Assessments of chromium pollution in surface sediment of the inner Gulf of Thailand

Miss Patcha Leelakun

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

การประเมินมลพิษของโครเมียมในตะกอนดินชั้นผิวของอ่าวไทยตอนใน

น.ส.พัชชา ลีละกุล

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาพิษวิทยาอุตสาหกรรมและการประเมินความเสี่ยง ภาควิชาวิทยาศาสตร์สิ่งแวดล้อม
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2564

Thesis Title	Assessments of chromium pollution in surface sediment of the inner Gulf of Thailand
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พัชชา ลีละกุล : การประเมินมลพิษของโครเมียมในตะกอนดินชั้นผิวของอ่าวไทยตอนใน. (Assessments of chromium pollution in surface sediment of the inner Gulf of Thailand) อ.ที่ปรึกษาหลัก : ผศ. ดร.สราวุธ ศรีทองอุทัย, อ.ที่ปรึกษาร่วม : รศ. ดร.ภศิชา ไชยแก้ว

อ่าวไทยตอนในเป็นทรัพยากรทางทะเลที่สำคัญในการพัฒนาประเทศทั้งด้านเศรษฐกิจและสังคม นอกจากนั้นยังเป็นระบบนิเวศทางทะเลที่มีความหลากหลายทางชีวภาพสูงและช่วยสร้างสมดุลสิ่งแวดล้อม แต่ขณะเดียวกันก็เป็นพื้นที่รองรับมลพิษจากหลายแหล่งกำเนิดจากอิทธิพลจากการพัดพาของแม่น้ำ โดยเฉพาะอย่างยิ่ง 4 แม่น้ำสายหลัก ได้แก่ แม่น้ำแม่กลอง แม่น้ำท่าจีน แม่น้ำเจ้าพระยา และแม่น้ำบางปะกง จากสาเหตุดังกล่าวสามารถก่อให้เกิดการปนเปื้อนของโครเมียมในบริเวณอ่าวไทยตอนในและกลายเป็นปัญหาสิ่งแวดล้อมที่ร้ายแรงสำหรับประเทศไทยได้ ดังนั้น งานวิจัยนี้จึงดำเนินการเก็บตัวอย่างตะกอนดินชั้นผิวคลอบคลุมพื้นที่อ่าวไทยตอนในทั้งหมด 58−60 สถานีในฤดูมรสุมตะวันตกเฉียงใต้ มรสุมตะวันออกเฉียงเหนือและฤดูแล้ง เพื่อศึกษารูปแบบการแพร่กระจายและการเปลี่ยนแปลงตามฤดูกาลของโครเมียมทั้งหมด เพื่อวิเคราะห์องค์ประกอบของรูปแบบทางธรณีเคมีของโครเมียม และเพื่อประเมินสถานภาพการปนเปื้อนและความเสี่ยงของโครเมียมในตะกอนดินชั้นผิวต่อระบบนิเวศปากแม่น้ำแม่กลอง แม่น้ำท่าจีน แม่น้ำเจ้าพระยา และแม่น้ำบางปะกง และอ่าวไทยตอนใน ผลการศึกษาพบว่าความเข้มข้นของโครเมียมทั้งหมดในตะกอนดินชั้นผิวของฤดูมรสุมตะวันตกเฉียงใต้ มรสุมตะวันออกเฉียงเหนือ และฤดูแล้ง อยู่ในช่วง 11.72−80.16 มิลลิกรัมต่อกิโลกรัม 5.61−107.45 มิลลิกรัมต่อกิโลกรัม และ 8.63−119.47 มิลลิกรัมต่อกิโลกรัม ตามลำดับ จะพบความเข้มข้นสูงที่บริเวณปากแม่น้ำและลดลงในบริเวณกลางอ่าวไทยตอนใน ความเข้มข้นของโครเมียมทั้งหมดในตะกอนดินชั้นผิวในแต่ละฤดูกาลไม่มีความแตกต่างกันอย่างมีนัยสำคัญ และจากข้อมูลองค์ประกอบของรูปแบบทางธรณีเคมีของโครเมียมพบว่าส่วนใหญ่อยู่ในรูปแบบที่ทำพันธะกับสารอินทรีย์ทั้งหมดและรูปแบบที่เหลือจากการสกัด ซึ่งแสดงให้เห็นว่าในบริเวณนั้นโครเมียมมีความเสี่ยงต่ำ เนื่องจากโครเมียมอยู่ในรูปแบบที่ไม่เคลื่อนที่และไม่สามารถปลดปล่อยออกสู่แหล่งน้ำได้ในสภาวะปกติ ด้านการศึกษาสถานการณ์ปนเปื้อนด้วยเกณฑ์คุณภาพตะกอนดินพบว่าโครเมียมในสถานีส่วนใหญ่ไม่ก่อให้เกิดผลกระทบทางชีวภาพที่ไม่พึงประสงค์ เมื่อพิจารณาค่าการสะสมโลหะหนักในตะกอนดินและดัชนีการสะสมทางธรณีพบว่าความเข้มข้นของโครเมียมทั้งหมดที่ตรวจพบในตะกอนดินชั้นผิวอยู่ในระดับต่ำและไม่มีการปนเปื้อน นอกจากนี้ระดับความเข้มข้นโครเมียมส่วนใหญ่ที่พบมีความเสี่ยงต่อระบบนิเวศบริเวณอ่าวไทยตอนในอยู่ในระดับต่ำ อย่างไรก็ตาม จากผลการประเมินโครเมียมในรูปแบบไอออนที่แลกเปลี่ยนได้และรูปแบบพันธะกับคาร์บอเนตพบว่าระดับความเสี่ยงสูงขึ้นโดยเฉพาะในฤดูแล้งมีระดับความเสี่ยงปานกลางเกือบทั้งหมด จากผลการวิจัยแสดงให้เห็นว่าอ่าวไทยตอนในมีการปนเปื้อนและความเสี่ยงต่อระบบนิเวศอยู่ในระดับที่ยอมรับได้ อย่างไรก็ตามบางพื้นที่ควรมีการเฝ้าระวังผลกระทบของโครเมียมอย่างใกล้ชิด รวมถึงการติดตามประเมินสถานภาพการปนเปื้อนในระยะยาวต้องดำเนินการอย่างต่อเนื่อง

สาขาวิชา	พิษวิทยาอุตสาหกรรมและการประเมินความเสี่ยง	ลายมือชื่อนิสิต .....
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6172159823 : MAJOR INDUSTRIAL TOXICOLOGY AND RISK ASSESSMENT
KEYWORD: CHROMIUM, SEDIMENT, ECOLOGICAL RISK ASSESSMENT, INNER GULF OF THAILAND

Patcha Leelakun : Assessments of chromium pollution in surface sediment of the inner Gulf of Thailand. Advisor: ASST. PROF. SARAWUT SRITHONGOUTHAI, Ph.D. Co-advisor: ASSOC. PROF. PASICHA CHAIKAEW, Ph.D.

The inner Gulf of Thailand is an important marine resource for economic and social developments of Thailand. Moreover, the inner Gulf of Thailand is a diverse of biological coastal ecosystem, which is make an equilibrium marine environment. On the other hand, this area is due mainly to a variety of pollutant sources from the surface runoff, particularly major large rivers including the Mae Klong, the Tha Chin, the Chao Phraya and the Bangpakong Rivers. As a result, chromium contamination can occur in the inner Gulf of Thailand and ultimately become a serious environmental issue in Thailand. Therefore, the surface sediments were collected from 58−60 stations entire the inner Gulf of Thailand in southwest monsoon season, northeast monsoon season, and dry season were also affected in the chromium accumulation in the surface sediment of the inner Gulf of Thailand in order to investigate spatial heterogeneity distributions and seasonal changes of total chromium contamination, to analyze geochemical fractions of chromium and to assess the contamination status and ecological risk of chromium. The results revealed that the concentration of chromium in surface sediment in southwest monsoon season, northeast monsoon season, and dry season in the range of 11.72−80.16 mg/kg, 5.61−107.45 mg/kg and 8.63−119.47 mg/kg, chromium contamination in surface sediment was decreased from the river estuaries to the lower of the inner Gulf of Thailand. Fractional distribution of Cr was mostly bound to organic matter and residual fraction. As a result, fraction includes the rest of the metals and is associated with minerals that are bound via their crystalline structure, immobilized, and that will not constitute a threat to the ecosystem. Based on the SQG_s, the most of areas may not cause any adverse biological effects, but some areas were occasionally associated with adverse biological effect within the inner Gulf of Thailand. Considering calculation of the enrichment factor (EF) and geo−accumulation index (I_{geo}) for chromium, indicated that the inner Gulf of Thailand was mostly minor enrichment and practically uncontaminated, respectively. Furthermore, the E_r of all stations was less than 40, which was indicated that in the inner Gulf of Thailand is not associated ecological risk. However, the concentrations of exchangeable and carbonate−bound chromium fractions were assessed the ecological risk, which were indicated that the risk level was increased, particularly at almost moderate risk in the dry season. As a result, the Cr concentrations were at low contamination and risk in the surface sediment of the inner Gulf of Thailand, however some area should be concerned, and long−term monitoring is needs to be investigated and assessed the concentration changes over the time.

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

ACKNOWLEDGEMENTS

It would not have been possible to write this thesis without the help and support of the kind people around me, to only some of whom it is possible to give particular mention here.

First, I would like to express Chulalongkorn University for financial, academic and technical support and providing guidance concerning project implementation for their supports in completing this research.

I would like to express my research advisor, Assistant Professor Sarawut Srithongouthai, Ph.D. and Co-advisor, Associate Professor Pasicha Chaikaew, Ph. D., who has supported me throughout my thesis with his invaluable knowledge, guidance, suggestion and inspiration all along the thesis process. Thank you for always stay beside me in every step.

I would like to thank to the chairman, Professor Wanida Jinsart, Ph.D., Chidsanuphong Chart-asa, Ph.D. and Assistant Professor Marut Suksomjit, Ph.D. for their suggestions and assistance of my research.

I am most grateful to Mr. Pathompong Vibhatabandhu, Ms. Anutsara Yottiam and Mr. Phuttiphat Lapat-Atiwat for assistance to sampling in the field. In addition, Ms. Ketsaraporn Kaenkaew and Ms. Pansuree Jariyavijit, the laboratory assistant who advises me about laboratory work.

In addition, I would also like to thank Science Program in Industrial Toxicology and Risk Assessment, Department of Environmental Science, Faculty of Science, Chulalongkorn University and also people in this organization for giving me such attention and time.

Special thanks go to my friend in Science Program in Industrial Toxicology and Risk Assessment, Department of Environmental Science, Faculty of Science, Chulalongkorn University for the keep interest shown to complete this thesis successfully.

The product of this research paper would not be possible without all of them.

Above all, I would like to thanks to my parents for support, encouragement and effort me throughout my life. In addition, special thanks to friends who always support me in every step.

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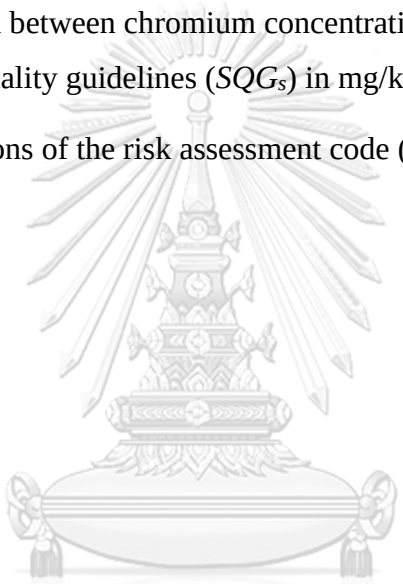

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CHAPTER I
INTRODUCTION

1.1 Background and Significance of the Research

The inner Gulf of Thailand is the very important marine resource for economic development of Thailand. Moreover, the inner Gulf of Thailand is also serving as a large breeding, nursery, and growth grounds for diverse marine organisms. However, the inner Gulf of Thailand is under immense pressure due to indiscriminate exploitation beyond its supportive capacity. The ecological degradation of the inner Gulf of Thailand is triggered by industrialization, urbanization, tourism, port development, marine transportation, marine transshipment and agriculturization [1]. These are anthropogenic activities, which have contributed runoff of mixed pollutants, particularly chromium into the ecosystem of the inner Gulf of Thailand via the four main rivers including the Mae Klong, the Tha Chin, the Chao Phraya and the Bangpakong Rivers [2].

Generally, the chromium enters into the matrix of various environments (air, soil and water) from various natural and anthropological sources, with the largest emissions coming from industrial establishments. The industries that contribute the most to the release of chromium are metal processing, tannery, chromate production, stainless steel welding and production of ferrochrome and chromium paint [3]. An increase in chromium concentrations in the environment has been linked to chromium emissions in air and wastewater, mainly from the metallurgy, refractory, and chemical industries. Most of the soluble chromium is present as Cr^{6+} or as soluble Cr^{3+} complexes and generally accounts for a small percentage of the total. Chromium is toxic, persistent, and non−biodegradable, also has the ability to accumulate in living organisms [4]. Moreover, chromium also poses serious problems for marine ecosystems and humans that rely on marine resources for food, industry, and recreation. The chromium toxicity refers to the toxic effects on organisms or cells

resulting from exposure to specific forms of chromium [5]. It damages genetic information in living cells, DNA mutations, and possibly the formation of cancerous tumors [6]. Although chromium has a negative effect on health and remains in the environment for a long time, but chromium exposure continues to increase in many parts of the world [5, 7]. Chromium released into the environment by human activities occurs mainly in the hexavalent form (Cr^{6+}). Hexavalent chromium (Cr^{6+}) is a toxic industrial pollution. It is classified as a human carcinogen by many regulatory and non-regulatory agencies [8, 9]. As a result, chromium contamination in marine ecosystems has become a global concern. This includes the inner Gulf of Thailand.

In fact, sediments have been identified as the main sink for chromium. After chromium entered marine environments, the dissolved chromium is transported into water bodies and moved downstream, while others settle in sediments [10]. Moreover, sediments can release chromium to the water column by remobilization processes, or they can retain the chromium [11]. Therefore, sediments are considered sink and source to the transmission and deposition of chromium.

Therefore, it is important to determine the spatial heterogeneity of chromium concentrations in the surface sediments of the inner Gulf of Thailand, to evaluate contamination status and to assess ecological risk by its presence in contaminated areas. The present study contributed to the understanding of the geochemical fraction of chromium in surface sediments and provides basic distribution information for environmental protection and pollution control by particularly important areas of the inner Gulf of Thailand.

1.2 Research Objectives

1.2.1 To investigate spatial heterogeneity distributions and seasonal changes of total chromium contamination in the surface sediment of the inner Gulf of Thailand.

1.2.2 To analyze geochemical fractions of chromium in the surface sediment of the inner Gulf of Thailand.

1.2.3 To assess contamination status and potential ecological risk of chromium in the surface sediment of the inner Gulf of Thailand.

1.3 Scope of the Research

1.3.1 Study areas: the inner Gulf of Thailand including the Mae Klong, the Tha Chin, the Chao Phraya and the Bangpakong River estuaries were chosen to study the spatial heterogeneity distributions, seasonal changes, geochemical fractions, contamination status and ecological risk of chromium in the surface sediments.

1.3.2 Samples: the surface layer of sediment (0−1 cm depth) is considered for chromium and physico−geo−chemical analysis in order to meet the goals of research.

1.3.3 Sampling points: total 63 sampling points were established in order to investigate spatial heterogeneity distributions of chromium, including 28 stations entire the inner Gulf of Thailand, and 35 stations are located in the river estuarine areas.

1.3.4 Sampling period: the sampling was carried out in July 2017 (southwest monsoon season), December 2017 (northeast monsoon season) and April 2018 (dry season) in order to evaluate effect of seasonal changes on chromium contamination in the surface sediment of the inner Gulf of Thailand.

1.3.5 Parameters: total concentration and five geochemical fractions (exchangeable, carbonate, Fe−Mn oxides, organic and residual forms) of chromium in the surface sediment were analyzed. In addition, total organic matter, total organic carbon, total phosphorus and acid volatile sulfide of surface sediment was also analyzed as the factors that were regulated the chromium concentrations in the surface sediment of the inner Gulf of Thailand.

1.3.6 Laboratory analysis: laboratory analysis was carried out during July 2019 to January 2020 at the Department of Environmental Science, Faculty of Science, Chulalongkorn University.

