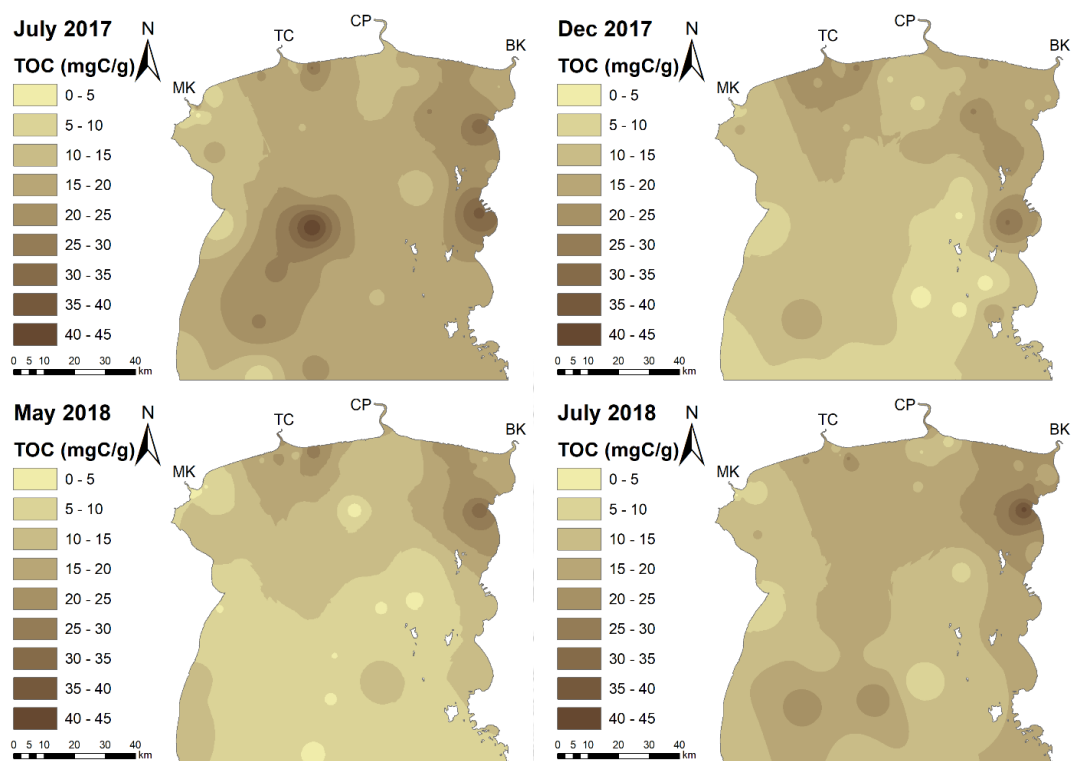
In dry season (May 2018), TOC concentration was varied between 2.76–35.50 mgC/g. The highest concentration was found at the inner area of the Tha Chin River (Stn.TC2), while the lowest concentration was found at the inner Gulf of Thailand (Stn.GT6). As TOC distribution (Figure 4.18), in the upper part of the inner Gulf was found the relative high concentration.

In southwest monsoon season (July 2018), TOC concentration was found in the range of 4.28–40.72 mgC/g. The highest concentration was found at the upper part of the Gulf (Stn.GT17) on the other hand the lowest concentration was found at the Mae Klong River estuary area (Stn.MK3). As Figure 4.18, the high concentration of TOC was shown around the middle of the Gulf and river estuaries.

Seasonal TOC concentration following a descending order of southwest monsoon season in 2017 ( $17.42 \pm 7.23$  mgC/g) > southwest monsoon in 2018 ( $17.03 \pm 7.02$  mgC/g) > northeast monsoon season in 2017 ( $15.08 \pm 6.33$  mgC/g) > dry season in 2018 ( $7.05 \pm 2.70$  mgC/g). According to mean comparison between seasonal, the TOC concentration of dry season was significantly lowest ( $p < 0.05$ )



while both of southwest monsoon season and northeast monsoon season were not different.



**Figure 4.18** Spatial distributions and seasonal variations of TOC concentration in the surface sediment of the inner Gulf of Thailand.

#### 4.2.3 Total phosphorus

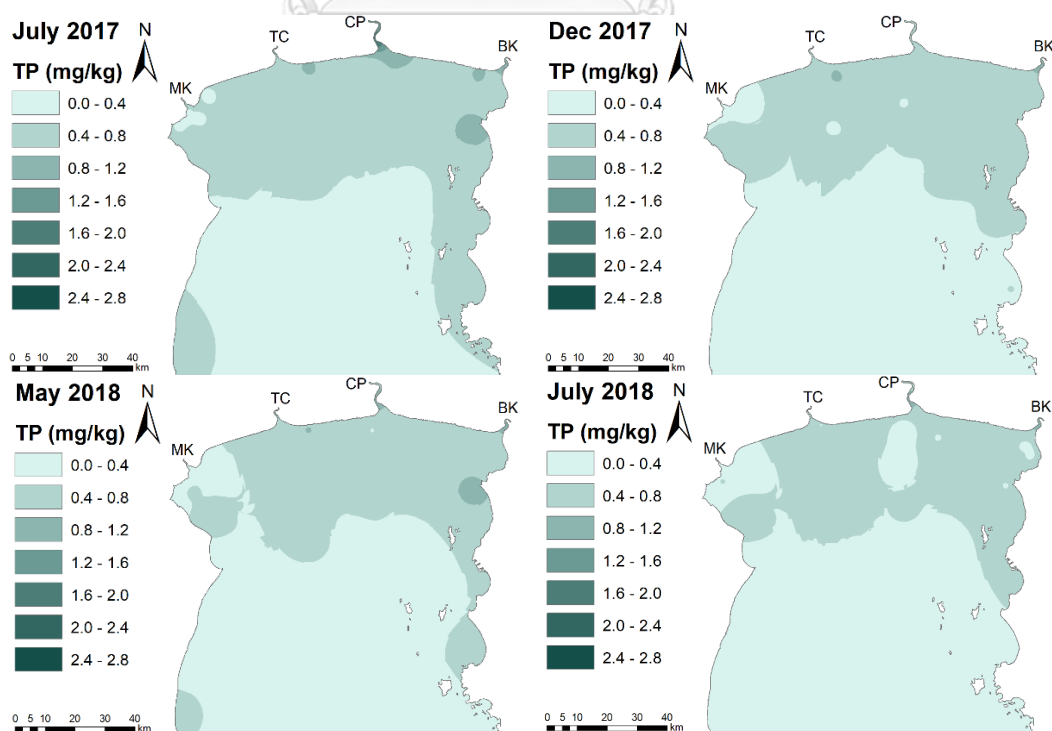
Total phosphorus (TP) concentration was found in the range of 0.19–1.89 mg/kg for southwest monsoon season (July 2017). The lowest concentration was found at the outside area of The Mae Klong River mouth (Stn.MK9) while the highest concentration was found at the river zone of the Chao Phraya River (Stn.CP1). According to TP distribution map (Figure 4.19), the TP concentration at the upper part of the Gulf was higher than the lower part.

In northeast monsoon season (December 2017), TP concentration was found in range of 0.09–1.08 mg/kg. The lowest concentration was found in the middle part of the Gulf (Stn.GT27) while the highest concentration was found at the inner the Bangpakong River (Stn.BK1). In this season, most of TP concentration were found in the upper half of Gulf.

In the dry season (May 2018), TP concentration was found in range of 0.15–1.14 mg/kg. The lowest concentration was found at the Mae Klong River estuary (Stn.MK4) by contrast the highest concentration was found at the inner Tha Chin River (Stn.TC2). The pattern of TP distribution in this season was alike the pattern in southwest monsoon season (July 2017).

In southwest monsoon season (July 2018), TP concentration was varied between non-detectable to 0.69 mg/kg. The lowest concentration of TP in this season was found in many areas, such as in the Mae Klong River estuary (Stn.MK9) and the inner Gulf of Thailand (Stn.GT34,36, and 40). The highest concentration was found at the Tha Chin River estuary (Stn.TC5). The pattern of TP distribution in this season, the TP concentration density was found in the upper part of the Gulf.

Seasonal TP mean concentration following a descending order of southwest monsoon season in 2017 ( $0.57 \pm 0.30$  mg/kg) > dry season ( $0.48 \pm 0.22$  mg/kg) > northeast monsoon season ( $0.46 \pm 0.21$  mg/kg) > southwest monsoon season in 2018 ( $0.44 \pm 0.20$  mg/kg). As mean comparisons result, the significant highest concentration was in southwest monsoon season (July 2017) ( $p < 0.05$ ).



**Figure 4.19** Spatial distributions and seasonal variations of TP concentration in the surface sediment of the inner Gulf of Thailand.

#### 4.2.4 Acid volatile sulfide

Acid volatile sulfide (AVS) was varied between non-detectable to 0.21 mg/g DW for the southwest monsoon season (July 2017). The lowest concentration was found in many areas, such as in the Mae Klong River estuary (Stn.MK9), the Bangpakong (Stn.BK9), and the inner Gulf of Thailand (Stn.GT30 and 40). While the highest concentration was found in the outer zone of the Tha Chin River estuary (Stn.TC14). The relatively high concentration was found near the Tha Chin River and the Bangpakong River estuaries.

In northeast monsoon season (December 2017), AVS concentration was found in the range of 0.00–2.21 mg/g DW. The lowest concentration was found in many spots at the inner Gulf of Thailand (Stn.GT9,11,19,27 and 29). While the highest concentration was found at the Tha Chin River estuary (Stn.TC14). As Figure 4.20, this season AVS distribution pattern was resembled with the AVS distribution in southwest monsoon season (July 2017).

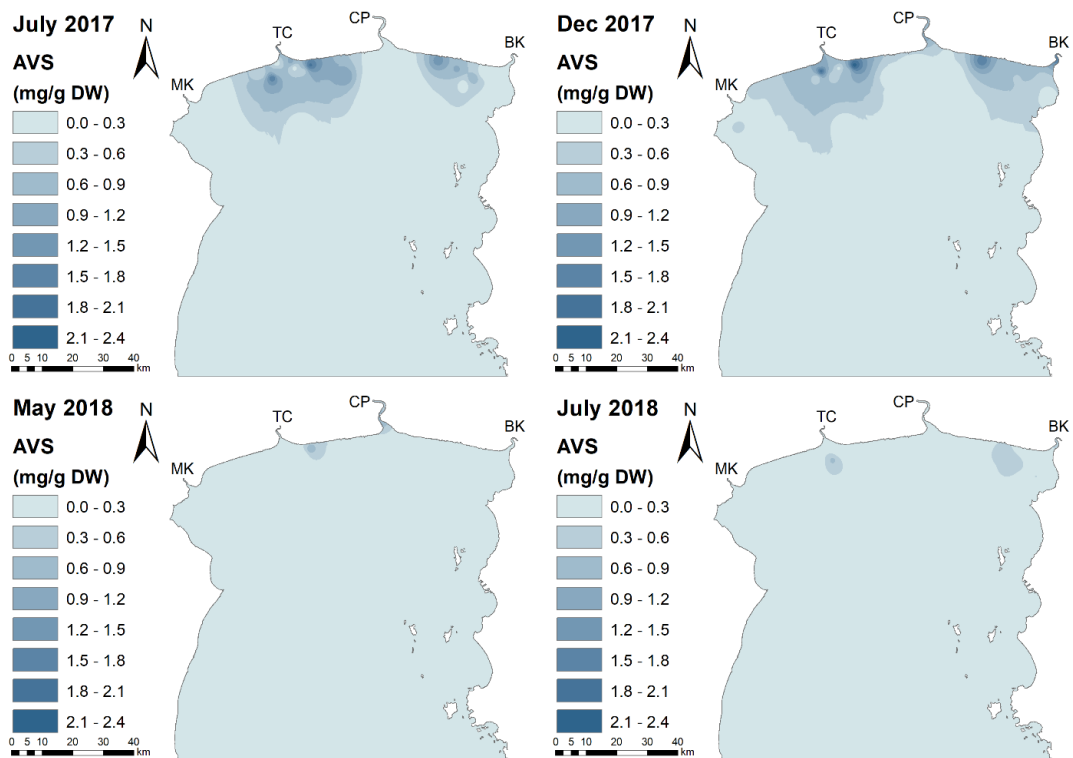
In the dry season (May 2018), AVS concentration was varied between 0.00–0.80 mg/g DW. As Figure 4.20, AVS concentration this study area generally was in between 0.00–0.30 mg/g DW the lowest concentration was found at The Mae Klong River estuary (Stn.MK3) and the inner Gulf of Thailand (Stn.GT2,29,36 40, and 41). By contrast the highest concentration was found at the inner zone of the Chao Phraya River (Stn.CP1).

In southwest monsoon season (July 2018), AVS concentration was found in the range of 0.00–0.69 mg/g DW. AVS distribution pattern in this season was similar to dry season (Figure 4.20). The highest concentration was found at the Tha Chin River estuary (Stn.TC5). While the lowest concentration can be found in many areas due to 0.00 mg/g DW such as in the Mae Klong River estuary (Stn.MK9) and in the inner Gulf of Thailand (Stn.GT34, 36, and 40).