1.3.7 Data analysis: spatial heterogeneity distributions of total chromium in the surface sediment were performed by deterministic interpolation technique

using ArcGIS™. Contamination status of total chromium were analyzed using enrichment factor and geo−accumulation index. While, potential ecological risk factor was used to assess ecological risk in the surface sediment of the inner Gulf of Thailand.

1.4 Research Outcomes

1.4.1 Improve understanding of spatial heterogeneity distributions, seasonal variations, contamination status and ecological risk of chromium in the surface sediments of the inner Gulf of Thailand.

1.4.2 Finding data are the solution of marine environmental problems that can be used to develop environmental policy for pollution controlling in the marine ecosystem of the inner Gulf of Thailand.

CHAPTER II
LITERATURE REVIEWS

The inner Gulf of Thailand is a semi−enclosed bay, which was a dynamic coastal ecosystem due to the complex hydrologic movements, seasonal variations, and tidal changes. Moreover, the inner Gulf of Thailand has a high biodiversity, which is serves a complex ecosystem. However, large amounts of pollutants from point sources and non–point sources were loading into the system, cause the risk to ecosystem and human health. In particular, estuaries receive more pollution inputs per unit surface area than any other type of ecosystem. For the understanding of this thesis, the fundamental knowledges including the definitions and theories of heavy metal, particular chromium are needed to descript. In addition, analysis tools, including contamination status, ecological risk assessment are needed to review. All data of the present study were totally explained as follows:

2.1 Heavy Metals

2.1.1 Definition

Heavy metals are a natural element which toxic at relatively high concentration. Heavy metal is known as metal with a specific weight higher than 5 gm/cm^3 or a high atomic mass. The heavy metals are a heterogeneous group of elements which greatly differ in their chemical properties and biological functions. According to [12], “heavy metals” is a collective term for metals of high atomic mass, particularly those transition metals that are toxic and cannot be processed by living organisms, such as lead, mercury, and cadmium.

2.1.2 Toxicity

Heavy metals are found in elemental form and in many other chemical compounds. Volatile and attached to fine particles can be widely transported on very large scales. Each form or compound has different properties, which affects what happens to it in the food chain, and food toxicity. Human activities have

dramatically altered the biochemical cycle and balance of some heavy metals [13].

According to [14], Heavy metals are extremely. They persist in the environment and can accumulate in plant and animal tissues. Industrial wastes are potential sources of heavy metal pollution. Heavy metal toxicity depends on factors, including dose, route of exposure, and the type of chemical, as well as the age, sex, genetics, and nutritional status of the person exposed. Due to their high levels of toxicity, arsenic, cadmium, chromium, lead, and mercury are among the major metals that are important to public health. These constituents are considered toxin that cause multiple organ damage to a lower level [15]. Heavy metals have been reported to affect cell organelles and components such as cell membranes, mitochondria, lysosomes, endoplasmic reticulum, nucleus, and certain enzymes. It is involved in metabolism, detoxification, and damage repair. Metal ions have been found to interact with cellular components such as DNA and nuclear proteins. This causes DNA damage and structural changes that can lead to cell cycle modulation, cancer, or cell death [6, 16]

2.1.3 Carcinogenicity

The International Agency for Research on Cancer (*IARC*) has developed a classification system to assess the carcinogenicity of this substance in humans [17]. Classification agents are based on scientific evidence derived from human and laboratory animal studies and from other mechanisms and information related. The list of categories and definitions is shown in Table 2.1.

Almost all heavy metals are toxic as carcinogens, arsenic, cadmium, chromium and nickel are classified as Group 1 carcinogens by the International Agency for Research on Cancer. In commercial use reports have shown that exposure to these agents leads to disruptions in the expression of tumor suppressor genes, damage repair process, and the enzymatic activity involved in oxidative stress induced by reactive oxygen species (ROS) is a well-known mechanism of heavy metal damage [18].

Table 2.1 Classifications of carcinogenic agents by the International Agency for Research on Cancer (*IARC*)

Group	Description	Definition	Number of agents
Group 1	Carcinogenic to humans	- Sufficient evidence of carcinogenicity or - Evidence of carcinogenicity in humans is less than sufficient, but there is sufficient evidence of carcinogenicity in experimental animals and strong evidence in exposed humans that the agent acts through a relevant mechanism of carcinogenicity.	121
Group 2A	Probably carcinogenic to humans*	- Limited evidence of carcinogenicity in humans and sufficient evidence of carcinogenicity in experimental animals or - Inadequate evidence of carcinogenicity in humans and sufficient evidence of carcinogenicity in experimental animals and strong evidence that the carcinogenesis is mediated by a mechanism that also operates in humans OR - Limited evidence of carcinogenicity in humans, but belongs, based on mechanistic considerations, to a class of agents for which one or more members have been classified in Group 1 or Group 2A.	89
Group 2B	Possibly carcinogenic to humans*	- Limited evidence of carcinogenicity in humans and less than sufficient evidence of carcinogenicity in experimental animals or - Inadequate evidence of carcinogenicity in humans but sufficient evidence of carcinogenicity in experimental animals or - Inadequate evidence of carcinogenicity in humans and less than sufficient evidence of carcinogenicity in experimental animals, but with supporting evidence from mechanistic and other relevant data.	318
Group 3	Not classifiable as to its carcinogenicity to humans	- Evidence of carcinogenicity is inadequate in humans and inadequate or limited in experimental animals or - Evidence of carcinogenicity is inadequate in humans but sufficient in experimental animals, but strong evidence that the mechanism of carcinogenicity in experimental animals does not operate in humans or - Agents that do not fall into any other group. Agents in Group 3 are not determined to be non-carcinogenic or safe overall, but often means that further research is needed.	499

* The terms probably carcinogenic and possibly carcinogenic have no quantitative significance and are used simply as descriptors of different levels of evidence of human carcinogenicity, with probably carcinogenic signifying a higher level of evidence than possibly carcinogenic.
Source: IARC (2021)

2.2 Chromium

2.2.1 Chemical properties

Chromium (Cr) is described as a hard, brittle, shiny metal that resists tarnishing and is highly polished. These attributes have made Cr a highly sought-after metal for generations of automobile enthusiasts. The Cr is the 22nd most common element in the earth's crust and average concentrations in uncontaminated soils are 100 mg/kg (range 1–300 mg/kg). Concentrations range from 5–800 µg/L in seawater and 26 µg/L to 5.2 mg/L in freshwater. Approximately 44% of the 8.7 million tons of chromium ore mined each year comes from South Africa, but Eastern Europe and Turkey are also the major mining regions. In nature, Cr occurs mainly as Cr^0 (element), Cr^{3+}, and Cr^{6+}, with Cr^{3+} being the most common and toxic hexavalent or Cr^{6+} [3].

2.2.2 Speciation in the marine environments

The aqueous chromium is either soluble or as a suspended solid that is adsorbed on clay, organic matter or iron oxides. Most of the soluble chromium is contained in Cr^{6+} or as a soluble Cr^{3+} complex and generally only a small proportion of the total soluble Cr^{6+} may remain partially in water but is ultimately reduced to Cr^{3+} by organic matter or other reducing agents in water [3]. Recommended Cr^{6+} reduction mechanisms for oxidized water include reaction with photochemical Fe^{2+} and organic matter [19, 20]. The most probable species were cited as $Cr(OH)_2 + 4H_2O$ and CrO_4^{2-}. In the oxygen-free zone where H_2S was present, Cr^{3+} was the dominant species. The presence and association of chromium-binding species depends on the amount of organic matter in seawater, as discussed by several authors [21]. It may be a complexing agent for chromium. The role of MnO_2 as a catalyst in reducing Cr^{6+} has been investigated [22].

2.2.3 Geochemical fractionation of Cr in sediments

Chromium is one of the most common pollutants in aquatic environments from either natural source, such as geologic weathering or anthropogenic sources such as industrial, agricultural, municipal and residential waste products [23]. Insoluble Cr is adsorbed and deposited at the bottom sediment [24]. The Cr is distributed between the aqueous phase and the suspended sediments during their

transport. The fraction in the sediment is not expected to present a direct danger, provided that the metal ions are immobilized due to encapsulation via variation of environmental conditions such as acidification, redox potential, and chelation, etc., and impose adverse effects on living organisms. The Cr in sediments can occur in five categories: exchangeable; carbonates; reducible forms (Fe and Mn oxides); organics and sulfides; and residual form [25] This variation is because metals can undergo different remobilization conditions under changing environmental conditions. This affects the absorption and solubility of those metals. The determination of the total content of Cr is insufficient to assess the environmental impact. Therefore, the determination of the geochemical profile of Cr is necessary to understand the metallurgical capacity and its environmental impact [26]. Factors for the absorption of Cr in the sludge as follows: (1) solid phase, such as AVS, particulate organic carbon, iron and manganese oxide hydroxide; (2) the aqueous phase, i.e., physical and chemical properties such as pH and redox potential (Eh).

1. **Sulfides: acid volatile sulfides (AVS)**

Reactive sulfide species, including aqueous sulfides, poorly crystalline FeS, mackinavite, gragite and pure metal sulfide minerals. It is important to monitor the binding and division of metals under nontoxic conditions [27]. The reduction of the SO_4^{2-} formula can be described as follows:

$$SO_4^{2-} + 8e^- + 8H^+ \rightarrow S^{2-} + 4H_2O \quad (2.1)$$

When Fe^{2+} exists in anoxic sediments, the reduction of SO_4^{2-} may cause the formation of poorly crystalline FeS.

$$Fe^{2+} + SO_4^{2-} + 8H^+ + 8e^- \rightarrow FeS + 4H_2O \quad (2.2)$$

Fe and Mn sulfides are important precipitations of AVS−metal in the sediment. The lowest Fe and Mn precipitation concentrations were observed in the more toxic sediment surface layer and may emphasize the importance of Fe and Mn oxide precipitation near the sediment -water interface, which can reduce the mobility of metal.

The chemical basis of AVS binding to metal ions is the displacement of iron in iron monosulfide (FeS) and divalent metasl (Me^{2+}) to form highly insoluble metal sulfides.

$$Me^{2+} + FeS(s) \rightarrow MeS(s) + Fe^{2+} \qquad (2.3)$$

Based on this reaction mechanism, sulfide phase shows low solubility in anoxic sediment. AVS concentrations are considered high enough to bind positively charged metals and reducing the threshold for final chronic effects on benthic invertebrates [23].

2. Organic matter (OM)

Organic matter accumulates on the sediment surface. It is mainly a result of the decomposition of phytoplankton material. Although the amount of organic matter in the sediment is usually small compared to clay but organic matter also has a strong influence on metal adhesion [28]. The retention potential of the metals coming from the humic layer of the sediment. This has important implications for the mobility of metals into the sediment and for the absorption of the metals into living organisms.

The mechanisms involved in metal retention by organic matter appear to include both formation of complexes and adsorption. This is reflected in the literature where some authors describe the interactions between metals and organic matter in terms of ion exchange [29] and others in terms of complexity. The active constituents in the organic metal binding are negatively charged functional groups such as phenol, carboxyl(-eth) and amino groups [30].

3. Fe-Mn oxide

Hydrous Fe and Mn oxides occur in clays as coatings on phyllosilicates and as free gels and crystals. Low concentrations of the oxides are often found in reducing environments [31]. Therefore, the influence of Fe and Mn anhydrous on the solubility of metals is often most important in relatively oxidizing environments. Oxides of Fe and Mn, which are the main constituents of minerals. It is a small metal remover, and these constituents can be deposited in the aerobic sediment in the surface [32]. Due to the large surface area, the "Fe–Mn oxide regulator" is therefore considered the predominant sorbent and a high significant positive load was observed on the metals. Oxyhydroxides of Fe and Mn, which digenetic enrich during the decomposition of Fe and Mn oxides under redox cycling, can also affect the metal flux and the mobilization of metal as well.

4. pH

The pH value is used to weigh the acidity or alkalinity in a sediment or water column and has a strong influence on the solubility of metals. A high pH promotes adsorption and precipitation, while a low pH can weaken the metal inclusion strength and hindering the retention of metal with sediment. In acidic conditions, adsorption is a more important process than solid phase precipitation in reducing the concentration of metal ions in solution and the reverse is true in alkaline conditions [33]. Specific adsorption is also highly dependent on pH [34]. At near neutral pH, complex formation may become an additional fixation mechanism.

5. Redox potential

Redox is a short term for reduction-oxidation reactions, which is a process involves the flow of electrons from the reducing agent (reducing agent) to the oxidizing agent (oxidizing). The redox reaction in the sediment is controlled by the water free electron activity pE, which can be expressed in the form of eh redox potential. The increasing ORP in sediment will facilitate the oxidization rate of sulfides and the degradation of organic compounds correspondingly, accelerating the liberation of the adsorbed/complexing heavy metal [35].

2.2.4 Sources and uses of chromium

Heavy metals are naturally occurring elements found throughout the earth's crust, most environmental contamination, and human exposure is the result of human activities such as mining and smelting, production and industrial use, and the use of metals and metal-containing compounds in the country and in agriculture [23] Environmental contamination can occur from metal corrosion, accumulation of atmosphere, soil erosion of metal ions and the leaching of leached heavy metals and evaporation of metals from water supplies to soil and groundwater [36]. Natural phenomena such as weather conditions and volcanic eruptions have been reported, which contributes to heavy metal pollution. Industrial sources include metal processing in refineries, coal burning in power plants, petroleum burning, nuclear power plants, plastics, textiles, microelectronics wood preservation plant and paper mill [37].

Chromium enters into the matrix of various environments (air, soil and water) from various natural and anthropological sources, with the largest emissions coming from industrial establishments. The industries that contribute the most to the release of chromium are metal processing, tannery, chromate production, stainless steel welding and production of ferrochrome and chromium paint [3]. An increase in chromium concentrations in the environment has been linked to chromium emissions in air and wastewater, mainly from the metallurgy, refractory, and chemical industries. Chromium released into the environment by human activities occurs mainly in the hexavalent form (Cr^{6+}) [3]. Hexavalent chromium (Cr^{6+}) is a toxic industrial pollution. It is classified as a human carcinogen by many regulatory and non-regulatory agencies [9]. Chromium is widely used in many industrial processes and, as a result, is a contaminant in many environmental systems. Chromium compounds are commercially used in industrial welding, chrome plating, dyes and pigments, tanning and wood preservation. Chromium is also used as an anticorrosive in cooking systems and boilers [38].

2.2.5 Fate and transport of chromium in the marine environments

In aquatic environmental, chromium is two difference components when the heavy metals runoff into water, includes particulate and dissolved heavy

metals, and thus changes of their toxicity. Chromium can accumulate in suspended particulates and regenerated into water under favorable conditions [39]. After the metals enter to marine ecosystem, the particulate heavy metals will react with particulate sediment by particle surface adsorption and will be deposited in the bottom sediment by sedimentation. Also, the particulate chromium can be released into the water column as dissolved heavy metals in response to certain disturbances. The dissolved chromium can be assimilated to primary producer, biomagnified (entered) to food chains and get into human body through consumption. After life period, the primary producer turns into particulate and sink down to the sediment through suspension and sedimentation. The bottom sediment provides habitats and a food source for benthic fauna and flora; thus, pollutants may be directly or indirectly toxic to the aquatic flora and fauna through biochemical process. Sediments can either retain metals or release them to the water column through various remobilization processes. Therefore, sediments are considered a key role in transmission and deposition of metals. As a result, chromium pollution in the marine ecosystem can cause ecological effects and human health effects (Figure 2.1).

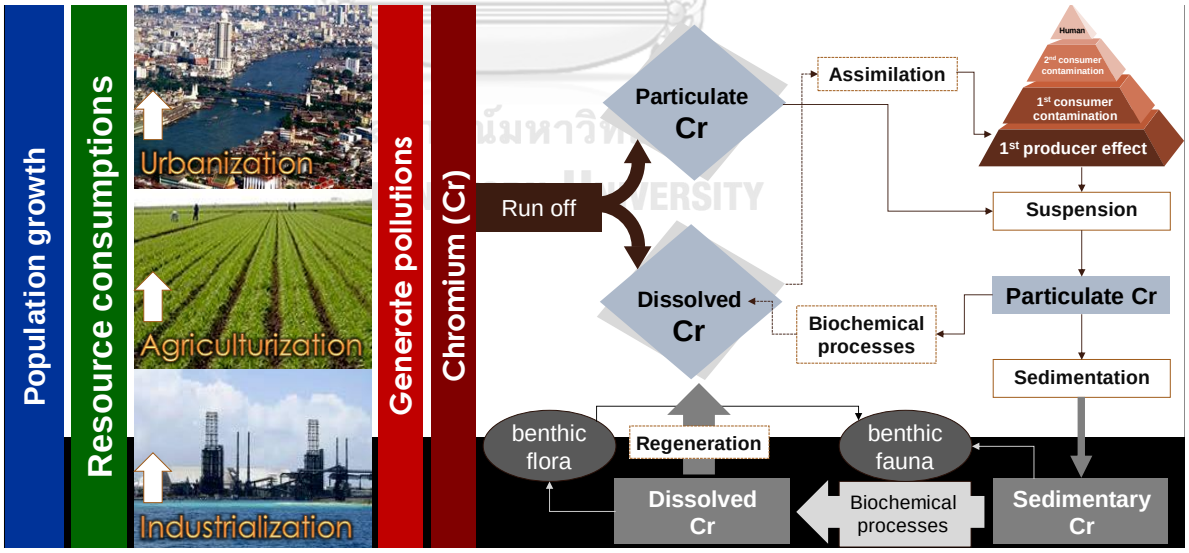


Figure 2.1 Causes, sources, uses, fate and transports of chromium in the marine ecosystem.

2.2.6 Effects of chromium

According to the characteristics of heavy metals which are having high atomic weight, bioaccumulation, persistent and non−biodegradable, these characteristics make heavy metals toxic and effects. Heavy metals contamination can pose effects on ecosystem and human health. The metals can cause ecological effects by assimilating to primary producer, which is phytoplankton, and the metals can accumulate into zooplankton by eating phytoplankton and following by accumulation in a small fish and a big fish which are upper tropic levels. Finally, the metals can be bio−magnified to human food chains. Then, get into the human body via food and pose human health effects [15].

1. Bioavailability

In general, the definition of bioavailability can be "the portion of a chemical in the environment that is available for biological action, such as uptake by an organism" [40]. In term of sediment contamination, bioavailability can be defined as "the fraction of the total contaminant in the interstitial water and on the sediment particles that is available for bioaccumulation" [41].

Bioavailability of aquatic organisms varies depending on their metal uptake. The organisms are divided into two types, which are regulators (excluders) and accumulators (non−excluders) [42]. The organisms are categorized by metal uptakes: regulators are classified by their low metal uptake, and accumulators are classified by their high metal uptake. Regulators have abilities to control metal accumulations and keep their intracellular metal concentrations constant among the conditions of high metal concentration; whereas accumulators are able to detoxify with high metal level in a body.

Reducing bioavailability, which includes solubility and mobility as well, complexing the metal at the organism surface, decreasing the permeability of epithelial surfaces, decreasing transport into the cell, and undertaking behavioral avoidance activity mostly are common mechanisms

limiting heavy metal uptakes [43]. Heavy metals may reveal both negative and positive effects, which are controlled by the kind and concentration of metal, after metals are absorbed or assimilated by an organism [44].

2. Bioconcentration and bioaccumulation

The bioaccumulation of chromium is influenced by chemical form and redox conditions of marine systems. Oxidation increases Cr^{6+} while Cr^{3+} is enhanced if the marine system is oxygen free. As previously stated, Cr^{3+} forms strong and adsorbed complexes on solid surfaces, whereas Cr^{6+} prefers to dissolve in seawater [45]. Chromium may accumulate differently in different tissue types. In fish gills, kidneys and liver, chromium concentrations were found to be highest while the muscles have very little ability to accumulate chromium, however, chromium does not seem to accumulate at higher nutritional levels in seafood [46].

3. Biomagnification

In the environment, chromium can be absorbed by humans and chromium receptors. Cr^{3+} + is generally absorbed through the cell membrane although it is significantly less than Cr^{6+}. This is because most of the biosphere is reduced for Cr^{6+} and Cr^{3+} is relatively immobile. Therefore, there is little bioconcentration or biomagnification of Cr^{6+}. Chromium appears to be a nutrient for at least some plants and animals, including humans. Although Cr^{6+} species have been reported to be toxic to bacteria, plants and animals, human toxicity includes lung cancer, liver, kidney and gastric damage. and skin irritation and allergic reactions. However, it is noted that the clinical, toxicological and epidemiological evidence indicates that some compounds containing Cr^{6+} are not carcinogenic [47].

2.3 Contamination Status Assessment

2.3.1 Chromium concentrations in the marine environments

Polprasert et al. (1982) studied the contamination of chromium in surface sediment in the Chao Phraya River estuary, Thailand, was collected 12 sampling station. Chromium was found rang from non−detectable to 47.50 mg/kg in sediment, in the first sampling period were consistently higher than in second sampling for chromium (Table 2.2).

Censi et al. (2006) studied the contamination of chromium in surface sediment in the western past the upper Gulf of Thailand. The contamination of chromium in surface sediment ranged from 17.41−46.72 mg/kg. The Mae Klong River is the most important river in the studied area. There are all stations have enrichment factor ≤2, was associated with zero to minor contamination (Table 2.2).

Khowhit et al. (2013) studied the concentration of chromium in the sediment of the coastal area receiving effluent from Phetchaburi municipal wastewater treatment system in Phetchaburi province. The sediment samples were collected 4 sites in August 2012 and March 2013 from the bottom depth 0−15 cm. The concentration was compared to the standard of the sediment qualities coastal area. The results investigated that the average of chromium was 10.454 mg/kg dry weight, respectively which were in line and accepted with the standard qualities (Table 2.2).

Ho et al. (2010) studied the distribution of chromium in surface sediment from Ha Long Bay, Vietnam, chromium concentration in surface sediment was found approximately 27 mg/kg. The distribution pattern of chromium is controlled by organic matter and clay minerals and determined by the distribution of the fine-grained fraction in the sediments. Chromium concentration compared with sediment quality guidelines, based on the used criteria, the risk of chromium is in principle not associated with adverse biological effects. Chromium has negative values of geo−accumulation index for these reference materials, which is evaluated as unpolluted and values of enrichment factor for chromium less than 1, can be classified as minor contamination (Table 2.2).

Qiao et al. (2015) studied the chromium contamination in surface sediment was collected 18 sediment samples in the upper Gulf of Thailand and along the river of the Mae Klong, the Tha Chin, the Chao Phraya, and the Bangpakong. Chromium concentrations ranged from 26.1−349.92 mg/kg and average is 138.94 mg/kg. The major distribution areas of chromium with higher concentrations were in the Chao Phaya River. The concentrations of chromium are higher than background data, and statistical analysis of geo-accumulation index indicates that the study area is moderately polluted by chromium (Table 2.2).

Han et al. (2016) studied the chromium contaminations in Yangtze River estuary, China, were collected sediment samples in August 2014. As a result, chromium was found approximately 34.64 mg/kg which was higher than background values. Distribution pattern of chromium was low concentration in the inner River but high in the adjacent sea area. Comparison with sediment quality guideline, chromium was within the effect range low, suggesting that chromium may cause rare adverse biological effect to local benthic organisms. Geo-accumulation index of chromium indicated low pollution level in the Yangtze River estuary (Table 2.2).

Trifuoggi et al. (2017) studied the distribution of metals in surface sediments of Gulf of Pozzuoli, Italy. Sampling of sediments was performed aboard a boat named Antilia in December 2015 in 22 sites. The chromium concentration ranged from 0.5−49.5 mg/kg. The results investigated that the average of chromium was 14.0 mg/kg dry weight. The enrichment factor values were outstandingly high, >1.5 with values which were often ≥100. The geo−accumulation index (I_{geo}) was very critical for chromium showing I_{geo} in the range of strongly polluted ($4<I_{geo}<5$) and very strongly polluted ($I_{geo}>5$). The principal component analysis and Pearson's correlation matrix excluded significant contribution from weathering products (Table 2.2).

Xu et al. (2017) studies chromium contamination in sediment along the Jiaozhou Bay catchment, China, was collected 47 sites in December 2015. The result of chromium concentration ranged from 12.2−185.5 mg/kg with mean value 69.3 mg/kg. Values of geo−accumulation index of chromium was less than

zero, indicating minor contamination and enrichment factor values of chromium was less than 1.5, suggesting that chromium not major concern. Based on the effect−range classification according to the threshold effect level/probable effect level of sediment quality guidelines for chromium was likely to have adverse biological impacts on local aquatic ecosystems (Table 2.2).

Zhao et al. (2016) studied the concentration of chromium from the Daya Bay and adjacent shelf was determined to evaluate their levels and spatial distributions. The measured concentrations ranged from 10–85 mg/kg for chromium. Chromium contaminations, which was lower than the primary standard criteria of China, exhibited special distribution decrease from west to east of the Daya Bay. Enrichment factor and geo−accumulation index result demonstrated that chromium was not pollution level, while principal component analysis showed that chromium likely originated from natural process (Table 2.2).

Baysala and Akmanb (2018) studied the determination and evaluation of chromium in Tuzla Aydinli Bay is an important subject since it is an industrial marine area. In this study, 32 samples were collected both from near the coastal shipyard activity to far of the activity areas in Tuzla Aydinli Bay, Istanbul (Turkey). The chromium concentration ranged from 0.50–5.27mg/kg. While chromium concentration in sediment samples was determined below the recommended limit values, the risk assessment approaches on the nickel and chromium in surface sediments showed that they varied no contamination to considerable contamination (Table 2.2).

Table 2.2
The comparison of chromium (Cr) concentrations in the surface sediment of the worldwide areas.

Locations	Cr concentrations (mg/kg)	References
Chao Phraya River estuary, Thailand	nd−47.50	[1]
The western past the upper Gulf of Thailand	17.41−46.72	[48]
Phetchaburi province, Thailand	10.454	[49]
Ha Long Bay, Vietnam	27	[50]
The upper Gulf of Thailand	26.1−349.92	[51]
Yangtze River estuary, China	34.64	[52]
Gulf of Pozzuoli (GoP), Italy	0.5−49.5	[53]
Jiaozhou Bay catchment, China	12.2−185.5	[54]
Daya Bay and adjacent shelf	10−85	[55]
Tuzla Aydinli Bay, Istanbul (Turkey)	0.50−5.27	[56]

Remark: nd is non−detectable

2.3.2 Sediment quality guidelines

Sediment quality guidelines (*SQG*s) are very useful to reveal sediment contamination by comparing the sediment concentration with the corresponding quality guideline [57]. These guidelines evaluate the degree to which the sediment-associated chemical status might adversely affect marine organisms and are designed to assist in interpreting sediment quality.

The weight−of−evidence approach to the development of numerical sediment quality guidelines has been described in detail . Sediment chemistry and biological effects from numerous reports have been compiled to support the acquisition of the guidelines. The weight-of-evidence approach involved three main steps. First, collect, evaluate, and compare all reported data on measurements of undesirable biological effects and chemical concentrations in the sediment. Next, identify the ranges that were rarely, occasionally, and frequently associated with adverse biological effects. Finally, determine the incidence of biological effects within each concentration range of each chemical as an accurate

estimate of the approach. The derivation of SQG_s involves the development of the biological effects database for sediments (BED_S) to collect relevant chemical and biological data from numerous studies conducted throughout North America. Nearly 350 publications were reviewed and screened for possible inclusion in the BED_S. Data from Balanced Segmentation Modeling, Biological analysis of sludge in the laboratory and in the field study on toxicity of sediments and benthos. The composition was assessed critically. For each chemical, BED_S data were retrieved and arranged in ascending concentration order in tabular form and summarize the available data for each chemical group considered [57].

The *ERL* and *ERM* measurements are expressed as the specific chemical concentrations of the toxic in the sediment. The *ERL* indicates the concentrations below which toxic effects are rarely observed or predicted: the *ERM* indicates which effects are observed by common or often observed above. The numerical values are included in the Sediment Quality Guidelines (SQG_s) developed by [58] for the National Oceanic and Atmospheric Administration (NOAA) National Status & Trends program as an official tool for assessing whether contaminant concentrations in sediments may be toxicological effects. These guidelines are for sediments separation for trace metals and organic contaminants. NOAA originally calculated *ERL/ERM* using available toxicity data collected from complete toxicity tests with different endpoints, including the effects on the organisms tested in general especially in the delicate period of life. This process is considered "weight of evidence approach", whose results are based on an extensive database of previously conducted studies. The studies used included a summary of the collected sediment chemical analysis and toxicity effect data. Using the data collected has the advantage of being able to make quick and inexpensive assessments with large datasets that can take much more time and costly specific toxicity testing. The collected datasets consisted of a variety of endpoints, including mortality, reproduction, growth rate, and juvenile survival in the sedimentary toxicity dataset for all organisms tested. The study was screened and only tests that use standardized methods and result in significant implications for *ERL/ERM* guidance [59, 60].

Two values were obtained for each chemical or chemical group. The lower 10^{th} percentile impact data for each chemical is identified and referred to as the low effects range (*ERL*). The median or 50^{th} percentile, of the impact data is identified and is called the effects range−median (*ERM*). Percentile of aquatic toxicity data was used by [61] to calculate seawater quality standards. Concentrations below the *ERL* value represent the least impact range. The range is intended to assess conditions in which impacts are unlikely to occur. Finally, concentrations equal to or above the *ERM* values represent the probable effect range can go which the effects tend to frequently occur.

The original acquisition procedure was modified to develop *TEL* and *PEL* for each analysis. Originally, the 10^{th} (*ERL*) and 50^{th} (*ERM)* percentile values were used to establish the SQG_s. This method is similar to the procedure used by [61] to standardize seawater quality in California. These authors argue that using percentile data of aquatic toxicity data effectively reduces the influence of a single data point on outcome assessment values. The original procedure did not use data in the no effect dataset. However, information on contaminant concentrations that are not related to effects may provide additional information for determining the relationship between contaminant exposure and effects. biological impact and therefore was used in this study.

Two SQG_s were obtained for each analysis using data in both the effects and non-effects datasets. The distribution of these datasets is determined using percentiles. For each analysis, *TEL* was obtained by calculating the geometric mean of the 15^{th} percentile of the effect dataset and the 50^{th} percentile of the no-effect dataset. Similarly, *PEL* were developed for each chemical, the geometric mean of the 50^{th} percentile of the effect dataset and the 85^{th} percentile of the no-effect dataset. *TEL* was intended to be assessed; the concentration of the chemical is below which side effects rarely occur. Similarly, *PEL* aims to provide a higher estimate of the concentration at which frequent side effects occur. Therefore, *TEL* and *PEL* were intended to define three concentration ranges for chemicals, including those that were rarely, occasionally, and frequently associated with adverse effects [62].

2.3.3 Enrichment factor

The enrichment factor (*EF*) approach to assessing man-made effects on sludge is to calculate the normalized enrichment factor (*EF*) for metal concentrations above the uncontaminated background level [63]. The *EF* attempts to reduce the metallurgical variability associated with mud/sand ratio variability and is a convenient tool for planning geochemical trends in large geographic areas. This can vary greatly in the mud (e.g., clay) to sand ratio. The *EF* is an indicator used to estimate the magnitude or degree of human pollution in sediments. The *EF* is calculated from reference element concentrations and the content of other metals is normalized in comparison with reference elements.

The reference element should be one that is stable in the soil, which is classified according to mobility and low degradation The most commonly used reference elements are Al, Fe, Mn, and Rb [64]. Aluminum is a conservative element mainly used by many scientists [65]. Fe is also used by many studies on marine and estuarine sediments [66]. This is because the Fe in most estuarine sediments comes from natural weathering processes and it is widely used to normalize the concentration of metals in order to reduce particle grain size influence because variations in Fe concentration can be explained by the difference in particle grain size, with fine-grained sediments having high Fe concentrations, besides geochemistry is similar to a trace metals and natural sediment concentrations have tendency to be consistent [67]. Earth crust and soil values were used as the background values for many years is that of average clay of deep-sea sediment [68]. The present study was used iron as a normalizer, subsequently the *EF* is calculated using equation 2.4

$$EF = \frac{\left(\frac{M}{X}\right)\text{sample}}{\left(\frac{M}{X}\right)\text{background}} \qquad (2.4)$$

where EF is metal enrichment factor for sediment

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

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

2.3.4 Geo-accumulation index

The geo-accumulation index (I_{geo}) approach to estimating the concentration of metals above the background or baseline concentration is to calculate the geo−accumulation index (I_{geo}) as proposed by [69], is commonly used to estimate anthropogenic inputs. According to these methods, the metal concentrations were normalized to the metal concentrations of average shale [70] or average crust. However, these metal levels tend to be very general and may be misleading in certain areas. The I_{geo} calculation was done using the following equation:

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5\ B_n}\right) \quad (2.5)$$

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.