AVS mean concentration following a descending order to northeast monsoon season ( $0.34 \pm 0.52$  mg/g DW) > southwest monsoon season in 2017 ( $0.26 \pm 0.47$  mg/g DW) > southwest monsoon season in 2018 ( $0.12 \pm 0.15$  mg/g DW) > dry season ( $0.06 \pm 0.15$  mg/g DW). After mean comparison analysis, the

significant highest concentration was found in northeast monsoon season ( $p<0.05$ ) and the significant lowest concentration was found in 2 seasons (dry season and southwest monsoon season in 2018) ( $p<0.05$ ).

In this study, AVS distribution as seasonal could be assume that separate into 2 distribution patterns (southwest monsoon season in 2017 with northeast monsoon season and dry season with southwest monsoon season in 2018).



**Figure 4.20** Spatial distributions and seasonal variations of AVS concentration in the surface sediment of the inner Gulf of Thailand.

### 4.3 Contamination Status of Heavy Metal Contaminations in the Surface Sediment

#### 4.3.1 Sediment quality guideline

In this study, sediment quality guideline of Thailand ( $SQG_T$ ) (Pollution Control Department, 2015) and sediment quality guidelines ( $SQG_s$ ) from National Oceanic and Atmospheric Administration's Screening Quick Reference Tables ( $TEL$ ,  $PEL$  and  $AET$ ) (Buchman, 2008; Long & MacDonald, 1998; Macdonald et

al., 1996) were used to prospecting the contamination status of surface sediment by compared with the heavy metal concentration.  $SQG_T$  shows the upper limit of concentration, which does not cause any effect on benthic fauna. *TELS* and *PELS* are define into three ranges of concentration; 1) below *TELS* values mean adverse effect was found rarely, 2) greater than *TELS* but less than *PELS* mean adverse effect was found occasionally, 3), greater than *PELS* values mean the heavy metal in surface sediment frequently associated with organisms. Apparent effects threshold is another benchmark based upon relationships between highest concentration and adverse effect which observed bioassay endpoints (M–Microtox, B–Bivalve, E–Echinoderm larvae, O–Oyster larvae, A–Amphipod, N–Neanthes, L–Larval bioassay, I–Infaunal community impacts) (Buchman, 2008) The result of comparison shown in Table 4.2.

In southwest monsoon season (July 2017), Cd is rarely associated with adverse effect following as the 100% of Cd concentration was lower than *TEL* value and  $SQG_T$ . 98.31% of Pb is rarely associated while 1.69% of Pb is occasionally associated with adverse effect. 13.56% of Cu concentration greater than  $SQG_T$  values. while comparing with *TEL–PEL* the 57.63% of Cu across the entire study areas are below the *TEL* values and the others between *TEL* and *PEL* is 42.37%. According to compared with *AET* values, 91.53% of Co concentration is higher. Compared with NOAA values, 66.10% of Ni is between *TEL* and *PEL* while 1.69% is over *PEL* values. As compared with *AET* value, the 96.61% of Mn is exceeded. Comparing with PCD values the Zn which higher than guideline is 23.73%. While compared with NOAA, the Zn concentration which in between *TEL* and *PEL* is 18.64%.

In northeast monsoon season (December 2017), Cd is rarely associated with adverse effect due to 100% lower than *TEL* and  $SQG_T$  values. 100% of Zn compared with PCD and 96.67% of Zn compared with NOAA are consider as low associate with adverse effect, while 3.33% of Zn is occasionally associated with adverse effect when compared with NOAA. Cu concentration compared with PCD and NOAA, 8.33% and 23.33% are higher than  $SQG_T$  and between *TEL–PEL* values, respectively. Co compared with NOAA, 75% of Co concentration which higher than *AET* values can cause adverse effect on benthic

bioassay. As comparing with PCD and NOAA, 100% and 40% of Ni is lower than  $SQG_T$  and  $TEL$  values, respectively. By contrast, the occasionally associated with an adverse effect of Ni concentration to benthic by 58.33% of Ni are in  $TEL-PEL$  values and 1.67% if Ni also frequently associated with adverse effect. The result of Mn concentration in study area compared with  $AET$  value, which 96.67% of Mn can impact the adverse effect on benthic bioassay. After comparing with  $SQG_T$ , the concentration of Zn which can found the adverse effect to benthic fauna following PCD guideline is 13.33%. The 95% of Zn is lower than  $TEL$  value show that the rarely associated with adverse effect to benthic organism, while 5% of Zn is between  $TEL-PEL$  values that indicated the occasionally associated with adverse effect.

In dry season (May 2018), 100% concentration of Cd and Pb are lower than  $SQG_T$  and  $TEL$  values then the Cd and Pb have very low associated with adverse effect to any benthic organism. Comparing Cu concentration with PCD and NOAA guideline, the 5.17% is higher than  $SQG_T$  and 12.07% is between  $TEL-PEL$  values show a slightly occasionally associated with adverse effect. As  $AET$  value, 84.48% of Co is likely to associated with adverse effect. Ni concentration which is lower than  $TEL$  is 29.31% and higher  $TEL$  but not greater than  $PEL$  is 70.69%. Show that over 70.69% of Ni can occasionally associated with adverse effect. 48.28% of Mn which is higher than  $AET$  value also shows the associated with adverse effect to benthic bioassay too. For identify Zn contamination level, 5.17% of Zn is exceed than  $SQG_T$  value and 1.72% of Zn is between  $TEL-PEL$  range, are occasionally associated with adverse effect.

In southwest monsoon season (July 2018), all of Cd concentrations are lower than  $SQG_T$  and  $TEL$  show that the associated with adverse effect is low or slightly. As  $SQG_T$ , Pb is not pose any effect to fauna benthic, but when comparing with NOAA the 1.92% of Pb is occasionally associated with adverse effect. Cu concentration in this study compared with  $SQGs$ , 13.46% is greater than  $SQG_T$  value and 36.54% is in the range of  $TEL-PEL$ , this result was shown that Cu is likely low chance to pose any effect to fauna benthic for PCD standard and over 36.54% was occasionally associated with adverse effect for NOAA guideline. When comparing Co concentration in this area to  $AET$  values, almost

of Co concentration (90.38%) noticeably to have observed toxicity benthic bioassay result. Following the  $SQG_T$ , Ni is no relative with the opportunity to impact the benthic organism. But while comparing with NOAA, almost of Ni (80.77% and 7.69%) are associated with adverse effect to fauna benthic as occasionally and frequently, respectively. 80.77% of Mn concentration is greater than  $AET$ , the observer toxicity benthic bioassay result could be found. 17.37% of Zn could be impact to benthic organism following as PCD sediment quality guideline, but in NOAA guideline its only 11.54% of Zn seems to have occasionally associated with adverse effect.

The result from selected heavy metal contamination compared with PCD of Thailand's sediment quality guidelines, NOAA's screening quick reference tables ( $TEL$ ,  $PEL$ ,  $AET$ ) the result, Cd concentration in the surface sediment is lower than  $SQG_T$ ,  $TEL$ ,  $PEL$  and  $AET$ . The Cd concentration in this study has low possibility of associated with any effect to organism. Following the  $SQG_T$ , the heavy metal which over guideline values in every season are Cu and Zn. As  $TEL$  and  $PEL$  comparison, the heavy metal in the dry season (May 2018) which have an exceeding value are Cu, Co, Ni, Mn, and Zn. While in the others season the heavy metal which have an exceeding value are Pb, Cu, Co, Ni, Mn, and Zn. According to  $AET$  the Co and Mn in all seasons are extremely over (75.00–96.67%) excluding in dry season (Mn= 8.28%).

**Table 4.2** Comparison of selected heavy metal concentration to sediment quality guidelines (SQGs)

Seasons	Guidelines	Cd	Pb	Cu	Co	Ni	Mn	Zn
Southwest monsoon season (July 2017)	> <i>SQG<sub>T</sub></i> (%)	0	0	13.56	-	-	-	23.73
	< <i>TEL</i> (%)	100	98.31	57.63	-	32.20	-	81.36
	<i>TEL-PEL</i> (%)	0	1.69	42.37	-	66.10	-	18.64
	> <i>PEL</i> (%)	0	0	0	-	1.69	-	0
	> <i>AET</i> (%)	0	0	0	91.53	0	96.61	0
Northeast monsoon season (December 2017)	> <i>SQG<sub>T</sub></i> (%)	0	0	8.33	-	-	-	13.33
	< <i>TEL</i> (%)	100	96.67	76.67	-	40.00	-	95.00
	<i>TEL-PEL</i> (%)	0	3.33	23.33	-	58.33	-	5
	> <i>PEL</i> (%)	0	0	0	-	1.67	-	0
	> <i>AET</i> (%)	0	0	0	75.00	0	96.67	0
Dry season (May 2018)	> <i>SQG<sub>T</sub></i> (%)	0	0	5.17	-	-	-	5.17
	< <i>TEL</i> (%)	100	100	87.93	-	29.31	-	98.28
	<i>TEL-PEL</i> (%)	0	0	12.07	-	70.69	-	1.72
	> <i>PEL</i> (%)	0	0	0	-	0	-	0
	> <i>AET</i> (%)	0	0	0	84.48	0	48.28	0
Southwest monsoon season (July 2018)	> <i>SQG<sub>T</sub></i> (%)	0	0	13.46	-	-	-	17.31
	< <i>TEL</i> (%)	100	98.08	63.46	-	11.54	-	88.46
	<i>TEL-PEL</i> (%)	0	1.92	36.54	-	80.77	-	11.54
	> <i>PEL</i> (%)	0	0	0	-	7.69	-	0
	> <i>AET</i> (%)	0	0	0	90.38	0	80.77	0

Remark; <sup>a</sup> = Coastal sediment quality standard of Thailand (Pollution Control Department, 2015)

<sup>b</sup> = NOAA Screening Quick Reference Tables (Buchman, 2008)



### 4.3.2 Enrichment factor

Enrichment factor (*EF*) is a tool for assess the quantity of anthropogenic concentration heavy metals deposition on surface sediment. Evaluation of *EF* values are calculated by normalized selected heavy metals with normalizer (Al) then compared with selected heavy metal's background concentration. The result of seasonal comparisons of *EF* values in surface sediment is displayed in Figure 4.21.

In southwest monsoon season (July 2017), *EF* values of Cd are found in range of 0.09–10.03. The lowest value is found at the inner Gulf of Thailand (Stn.GT26), while the highest value is found at the Chao Phraya River (Stn.CP7). As *EF* tier classification (Figure 4.21), 11.86% of Cd values in this season are no enrichment, 74.58% of values are minor enrichment, 3.39% of values are moderate enrichment, 8.47% of values are moderately enrichment, and 1.69% of values are severe enrichment. *EF* values of Pb are found in the range of 0.09–3.49. The lowest and highest values are found at the inner Gulf of Thailand (Stn.GT1) and the Chao Phraya River (Stn.CP1), respectively. While *EF* tier classification is followed; 61.02% are no enrichment, 35.59% are minor enrichment, 3.39% are moderate enrichment. *EF* values of Cu are varied between 0.01–1.58. The lowest and highest values are found at the inner Gulf of Thailand (Stn.GT17) and the Chao Phraya River (Stn.CP), respectively. *EF* values of Co are in the range of 0.19–5.18. The lowest *EF* value is found at the inner Gulf of Thailand (Stn.GT26) and the highest *EF* value is found at the Chao Phraya River (Stn.CP7). As *EF* values order by tier, 40.68% of *EF* values are found no enrichment, 49.15% are found in minor enrichment tier, 8.47% are in moderate enrichment, and 1.69% are found as moderately enrichment. *EF* values of Ni are found in the range of 0.08–1.74, the lowest and the highest values of *EF* are found at the inner Gulf of Thailand (Stn.GT26) and the Chao Phraya River (Stn.CP7) afterwards. *EF* values of Ni also found classification following as; 89.83% of values are no enrichment and 10.17% of values are minor enrichment. Mn's *EF* values are varied between 0.01–1.88. While the lowest and the highest values have been found at the inner Gulf of Thailand (Stn.GT17) and the Chao

Phraya River (Stn.CP8). The classification of Ni's *EF* values by 89.83% of values are no enrichment and 10.17% of values are in minor enrichment. The *EF* values of Zn are found between 0.53–6.67. The inner Gulf of Thailand (Stn.GT35) is the lowest *EF* value while the highest is found in the Chao Phraya River (Stn.CP12). The classification of Zn following EF tier show that the 27.12% of values are no enrichment, 50.85% of values are minor enrichment, 11.86% of values are moderate enrichment, and the rest (10.17%) are moderately enrichment.

In northeast monsoon season (December 2017), Cd enrichment factor values are found in the range of 0.05–4.30. The lowest and highest value is found at the inner Gulf of Thailand (Stn.GT24) and The Mae Klong River (Stn, MK1) respectively. Cd's *EF* are separated in 3 tiers; 1) 56.67% is no enrichment 2) 40.00% is minor enrichment 3) 3.33% is moderate enrichment. *EF* values of Pb are varied between 0.18–2.06. The lowest value is located in the inner Gulf of Thailand (Stn.GT25) while the highest value is located in The Mae Klong River (Stn. MK2). All Pb enrichment factor values in this season can be defined in 2 classes; firstly, the 81.67% of values are no enrichment and the second are minor enrichment (18.33%). For enrichment factor evaluation of Cu, all of values are no enrichment (100%). The highest and lowest value can be found at Tha Chin River estuary (Stn.TC1; 0.80) and the inner Gulf of Thailand (Stn.GT38; 0.04). The lowest and the highest value of Enrichment factor of Co are found in range of 0.40–2.12 (Stn.GT9–Stn.CP16). The 73.33% of Co values are found no enrichment and 26.67% of values are minor enrichment. As the enrichment factor of Ni values in the range of 0.09–0.86 in this season. And all Ni are no enrichment. The lowest and the highest of Mn values are both found at the inner Gulf of Thailand (Stn.GT38; 0.13–Stn.GT20; 1.40). The classification of Mn following EF values that the 100% of Mn values are no enrichment. While the range of Zn's enrichment factor values are 0.01–6.28 (Stn.GT28–Stn.TC1), the 65.00% of Zn values are no enrichment, the 21.67% of Zn values are minor enrichment, the 10.00% of Zn values are moderate enrichment, and the last portion (3.33%) are moderately enrichment.