C_n is the measured concentration of the element "n" in the pelitic sediment fraction (< 2 μm) and B_n is the geochemical background value in fossil argillaceous sediment (average shale; the factor 1.5 is used because of possible variations of the background data due to lithogenic effects [71]. Therefore, several researchers have recommended the use of regional background values. The I_{geo} value can be classified into 7 classes: The I_{geo} is classified by I_{geo} <0 practically unpolluted, 0–1 unpolluted to moderately polluted, 1–2 moderately polluted, 2–3 moderately to strongly polluted, 3–4 polluted, 4–5 strongly to very strongly polluted, and >5 very strongly polluted.

To determine the extent of pollution in aquatic systems using the heavy metal content in the sediments. The first priority is to determine the natural levels of these substances, i.e., "pre-industrial" levels, and then subtract them from the existing values for metal concentrations to obtain all enrichment caused by human influence, in order to obtain an optimal benchmarking basis for environmental studies. The

following criteria should be met to achieve representative values for metal concentrations: a large number of sediments must be analyzed corresponding to recent deposition in (1) grain size distribution, (2) material composition, and (3) conditions of origin. The fourth criterion is the sample must not be contaminated by the influence of civilization.

Several possibilities have been discussed to establish background values for trace metals [72]:

1. average shale composition as a global standard value;
2. fossil aquatic sediments from defined environments as a standard, taking into account natural allochthonous and autochthonous factors and mechanisms as well as regional influences;
3. recent deposits in relatively unpolluted areas;
4. short, dated sedimentary cores, which provide a historical record of events occurring in the watershed of a particular river or estuary.

These would enable an estimation of both the background level and the element's input change to be evaluated over a period of time. The most suitable data for international standards prove that for fossil strata and the data collected by [68] are often used as a universal basis for comparing metal contaminated sediments. For some metals, e.g., manganese, zinc and lead, the values of this so-called shale standard fall quite well with the average concentrations measured in recent shallow sediments in less polluted areas. For other examples, especially the composition is rich in basic stones. The values of the shale appear to be too high to compare with modern sediments from inland and coastal waters. Such elements, such as Cr, Ni, Co and Cu, the corresponding concentrations in fossil Rhine sediments [73] and in soils [74], underscoring the tendency to lower the background values of these metals. The characteristics of the limestone of the reservoir must be considered accordingly, especially for inspections that cover a limited surface area.

2.4 Ecological Risk Assessment

As the toxicity of heavy metal can pose an effect on marine organism, an analysis of ecological risks posed by anthropogenic activities should be conducted. In

the present, there are many indexes that calculate for determining the degree of pollution. Potential ecological risk index, which was developed by [75], is a popular methodology used to assess ecological risks for 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. Hakansan 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: the concentration requirement, the number requirement, the toxic factor requirement, and the sensitivity requirement.

Additionally, the marine environment can be defined by variables such as salinity, temperature, retention time, depth, pH, alkalinity, biological yield index oxygen concentration, etc. All these environmental variables may be directly or indirectly separated or combined, the distribution affects the water, sediments, and organisms and thereby affects the potential ecosystem of a given toxicant or a given wastewater discharge. Various water systems in this context are known as receivers, have different sensitivity to toxic substances. As the toxicity of heavy metal can pose an effect on marine organism, an analysis of ecological risks posed by anthropogenic activities should be conducted. In the present, there are many indexes that calculate for determining the degree of pollution.

Hakanson (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 should at least, account for the following four requirements:

1. The concentration requirement
2. The number of substance requirement

$$C_d = \sum_{i=1}^{n} C_f^i = \sum_{i=1}^{n} \frac{C_{o-1}^i}{C_n^i} \quad (2.6)$$

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

4. sensitivity requirement

$$RI = \sum_{i=1}^{n} E_r^i = \sum_{i=1}^{n} T_r^i \cdot C_f^i \quad (2.7)$$

where

RI =the requested potential ecological risk index for the basin/lake.

E_r^i =the potential ecological risk factor for the given substance (i).

T_r^i =the "toxic response factor" for the given substance, i.e. PCB=40·BPI/5, Hg=40·5/BPI, Cd=30·$\sqrt{5}/\sqrt{\text{BPI}}$, As=10, Pb=Cu=5·$\sqrt{5}/\sqrt{\text{BPI}}$, Cr=2·$\sqrt{5}/\sqrt{\text{BPI}}$ and Zn=1·$\sqrt{5}/\sqrt{\text{BPI}}$, where BPI=the bioproduction index that come from lake bioproductivity obtained ignition loss and nitrogen content of superficial sediment.

Hakanson (1980) suggested that to meet the requested demands for accuracy, simplicity and rapidity, the risk index discussed in this context will be based

exclusively on sediment data. There are several reasons why a focus on the sediments may be fruitful in this case:

1. Data from the sediments provide time-integrated mean values of considerable time-stability compared to data on pollutants from, for example, water samples.
2. Sediment samples are comparatively easy to collect in the field.
3. The sample representatively in time and space may be evaluated in a rather simple way.
4. The adopted analytical procedure can generally provide both cheaper and better data from sediments than from, for example, water samples, because the concentrations are generally much higher in the sediments.

Potential ecological risk index (*RI*), which was developed by [75], is a popular method for assessing ecological risks for water pollution control. This method is based on the assumption that the sensitivity of the water system depends on the yield. The objective of creating an ecological risk index to be used in the control of aquatic environmental pollution. Hakansan 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: the concentration requirement, the number requirement, the toxic factor requirement, and the sensitivity requirement.

Values of natural background levels or preindustrial reference levels for the substances were considered. These values come from determining about 50 lakes from Europe and America, which are as follows (in ppm): PCB = 0.01, Hg = 0.25, Cd = 1.0, As = 15, Cu = 50, Pb = 70, Cr = 90 and Zn = 175.

It is widely implemented in many studies to assess the degree of the risk posed by heavy metal pollution in sediments. Results of the studies often showed the risk of heavy metal in sediments varied from low ecological risk to high ecological risk [5, 76, 77].

2.5 Problems of Chromium Analysis

The determination of heavy metals in sediment by atomic adsorption spectroscopy depends on the digestion method used [78]. Digestion procedures often use strong oxidizing acids. The solution is nitric acid, perchloric acid, hydrochloric acid, hydrofluoric acid, hydrogen peroxide and sulfuric acid. The use of nitric acid has been reported to measure Ca, Al, Mg, K, As, Pb, Cd, Fe and Zn in various environmental and biological samples [79]. It was concluded that HNO_3−HCl extraction followed by AAS is both accurate and precise in the determination of Cr, Mn, Zn, Ni, Cu, Pb, Hg, V and As, but low results were obtained for Fe, Cd, Co and Sb in NBS SRM 1645 standard river sediments and river sediments [80].

The three of the most effective acid mixtures were used in microwave digestion to see if the metal recovered. The power supplied to the microwave oven and the digestion time used vary with each acidic mixture. The recoveries of 9 heavy metals were compared with the certified values in Table 2.3. The standard sediment samples were tripled with each acid mixture in a closed Teflon vessel equipped with a pressure relief valve [81].

The use of aqua regia with microwave digestion resulted in recovery between 43 and 77% for all metals as shown in Table 2.3. These low recovery levels may be due to incomplete sediments degradation, which may contain silicates or other minerals. Loring and Rantala report that strong acid digestion without HF results in incomplete digestion. Since silicates and other refractory oxides are insoluble, the recoveries of Pb, Cd, Cu, Zn, Mn, Ni, Co, Fe and Cr obtained using of HNO_3−H_2O_2 (1:1), HNO_3−HCl (3:1) and HNO_3−HCl (1:3) by microwave digestion are summarized in Table 2.3 [81].

Table 2.3 Influence of acid mixture on the metal recoveries obtained by microwave digestion.

Metal (µg/g)	HNO_3^-:H_2O_2 (1:1)	HNO_3^-:HCl (3:1)	HNO_3^-:HCl (1:3)	R
Pb	22.5±1.4	27.55±0.6	16.63±1.7	31±1.6
Cu	19.18±1.6	27.31±0.2	12.59±19	26±2.6
Cd	7.49±0.2	8.27±0.06	6.64±1.0	9.2±0.4
Zn	51.21±2.8	77.14±0.6	62.11±0.6	81±7.1
Ni	12.14±0.8	14.44±0.7	11.66±0.6	16±1.2
Mn	243.7±11.6	346.8±0.1	245.5±9.3	359±24
Fe	19,219±1,144	20,400±50	12,414±1,202	25,900±1,500
Co	8.27±0.2	9.84±0.5	5.66±1.0	9.6±0.8
Cr	17.35±0.9	20.31±1.0	10.26±0.7	24±2.0

Remark: Power 100%; Digestion time = 20 minutes; n = 3 R = Certified value of standard reference (AGAL-11)

The use of HNO_3–H_2O_2 yielded a recovery of between 63−86%. This low recovery may be due to the fact that the mixture was ineffective at separating the 9 elements from the sediments at high pressure and temperature. The high pressure inside the Teflon vessel was released automatically, some of the HNO_3–H_2O_2 solution escaped. However, the most effective acidic mixture was found in microwave digestion (set at 100% power at 1000 watts for 20 minutes) is reverse aqua regia. It provides good yields (85-105%) for Pb, Cd, Cu, Zn, Mn, Ni, Co and Cr, but only 79% for Fe. This low iron recovery may result from decomposition of iron locked in incomplete crystals. The reverse aqua regia was then optimized by modifying the power and time settings [81].

The aqua regia (HNO_3–HCl, 1:3) digestion process (ISO standard 11466) was considered sufficient for the analysis of all recoverable heavy metals in the soil of some regions and it is used to assess the availability of maximum constituents for plants [82]. This technique enables fast, safe and efficient digestion. However, the aqua regia digestion failed to accurately quantify the 20 trace elements in some sediments [83]. [84]reported that aqua regia extracted < 70% of Cd, Mn, and Ni from

some sediments. Recovery of 43 to 77% for Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn from AGAL−11 reference sediment was also reported by [81].

Nadkarni (1984) reported that a mixture of aqua regia, HF, and H_3BO_3 provides satisfactory precision and accuracy for dissolving silica matrices. The addition of boric acid in the second stage of digestion not only causes the free fluoride in the solution to form a complex [85]. In the modified method, HF was added to the solid 16 h before the aqua regia addition and the mixture was then subjected to microwave heating [79]. Recovery of all constituents obtained using aqua regia and aqua regia+HF of microwave digestion. They are summarized in Table 2.4.

Table 2.4 Certified concentrations and recoveries obtained using two digestion procedures with National Institute of Standards and Technology (NIST) standard reference materials (SRMs).

Metal	% Recovery		Certified concentrations (mg/g)
	Aqua regia	Aqua regia+HF	
Al	60	95	60.9
Fe	87	91	41.1
Cd	90	96	3.45
Cr	72	89	135
Cu	96	110	114
Mn	89	105	555
Ni	92	91	44.1
Pb	99	95	161
Zn	95	95	438

Remark: SRMs 2074 from NIST, representing river sediment

2.6 The Gulf of Thailand

The Gulf of Thailand extends from the shallow western part of the South China Sea over 750 km to the north-west between the Thai−Malaysian Penninsula and Indo−China (Figure 2.2). Its northern boundary is the collected from the coast of the

central plain of Thailand. There are four major rivers flowing into the inner Gulf, namely, the Chao Phraya, the Bangpakong, the Tha Chin and the Mae Klong: the approximate ratio of their fresh water discharges as recorded by the Royal Irrigation Department is 10:4:1:6. The Chao Phraya River, the most important, passes through the capital city of Bangkok (population of 5 millions) and has an average discharge varying from 8000×10^6 to $34{,}000\times10^6$ m^3/year in the dry and wet seasons, respectively. Agricultural development along the northern section of the river and industrial development along the riverbanks and south of the Bangkok Metropolis have been proceeding rapidly during the last decade. Since Thailand does not yet have effective laws and measures for pollution control, these domestic, agricultural, and industrial wastes, either partially treated or without treatment, are being discharged into the river, metals, grease and oil and phenolic compounds [1].

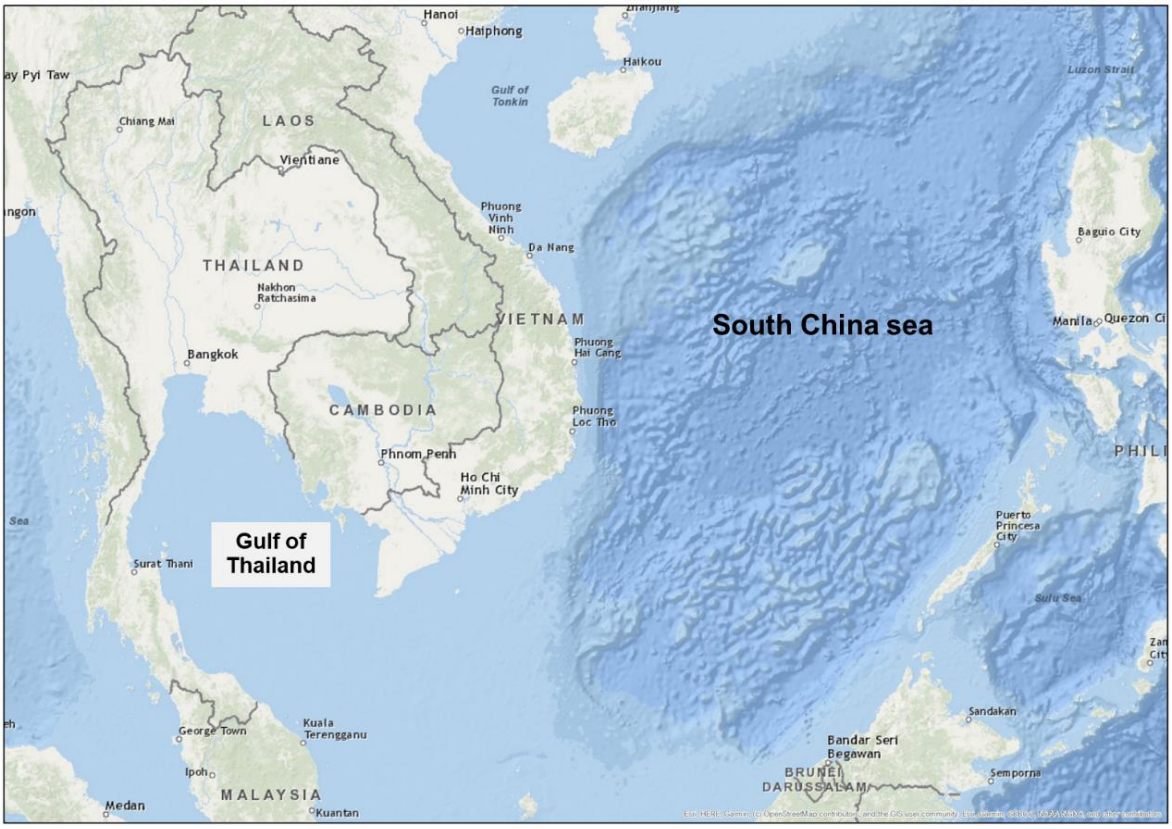


Figure 2.2 Map of the Gulf of Thailand.

2.6.1 The inner Gulf of Thailand

1) Geological characterizations

The inner Gulf of Thailand is a semi−enclosed square bay which surrounded by land in three directions and in the southern part is connected to a central Gulf. It is located at latitude 13°20'N and longitude 100°45'E and with a total area of approximately 90×90 km^2 [88] (Figure 2.3). Around the Gulf is full of the highly populated area and some heavily polluting industries. Industrial sites have been discharging untreated effluence into the inner Gulf. In addition, domestic wastewater generated by residents in and around the area is discharged into open ditches, which ultimately drains into the Gulf. The inner Gulf have been collected the contaminants and nutrients from the four major rivers at the head of the inner Gulf which is the Mae Klong River (MK), the Tha Chin River (TC), the Chao Phraya River (CP) and the Bangpakong River (BK) about 50 percent. Thus, frequent algae blooms have become common in the Gulf [2].

The inner Gulf of Thailand, where is influenced by tide and wind flow. The current is controlled by monsoon winds. The Gulf of Thailand is under the two monsoons, the northeast monsoon (November to January) and the southwest monsoon (May to August) (Figure 2.4).

For the period of the northeast monsoon, the current moves counterclockwise along the coastline. The direction of the circulation flows from the east to west and then moves southward to the southwestern part of the Gulf. In the transition period (February−April), the circulation pattern slightly changes. Northward currents occur along the eastern coast with the weaker counterclockwise flow (Figure 2.4).

During the southwest monsoon, the clockwise flow occurs. The current flows from the southwestern part to the north along the west coast, also it moves from northeastern part to the central of the lower part of the Gulf (Figure 2.4) [86]. The northward current flowing along the eastern coast and islands is still be seen, but it becomes weaker compared to those in the previous seasons. The current in the Gulf becomes weaker and more

complicate in the transition time occurring between September and October. In this transition period, the clockwise flow becomes weaker. Strongest currents from main rivers are observed because of high river discharges.

2) Ecological and economic services

The inner Gulf of Thailand is very important coastal area. It was providing not only ecological service, but also economic service. Major marine resources in the inner Gulf of Thailand are fisheries, coral, mangrove, oil, and mineral. Industrial sites have been discharging untreated effluence into the inner Gulf. In addition, wastewater from homes generated by residents in and around the area was released into an open ditch, which eventually flows into the Gulf of Thailand [2].

3) Sink and source of pollutions

Coastal and marine water pollution in Thailand is primarily caused by direct emissions from rivers, surface runoff and drainage from the port area. The city centers in Thailand are usually located on the coast and estuaries and most domestic waste and waste is disposed directly into shallow coastal environments, so rivers are generally heavily contaminated with municipal sewage, industrial wastewater, and sediments [87].

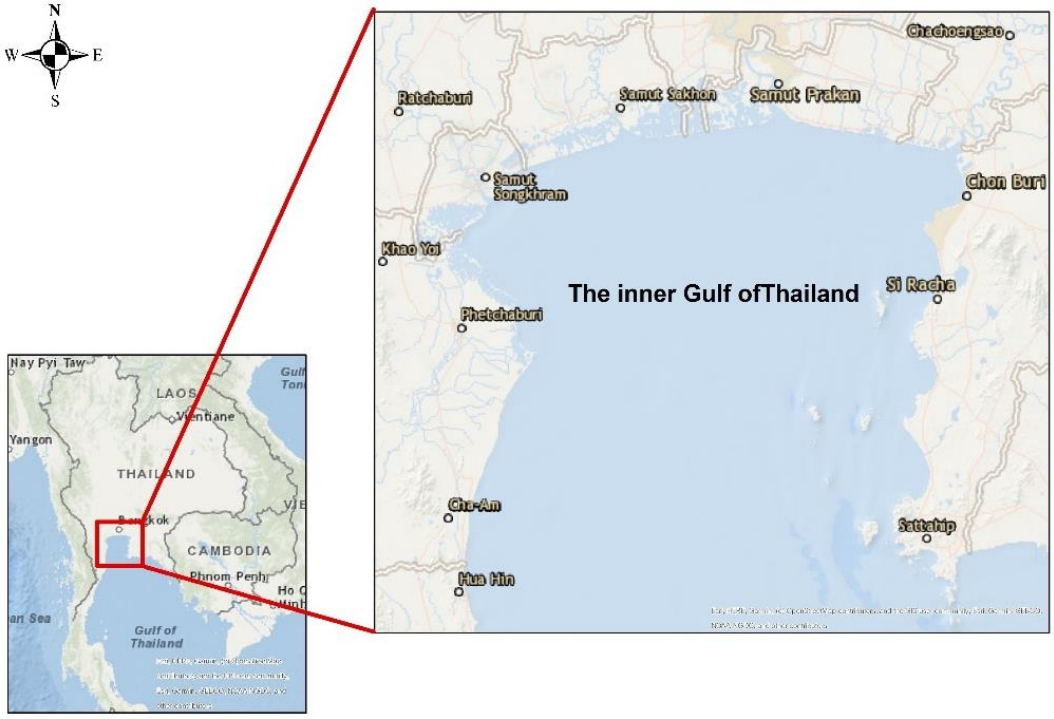


Figure 2.3 Map of the inner Gulf of Thailand.

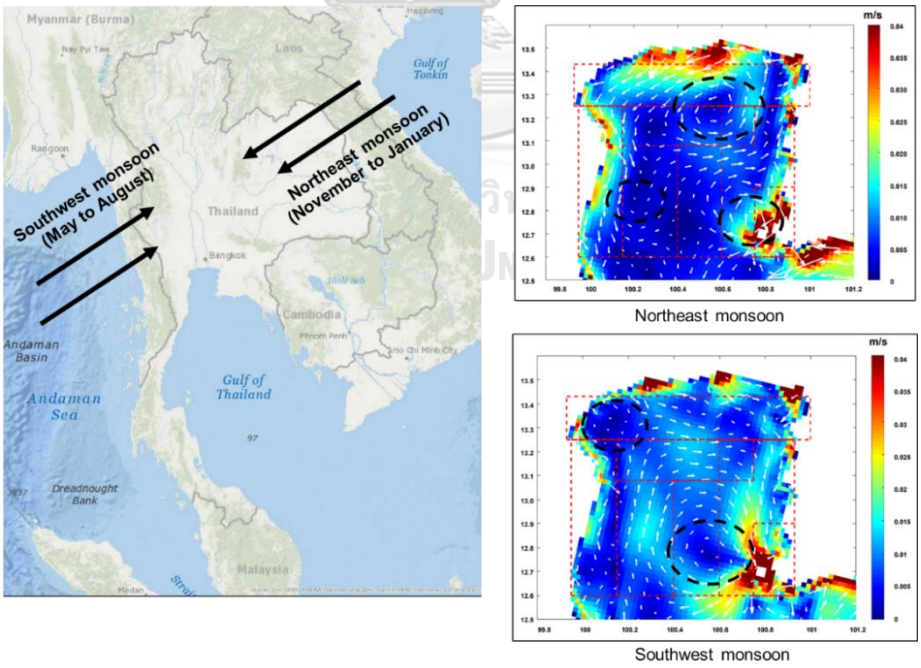


Figure 2.4 Map of monsoon and average current throughout the depth of water in the Gulf of Thailand.

Source: Meksumpun (2019)

2.6.2 Mae Klong River

1) Geological characterizations

The geological features of the Mae Klong River hydrographical basin has a strong influence on river chemistry and the flux of minor elements in the central part of the coastal areas studied. Especially, the Mae Klong River is the most important river in the study area and located in the west of the upper Gulf of Thailand. The surrounding coastal areas are characterized by exponential population growth in accordance with relevant industrial and economic developments. The 138 km long river begins at the confluence of the Kwai Noi and Kwai Yai rivers in Kanchanaburi and flows through Ratchaburi and Samut Songkhram enters the Gulf of Thailand, where one of the most important tin production areas in Southeast Asia is located [88] (Figure 2.5).

2) Ecological and economic services

The Mae Klong River supplies water for irrigation and supports aquaculture industries such as fish ponds and shrimp farms. The Mae Klong is occupied by agricultural fields such as rice fields, vegetable farms, orchards and industries such as the chemical industry, paper mills and backup battery factories. Water Runoff from agricultural effluents from aquaculture and household waste flows directly into the river through sewers and tributaries [89].

3) Source of pollutions

The Mae Klong River received a lot of untreated wastewater and other waste from industrial, agricultural, and community activities. Heavy metal from these activities was one of pollution loading into the rivers, causing degraded aquatic environment [90].

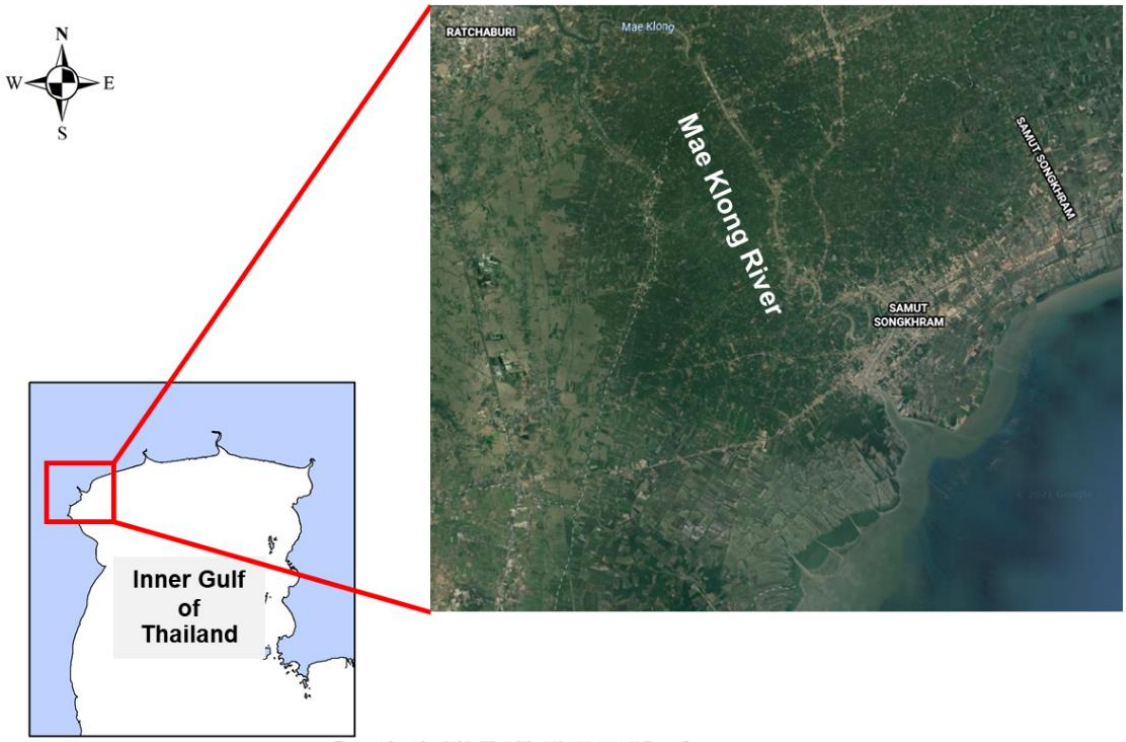


Figure 2.5 Map of the Mae Klong River.

2.6.3 Tha Chin River

1) Geological characterizations

Tha Chin River is located in a large basin in central Thailand and is the second most important river in the country. The Tha Chin River is a tributary of the Chao Phraya River, which is a waterway that drains from the central basin. The starting point of the Tha Chin River is the confluence of the Chao Phraya River, which is far from Bangkok about 180 km north and flows into the upper Gulf of Thailand. Approximately 60 km east of the city, the basin covers an area of 13,000 square kilometers and has a population of approximately 2 million people. The main channel of the Tha Chin River is 325 km long and flows through four provinces [91] (Figure 2.6).

2) Ecological and economic service

The lower Tha Chin region is the first 82 km downstream, covering an area of 1306 km^2 (11% of the watershed). The region is affected by tidal

conditions from the Gulf of Thailand and aquaculture and activities. The central region of Tha Chin District starts from 82 km up to Chao Phraya at a distance of 202 km downstream. The land use in the central region is a complex blend of agriculture, aquaculture, and raising pigs. The region covers 4263 km^2, or 36% of the total watershed area. The remainder is the Upper Tha Chin region, which is almost entirely covered by paddy fields and small communities [92].

3) Source of pollutions

The Tha Chin River basin is an intensely used area with a wide variety of different pollution sources from domestic, agricultural, and industrial activities. In the Tha Chin River basin, densely populated areas, often concentrated along the riverbank, are the major source of domestic wastewater. Agricultural pollution sources can be divided into point- and non-point such as pig, chicken and fish farms generate large amounts of wastewater. Industrial wastewater is a significant point-source pollution factor, especially in the lower basin, where large factories predominate and industrial growth rates are high, such as food processing, textile manufacturing, dyeing and bleaching factories [93].

Figure 2.6 Map of the Tha Chin River.

2.6.4 Chao Phraya River

1) Geological characterizations

The Chao Phraya River is the largest river located in northern and central Thailand. It accounts for about half of the rivers flowing into the Gulf of Thailand. The Chao Phraya River is the largest river located in northern and central Thailand (Fig. 2.7), accounting for about half of the river flowing into the Gulf of Thailand. Rivers and estuaries are Bangkok's main sea routes. It was therefore influenced by domestic and industrial activities there prior to interaction with the Gulf of Thailand, which is the shallow arm of the South China Sea [94].

2) Ecological and economic services

The Chao Phraya River is the largest river in Thailand, formed by four main rivers in northern Thailand. The benefits of this river are many for industries, fishery, agriculture, transportation, domestic consumption, etc., which most communities and consumers especially in Bangkok must rely mainly on this river [95].

3) Source of pollutions

The Chao Phraya River is heavily affected by a wide range of human activities along the river [87]. Pollution flowing into the river comes from the waste of cities located on its banks. There it receives large quantities of wastewater from households, agriculture and industry. There are many domestic and industrial waste sources, leading to an increase in the heavy metal content in water and sediment [96].

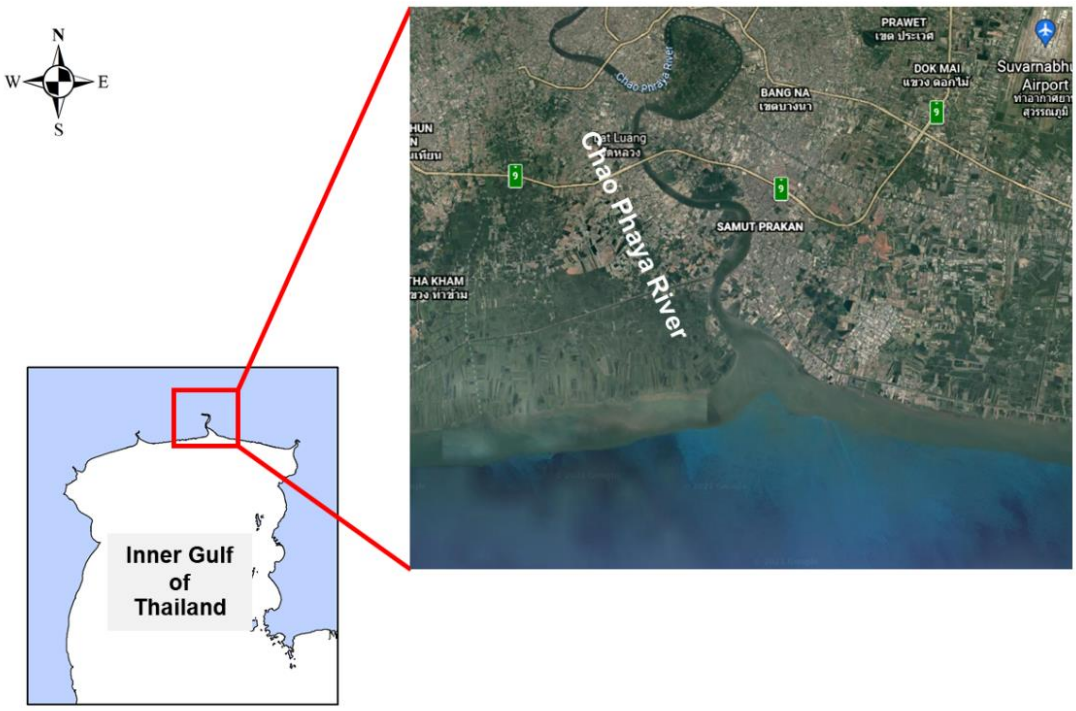


Figure 2.7 Map of the Chao Phraya River.

2.6.5 Bangpakong River

1) Geological characterizations

The Bang Pakong River is the most important watershed in eastern Thailand and is an important source of water for irrigation as well as heavy and light industry, aquaculture, animal husbandry, municipal procurement, and wastewater dilution (Figure 2.8). The basin covers an area of 18,500 km^2 and rivers are the result of the merger of two smaller rivers. The river flows into the Gulf of Thailand during the dry season, salt invasion can travel 150 km upstream [97].

2) Ecological and economic services

The Bangpakong river is located in the eastern region of Thailand. The water resources of the Bangpakong river are already heavily exploited for productive use in agriculture, industry, and tourism. The Bangpakong river supports a large agricultural community, mainly involved in

agro−forestry (e.g., trees such as mango, coconut, and rubber), irrigated crops (e.g., rice, cassava, maize, and other annual crops), livestock (such as chicken and pigs), and fisheries, and a wide range of growing industries [98].

3) Source of pollutions

The main sources of nutrients for drainage are municipal communities, agricultural, poultry, and aquaculture soils located in the watershed. The Bang Pakong River is an important source of nutrients due to the large number of contaminants from urban, rural areas, pig farms, rice fields, fish and shrimp ponds. Therefore, plankton bloom frequently in the eastern part of the inner Gulf of Thailand [97].