In the dry season (May 2018), the enrichment of Cd values is found in the range of 0.05–2.30. The bottom value of Cd enrichment is found at The Mae Klong River (Stn.MK3) and the tops value is found at the Bangpakong River (Stn.BK16). As *EF* values classification, 71.19% Cd values are no enrichment and the 28.81% of Cd values are minor enrichment. This season found the enrichment factor of Pb in the range of 0.14–1.27 at the inner Gulf of Thailand (both lowest and highest values; Stn.GT17 and Stn.GT4). A few of Pb which found in minor enrichment (3.39%). Although the enrichment factor of Cu is found in range of 0.00–0.49, but all the Cu values are no enrichment. After Co enrichment factor assessed, the 79.66% of values are no enrichment and the 20.34% are minor enrichment. The range of Co *EF* values are found in the range of 0.30–1.69 (Stn.MK10–Stn.GT4). As the enrichment factor of Ni are varied between 0.09–0.92, 100% of *EF* values are no enrichment. The lowest and the highest values of *EF* from Mn are 0.00–1.17 (Stn.MK5 and TC8–Stn.GT3), which the few are found as minor enrichment (1.69%). Enrichment factor of Zn values are varied between 0.04–3.02 by lowest value at the mouth of the Mae Klong River(Stn.MK10) and highest value at (Stn.BK16). These enrichment factor values are in 3 different classes 1. 84.75% is no enrichment 2) 13.56% is minor enrichment to the environment 3.) 1.69% of Zn are moderately enrichment.

The southwest monsoon season (July 2018), 0.37–5.47 are the range of Cd enrichment factor which are found in this season. The Chao Phraya River estuary and the inner Gulf of Thailand are shown as lowest and highest values, respectively. Moderately enrichment is found in the 1.92% of Cd values, 3.85% of Cd values is moderate enrichment, 61.54% of Cd also in minor enrichment class, the other 32.69% are no enrichment. Enrichment factor values of Pb are found in a range of 0.25–1.82, the lowest value is in the Bangpakong River estuary (Stn.BK12) and the highest value is in the Mae Klong River estuary (Stn.MK9). The enrichment factor of Pb in this season are sorted by *EF* values by 2; firstly, the no enrichment is 82.69% and the second is minor enrichment is 17.31%. Enrichment factor values of Cu are found in the range of 0.01–0.66, while the lowest is Stn.GT4 and the highest at Stn.GT36. The full of Cu enrichment factor values are shown no enrichment. The range of Co *EF* values is

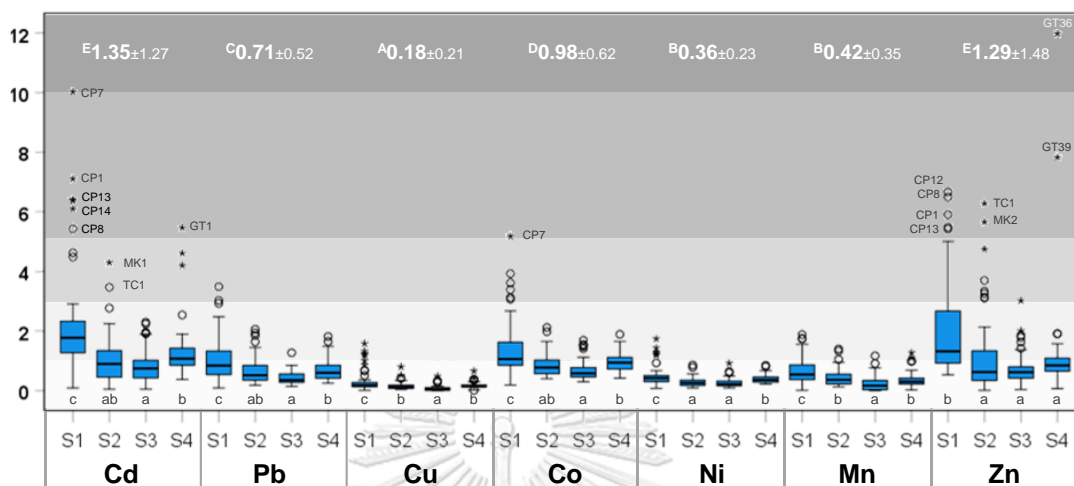
0.42–1.89. The tops value is found at GT40 station, and the bottoms value is found at MK3 station. *EF* classification for Co value show that the 59.62% is no enrichment while the 40.38% is minor enrichment. As the range of Ni values (0.22–0.85) which are found in the inner Gulf of Thailand at GT26 station and GT36 station, respectively. As Figure 4.21, Ni values usually are no enrichment. In Mn enrichment factor evaluation, at few (3.85%) of value are minor enrichment from the range of value at 0.02–1.27. The enrichment factor value range of Zn (0.07–11.98) classified following *EF* assessment show that the 1.92% of values are severe enrichment, 1.92% of values also are moderately enrichment, the 26.92% of values are minor enrichment, and the biggest portion (69.23%) are no enrichment.

The mean values of *EF* in the selected heavy metals follows a descending order of Cd ( $1.35 \pm 1.27$ ) > Zn ( $1.29 \pm 1.48$ ) > Co ( $0.98 \pm 0.62$ ) > Pb ( $0.71 \pm 0.52$ ) > Mn ( $0.42 \pm 0.35$ ) > Ni ( $0.36 \pm 0.23$ ) > Cu ( $0.18 \pm 0.21$ ). According to *EF* mean values comparison between heavy metals (Figure 4.21) show that the *EF* values of Cd and Zn are significantly highest, while the significantly lowest is Cu. By contrast the mean of *EF* values comparison between season in each heavy metal result show that all the heavy metals in this study are significantly highest in southwest monsoon season (July 2017) ( $p < 0.05$ ) and the significantly lowest mean *EF* values are from dry season (May 2018) ( $p < 0.05$ ) in all metals.

Although, the *EF* values in this study shown that most of heavy metals concentration were not affected by anthropogenic source ( $EF < 2$ ) (Barbieri, 2016) except in some areas which found enriched ( $EF > 3$ ) (Barbieri, 2016) in southwest monsoon season (2017) Cd, Co and Zn were defined as significant enrichment at the Chao Phraya River estuarine area. And in northeast monsoon season found the enrichment of Cd and Zn at the Tha Chin River and the Mae Klong River estuarine areas. By contrast, the enrichment of Cd and Zn were found in 2018's southwest monsoon season. Assume that the Cd and Zn accumulation that found in 2017 southwest monsoon season transferred to sunk to the inner Gulf of Thailand later in 2018 southwest monsoon season. As result, heavy metals concentration which found in this study were influenced by human

activates such as industrial plant especially electrical production (Clemens Reimanna, 2005)

### EF value



Remark: S1 is July 2017, S2 is December 2017, S3 is May 2018 and S4 is July 2018  
Alphabet indicated the significant differences between seasons and areas ( $p < 0.05$ )

**Figure 4.21** Seasonal comparisons of enrichment factor (EF) of selected heavy metals in the surface sediment.

### 4.3.3 Geo-accumulation index

Geo-accumulation index ( $I_{geo}$ ) is another tool for identifying the anthropogenic sources from contamination, instead of normalized the concentration of heavy metals with commonly earth's crust mineral such as Al. But this study, the geochemical background value of heavy metals was used to calculated. The result is displayed in Figure 4.22.

In southwest monsoon season (July 2017), the lowest  $I_{geo}$  value of Cd is found in the inner Gulf of Thailand (Stn.GT26; -5.13) and the highest is found at Bangpakong River estuary (Stn.BK12; -0.80). The  $I_{geo}$  value of Pb are found in range of -6.00 to -1.72, the lowest value is found in the inner Gulf of Thailand (Stn.GT1) while the highest value is found in Mae Klong River estuary (Stn.MK1). The  $I_{geo}$  values of Cu are varied from -8.29 to -2.95, the upper value is found at and the lower value at the inner Gulf of Thailand (Stn.GT27) and the bottoms value is found at Tha Chin River (Stn.TC1).  $I_{geo}$  of Co are varied by the lowest is from at (Stn.GT26; -4.05) and the highest it found from at the

Bangpakong River estuary (Stn.BK7; -1.41). The range of Ni  $I_{geo}$  which found in this study area are -5.41 to -2.93 while the lowest value is found at the inner Gulf of Thailand (Stn.GT27) and the highest is found at Tha Chin River estuary (Stn.TC14). The location of the highest  $I_{geo}$  value of Mn is found at Mae Klong River estuary (Stn.MK4;-2.24) and the lowest  $I_{geo}$  value of Mn is found at the inner Gulf of Thailand (Stn.GT17; -8.51). The range of  $I_{geo}$  values of Zn which found start from the lowest at the inner Gulf of Thailand (Stn.GT34; -4.52) and the highest value is found at Tha Chin River estuary (Stn.TC1; -0.28). As Figure 4.22 show that all heavy metals are practically uncontaminated from anthropogenic source.

In northeast monsoon season (December 2017), the range of  $I_{geo}$  from Cd by the lowest is found at the inner Gulf of Thailand (Stn.GT39; -7.71) and the highest value is found at The Chao Phraya River estuary (Stn.CP7; -0.92). The highest  $I_{geo}$  of Pb is found at Tha Chin River estuary (Stn.TC1; -1.85) and the lowest  $I_{geo}$  of Pb is found at the inner Gulf of Thailand (Stn.GT39;-5.06). The  $I_{geo}$  of Cu are varied between -8.98 to -3.11, the highest value is found at Tha Chin River estuary (Stn.TC1) and the lowest value is found at the inner Gulf of Thailand (Stn.GT20). The  $I_{geo}$  values of Co which the lowest is found at the inner Gulf of Thailand (Stn.GT20; -5.43) while the highest  $I_{geo}$  value is found at The Chao Phraya River estuary (Stn.CP8; -1.81). The lowest  $I_{geo}$  value of Ni which is found at the inner Gulf of Thailand (Stn.GT20;-7.83) and the highest  $I_{geo}$  value is found at The Chao Phraya River estuary (Stn.CP8; 2.96). The  $I_{geo}$  values are ranged in between -6.59 at the inner Gulf of Thailand (Stn.GT38) and -2.70 at the Bangpakong River estuary (Stn.BK7). The maximum of  $I_{geo}$  value from Zn is found at Tha Chin River estuary (Stn.TC1 ; -0.15) while the minimum of  $I_{geo}$  value from Zn is found at the inner Gulf of Thailand (Stn.GT28 ; -11.27). As Figure 4.22, every  $I_{geo}$  values are practically uncontaminated.

In dry season (May 2018), the range of  $I_{geo}$  values from Cd by start with the lowest at the inner Mae Klong River estuary (Stn.MK3; -7.08) and the highest value in Tha Chin River estuary (Stn.TC2 ; -0.86).  $I_{geo}$  values of Pb are varied between -6.04 to -2.27, the lowest value is located at the inner Gulf of Thailand (Stn.GT2) and the highest value is located at Tha Chin River estuary (Stn.TC2).

$I_{geo}$  values of Cu are found in range of -10.55 to -3.42, by found lowest value at Mae Klong River estuary (Stn.MK6) and found highest value at Tha Chin River estuary (Stn.TC2).  $I_{geo}$  values of Co are varied by lowest at the inner Gulf of Thailand (Stn.GT26; -4.33) while the highest is found at the Bangpakong River estuary (Stn.BK7;-1.41). According to  $I_{geo}$  values of Ni are in ranged between -5.96 to -3.03, the highest value is found at the Bangpakong River estuary (Stn.BK7) and the lowest value is found at Mae Klong River estuary (Stn.MK4). The range of  $I_{geo}$  values (-11.38 to -2.15) is found both in Tha Chin River estuary, Stn.TC8 and Stn.TC11 are lowest and highest value, respectively. The  $I_{geo}$  values of Zn are found in the range -6.57 to -0.75, for the lowest value is found at the inner Gulf of Thailand (Stn.GT26) while the highest is found in Tha Chin River estuary (Stn.TC2). The result of enrichment evaluation, all  $I_{geo}$  values in dry season are practically uncontaminated.