Figure 2.8 Map of the Bangpakong River

CHAPTER III
MATERIALS AND METHODS

The inner Gulf of Thailand is a very important coastal area. It was providing not only ecological service but also economic service. However, rapid agriculturization, urbanization, and industrialization of Thailand have been generated pollution into coastal environments via river runoff. One of the serious pollutions is Cr, which was discharged from 4 major rivers into the inner Gulf of Thailand. All materials and methods of the present study were totally explained and describes as follows:

3.1 Study Areas

The inner Gulf of Thailand is a semi−enclosed square bay, where is located at latitude 13º20'N and longitude 100º45'E. Its total shoreline is approximately 350 km long, with a total area of approximately 90×90 km^2, and its average depth is 15 m. Moreover, the inner Gulf of Thailand is a transition area between land and sea. It has a limited water exchange with the lower Gulf, while there are high inflows from four major rivers (the Mae Klong, the Tha Chin, the Chao Phraya and the Bangpakong rivers) carrying high suspended load into the Gulf. Additionally, the inner Gulf of Thailand is a very important marine resource for economic developments in Thailand. In the past century, the industrial, agriculture and urban areas have been continued to expand around the Gulf. Moreover, the Gulf's waters are used increasingly for recreation and fishing by commercial fishermen. According to the mention above, the inner Gulf of Thailand is receiving large amounts of macro and micro pollutants due to industrialization, agriculturization and urbanization. Therefore, the inner Gulf of Thailand, including the Mae Klong, the Tha Chin, the Chao Phraya and the Bangpakong River estuaries are chosen as the study areas.

3.2 Sampling Points

A total of 63 sampling sites were established in order to assess distribution of total chromium contamination in the surface sediment of the inner Gulf of Thailand.

For river estuaries, station MK1, TC1, CP1 and BK1 were established in the river influences zone in order to characterize effects of river runoff as sources of pollutants (Figure 3.1). While, other stations were established in the sedimentation zones of the river estuaries in order to characterize the deposition of chromium in the surface sediments (Figure 3.1). Total sites were established in total of 7 sites in the Mae Klong, 9 sites in the Tha Chin, 9 sites in the Chao Phraya and 9 sites in the Bangpakong Rivers estuaries in order to identify different effects of chromium in the surface sediments (Figure 3.1).

For the inner Gulf of Thailand, 28 sampling sites were established in different depths entire the inner Gulf of Thailand (Figure 3.2). Water depth of station GT1, GT3, GT4, GT9, GT10 and GT11 was in range of 0−10 m. Station GT16, GT17, GT18 and GT20 were ranged of 10−15 m of water depth. Water depth at 15−20 m was found in station GT23, GT24, GT25, GT26, GT27, GT28 and GT32. Station GT19, GT29, GT30, GT31, GT33, GT35 and GT36 were ranged of 20−25 m. Finally, water depth of station GT34, GT39, GT40 and GT41 was in the range of 25−30 m (Figure 3.2).

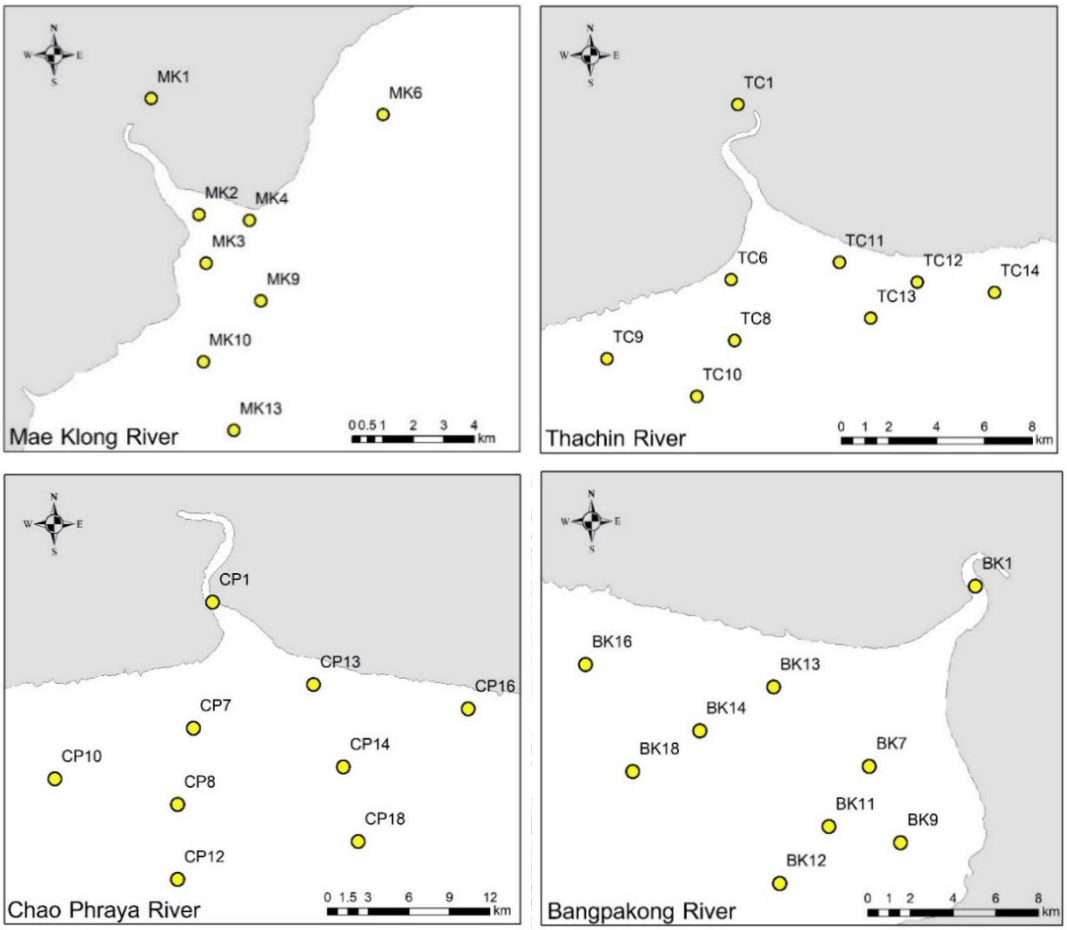


Figure 3.1 Map of sampling sites in the Mae Klong, the Tha Chin, the Chao Phraya and the Bangpakong River estuaries.

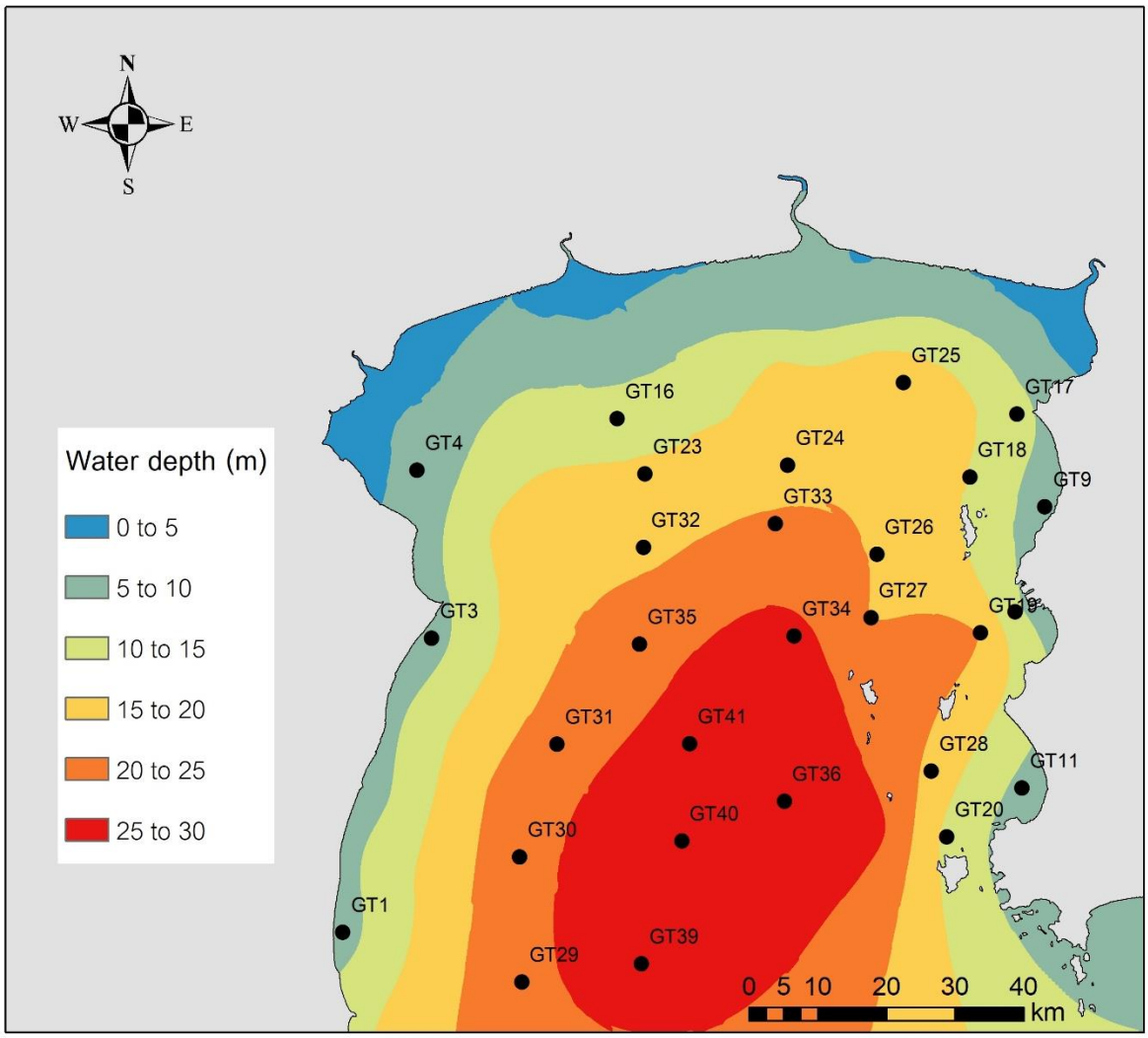


Figure 3.2 Map of water depth contour and sampling sites entire the inner Gulf of Thailand.

3.3 Research Materials

3.3.1 Sampling cruise

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

3.3.2 Sediment sampling

1) Ekman grab sampler
2) Smith−McIntyre grab sampler
3) Projector scale

4) Polyethylene spoon
5) Polyethylene zip bag
6) Water proof labeling pen
7) Cooling container

3.3.3 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) Atomic absorption spectrophotometer (Agilent 240AA, USA)
5) TOC analyzer (Analtik Jena Multi N/C® 3100, Germany)
6) Muffle furnace (Nabertherm LT5/12, Germany)
7) Spectrophotometer (UNICO Spectrophotometers 1200)

3.3.4 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

3.3.5 Chemical substances

1) HNO_3 (QReC, AR, New Zealand)
2) HCl (QReC, AR, New Zealand)
3) HF (MERCK, AR, Germany)
4) H_2O_2 (MERCK, AR, Germany)
5) NaOAc (Sigma−Aldrich, AR, USA)
6) $NH_2OH.HCl$ (Sigma−Aldrich, AR, USA)
7) $MgCl_2.6H_2O$ (KemAus, AR, Australia)
8) $Mg(NO_3)_2$ (Sigma−Aldrich, AR, USA)
9) Ammonium acetate (QReC, AR, New Zealand)

8) Heavy metals standard solution (Agilent, AR, USA)

3.4 Measurement Parameters

3.4.1 Total heavy metals

1) Chromium (Cr)
2) Iron (Fe)

3.4.2 Sequential fractions

In defining the desired partitioning of chromium [25], analysis was taken to choose fractions likely to be affected by various environmental conditions; the following five fractions were selected as follow:

1) **Exchangeable form:** numerous studies performed on sediments or on their major constituents (clays, hydrated oxides of iron and manganese, humic acids) have demonstrated the adsorption of trace metals; changes in water ionic composition (e.g., in estuarine waters) are likely to affect sorption−desorption processes.
2) **Bound to carbonates form:** several workers have shown that significant trace metal concentrations can be associated with sediment carbonates; this fraction would be susceptible to changes of pH.
3) **Bound to iron and manganese oxides form:** it is well established that iron and manganese oxides exist as nodules, concretions, cement between particles, or simply as a coating on particles; these oxides are excellent scavengers for trace metals and are thermodynamically unstable under anoxic conditions (i.e., low Eh).
4) **Bound to organic matter form:** trace metals may be bound to various forms of organic matter: living organisms, detritus, coatings on mineral particles, etc. The complexation and peptization properties of natural organic matter (notably humic and fulvic acids) are well recognized, as is the phenomenon of bioaccumulation in certain living organisms. Under oxidizing conditions in natural waters, organic matter can be degraded, leading to a release of soluble trace metals.
5) **Residual form:** once the first four fractions have been removed, the residual solid should contain mainly primary and secondary minerals,

which may hold trace metals within their crystal structure. These metals are not expected to be released in solution over a reasonable time span under the conditions normally encountered in nature.

3.4.3 Related parameters

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

3.5 Sampling and Sample Preparations

3.5.1 Sediment sampling

All sediment samplings were carried out in different seasons, including July 2017 (southwest monsoon season), December 2017 (northeast monsoon season), and April 2018 (dry season). The sampling is separated into 2 teams. First team was carried out on broad of Kasetsart Research Vessel, which was collected the sample for the central station of the Gulf. The second team was carried out on broad of Marine Research Vessel, which was collected the sample for the river estuarine stations and near coastal line stations.

The surface sediment samples (0−1 cm) were collected from four river estuaries and some stations of the inner Gulf of Thailand including station GT1, GT3, GT4, GT9, GT10, GT11, GT16, GT17, GT18, GT19, GT20 and GT25 using the Ekman grab sampler, while the surface sediment samples remained in the inner Gulf of Thailand including station GT23, GT24, GT26, GT27, GT28, GT29, GT30, GT31, GT32, GT33, GT34, GT35, GT36, GT39, GT40 and GT41 were sampled using the Smith−McIntyre grab sampler. All surface sediment samples were placed in cleaned polyethylene zip bag and stored on cooling container (4 °C) in the dark at field sampling until laboratory analysis.

3.5.2 Sample preparations

At laboratory, the wet sediment samples were then divided into two sub−samples. The first sub−sample was used to determine the AVS and water content. The remaining sediment sub−sample was dried at −40 °C for 72 hours

using a freeze−dryer (LABCONCO, Freezone 6, USA). Subsequently, dried sediment samples were sieved through a 1 mm using American standard test sieve series (ASTM, E11, USA), in order to remove coarse debris and fragments of shells. Each sieved sediment samples were ground to obtain texture powder using an agate mortar. All homogenous sediment samples were stored in acid−washed polyethylene tube in desiccators for later analysis of total chromium, sequential fractions, TOM, TOC and TP.

3.6 Chemical Analysis

3.6.1 Total chromium and iron analysis

For total chromium and iron analysis, 0.5 g dry weight of each homogenized sediment sample was placed to acid−cleaned Teflon vessels. Then, 4 ml of concentrated hydrofluoric acid (HF) and leaved to react overnight at room temperature. Following the initial reaction period, 2 ml of aqua regia ($HCl:HNO_3$ at a ratio 3:1 v/v) added to sample. Each sediment sample were digested for 15 min at 180 °C using the high performance microwave digester (Mileston, Series 135931, Italy). After the digestion, 2 g of boric acid (H_3BO_3) was added to neutralize excess HF before analysis. The samples were filtered using paper filter (Whatman No.42, UK) and diluted with distilled water to 50 ml [64, 79]. The filtrate samples were stored in acid−washed polyethylene bottle until analysis. Total chromium and iron were determined using a flame Atomic Absorption Spectrophotometer (Agilent 240AA, USA).

3.6.2 Sequential fraction of chromium

A sequential extraction method proposed by [42]. The major mechanism chromium in sediment leads to existence of five categories, including exchangeable, bound to carbonate (acid−soluble), bound to Fe−Mn oxide (reducible), bound to organic matter bond (oxidizable) and residual fraction (silicate). Each difference form respected for bio−availability and remobilization of chromium.

Each sediment (MK1, MK6, MK13, TC1, TC9, TC14, CP1, CP10, CP16, BK1, BK9, BK16, GT3, GT9, GT16, GT32, GT39, GT40 and GT41) were divided into the following fractions:

1) **Exchangeable form:** numerous studies on sediment or its primary constituents (clay, iron and manganese hydrides, humic acids) have shown the adsorption of trace metals and changes in the ionic composition of water (e.g., in estuary waters) tend to affect the adsorption-transpiration process.
2) **Bound to carbonates form:** many workers have shown that significant trace metal concentrations can be linked to carbonate precipitates. This part is sensitive to changes in pH.
3) **Bound to iron and manganese oxides form:** it is well established that iron and manganese oxides exist in the form of lumps, solidification, inter-particle cement or just as a coating on the particles. These oxides are excellent waste collectors for small metals. and is thermodynamically unstable under anoxic conditions.
4) **Bound to organic matter form:** trace metals may bind to various forms of organic matter: organisms, debris, coatings on mineral particles, etc. The complex and foaming properties of natural organic matter are well recognized as the phenomenon of bioaccumulation in some organisms. Under oxidizing conditions in natural water, organic matter is degradable, leading to the release of small amounts of soluble metal.
5) **Residual form:** the remaining solids should contain mostly primary and secondary minerals, which may retain the trace metal within the crystal structure. These metals are not expected to be released in solution for a reasonable period of time under normal conditions found in nature.

All extracted samples were determined chromium concentration in different extracts using a flame Atomic Absorption Spectrophotometer (Agilent 240AA, USA).

3.6.3 Total organic matter analysis

Weight loss was measured after heating the samples overnight at 100 ºC to remove water, at 550 ºC for 4 hours to remove organic matter. The

difference in mass before and after the ignition process were used to calculate the TOM.

3.6.4 Total organic carbon analysis

The TOC was a measure of the basic chemical compositions of organic matter, which is used as an indicator of its presence in the sediment. It is an important component of environmental characterization. TOC is also the most important component of sediments, because it can be used to distinguish the sources of marine and terrestrial organic matter, environmental deposition conditions, pollution index, and indicators of sediment quality and yield. All samples of TOC in surface sediment were determined in the sample segment after carbonate removal with 1.2 N HCl (at 60 ºC, 24 hours) using a TOC analyzer (Analytik Jena, multi N/C® 3100, Germany)

3.6.5 Total phosphorus analysis

The TP determination consisted of initial ash determination of dry samples containing 5% (w/v) $Mg(NO_3)_2$ as the oxidant [103] at 550 ºC for 2 hours followed by extraction with 1 N HCl as 16 hours at room temperature [104]. The extracted samples were analyzed for orthophosphate using the acid molybdate–ascorbic method [105].

3.6.6 Acid volatile sulfide analysis

The wet sediment sample (0.5−1.0 g) was reacted with 18 N H_2SO_4 in colorimetric gas detection tubes (Gastec, 201LH, Japan) to release hydrogen sulfide (H_2S) from solid phase sulfide in the sediment. The produced gas is accumulated in milligrams of gas detection tubes.

3.6.7 Water content

The method relies on the sediment moisture by oven drying the sediment sample to constant weight. The water content (%) was calculated from the sample weight before and after drying. Weigh the same amount of each wet sludge sample. The samples were then dried for 24 hours, after which each sample was weighed again. Compare the weight of each sludge sample before and after drying to determine the mass ratio.

3.7 Data Analysis

3.7.1 Spatial distributions

Spatial heterogeneity distributions of total chromium concentration and related parameters in the surface sediment were performed by deterministic interpolation technique using an inverse distance weighting (IDW) of ArcGIS™ v.10.4 software.

3.7.2 Contamination status of chromium

1) Sediment quality guidelines

Sediment quality guidelines (*SQG*$_s$) are very useful in terms of disclosing sludge contamination by comparing sludge concentrations with relevant quality guidelines [57]. These guidelines evaluate the degree to which the sediment−associated chemical status might negative effects on marine life and is designed to assist in the interpretation of sediment quality.

The chromium contamination was compared with US National Oceanic and Atmospheric Administration (NOAA), Canadian *SQG*$_s$, National Oceanic Administration of China (NOAC) and Australian and New Zealand Environment and Conservation Council (ANZECC) including *ERL* (effect range low) and *ERM* (effect range median) (Table 4). The level of chemical contamination is classified according to Long et al. (1995) as follow:

- The concentrations below *ERL* represent a minimal−effects range, which effects would be rarely observed.
- The concentrations between *ERL* and *ERM* represent a possible−effects range which effects would occasionally occur.
- The concentrations above *ERM* represent a probable−effects range, which effects would frequently occur.

In addition, the comparison with Canadian and Wisconsin united states sediment guideline quality including *TEL* (threshold effect level) were identified to adverse effects only rarely occurred and *PEL* (probable effect level) were identified to adverse effects frequently occurred (Table

3.1). The *TEL* and *PEL* were intended to define three concentration ranges according to MacDonald et al. (1996) as follow:

- Chemical concentrations below *TEL* that rarely associate with adverse effect.
- Chemical concentrations between *TEL* and *PEL* that occasionally associate with adverse effect.
- Chemical concentrations above *PEL* frequently associated with adverse effects.

Table 3.1 The values of chromium concentration in different sediment quality guidelines; all unit is in mg/kg.

Condition	Sediment Quality Guidelines					
	NOAA, USA	Wisconsin	Canadian	Thailand	NOAC, China	ANZECC
Effects range low (*ERL*)	80		81		80	81
Effects range median (*ERM*)	145		370		270	370
Threshold effect level (*TEL*)		43	52.3			
Probable effect level (*PEL*)		110	160			
SQG_T				42		
Reference	NOAA (2006)	WDNR (2003)	Macdonald et al. (1996)	PCD (2015)	NOAC (2002)	ANZECC (1997)

2) Enrichment factor

This method normalizes the measured metal concentration compared to the reference metal and is often used as a pollution indicator [99]. The continental shale abundance metal concentrations were used as the background chromium contents. In general, aluminum is a major constituent of clay minerals and is used as a reference element to assess

the presence of heavy metal pollution in some environments. However, iron can be used as a reference element due to its conservative nature [68]. The present study was used iron as a normalizer, subsequently the *EF* is calculated using equation 3.1.

$$EF = \frac{\left(\frac{C_n}{Fe}\right)\text{sample}}{\left(\frac{C_n}{Fe}\right)\text{background}} \quad (3.1)$$

where

$\left(\frac{C_n}{Fe}\right)$ sample is chromium and iron ratio observed for sediment sample.

$\left(\frac{C_n}{Fe}\right)$ background is natural chromium and iron ratio for reference sediment. [58].

The degrees of chromium pollution are classified as seven tiers of *EF* indices are defined in Table 3.2.

Table 3.2 Tiers of chromium 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: [100]

3) Geo−accumulation index

The I_{geo}, is commonly used to estimate anthropogenic inputs. According to these methods, chromium concentrations were normalized to the chromium concentrations of average crust. The I_{geo} calculation was done using the following equation:

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5\ B_n}\right) \quad (3.2)$$

Where C_n is chromium concentration in the surface sediment (mg/kg).

B_n is the geochemical background value of chromium (mg/kg). In this study, the value of 90 was used according to [68].

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

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

Table 3.3

Classes of chromium contamination status in the surface sediment based on different the I_{geo} values.

Class	I_{geo} Values	Level of contaminations
1	$I_{geo} < 0$	practically uncontaminated
2	$0 < I_{geo} < 1$	uncontaminated to moderately
3	$1 < I_{geo} < 2$	moderately contaminated
4	$2 < I_{geo} < 3$	moderately to heavily contaminated
5	$3 < I_{geo} < 4$	heavily contaminated
6	$4 < I_{geo} < 5$	heavily to extremely contaminated
7	$I_{geo} > 5$	extremely contaminated

Source: [69]

4) Potential ecological risk assessment

Potential ecological risk (E_r) is an index of ecological risk assessment proposed by [75] and widely used to evaluate the degree of pollution of element in the sediment.

$$\boldsymbol{E_r = T_r^i \times C_f^i} \quad (3.3)$$

where $\boldsymbol{E_r}$ is the potential risk of chromium.

$\mathbf{T_r^i}$ is the toxic−response factor (TRF) for chromium

$$\boldsymbol{C_f^i = \frac{C_D^i}{C_r^i}} \quad (3.4)$$

Where $\mathbf{C_f^i}$ is the contamination factor.

$\mathbf{C_D^i}$ is the mean concentration of chromium for present study.

$\mathbf{C_r^i}$ is the preindustrial reference value of chromium in the sediments. In this study, the value of 90 was 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

Classifications of potential ecological risk factor (E_r) of chromium pollution in the surface sediment.

Class	E_r Values	Level of risk
1	$E_r < 40$	low potential ecological risk
2	$40 \leq E_r < 80$	moderate potential ecological risk
3	$80 \leq E_r < 160$	considerable potential ecological risk
4	$160 \leq E_r < 320$	high potential ecological risk
5	$E_r \geq 320$	very high potential ecological risk

Source: [75]

3.8 Quality Control

The relative accuracy and precision for all chromium determinations are verified against certified reference materials (sediment reference material MESS−4, a polluted marine sediment standard prepared by the National Research Council of Canada). Quality control was performed by including CRM and blank methods in each sample group. At the same time, there is a sufficient number of iterations along with the example.

For accuracy, the CRM was digested and determined Cr and Fe concentration using selected method. After that %recovery was calculated between the standard concentration of CRM and detected concentration.

For precision of QC standard, the CRM was digested and determined Cr and Fe concentration in 5 sets. And then, %RSD was calculated among those 5 sets.

QC sample, 20% of sediment samples was randomly chosen. Triplicate at each random sample was digested and determined Cr, Fe and regulating factor. And then, %RSD was calculated among the samples.

3.9 Statistical Analysis

This study, One−way ANOVA was held to evaluate the difference between the results from mean value of total chromium from difference area are frequently compared in the inner Gulf of Thailand. Pearson correlation analysis was conducted to identify the relationships between the detected sediment properties and total chromium. Differences was considered to be significant if $p<0.05$. Principal component analysis (*PCA*) was conducted for all the variable to assess their relationship for Cr distribution, the sampling adequacy of the dataset was determined using the Kaiser-Meyer-Olkin (*KMO*) and the strength of the interrelationship between the variables was evaluated using Bartlett's test of Sphericity. The *KMO* values > 0.5 and Bartlett's test with p-value < 0.05 were found in all station models, which provided a minimum standard to proceed with the *PCA*. All statistical analysis were performed using SPSS v.22.0 for Windows software package.

CHAPTER IV

RESULTS AND DISCUSSION

The inner Gulf of Thailand is loaded with heavy metals, particularly Cr from anthropogenic sources due to runoff of the Mae Klong, the Tha Chin, the Chao Phraya and the Bangpakong Rivers. The present study is designed in order to evaluate spatial distributions and seasonal variations of total concentration of Cr coupling with physicochemical factors in the surface sediment in the inner Gulf of Thailand, including the Mae Klong, the Tha Chin, the Chao Phraya and the Bangpakong Rivers estuaries. Moreover, fractional forms of Cr were additionally analyzed and discussed in different toxic responses. Then, the contamination status of Cr was evaluated using the sediment quality guidelines, enrichment factor and geo−accumulation index. Subsequently, potential risk was assessed ecologically in order to predict risk levels of the inner Gulf of Thailand. Finally, the regulating factors of Cr changes in the surface sediment of the inner Gulf of Thailand were analyzed due to the physicochemical conditions of the study areas. All results and discussion of the present study were totally explained and discussed as follows:

The quality assurance and quality control were done by method blanks and standard reference materials. Blank samples were also performed throughout all the analyses. To explicitly guarantee the analytical precision, 20% of sediment samples were determined in triplicate. Precision, expressed as relative standard deviation, was less than 20%. The accuracy and precision of the analytical procedures were checked by analyzing certified reference materials (sediment reference material MESS−4, a polluted marine sediment standard prepared by the National Research Council of Canada).

Quality control for the total Cr and Fe concentrations was performed using a certified reference material, and the indicated Cr and Fe in marine sediments were analyzed (Table 4.1). Results accuracy ranged from 70-120% (n=5). The analytical

process accuracy is defined as the relative standard deviation (RSD). The standard solution analysis accuracy is within 20%.

Table 4.1 Comparison of the analytical results of the certified reference materials sediment reference material MESS−4, a polluted marine sediment standard prepared by the National Research Council of Canada) with the measured data.

Element	Certified value	Instrument	Measured value	Instrument	% Recovery
Chromium (Cr)	94.3±1.8 mg/kg	ICP−MS, ICP−AES and INAA	68.26±3.14	AAS	72.38
Iron (Fe)	37.9±1.6 mg/kg	ICP−AES, INAA and XRF	42.10±8.18	AAS	111.09

4.1 Spatial Distributions and Seasonal Variations of Chromium

Data of the present study are provided a bay–wide synaptic distribution of surface sedimentary Cr and physicochemical characteristics of the inner Gulf of Thailand during the different seasons, including southwest monsoon, northeast monsoon, and dry seasons. Noticeable data on the surface sediment at the 58−60 frequently sampled sites and total 177 sediment samples over the study periods showed spatial and seasonal variations (Figure 4.1). Heterogeneity distributions of heavy metal and physicochemical factors in the surface sediment were indicated entire the inner Gulf of Thailand. Moreover, Cr was differently accumulated in the Mae Klong, the Tha Chin, the Chao Phraya and the Bangpakong River estuaries. While, southwest monsoon season, northeast monsoon season, and dry season were also affected in the Cr accumulation in the surface sediment of the inner Gulf of Thailand. Data of the present study were much and complicated, however all data were carefully analyzed and detailly reported as follow:

4.1.1 The inner Gulf of Thailand

The spatial heterogeneity distributions of Cr in the surface sediment were indicated entire the inner Gulf of Thailand (Figure 4.1a−c). In the southwest monsoon season (July 2017), the lowest Cr concentration was 11.72 mg/kg (GT26), where occurred at middle part of the inner Gulf of Thailand, while the

highest value of 80.16 mg/kg (CP13) was occurred at the mouth of the Chao Phraya River (Figure 4.1a). According to the distribution pattern, the relative high Cr concentrations were observed in the Chao Phraya, the Bangpakong and the Tha Chin River estuaries, subsequently decreasing concentrations were occurred from the river mouths to the lower part of the Gulf (Figure 4.1a). The average Cr in the surface sediment was 36.04±16.72 mg/kg, which was higher than the western part upper Gulf of Thailand [48], Phetchaburi province, Thailand [49] but lower than those previously determined in the upper Gulf of Thailand by [51]. In addition, Cr concentration was significantly lower than those found in the northern Kaohsiung Harbor, Taiwan [101], the Pearl River estuary, China [102], the upstream Yangtze River, China [103], the Jiaozhou Bay, China [54], Masam Bay, Korea [104], Yellow River, China [105], Daya bay and adjacent shelf [55], and San Simon Bay, Spain [106]. Furthermore, Cr concentrations were higher than those reported Laizhou Bay, China protected area, China [107], the Yangtze River, China [52], Nyanza Gulf of Lake Victoria, East Africa [108], Halong bay, Vietnam [50], Gulf of Pozzuoli, Italy [53], Admiralty Bay, Antarctica [109], and Tuzla Aydinli Bay, Istanbul [56]. As the result, the average Cr concentration in southwest monsoon season which was relatively low to moderate concentration when compared to another coastal surface sediments (Table 4.2). Sediment quality guidelines are commonly used for the assessment of sediment quality in Thailand, and have been widely applied in environmental studies [110]. Compared with these criteria (42 mg/kg), the average concentration of Cr in the inner Gulf of Thailand was low.