In southwest monsoon season (July 2018), the  $I_{geo}$  values of Cd are in range from lowest at the inner Gulf of Thailand (Stn.GT36; -4.41) to highest at The Chao Phraya River estuary (Stn.CP12 ; -0.91). According to  $I_{geo}$  values of Pb are found varied in -3.93 to -1.42, the lowest value is occurred at the inner Gulf of Thailand (Stn.GT36) and the highest value is occurred at Mae Klong River estuary (Stn.MK1). The  $I_{geo}$  values of Cu range are found by lowest at the inner Gulf of Thailand (Stn.GT4;-9.57) and the highest found at Tha Chin River estuary (Stn.TC5; -3.12). As the  $I_{geo}$  values range of Co (-4.09 to -1.34) by the lowest which found at the inner Gulf of Thailand (Stn.GT36) and the highest is found at the Bangpakong River estuary (Stn.BK1).  $I_{geo}$  values of Ni are varied between -4.74 and -2.83, while the lowest value is found at the inner Gulf of Thailand (Stn.GT36) and the highest value is found at the Bangpakong River estuary (Stn.BK1).  $I_{geo}$  values of Mn are found lowest at the Maeklong River estuary (Stn.MK3; -8.09) by contrast the highest is found at the mouth of the Bangpakong river (Stn.BK13; -2.67). As Figure 4.22 the range of Zn- $I_{geo}$  values are found between -6.88 to -0.69, whereas the area that found the lowest and highest values are the inner Gulf of Thailand (Stn.GT4) and in the mouth of Tha Chin River (Stn.TC5). As be seen in Figure 4.22, the level of contamination

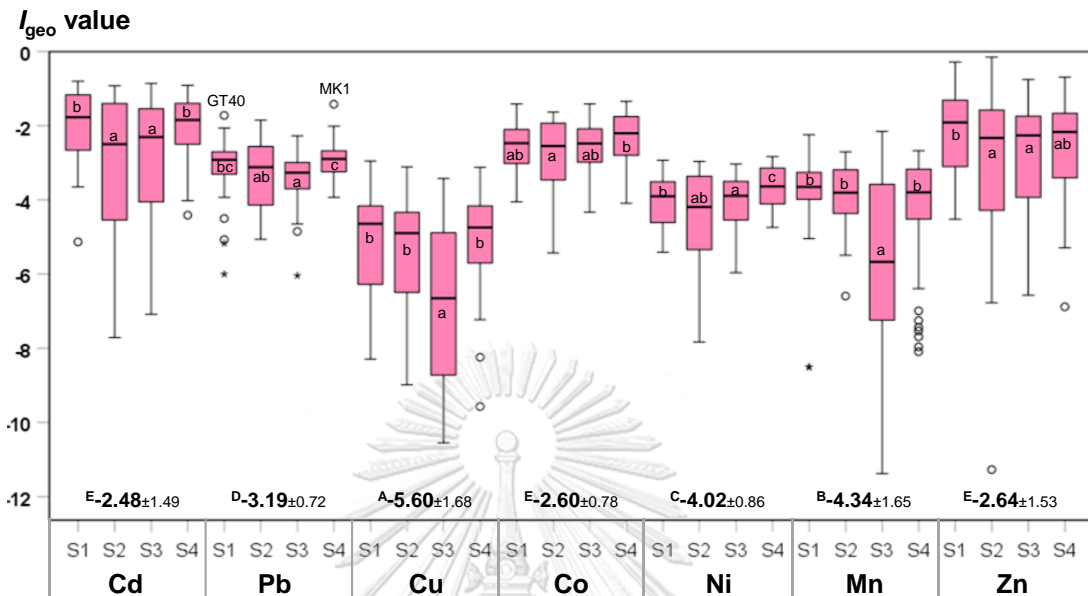
evaluation result shown that the  $I_{geo}$  values in this season are below practically uncontaminated.

As variable seasonal, the  $I_{geo}$  mean values of each heavy metals can be ordered by descending of Cd ( $-2.48 \pm 1.49$ ) > Co ( $-2.60 \pm 0.78$ ) > Zn ( $-2.64 \pm 1.53$ ) > Pb ( $-3.19 \pm 0.72$ ) > Ni ( $-4.02 \pm 0.86$ ) > Mn ( $-4.34 \pm 1.65$ ) > Cu ( $-5.60 \pm 1.68$ ). The highest  $I_{geo}$  mean value among the heavy metals are group of Cd and Zn ( $p < 0.05$ ) and the lowest mean value is Cu ( $p < 0.05$ ). The mean comparison of  $I_{geo}$  of heavy metals between seasonal, firstly Cd in southwest monsoon season in 2017 ( $-1.97 \pm 0.90$ ) is the highest while the Cd in southwest monsoon season in 2018 ( $-2.05 \pm 0.84$ ) is lower but also higher than northeast monsoon season ( $-2.98 \pm 1.86$ ) and dry season ( $-2.85 \pm 1.67$ ) ( $p < 0.05$ ). The highest mean  $I_{geo}$  of Pb is in southwest monsoon season in 2018 ( $-2.92 \pm 0.47$ ) ( $p < 0.05$ ) and the lowest mean is found in dry season ( $-3.37 \pm 0.62$ ) ( $p < 0.05$ ). The mean  $I_{geo}$  values of Cu in both southwest monsoon season (2017;  $-5.11 \pm 1.28$  and 2018;  $-5.01 \pm 1.26$ ) and northeast monsoon season ( $-5.43 \pm 1.41$ ) are not significantly different, but the lowest of mean value is found in dry season ( $-6.79 \pm 2.00$ ) ( $p < 0.05$ ). The significantly highest mean Co -  $I_{geo}$  value is in southwest monsoon season in 2018 ( $-2.36 \pm 0.68$ ) ( $p < 0.05$ ) and the significantly lowest is in northeast monsoon season ( $-2.64 \pm 0.69$ ) ( $p < 0.05$ ). The mean  $I_{geo}$  value of Ni in both southwest monsoon seasons show that mean  $I_{geo}$  value in 2018 ( $-3.65 \pm 0.54$ ) is significantly higher than mean  $I_{geo}$  value in 2017 ( $-4.05 \pm 0.65$ ) ( $p < 0.05$ ) while the lowest mean value in this season is northeast season ( $-4.38 \pm 1.19$ ) ( $p < 0.05$ ). In both southwest monsoon season in 2017 ( $-3.74 \pm 1.08$ ), in 2018 ( $-4.26 \pm 1.56$ ) and northeast monsoon season ( $-3.87 \pm 0.82$ ) the mean  $I_{geo}$  of Mn are not significantly different, but the lowest mean is found in dry season ( $-5.50 \pm 2.17$ ) ( $p < 0.05$ ). The mean of Zn in July 2017's southwest monsoon season ( $-2.14 \pm 1.14$ ) has not significantly different with the mean value in July 2018's southwest monsoon season ( $-2.47 \pm 1.25$ ) but higher than northeast monsoon season ( $-2.98 \pm 1.91$ ) and ( $-2.95 \pm 1.50$ ) ( $p < 0.05$ ).

According to the  $EF$  values which present the disturbance unnatural source in heavy metals concentration. By contrast the  $I_{geo}$  values (Figure 4.22) shown no contaminated in all heavy metals concentration which were found in this study



might be from selected background values of heavy metals in this study were likely to similar amount in study area. (Birch, 2017)



Remark: S1 is July 2017, S2 is December 2017, S3 is May 2018 and S4 is July 2018  
Alphabet indicated the significant differences between seasons and areas

**Figure 4.22** Seasonal comparisons of Geo-accumulation index ( $I_{geo}$ ) of selected heavy metals in the surface sediment.

## 4.4 Risk of Heavy Metal Contaminations in the Surface Sediment

### 4.4.1 Potential ecological risk

As the result of heavy metal contaminations in surface sediment, the concentration of each element which exceeded sediment quality guidelines can affected the benthic organism. However, organisms could receive one or more pollutants. Then potential ecological risk ( $E_r$ ) is an index of ecological risk assessment which commonly use to evaluate the level of pollution of various elements in surface sediment.

In southwest monsoon season (July 2017),  $E_r$  values of Cd are found in range of 0.54 – 10.83, while the lowest  $E_r$  is found at the inner Gulf of Thailand (Stn.GT26) and the highest  $E_r$  is found at the Bangpakong River estuary (Stn.BK12).  $E_r$  values of Pb are varied in range start with the lowest at the inner Gulf of Thailand(Stn.GT1; 0.13) to the highest at the Mae Klong River estuary (Stn.MK1; 2.6). The highest  $E_r$  values of Cu in this season is at the inner part of

the Tha Chin River estuary (Stn.TC1; 4.85) while the lowest  $E_r$  values located at the inner Gulf of Thailand (Stn.GT17; 0.12).  $E_r$  values of Co are found in range of 1.81 – 11.27, the lowest  $E_r$  is located at the inner Gulf of Thailand (Stn.GT26) while the highest  $E_r$  is found at the Bangpakong River estuary (Stn.BK7). The lowest  $E_r$  of Ni in this season is located at the inner Gulf of Thailand (Stn.GT27; 0.80) and the highest  $E_r$  is in the Tha Chin River estuary (Stn.TC14; 4.46).  $E_r$  values of Mn are found in range of 0.07 – 5.78, by the lowest is found at the inner Gulf of Thailand (Stn.GT17) and the highest is found at Mae Klong River estuary (Stn.MK1).  $E_r$  values of Zn are found in the range of 0.06 – 1.16, the lowest is located at the inner Gulf of Thailand (Stn.GT35) and the highest is found at Tha Chin River estuary (Stn.TC1).

In northeast monsoon season (December 2017),  $E_r$  values of Cd are found in range of 0.09 – 9.97. The lowest  $E_r$  value is located at the inner Gulf of Thailand (Stn.GT39) while the highest is located at The Chao Phraya River estuary (Stn.CP7).  $E_r$  values of Pb are varied from the lowest at the inner Gulf of Thailand (Stn.GT39; 0.26) to the highest which be found at Tha Chin River estuary (Stn.TC1; 2.39).  $E_r$  values of Cu are found in the range of 0.07 – 4.34, the lowest  $E_r$  is found at the inner Gulf of Thailand (Stn.GT20) and the highest  $E_r$  is found at Tha Chin River estuary (Stn.TC1).  $E_r$  values of Co are found in the range of 0.70 – 9.66, the lowest  $E_r$  is located at the inner Gulf of Thailand (Stn.GT20) and the highest is located at The Chao Phraya River estuary (Stn.CP8).  $E_r$  values of Ni are found varied from lowest at the inner Gulf of Thailand (Stn.GT20;0.15) while the highest is located at The Chao Phraya River estuary (Stn.CP8;4.36).  $E_r$  values of Mn are found in the range of 0.28 – 4.21, the lowest  $E_r$  is found at the inner Gulf of Thailand (Stn.GT38) and the highest  $E_r$  is found at the Bangpakong River estuary (Stn.BK7).  $E_r$  values of Mn are found in the range of 0.00 – 1.28, the lowest value is found at the inner Gulf of Thailand (Stn.GT28) and the highest value is found at Tha Chin River estuary (Stn.TC1).

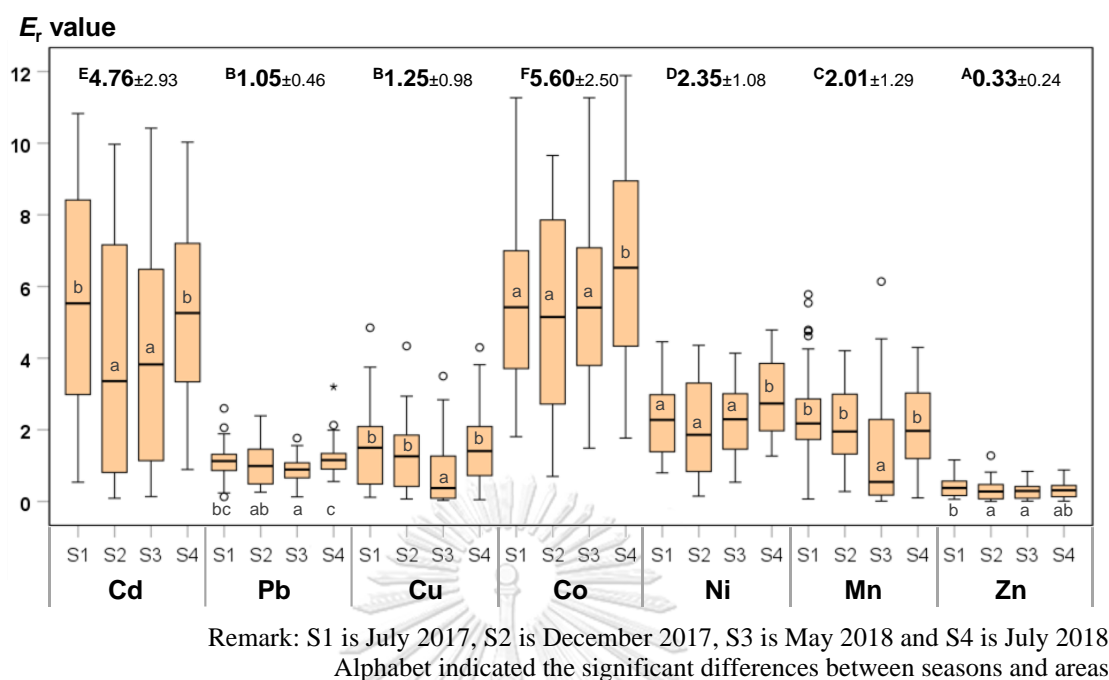
In dry seasons (May 2018),  $E_r$  values of Cd are found lowest at the inner Gulf of Thailand (Stn.GT39;0.09) and the highest at The Chao Phraya River estuary(Stn.CP7;9.97).  $E_r$  values of Pb are found in range of 0.26 – 2.39, the lowest is found at the inner Gulf of Thailand (Stn.GT39) and the highest is found

at the Tha Chin River estuary (Stn.TC1).  $E_r$  values of Cu are varied from 0.07 to 4.34, the lowest  $E_r$  is found at the inner Gulf of Thailand (Stn.GT20) and the highest  $E_r$  is found at the the Tha Chin River estuary (Stn.TC1). The lowest of Cobalt's  $E_r$  value is found at the inner Gulf of Thailand (Stn.GT20; 0.70) while the highest  $E_r$  values is found at the Chao Phraya River estuary (Stn.CP8; 9.66).  $E_r$  values of Ni are found in range of 0.15 – 4.36, the lowest  $E_r$  value is occurred at the inner Gulf of Thailand (Stn.GT20) and the highest  $E_r$  value is occurred at the Chao Phraya River estuary (Stn.CP8).  $E_r$  values of Mn are found in the range of 0.28 – 4.21, the lowest  $E_r$  value is found at the inner Gulf of Thailand (Stn.GT38) and the highest  $E_r$  values is found at the Bangpakong River estuary (Stn.BK7).  $E_r$  values of Zn are found in the range of 0.00 – 1.28, the lowest  $E_r$  value is located at the inner Gulf of Thailand (Stn.GT28) and the highest  $E_r$  value is located at Tha Chin River estuary (Stn.TC1).

In southwest monsoon season (July 2018),  $E_r$  values of Cd are found in the range of 0.89 – 10.03. The minimum  $E_r$  value is found at the inner Gulf of Thailand (Stn.GT36) while the maximum  $E_r$  value is located at the Chao Phraya River estuary (Stn.CP12).  $E_r$  values of Pb are found in the range of 0.56 – 3.20, the lowest  $E_r$  value is found at the inner Gulf of Thailand (Stn.GT36).  $E_r$  values of Cu are found in the range of 0.05 – 4.30, the lowest  $E_r$  value is found at the inner Gulf Thailand (Stn.GT4) and the highest  $E_r$  value is found at the Tha Chin River estuary (Stn.TC5). The lowest  $E_r$  value of Co is found at the inner Gulf of Thailand (Stn.GT36; 1.77) while the highest  $E_r$  value is found at the Bangpakong River estuary (Stn.BK1; 11.89).  $E_r$  values of Ni are found in range of 1.27 – 4.79, the lowest is found at the inner Gulf of Thailand (Stn.GT36) and the highest is found at the Bangpakong River estuary (Stn.BK7).  $E_r$  values of Mn are found in range of 0.10 – 4.30, the lowest  $E_r$  is found at the Mae Klong River estuary (Stn.MK3) and the highest  $E_r$  is found at the Bangpakong River estuary (Stn.BK13). The lowest  $E_r$  value of Zn is found at the inner Gulf of Thailand (Stn.GT4; 0.01) while the highest  $E_r$  value is found at the Tha Chin River estuary (Stn.TC5; 0.88).

According to level of risk index classification in Figure 4.23, all  $E_r$  values in this study are considered as low potential ecological risk. The  $E_r$  mean values

of each heavy metals can be ordered by descending of Co ( $5.60 \pm 2.50$ ) > Cd ( $4.76 \pm 2.93$ ) > Ni ( $2.35 \pm 1.08$ ) > Mn ( $2.01 \pm 1.29$ ) > Cu ( $1.25 \pm 0.98$ ) > Pb ( $1.05 \pm 0.46$ ) > Zn ( $0.33 \pm 0.24$ ). For Cd, southwest monsoon season in 2017 ( $5.68 \pm 2.94$ ) and 2018 ( $5.25 \pm 2.40$ ) are significantly higher ( $p < 0.05$ ) than northeast monsoon season ( $4.15 \pm 3.19$ ) and dry season ( $4.04 \pm 2.68$ ). For Pb, mean  $E_r$  of southwest monsoon season in 2018 ( $1.20 \pm 0.43$ ) is significantly higher ( $p < 0.05$ ) than southwest monsoon season in 2017 ( $1.12 \pm 0.45$ ) and northeast monsoon season ( $1.00 \pm 0.55$ ). The significantly lowest mean of Pb is from dry season ( $0.89 \pm 0.31$ ) ( $p < 0.05$ ). Both southwest monsoon season in 2017 ( $1.48 \pm 1.00$ ), 2018 ( $1.55 \pm 1.00$ ), and northeast monsoon season ( $1.25 \pm 0.89$ ) of Cu are higher than dry season ( $0.74 \pm 0.83$ ) ( $p < 0.05$ ). The mean value of Co in 2018's southwest monsoon season ( $6.47 \pm 2.65$ ) is higher ( $p < 0.05$ ) than mean value in 2017's southwest monsoon ( $5.52 \pm 2.24$ ), northeast monsoon ( $5.20 \pm 2.74$ ), and dry seasons ( $5.31 \pm 2.12$ ). The mean value of Ni in 2018's southwest monsoon season ( $2.90 \pm 1.02$ ) is higher ( $p < 0.05$ ) than 2017's southwest monsoon ( $2.25 \pm 0.92$ ), northeast monsoon ( $2.12 \pm 1.27$ ), and dry seasons ( $2.21 \pm 0.90$ ). The mean value of Mn in southwest monsoon in 2017 ( $2.43 \pm 1.18$ ), in 2018 ( $2.07 \pm 1.26$ ), and northeast monsoon seasons ( $2.15 \pm 1.04$ ) are higher ( $p < 0.05$ ) than dry season ( $1.37 \pm 1.42$ ). The mean value of Zn in 2017's southwest monsoon season ( $0.42 \pm 0.27$ ) is significantly higher than northeast monsoon ( $0.31 \pm 0.25$ ) and dry season ( $0.27 \pm 0.19$ ) while the significantly difference between mean value of southwest monsoon season in 2018 ( $0.34 \pm 0.22$ ) and the others are not observed.



**Figure 4.23** Seasonal comparisons of Potential ecological risk ( $E_r$ ) of selected heavy metals in the surface sediment.

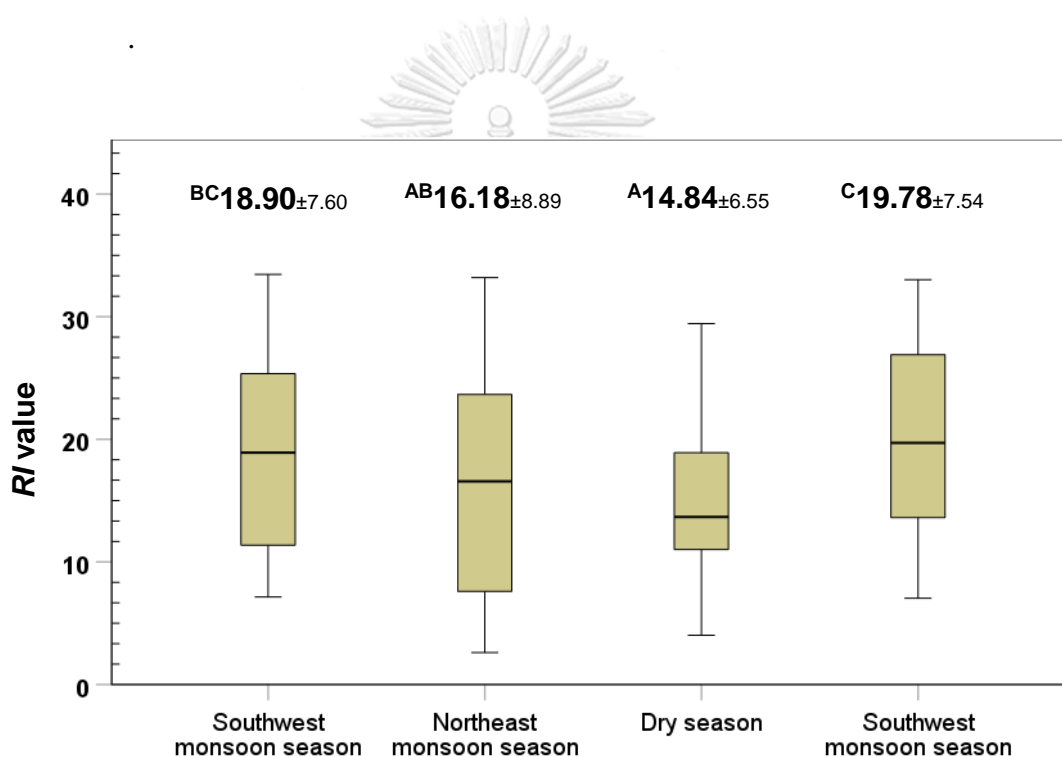
#### 4.4.2 Risk index

Risk index ( $RI$ ) was calculated from combined selected heavy metal's  $E_r$  in each station. As although all  $E_r$  values in study area are considered as low potential ecological risk, but the various pollutants can be sink surface sediment the combined  $E_r$  or  $RI$  could be more advantage to discuss the hazard identify in ecological.

First, the highest  $RI$  value in southwest monsoon season (July 2017) is found at the Bangpakong River estuary (Stn.BK1;  $RI = 33.45$ ) and the lowest is found at the inner Gulf of Thailand (Stn.GT34;  $RI = 7.04$ ). Then in northeast monsoon season (December 2017), the highest  $RI$  value is found at the Tha Chin River estuary (Stn.TC1;  $RI = 33.20$ ) while the lowest is found at the inner Gulf of Thailand (Stn.GT38;  $RI = 2.61$ ). In dry season (May 2018), the highest  $RI$  value is found at the the Tha Chin River estuary (Stn.TC2;  $RI = 29.44$ ) whereas the lowest  $RI$  value is found at the Mae Klong River estuary (Stn.MK4;  $RI = 4.02$ ). Lastly, the highest  $RI$  value in southwest monsoon season (July 2018) is found at the Bangpakong River estuary (Stn.BK1;  $RI = 33.02$ ) and the lowest is found at

the inner Gulf of Thailand (Stn.GT34;  $RI = 7.04$ ). As seen in Figure 4.24, every seasonal  $RI$  value are considered as low risk level ( $RI < 150$ ).

However, the results suggest all of station in 4 seasons were considered as low ecological risk but the seasonal mean  $E_r$  values of Cd and Co were at least 2-fold higher than the other metals. Then the concentration of Cd and Co might act as main contributor of seasonal ecological risk in this study, neither the Zn concentration which also was influenced by anthropogenic source but was not main contributor.



Remark: Alphabet indicated the significant differences between seasons and areas  
**Figure 4.24** Seasonal comparisons of risk index (RI) in the surface sediment of selected heavy metals.

#### 4.5 Regulating factors of Heavy Metal Concentration in the Surface Sediment

The correlation between heavy metals and sedimentary properties is represented in Table 4.3 in order to determine the regulating factors of heavy metal changes in the surface sediment of the inner Gulf of Thailand. The Pearson's correlation coefficient represented significant relationship ( $p < 0.01$ ) of almost all heavy metals have strong correlation excluding the pair of these the significant correlation in  $p < 0.05$  level; Zn-

Pb in southwest monsoon season (July 2017), Cu-Pb and Ni-Mn in dry season, Cd-Pb Cd-Zn Pb-Al, Zn-Al, and Mn-Al in southwest monsoon season (July 2018), by contrast in these pairs relationship are not found following seasons; first in southwest monsoon season (July 2017) are Pb-Al and Zn-Mn, in northeast monsoon season (December 2017) are Pb-Al and Zn-Al, in dry season are Cd-Mn, Pb-Mn, and Pb-Mn in southwest monsoon season (July 2018).

As a result, strong positive correlations between the heavy metals indicate that those metals might have derived from common sources with mutual dependency and similar behavior during their transport. Whereas, a weak correlation between some of the metals indicate that the concentration of these metals might have been influenced by a combination of a number of factors such as variable contribution and mixing of sediments derived from varied geological units, sediment textural variability, geochemical affinity and mobility of metals, variation in natural and anthropogenic sources as well as the properties of these heavy metals, including TOM, TOC, TP and AVS.

The positive correlation coefficients are shown to represent the significant correlation ( $p < 0.01$ ) between heavy metal and related parameters (TOM, TOC, TP, AVS, and WC) excepts these pairs following as season; southwest monsoon season in July 2017 (Ni-TOC, Al-TP, Co-AVS, Mn-AVS, and Mn-WC), dry season (Cd-TOM, Mn-TOM, Mn-TP, Cd-AVS, Pb-AVS, Al-AVS, Pb-WC, and Mn-WC), southwest monsoon season in July 2018 (Pb-TOM, Mn-TOM, Cd-TOM, Mn-TOM, Cd-TOC, Zn-TOC, Cd-AVS, and Pb-AVS) are found significant correlated at  $p < 0.05$  level. While in these pairs the correlations are not show; in southwest monsoon season in 2017 (Cd-TOC, Pb-TOC, Cu-TOC, Co-TOC, Mn-TOC, Zn-TOC, and Al-TOC), in northeast monsoon season in December 2017 (Al-AVS), in dry season (Pb-TOM), and southwest monsoon season in July 2018 (Zn-TOM, Al-TOC, Al-TP, Al-AVS, and Pb-AVS).

As a result, the metals like Cd, Pb, Cu, Co, Ni, M and Zn almost showed a positive correlation with TOM in the surface sediment. TP also has positive relation with clay particles. ((Sheela et al., 2014). The heavy metals are adsorbed onto the clay particles due to the increase in specific surface area and a net negative charge on the

surface of clay particles (Grant & Middleton, 1990). Sand and silt fractions are mainly composed of primary minerals like quartz, which are very weak adsorbent for heavy metals (Yao et al., 2021). Apart from the natural sources of the heavy metals, the input from agricultural lands and Kule farming sites might also have contributed to the higher concentration of heavy metals in the upstream sites. These paddy fields occupy a significant part of the backwater, where the seasonal paddy cultivation is carried out mainly during the summer season (Razia Beevi et al., 2009). It was also observed that Mn concentrations were high during monsoon season at all the stations (Fig. 4), which is possibly due to the increased supply through different hydrological regimes (i.e., rain, flooding, and inundation). The cycling of Mn in estuaries is dominated by natural processes such as river inputs, particle desorption, and sediment remobilization (M. Yang & Sañudo-Wilhelmy, 1998). Geological units such as Charnockite Group rocks and Quaternary sequences present in the study area might have contributed to high Mn through weathering processes and river discharge. Mn is also sensitive to the redox condition which regulates the mobility of Mn and explains relatively high concentration in estuarine and marine waters (Dehairs et al., 1989; Dehairs et al., 1989; Ouddane et al., 1997). It is reported that these hydrological systems can influence metal transport (Conrad et al., 2020). The regulator mechanism in the back-water which act as a corridor for water circulation may also influence the sediment flux entering or exiting the Biyyam Kayal during its seasonal operation and might as well contribute to the spatial and seasonal variation in heavy metal (such as high Mn) concentration in the back-water. Also, few studies suggest that groundwater discharge through floodwater subsidence constitutes a considerable portion of metal loading to downstream waterways (Berka et al., 2001; Santos et al., 2011).



**Table 4.3** Correlation among Heavy metal and Physicochemical Characteristics of the Surface Sediment

	Cd	Pb	Cu	Co	Ni	Mn	Zn	Al	TOM	TOC	TP	AVS	WC	
Southwest monsoon season (July 2017)	Cd	1	.439**	.594**	.898**	.871**	.481**	.445**	.455**	.408**	0.181	.650**	.344**	.724**
	Pb		1	.476**	.289*	.492**	.415**	.274*	0.242	0.070	0.005	.462**	0.213	0.174
	Cu			1	.547**	.739**	.423**	.748**	.342**	.420**	0.074	.740**	.512**	.626**
	Co				1	.837**	.507**	.531**	.490**	.449**	0.201	.563**	.309*	.684**
	Ni					1	.461**	.652**	.543**	.612**	.295*	.699**	.522**	.826**
	Mn						1	0.219	.481**	0.051	-0.033	.356**	0.229	.328*
	Zn							1	.489**	.519**	0.166	.547**	.356**	.625**
	Al								1	.338**	0.153	.304*	.343**	.570**
	TOM									1	.660**	.342**	.338**	.690**
	TOC										1	0.212	0.146	.330*
	TP											1	.335**	.582**
	AVS												1	.464**
	WC													1
	Northeast monsoon season (December 2017)	Cd	1	.651**	.701**	.752**	.744**	.567**	.579**	.606**	.513**	.408**	.503**	.295*
Pb			1	.805**	.724**	.732**	.704**	.902**	0.219	.523**	.309*	.490**	.408**	.553**
Cu				1	.868**	.880**	.651**	.806**	.477**	.709**	.552**	.695**	.524**	.795**
Co					1	.976**	.734**	.649**	.678**	.788**	.470**	.664**	.499**	.869**
Ni						1	.688**	.641**	.691**	.812**	.506**	.665**	.514**	.880**
Mn							1	.627**	.359**	.538**	.415**	.584**	.469**	.703**
Zn								1	0.158	.465**	.304*	.463**	.364**	.475**
Al									1	.612**	.457**	.425**	0.191	.694**
TOM										1	.540**	.634**	.456**	.811**
TOC											1	.647**	.522**	.712**
TP												1	.588**	.751**
AVS													1	.617**
WC														1
Dry season (May 2018)		Cd	1	.471**	.397**	.689**	.677**	0.142	.600**	.466**	.285*	.572**	.559**	.315*
	Pb		1	.292*	.553**	.604**	0.154	.344**	.548**	0.242	.441**	.445**	.312*	.292*
	Cu			1	.360**	.469**	.819**	.755**	.344**	.524**	.634**	.547**	.461**	.584**
	Co				1	.906**	0.217	.653**	.636**	.546**	.593**	.625**	.370**	.662**
	Ni					1	.280*	.674**	.602**	.646**	.656**	.630**	.446**	.674**
	Mn						1	.533**	.270*	.328*	.368**	.310*	.402**	.337*
	Zn							1	.535**	.566**	.706**	.714**	.441**	.754**
	Al								1	.390**	.471**	.503**	.344*	.505**
	TOM									1	.706**	.579**	0.252	.686**
	TOC										1	.820**	.417**	.761**
	TP											1	.546**	.692**
	AVS												1	.274*
	WC													1
	Southwest monsoon season (July 2018)	Cd	1	.295*	.464**	.655**	.580**	.507**	.329*	.366**	.327*	.313*	.306*	.347*
Pb			1	.559**	.457**	.522**	0.036	.356**	.280*	0.228	.300*	.464**	.355*	0.166
Cu				1	.769**	.830**	.599**	.857**	.361**	.494**	.566**	.693**	.590**	.592**
Co					1	.942**	.735**	.614**	.636**	.568**	.556**	.643**	.517**	.716**
Ni						1	.636**	.647**	.594**	.679**	.634**	.698**	.584**	.727**
Mn							1	.598**	.302*	.333*	.410**	.474**	.430**	.609**
Zn								1	.278*	0.263	.340*	.487**	.492**	.400**
Al									1	.390**	0.190	0.209	0.081	.372**
TOM										1	.791**	.470**	.357*	.656**
TOC											1	.558**	.355*	.567**
TP												1	.510**	.551**
AVS													1	.444**
WC														1

Remark: \* Correlation is significant at the 0.05 level, \*\* Correlation is significant at the 0.01 level.

Principal component analysis (PCA) was also applied to further analyze the sources of the heavy metals in the sediment, which can reduce a large number of variables to a few component variables that explain the variability. The PCA was preceded by a Kaiser Meyer Olkin (KMO) test to ensure the sampling adequacy. The KMO statistic values were 0.780, 0.870, 0.840, 0.854 and 0.884 for southwest monsoon and northeast monsoon seasons (2017), dry season (2018), southwest monsoon season (2018) and all seasons, respectively. The significance probabilities of Bartlett's spherical test were 0.000, which were valid for the further analyzes. Here, the concentrations of Cd, Pb, Cu, Co, Ni, Mn, Zn, Al and sediment properties including TOM, TOC, TP, AVS and WC were subjected to PCA after the correlation test (Table 4.4–5).

In southwest monsoon season of 2017, two principal components explained 63.46% of the total variance (Table 4.4). The PC1 accounted for 42.28% of the variance and presented high positive loadings for Ni, Cd, Cu, Co, Mn, Pb, Zn, TP, and WC. It indicated that they may have homologous sources and similar geochemical behaviors. The PC2 contributed 21.18% of the variance and presented high positive loadings for WC, TOM and TOC.

In northeast monsoon season of 2017, three principal components were extracted from PCA in surface sediment; they explained 27.93%, 27.77% and 25.91% of the total variance, respectively (Table 4.4). The PC1 of the variance and presented high positive loadings Zn, Pb and Cu. It indicated that they may have homologous sources and similar geochemical behaviors. While the PC2 of the variance and presented high positive loadings for Al, Ni, Co, Cd, TOM, and WC. Finally, the PC3 of the variance and presented high positive loadings for WC, AVS and TOC. Three principal components explained 81.64% of the total variance.

In dry season 2018, three components were extracted, accounting for 75.74% of the total variance (Table 4.4). The PC 1 accounted for 30.67% of the variance; TOM, WC, TOC, TP, and Zn had a higher positive load (0.645–0.861). The PC2 accounted for 25.51% of the variance and Pb, Co, Ni, Al and Cd had a higher positive load (0.683–0.856). The PC3 accounted for 18.55% of the variance and Mn, Cu and AVS had the largest positive load (0.611–0.919).

In southwest monsoon season of 2018, three principal components explained 75.50% of the total variance (Table 4.4). The PC1 accounted for 32.78% of the

variance and presented high positive loadings for Mn, Co, Al, Zn, Ni, Cd and WC. It indicated that they may have homologous sources and similar geochemical behaviors. The PC2 contributed 22.42% of the variance and presented high positive loadings for WC, TOM and TOC. the PC3 contributed 20.29% of the variance and presented high positive loadings for Cu and TP.

For all data of four different seasons, the results showed that a total of 3 factors, which represent 70.02 % of a total variance, were extracted by PCA and a factor loading matrix after varimax rotation was obtained (Table 4.5). Factor 1, with 26.77% of variance after rotation, is positively loaded with strong loadings for Cu, Pb, Zn, and Mn. Factor 2, with 23.21% of variance after rotation, is positively loaded with high loadings for TOM, TOC and WC, so that is a factor related to organic matter and carbon, also representing the origin from anthropogenic source. Factor 3, with 20.05% of variance, is positively loaded with Al, Co and Ni. Therefore, factor 3 represents terrigenous aluminum minerals, indicated that Co and Ni can be identified to be originated from lithogenic source (Karageorgis et al., 2012).

In coastal enclosed bay systems, the distribution and migration of heavy metals in sediments is largely controlled by the complex interactions of various physical and biochemical processes (Sun et al., 2018). According to correlation analysis and PCA, the present study was also indicated that Cd, Pb, Cu, Co, Ni, Mn, Zn concentrations in the surface sediments of the inner Gulf of Thailand are controlled due to various processes entire the area and variations of season.

**Table 4.4** Principal component analysis of heavy metals and other environmental factors in the surface sediment of the inner Gulf of Thailand.

Season	Variable	Component			h <sup>2</sup>
		1	2	3	
Southwest monsoon season (2017)	Ni	0.844			0.918
	Cd	0.822			0.750
	Cu	0.800			0.695
	Co	0.768			0.699
	TP	0.740			0.603
	Mn	0.713			0.549
	Pb	0.664			0.486
	Zn	0.607			0.558
	WC	0.640		0.626	0.802
	TOM			0.890	0.852
	TOC			0.795	0.636
	Al				0.394
	AVS				0.308
	Eigen values		5.496	2.753	
% of Variance		42.276	21.180		
Cumulative %		42.276	63.457		
Northeast monsoon season (2017)	Zn	0.936			0.911
	Pb	0.929			0.933
	Cu	0.684			0.866
	Al			0.935	0.900
	Ni			0.723	0.931
	Co			0.711	0.920
	Cd			0.637	0.695
	TOM			0.621	0.707
	WC			0.648	0.920
	AVS				0.649
	TOC				0.855
	TP				0.778
	Mn				0.759
	Eigen values		3.634	3.611	3.368
% of Variance		27.953	27.775	25.911	
Cumulative %		27.953	55.728	81.639	
Dry season (2018)	TOM	0.861			0.775
	WC	0.840			0.822
	TOC	0.795			0.790
	TP	0.664			0.685
	Zn	0.645			0.772
	Pb			0.856	0.736
	Co			0.743	0.850
	Ni			0.712	0.850
	Al			0.706	0.632
	Cd			0.683	0.590
	Mn				0.919
	Cu				0.826
	AVS				0.611
	Eigen values		3.988	3.446	2.412
% of Variance		30.674	26.509	18.553	
Cumulative %		30.674	57.183	75.736	
Southwest monsoon season (2018)	Ni	0.882			0.812
	Co	0.760			0.900
	Al	0.739			0.727
	Zn	0.665			0.749
	Ni	0.651			0.915
	Cd	0.636			0.495
	WC	0.616		0.605	0.749
	TOM			0.884	0.843
	TOC			0.804	0.759
	Pb	0.607			0.670
	Cu				0.881
	TP				0.692
	AVS				0.484
	Eigen values		4.261	2.915	2.638
% of Variance		32.780	22.422	20.295	
Cumulative %		32.780	55.202	75.496	

**Table 4.5** Principal component analysis of heavy metals and other environmental factors in all surface sediment during four different seasons of the inner Gulf of Thailand.

Variable	Component			h <sup>2</sup>
	1	2	3	
Cu	0.795			0.830
Pb	0.764			0.642
Zn	0.723			0.661
Mn	0.642			0.492
TOM		0.823		0.766
TOC		0.766		0.660
WC		0.695		0.803
Al			0.854	0.747
Co			0.729	0.876
Ni			0.678	0.881
Cd				0.639
TP				0.583
AVS				0.524
Eigen values	3.480	3.017	2.606	
% of Variance	26.771	23.206	20.047	
Cumulative %	26.771	49.977	70.025	



# CHAPTER 5

## RESEARCH CONCLUSION

---

The Master's Thesis describes the results of a four-season research into the spatiotemporal distribution of heavy metals and environmental variables in a coastal environment of the inner Gulf of Thailand. Data analysis by making a comparison of  $SOG_s$ ,  $EF$  and  $I_{geo}$  values and linking them with  $E_r$  and  $RI$  of the whole study area with the help of the highest and lowest measured concentration of each heavy metal gave a great result in specifying more comprehensive and unique understanding to the overall and specific contamination and risk of the studied area. The specific results of my deliberation can be concluded as follow:

### 5.1 Spatiotemporal Heterogeneity Distributions and Regulating Factors

5.1.1 The concentration of Cd, Pb, Cu, Co, Ni, Mn and Zn in the surface sediment of the inner Gulf of Thailand varied spatially in the range of 0.003–0.36 mg/kg, 1.82–44.86 mg/kg, 0.25–48.54 mg/kg, 2.58–44.00 mg/kg, 1.48–47.57 mg/kg, 3.77–2259.28 mg/kg, and 0.10–223.37 mg/kg, respectively. Average heavy metal concentrations in the surface sediments followed the order Mn ( $738.43 \pm 475.20$  mg/kg) > Zn ( $58.49 \pm 42.45$  mg/kg) > Ni ( $23.40 \pm 10.74$  mg/kg) > Co ( $20.72 \pm 9.24$  mg/kg) > Pb ( $14.69 \pm 6.43$  mg/kg) > Cu ( $12.48 \pm 9.83$  mg/kg) > Cd ( $0.16 \pm 0.10$  mg/kg). As a result, heavy metals were relatively high concentrations in the river estuaries, which are much more subjected to anthropogenic pressures, resulting in a higher sedimentation rate of various pollutants, particularly heavy metals.

5.1.2 Spatiotemporal distribution in the southwest monsoon, the northeast monsoon and the dry seasons demonstrated the seasonal changes were significantly influenced the heavy metal concentrations in the surface sediment of the inner Gulf of Thailand, particularly the dry season of 2018 and southwest monsoon of 2018.

5.1.3 Pearson correlation analysis showed Cd, Pb, Cu, Co, Ni, Mn and Zn were positively correlated with Al, TOM, TOC, TP and AVS in the surface sediment. Spatial variation can be explained by the variations in the environmental conditions. It has been observed that the spatial distribution of the heavy metals is strongly associated with the sediment, which in turn is a direct result of the physicochemical properties of the sediment, each with a varying tendency to accumulate metals. As a result, interact with heavy metal pollution by affecting organic matter productions and the redox potentials and indicating similar metal sources. Moreover, our findings suggest that sediment physicochemical factors, such as TOM, TOC, TP and AVS, strongly influenced the distribution and fate of heavy metals.

## 5.2 Contamination Status

The comprehensive assessments of  $SQGs$ ,  $EF$  and  $I_{geo}$  in the surface sediment of the inner Gulf of Thailand exhibited no enrichment and no contamination for Cd, Pb, Cu, Co, Ni, Mn and Zn. while Cd and Zn fluctuated from minor to moderately severe enrichment and contamination, whereas Pb and Co recorded minor enrichment but did not reach the point of contamination. The pollution degree from 7 heavy metals decreased in the sequence of  $Cd > Zn > Co > Pb > Mn > Ni > Cu$  for the  $EF$  and  $I_{geo}$ .

## 5.3 Potential Ecological Risk

The  $E_r$  of heavy metals of all station are considered as low potential ecological risk ( $E_r < 40$ ). The  $RI$  of Cd, Pb, Cu, Co, Ni, Mn and Zn are between 2.61–33.45 then all stations are considered as low risk level due to the  $RI$  in all seasons ( $RI < 150$ ).

## 5.4 Future Research

Further studies are needed to better understand the dynamics of pollutants, particularly heavy metals in this area, and adopt consequently strict recommendations to decrease the level of metallic pollution in this transitional system. Additional

studies will be additionally and continuously investigated according to various reasons as follow:

1. Detected heavy metals are needed to define exact sources because the identifying the sources of pollution and the factors controlling heavy metals release are equally important, to protect the local environment.
2. Total content is not sufficient since the toxicity, bioavailability and mobility are largely depended on the chemical fractions and binding state rather than total content. Heavy metal fractionations can provide more accurate indexes about the pollution level of bioavailability and mobility. The risk assessment code (RAC) calculated as the ratios of exchangeable and carbonate fractions to total contents is often used to represent the mobility, and bioavailability of heavy metals in sediment. Therefore, the optimization of the sequential extraction procedure for analysis of chemical fractionations of heavy metals in the surface sediment.
3. The findings of this study indicated that it is very necessary to operate long-term continuously monitoring and ecological risk assessment of these heavy metals, especially Cd and Co, in the inner Gulf of Thailand reclaimed for food security and human health



## REFERENCES

- Aspila, K. I., Agemian, H., & Chau, A. S. Y. (1976). A semi-automated method for the determination of inorganic, organic and total phosphate in sediments. *The Analyst*, *101*(1200), 187. <https://doi.org/10.1039/an9760100187>
- Barbieri, M. (2016). The Importance of Enrichment Factor (EF) and Geoaccumulation Index (Igeo) to Evaluate the Soil Contamination. *Journal of Geology & Geophysics*, *5*(1). <https://doi.org/10.4172/2381-8719.1000237>
- Berka, C., Schreier, H., & Hall, K. (2001). Linking Water Quality with Agricultural Intensification in a Rural Watershed. *Water, Air, and Soil Pollution*, *127*(1/4), 389–401. <https://doi.org/10.1023/A:1005233005364>
- Birch, G. F. (2017). Determination of sediment metal background concentrations and enrichment in marine environments – A critical review. *Science of The Total Environment*, *580*, 813–831. <https://doi.org/10.1016/j.scitotenv.2016.12.028>
- Bordalo, A. A., Nilsumranchit, W., & Chalermwat, K. (2001). Water quality and uses of the Bangpakong River (eastern Thailand). *Water Research*, *35*, 3635–3642. [https://doi.org/10.1016/s0043-1354\(01\)00079-3](https://doi.org/10.1016/s0043-1354(01)00079-3)
- Buchman, M. F. (2008). NOAA Screening Quick Reference Tables. *NOAA: Seattle*, 1–34.
- Cai, P., Cai, G., Chen, X., Li, S., & Zhao, L. (2021). The concentration distribution and biohazard assessment of heavy metal elements in surface sediments from the continental shelf of Hainan Island. *Marine Pollution Bulletin*, *166*(March), 112254. <https://doi.org/10.1016/j.marpolbul.2021.112254>
- Censi, P., Spoto, S. E., Saiano, F., Sprovieri, M., Mazzola, S., Nardone, G., Di

- Geronimo, S. I., Punturo, R., & Ottonello, D. (2006). Heavy metals in coastal water systems. A case study from the northwestern Gulf of Thailand. *Chemosphere*, 64(7), 1167–1176. <https://doi.org/10.1016/j.chemosphere.2005.11.008>
- Chaiyarak, B., Tattiyakul, G., & Karnsunthad, N. (2019). *Climate Change Vulnerability Assessment Bang Pakong River Wetland, Thailand*. 76.
- Christophoridis, C., Bourliva, A., Evgenakis, E., Papadopoulou, L., & Fytianos, K. (2019). Effects of anthropogenic activities on the levels of heavy metals in marine surface sediments of the Thessaloniki Bay, Northern Greece: Spatial distribution, sources and contamination assessment. *Microchemical Journal*, 149(March), 104001. <https://doi.org/10.1016/j.microc.2019.104001>
- Conrad, S. R., Santos, I. R., White, S. A., Hessey, S., & Sanders, C. J. (2020). Elevated dissolved heavy metal discharge following rainfall downstream of intensive horticulture. *Applied Geochemistry*, 113, 104490. <https://doi.org/10.1016/j.apgeochem.2019.104490>
- D. Krom, M., & A. Berner, R. (1981). The diagenesis of phosphorus in a nearshore marine sediment. *Geochimica et Cosmochimica Acta*, 45(2), 207–216. [https://doi.org/10.1016/0016-7037\(81\)90164-2](https://doi.org/10.1016/0016-7037(81)90164-2)
- Das, K. K., Reddy, R. C., Bagoji, I. B., Das, S., Bagali, S., Mullur, L., Khodnapur, J. P., & Biradar, M. S. (2019). Primary concept of nickel toxicity – an overview. *Journal of Basic and Clinical Physiology and Pharmacology*, 30(2), 141–152. <https://doi.org/10.1515/jbcpp-2017-0171>
- Dash, S., Borah, S. S., & Kalamdhad, A. S. (2021). Heavy metal pollution and potential

- ecological risk assessment for surficial sediments of Deepor Beel, India. *Ecological Indicators*, 122(December 2020), 107265. <https://doi.org/10.1016/j.ecolind.2020.107265>
- Dehairs, F., Baeyens, W., & Van Gansbeke, D. (1989). Tight coupling between enrichment of iron and manganese in North Sea suspended matter and sedimentary redox processes: Evidence for seasonal variability. *Estuarine, Coastal and Shelf Science*, 29(5), 457–471. [https://doi.org/10.1016/0272-7714\(89\)90080-2](https://doi.org/10.1016/0272-7714(89)90080-2)
- Ding, X., Ye, S., Yuan, H., & Krauss, K. W. (2018). Spatial distribution and ecological risk assessment of heavy metals in coastal surface sediments in the Hebei Province offshore area, Bohai Sea, China. *Marine Pollution Bulletin*, 131(May), 655–661. <https://doi.org/10.1016/j.marpolbul.2018.04.060>
- El Zrelli, R., Yacoubi, L., Wakkaf, T., Castet, S., Grégoire, M., Mansour, L., Courjault-Radé, P., & Rabaoui, L. (2021). Surface sediment enrichment with trace metals in a heavily human-impacted lagoon (Bizerte Lagoon, Southern Mediterranean Sea): Spatial distribution, ecological risk assessment, and implications for environmental protection. *Marine Pollution Bulletin*, 169(January). <https://doi.org/10.1016/j.marpolbul.2021.112512>
- Emmerson R.H.C., O'Reilly-Wiese S.B., Macleod C.L., & Lester J.N. (1997). A multivariate assessment of metal distribution in inter-tidal sediments of the Blackwater Estuary, UK. *Marine Pollution Bulletin*, 34(11), 960–968. [https://doi.org/10.1016/S0025-326X\(97\)00067-2](https://doi.org/10.1016/S0025-326X(97)00067-2)
- Flemming, C. A., & Trevors, J. T. (1989). Copper toxicity and chemistry in the

- environment: A review. *Water, Air, and Soil Pollution*, 44(1–2), 143–158.  
<https://doi.org/10.1007/BF00228784>
- Frankowski, M., Ziola-Frankowska, A., Kowalski, A., & Siepak, J. (2010). Fractionation of heavy metals in bottom sediments using Tessier procedure. *Environmental Earth Sciences*, 60(6), 1165–1178.  
<https://doi.org/10.1007/s12665-009-0258-3>
- Ganugapenta, S., Nadimikeri, J., Chinnapolla, S. R. R. B., Ballari, L., Madiga, R., K, N., & Tella, L. P. (2018). Assessment of heavy metal pollution from the sediment of Tupilipalem Coast, southeast coast of India. *International Journal of Sediment Research*, 33(3), 294–302. <https://doi.org/10.1016/j.ijsrc.2018.02.004>
- Gautam, P. K., Gautam, R. K., Banerjee, S., Chattopadhyaya, M. C., & Pandey, J. D. (2016). *HEAVY METALS IN THE ENVIRONMENT: FATE, TRANSPORT, TOXICITY AND REMEDIATION TECHNOLOGIES*. 30.
- Gopal, V., Krishnamurthy, R. R., Sreeshma, T., Chakraborty, P., Nathan, C. S., Kalaivanan, R., Anshu, R., Magesh, N. S., & Jayaprakash, M. (2021). Effect of a tropical cyclone on the distribution of heavy metals in the marine sediments off Kameswaram, Southeast coast of India. *Marine Pollution Bulletin*, 171(January), 112741. <https://doi.org/10.1016/j.marpolbul.2021.112741>
- Grant, A., & Middleton, R. (1990). An assessment of metal contamination of sediments in the humber estuary, U.K. *Estuarine, Coastal and Shelf Science*, 31(1), 71–85.  
[https://doi.org/10.1016/0272-7714\(90\)90029-Q](https://doi.org/10.1016/0272-7714(90)90029-Q)
- Hakanson, L. (1980). An ecological risk index for aquatic pollution control: a sedimentological approach. *Water Research*, 14(8), 975–1001.

[https://doi.org/10.1016/0043-1354\(80\)90143-8](https://doi.org/10.1016/0043-1354(80)90143-8)

Howe, P. D., Malcolm, H. M., & Dobson, S. (2004). *Manganese and its compounds: Environmental aspects*. World Health Organization.

Hungspreugs, M., & Yuangthong, C. (1983). A history of metal pollution in the Upper Gulf of Thailand. *Marine Pollution Bulletin*, 14(12), 465–469.

[https://doi.org/10.1016/0025-326X\(83\)90047-4](https://doi.org/10.1016/0025-326X(83)90047-4)

Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B. B., & Beeregowda, K. N. (2014).

Toxicity, mechanism and health effects of some heavy metals. *Interdisciplinary Toxicology*, 7(2), 60–72. <https://doi.org/10.2478/intox-2014-0009>

Jamshidi-Zanjani, A., & Saeedi, M. (2013). Metal pollution assessment and multivariate analysis in sediment of Anzali international wetland. *Environmental Earth Sciences*, 70(4), 1791–1808. <https://doi.org/10.1007/s12665-013-2267-5>

Klapow Lawrence A., & Lewis Robert H. (1979). Analysis of Toxicity Data for California Marine Water Quality Standards. *Water Pollution Control Federation*, 51, 2054–2070.

Kolawole, T. O., Olatunji, A. S., Jimoh, M. T., & Fajemila, O. T. (2018). Heavy Metal Contamination and Ecological Risk Assessment in Soils and Sediments of an Industrial Area in Southwestern Nigeria. *Journal of Health and Pollution*, 8(19), 180906. <https://doi.org/10.5696/2156-9614-8.19.180906>

Lee, C.-L., Fang, M.-D., & Hsieh, M.-T. (1998). Characterization and distribution of metals in surficial sediments in Southwestern Taiwan. *Marine Pollution Bulletin*, 36(6), 464–471. [https://doi.org/10.1016/S0025-326X\(98\)00006-X](https://doi.org/10.1016/S0025-326X(98)00006-X)

Leyssens, L., Vinck, B., Van Der Straeten, C., Wuyts, F., & Maes, L. (2017). Cobalt

- toxicity in humans—A review of the potential sources and systemic health effects. *Toxicology*, 387, 43–56. <https://doi.org/10.1016/j.tox.2017.05.015>
- Long, E. R., & MacDonald, D. D. (1998). Recommended Uses of Empirically Derived, Sediment Quality Guidelines for Marine and Estuarine Ecosystems. *Human and Ecological Risk Assessment: An International Journal*, 4(5), 1019–1039. <https://doi.org/10.1080/10807039891284956>
- Lopez, A. M., Brandon, A. D., Ramos, F. C., Fitzsimmons, J. N., Dellapenna, T. M., & Adams, H. M. (2021). Lead geochemistry of sediments in Galveston Bay, Texas. *Environmental Advances*, 4, 100057. <https://doi.org/10.1016/j.envadv.2021.100057>
- Lopez, A. M., Fitzsimmons, J. N., Adams, H. M., Dellapenna, T. M., & Brandon, A. D. (2021). A time-series of heavy metal geochemistry in sediments of Galveston Bay estuary, Texas, 2017-2019. *Science of The Total Environment*, 806, 150446. <https://doi.org/10.1016/j.scitotenv.2021.150446>
- Lopez, A. M., Fitzsimmons, J. N., Adams, H. M., Dellapenna, T. M., & Brandon, A. D. (2022). A time-series of heavy metal geochemistry in sediments of Galveston Bay estuary, Texas, 2017-2019. *Science of The Total Environment*, 806, 150446. <https://doi.org/10.1016/j.scitotenv.2021.150446>
- Loring, D. H. (1990). Lithium—A New Approach for the Granulometric Normalization of Trace Metal Data. *Mar. Chem*, 29, 155–168.
- Loring, D. H., & Rantala, R. T. T. (1992). Manual for the geochemical analyses of marine sediments and suspended particulate matter. *Earth-Science Reviews*, 32(4), 235–283. [https://doi.org/10.1016/0012-8252\(92\)90001-A](https://doi.org/10.1016/0012-8252(92)90001-A)

- Macdonald, D. D., Carr, R. S., Calder, F. D., Long, E. R., & Ingersoll, C. G. (1996). Development and evaluation of sediment quality guidelines for Florida coastal waters. *Ecotoxicology*, 5(4), 253–278. <https://doi.org/10.1007/BF00118995>
- MacDonald, D. D., Ingersoll, C. G., & Berger, T. A. (2000). Development and Evaluation of Consensus-Based Sediment Quality Guidelines for Freshwater Ecosystems. *Archives of Environmental Contamination and Toxicology*, 39(1), 20–31. <https://doi.org/10.1007/s002440010075>
- Mahboob, S., Ahmed, Z., Farooq Khan, M., Virik, P., Al-Mulhm, N., & Baabbad, A. A. (2022). Assessment of heavy metals pollution in seawater and sediments in the Arabian Gulf, near Dammam, Saudi Arabia. *Journal of King Saud University - Science*, 34(1), 101677. <https://doi.org/10.1016/j.jksus.2021.101677>
- Norton, S. B., Rodier, D. J., van der Schalie, W. H., Wood, W. P., Slimak, M. W., & Gentile, J. H. (1992). A framework for ecological risk assessment at the EPA. *Environmental Toxicology and Chemistry*, 11(12), 1663–1672. <https://doi.org/10.1002/etc.5620111202>
- Ouddane, B., Martin, E., Boughriet, A., Fischer, J. C., & Wartel, M. (1997). Speciation of dissolved and particulate manganese in the Seine river estuary. *Marine Chemistry*, 58(1), 189–201. [https://doi.org/10.1016/S0304-4203\(97\)00034-0](https://doi.org/10.1016/S0304-4203(97)00034-0)
- Parsons, T., YR, M., & Lalli, C. (1984). A Manual of Chemical & Biological Methods for Sea Water Analysis. *Pergamon Press, Oxford*, 70. <https://doi.org/10.1016/B978-0-08-030287-4.50034-7>
- Plum, L. M., Rink, L., & Haase, H. (2010). The Essential Toxin: Impact of Zinc on Human Health. *International Journal of Environmental Research and Public*

- Health*, 7(4), 1342–1365. <https://doi.org/10.3390/ijerph7041342>
- Qiao, S., Shi, X., Fang, X., Liu, S., Kornkanitnan, N., Gao, J., Zhu, A., Hu, L., & Yu, Y. (2015). Heavy metal and clay mineral analyses in the sediments of Upper Gulf of Thailand and their implications on sedimentary provenance and dispersion pattern. *Journal of Asian Earth Sciences*, 114, 488–496. <https://doi.org/10.1016/j.jseaes.2015.04.043>
- Rani, S., Ahmed, M. K., Xiongzi, X., Keliang, C., Islam, M. S., & Habibullah-Al-Mamun, M. (2021). Occurrence, spatial distribution and ecological risk assessment of trace elements in surface sediments of rivers and coastal areas of the East Coast of Bangladesh, North-East Bay of Bengal. *Science of the Total Environment*, 801, 149782. <https://doi.org/10.1016/j.scitotenv.2021.149782>
- Ryan J.D. & Windom H.L. (1988). Metals in Coastal Environments of Latin America. In *A Geochemical and Statistical Approach for Assessing Metal Pollution in Coastal Sediments* (pp. 47–58). Springer Berlin Heidelberg.
- Santos, I. R., de Weys, J., & Eyre, B. D. (2011). Groundwater or Floodwater? Assessing the Pathways of Metal Exports from a Coastal Acid Sulfate Soil Catchment. *Environmental Science & Technology*, 45(22), 9641–9648. <https://doi.org/10.1021/es202581h>
- Sheela, A. M., Letha, J., Sabu, J., Jobin, T., & Justus, J. (2014). Effect of Nutrients on Bioaccumulation of Heavy Metals in a Tropical Urban Coastal Lacustrine System. *Water Environment Research*, 86(6), 513–523. <https://doi.org/10.2175/106143014X13975035525104>
- Sinex, S. A., & Wright, D. A. (1988). Distribution of trace metals in the sediments and



- biota of Chesapeake Bay. *Marine Pollution Bulletin*, 19(9), 425–431.  
[https://doi.org/10.1016/0025-326X\(88\)90397-9](https://doi.org/10.1016/0025-326X(88)90397-9)
- Sirirattanachai, S., & Utoomprurkporn, W. (2005). *Mercury in the Chao Phraya River Estuary, Thailand*. 10(1), 14.
- Sutherland, R. A., Tolosa, C. A., Tack, F. M. G., & Verloo, M. G. (2000). Characterization of selected element concentrations and enrichment ratios in background and anthropogenically impacted roadside areas. *Archives of Environmental Contamination and Toxicology*, 38(4), 428–438.  
<https://doi.org/10.1007/s002449910057>
- Tchounwou, P. B., Yedjou, C. G., Patlolla, A. K., & Sutton, D. J. (2012). Heavy Metal Toxicity and the Environment. In A. Luch (Ed.), *Molecular, Clinical and Environmental Toxicology* (Vol. 101, pp. 133–164). Springer Basel.  
[https://doi.org/10.1007/978-3-7643-8340-4\\_6](https://doi.org/10.1007/978-3-7643-8340-4_6)
- Tessier, A., Campbell, P. G. C., & Bisson, M. (1979). Sequential Extraction Procedure for the Speciation of Particulate Trace Metals. *Analytical Chemistry*, 51(7), 844–851. <https://doi.org/10.1021/ac50043a017>
- Tessier, E., Garnier, C., Mullet, J.-U., Lenoble, V., Arnaud, M., Raynaud, M., & Mounier, S. (2011). Study of the spatial and historical distribution of sediment inorganic contamination in the Toulon bay (France). *Marine Pollution Bulletin*, 62(10), 2075–2086. <https://doi.org/10.1016/j.marpolbul.2011.07.022>
- Turekian, K. K., & Wedepohl, K. H. (1961). Distribution of the Elements in Some Major Units of the Earth's Crust. *Geological Society of America Bulletin*, 72(2), 175. [https://doi.org/10.1130/0016-7606\(1961\)72\[175:DOTEIS\]2.0.CO;2](https://doi.org/10.1130/0016-7606(1961)72[175:DOTEIS]2.0.CO;2)

- US EPA. (1992). Guidelines for Exposure Assessment, EPA/600/Z-92/001. *Risk Assessment Forum, Washington, DC, 1992.*, 57(May), 22888–22938.
- Usese, A., Chukwu, O. L., Rahman, M. M., Naidu, R., Islam, S., & Oyewo, E. O. (2017). Enrichment, contamination and geo-accumulation factors for assessing arsenic contamination in sediment of a Tropical Open Lagoon, Southwest Nigeria. *Environmental Technology and Innovation*, 8, 126–131. <https://doi.org/10.1016/j.eti.2017.06.006>
- Wang, Z., Wang, Y., Chen, L., Yan, C., Yan, Y., & Chi, Q. (2015). Assessment of metal contamination in coastal sediments of the Maluan Bay (China) using geochemical indices and multivariate statistical approaches. *Marine Pollution Bulletin*, 99(1–2), 43–53. <https://doi.org/10.1016/j.marpolbul.2015.07.064>
- Wattayakorn, G. (2006). Environmental Issues in the Gulf of Thailand. In E. Wolanski (Ed.), *The Environment in Asia Pacific Harbours* (pp. 249–259). Springer-Verlag. [https://doi.org/10.1007/1-4020-3655-8\\_16](https://doi.org/10.1007/1-4020-3655-8_16)
- Wattayakorn, G., & Jaiboon, P. (2014). *AN ASSESSMENT OF BIOGEOCHEMICAL CYCLES OF NUTRIENTS IN THE INNER GULF OF THAILAND*. 5.
- Wattayakorn, G., King, B., Wolanski, E., & Suthanaruk, P. (1998). Seasonal dispersion of petroleum contaminants in the Gulf of Thailand. *Continental Shelf Research*, 18(6), 641–659. [https://doi.org/10.1016/S0278-4343\(97\)00072-1](https://doi.org/10.1016/S0278-4343(97)00072-1)
- Xu, X., Cao, Z., Zhang, Z., Li, R., & Hu, B. (2016). Spatial distribution and pollution assessment of heavy metals in the surface sediments of the Bohai and Yellow Seas. *Marine Pollution Bulletin*, 110(1), 596–602. <https://doi.org/10.1016/j.marpolbul.2016.05.079>

- Yang, M., & Sañudo-Wilhelmy, S. A. (1998). Cadmium and manganese distributions in the Hudson River estuary: Interannual and seasonal variability. *Earth and Planetary Science Letters*, *160*(3), 403–418. [https://doi.org/10.1016/S0012-821X\(98\)00100-9](https://doi.org/10.1016/S0012-821X(98)00100-9)
- Yang, X., Wu, P., Yin, A., Zhang, H., Zhang, M., & Gao, C. (2017). Distribution and source analysis of heavy metals in soils and sediments of Yueqing Bay basin, East China Sea. *Marine Pollution Bulletin*, *115*(1–2), 489–497. <https://doi.org/10.1016/j.marpolbul.2016.11.046>
- Yao, W., Hu, C., Yang, X., & Shui, B. (2021). Spatial variations and potential risks of heavy metals in sediments of Yueqing Bay, China. *Marine Pollution Bulletin*, *173*(PA), 112983. <https://doi.org/10.1016/j.marpolbul.2021.112983>
- Yottiam, A., Chaikew, P., & Srithongouthai, S. (2019). Arsenic pollution assessment in surface sediment of the inner Gulf of Thailand. *IOP Conference Series: Earth and Environmental Science*, *345*, 012010. <https://doi.org/10.1088/1755-1315/345/1/012010>
- Zhang, C., Yu, Z., Zeng, G., Jiang, M., Yang, Z., Cui, F., Zhu, M., Shen, L., & Hu, L. (2014). Effects of sediment geochemical properties on heavy metal bioavailability. *Environment International*, *73*, 270–281. <https://doi.org/10.1016/j.envint.2014.08.010>



จุฬาลงกรณ์มหาวิทยาลัย  
**CHULALONGKORN UNIVERSITY**

## VITA

**NAME** Phuttiaphat Lapat-Atiwat

**DATE OF BIRTH** 11 January 2534

**PLACE OF BIRTH** Bangkok, Thailand

**INSTITUTIONS ATTENDED** Chulalongkorn University, 2009 - 2013  
Bachelor of Science (Environmental Science)

**HOME ADDRESS** 158 Barromrachchonnanee Road, Salathammasop, Thawiwatthana,  
Bangkok, 10170



จุฬาลงกรณ์มหาวิทยาลัย  
CHULALONGKORN UNIVERSITY