In the northeast monsoon season (December 2017), the lowest Cr concentration was 5.61 mg/kg (GT28), where occurred at middle part of the inner Gulf of Thailand, while the highest value of 107.45 mg/kg (CP1) was occurred in the inner of the Chao Phraya River (Figure 4.1b). According to the distribution pattern, the relative high Cr concentrations were observed in the Chao Phraya, the Bangpakong and the Tha Chin River estuaries, subsequently decreasing concentrations were occurred from the river mouths to the eastern and western lower part of the Gulf (Figure 4.1b). The average Cr in the surface sediment was 38.14±22.19 mg/kg, which was higher than the western part upper Gulf of

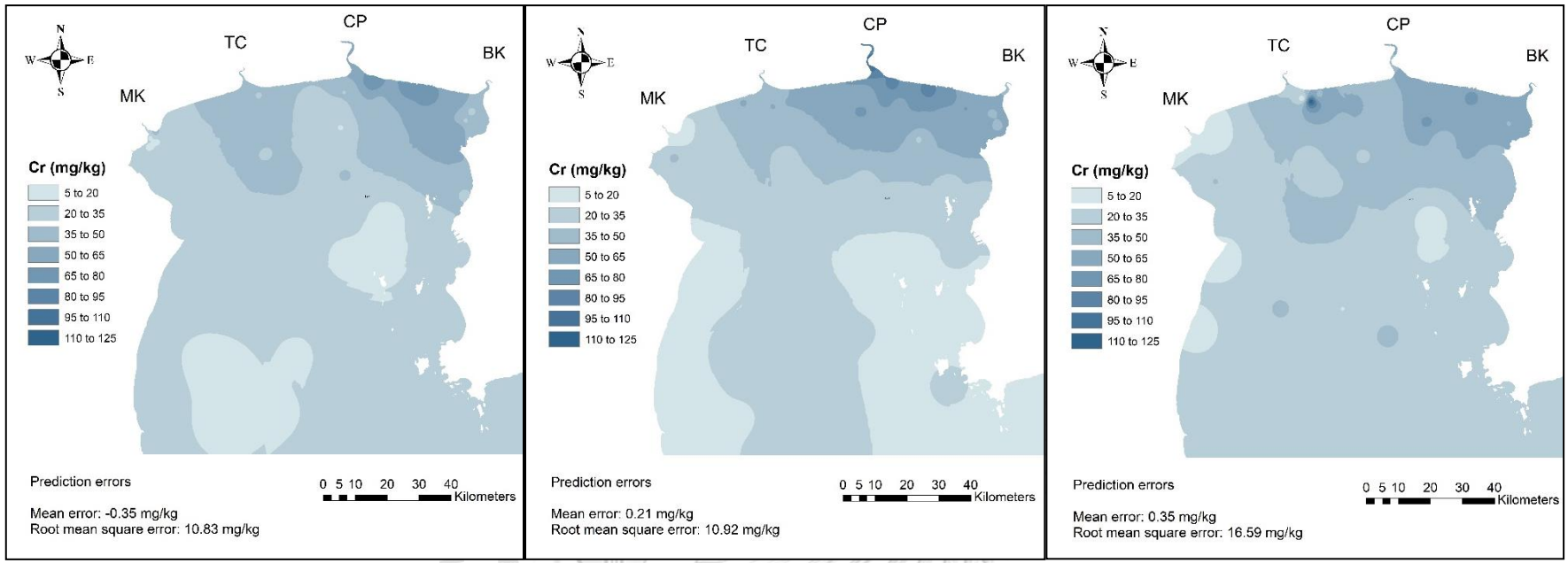
Thailand [48], Phetchaburi province, Thailand [49] but lower than those previously determined in the upper Gulf of Thailand by [51]. In addition, Cr concentration was significantly lower than those found in the northern Kaohsiung Harbor, Taiwan [101], the Pearl River estuary, China [102], the upstream Yangtze River, China [103], the Jiaozhou Bay, China [54], Masam Bay, Korea [104], Yellow River, China [105], Daya bay and adjacent shelf [55], and San Simon Bay, Spain [106]. Furthermore, Cr concentrations were higher than those reported Laizhou Bay, China protected area, China [107], the Yangtze River, China [52], Nyanza Gulf of Lake Victoria, East Africa [108], Halong bay, Vietnam [50], Gulf of Pozzuoli, Italy [53], Admiralty Bay, Antarctica [109], and Tuzla Aydinli Bay, Istanbul [56]. As the result, the average Cr concentration in southwest monsoon season which was relatively low to moderate concentration when compared to another coastal surface sediments (Table 4.2). Sediment quality guidelines are commonly used for the assessment of sediment quality in Thailand, and have been widely applied in environmental studies [110]. Compared with these criteria (42 mg/kg), the average concentration of Cr in the inner Gulf of Thailand was low.

In the dry season (May 2018), the spatial heterogeneity distribution of Cr concentrations in the surface sediment of the inner Gulf of Thailand was ranged from 8.63−119.47 mg/kg (Figure 4.1c). Surprisingly, both the lowest and highest Cr concentrations were occurred at TC13 and TC15, which located in the mouth of the Tha Chin River (Figure 4.1c). According to the distribution pattern, the relative high Cr concentrations were occurred at the Bangpakong, the Chao Phraya and Tha Chin River estuaries and trend to decrease to the lower part of the Gulf (Figure 4.1c). The average Cr concentration in the surface sediment was 37.67±19.29 mg/kg, which was higher than the western part upper Gulf of Thailand [48], Phetchaburi province, Thailand [49] but lower than those previously determined in the upper Gulf of Thailand by [51]. In addition, Cr concentration was significantly lower than those found in the northern Kaohsiung Harbor, Taiwan [101], the Pearl River estuary, China [102], the upstream Yangtze River, China [103], the Jiaozhou Bay, China [54], Masam Bay, Korea [104], Yellow River, China [105], Daya bay and adjacent shelf [55], and San

Simon Bay, Spain [106]. Furthermore, Cr concentrations were higher than those reported Laizhou Bay, China protected area, China [107], the Yangtze River, China [52], Nyanza Gulf of Lake Victoria, East Africa [108], Halong bay, Vietnam [50], Gulf of Pozzuoli, Italy [53], Admiralty Bay, Antarctica [109], and Tuzla Aydinli Bay, Istanbul [56]. As the result, the average Cr concentration in southwest monsoon season which was relatively low to moderate concentration when compared to another coastal surface sediments (Table 4.2). Sediment quality guidelines are commonly used for the assessment of sediment quality in Thailand, and have been widely applied in environmental studies [110]. Compared with these criteria (42 mg/kg), the average concentration of Cr in the inner Gulf of Thailand was low.

The mean concentrations of Cr in the surface sediment of the inner Gulf of Thailand in the southwest monsoon season (36.04 mg/kg) compared to the northeast monsoon season (38.14 mg/kg) and dry season (37.67 mg/kg) (Figure 4.2). The mean difference of Cr in the surface sediment between the seasonal variation did not vary significantly (p>0.05). The mean concentration of Cr in the surface sediments of the inner Gulf of Thailand changes similarly in three seasons. In other words, the average concentration of Cr in surface sediments in southwest monsoon and dry season is lower than that in northeast monsoon season. The amounts of Cr concentration in surface sediment varied seasonally as follows: northeast monsoon season > dry season > southwest monsoon season. The reason for the change was that there was more rainfall in the southwest monsoon season, causing tides in the inner Gulf of Thailand. Due to increased flow turbulence, some of the sediment and Cr in the sediment are displaced and washed away from the riverbed. As northeast monsoon season and the dry season begin increased temperature and evaporation and the termination of the precipitation period led to an increase in the concentration of Cr in the water and ultimately precipitate as Cr transfer from water to the sediment [111]. Industrial activities are one of the major sources of heavy metal contamination of the environment, especially in developing countries. Floods also lead to the distribution of toxic into the environment, about the floods of Thailand in 2011

due to some industrial estates affected. Raising concerns about heavy metals from industrial wastewater contamination [112].



(a) (b) (c)

Figure 4.1 Spatial heterogeneity distributions of chromium concentration in the surface sediment and seasonal variations in the southwest monsoon season (a), the northeast monsoon season (b), and the dry season (c) entire the inner Gulf of Thailand.

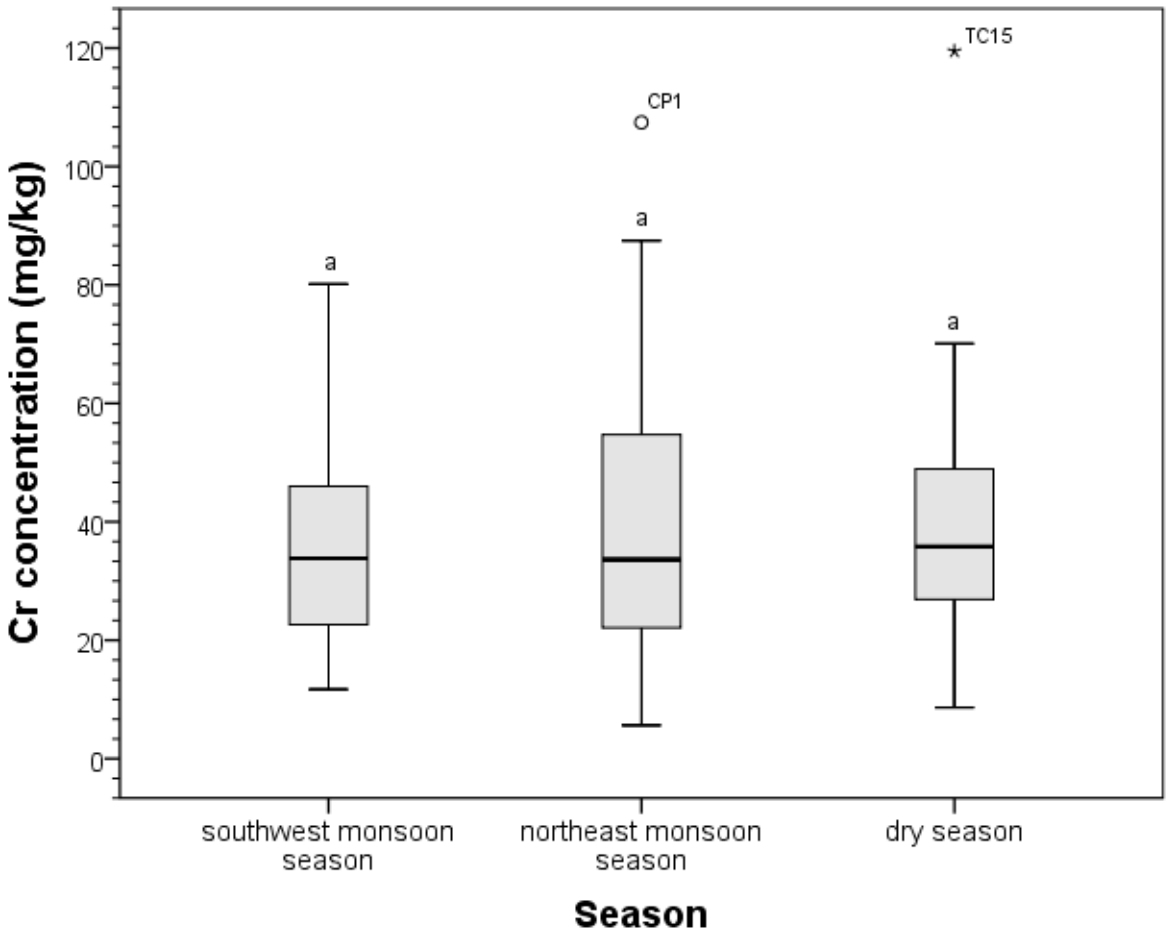


Figure 4.2 A comparison of the chromium concentration in surface sediments of the inner Gulf of Thailand between southwest monsoon season, northeast monsoon season and dry season. The box shows the 25th and the 75th percentiles, and the whiskers represent the smallest and the largest concentration. (alphabet indicated significant difference at p<0.05 using the DMRT analysis).

Table 4.2 Comparison of Cr concentration of surface sediments in the inner Gulf of Thailand with other regions.

Locations		Cr (mg/kg)	References
The upper Gulf of Thailand		138.9	[51]
Northern Kaohsiung Harbor, Taiwan		113.5	[101]
Pearl river estuary, China		106	[102]
The upstream Yangtze River, China		101.43	[103]
Jiaozhou Bay catchment, China		69.30	[54]
Masam Bay, Korea		67.1	[104]
Yellow River, China		62.4	[105]
Daya Bay and adjacent shelf		59.03	[55]
San Simon Bay, Spain		42.46	[106]
The inner Gulf of Thailand	southwest monsoon season	**36.04±16.72**	**This study**
	northeast monsoon season	**38.14±22.19**	
	dry season	**37.67±19.29**	
Liazhou River protected area, China		35.06	[107]
Yangtze River estuary, China		34.64	[52]
Nyanza Gulf, of Lake Victoria (East Africa)		33.85	[108]
Ha Long Bay, Vietnam		27.00	[50]
Western past the upper Gulf of Thailand		23.84	[48]
Gulf of Pozzuoli (GoP), Italy		14.00	[53]
Phetchaburi province, Thailand		10.45	[49]
Admiralty Bay, Antarctica		8.10	[109]
Tuzla Aydinli Bay, Istanbul (Turkey)		1.66	[56]

4.1.2 River estuary

1) Southwest monsoon season

The spatial distribution of Cr in the surface sediment of 4 river estuaries are shown in Figure 4.3. The Cr concentrations of the Mae Klong

River estuary were ranged from the lowest value of 15.31 mg/kg at MK10, where located at the mouth of the river, while the highest value (54.63 mg/kg at MK1) was found at inner part of the river, which corresponding to an average concentration of 29.32±5.05 mg/kg (Figure 4.3a). For the Tha Chin River estuary, the Cr concentration ranged from 32.53 (TC13) to 54.29 (TC1) mg/kg. The lowest concentration was found at the mouth of the river, while the highest value was occurred at the inner of the river. An average concentration was 45.03±7.58 mg/kg (Figure 4.3b). The Cr concentration of the Chao Phraya River estuary varied from 19.02 mg/kg at CP12, where located at outside area of the river, to 80.16 mg/kg at CP13, where located at the mouth of the river with an average concentration of 45.03±7.58 mg/kg (Figure 4.3c). The Cr concentrations of the Bangpakong River estuary were in the ranged of 31.32 mg/kg at BK7, where occurred at the mouth of the river, while the highest value of 79.93 mg/kg at BK16 was occurred at the mouth of the Bangpakong River with 51.36±5.35 mg/kg of an average concentration (Figure 4.3d).

Comparisons of Cr concentration the chromium concentration in surface sediments of four river estuaries and three parts from the inner Gulf of Thailand are shown in Figure 4.4. In general, mean±SD concentrations of Cr in the surface sediment were ranked, in decreasing order as follows: Bangpakong (51.36±5.35 mg/kg) > Chao Phraya (45.03±7.58 mg/kg) > Tha Chin (45.03±7.58 mg/kg) > Eastern of GT (35.63±6.37 mg/kg) > Western of GT (26.46±3.70 mg/kg) > Mae Klong (29.32±5.05 mg/kg) > Middle of GT (26.46±3.70 mg/kg). Surface sediment profile of chromium concentrations was non−significant difference at Mae Klong, Tha Chin, Western of GT, Middle of GT and Eastern of GT, while chromium concentrations in Mae Klong, Tha Chin, Chao Phraya and Eastern of GT were non-significant difference and chromium concentrations in Bangpakong was non-significant difference with Tha Chin and Chao Phraya. Sediment quality guidelines are commonly used for the assessment of sediment quality in Thailand, and have been widely applied in environmental studies [110]. Compared with these criteria, the average of

Cr concentration in Eastern of GT (35.63±6.37 mg/kg), Western of GT (26.46±3.70 mg/kg), Mae Klong (29.32±5.05 mg/kg) and Middle of GT (26.46±3.70 mg/kg) were low. But the average of Cr concentration in Bangpakong (51.36±5.35 mg/kg), Chao Phraya (45.03±7.58 mg/kg) and Tha Chin (45.03±7.58 mg/kg) were higher than sediment quality guidelines Thailand. The result of Cr concentration was higher than sediment quality guidelines Thailand including MK1 (54.63 mg/kg), MK4 (42.83 mg/kg), TC1 (54.29 mg/kg), TC8 (48.26 mg/kg), TC14 (48.67 mg/kg), TC15 (44.38 mg/kg), CP1 (64.81 mg/kg), CP13 (80.16 mg/kg), CP16 (73.88 mg/kg), BK12 (60.44 mg/kg), BK13 (62.69 mg/kg), BK14 (58.13 mg/kg), BK16 (79.93 mg/kg), BK18 (55.35 mg/kg), GT17 (52.93 mg/kg), GT23 (43.79 mg/kg) and GT25 (48.55 mg/kg), where located near coastal area and the emitting source with frequent anthropogenic activities. Therefore, the results reflect that the high concentrations of the Cr could come from the human activities. The major distribution areas of Cr with higher concentrations were in the Chao Phaya River estuary and with lower concentrations were in the middle area. As a result, the increase in industrial activity has contributed to environmental pollution throughout the country, cause health concerns. The Chao Phraya River and Pa Sak are important water bodies in Thailand's Chao Phraya River basin. More than 30,000 factories located in the Chao Phraya River basin contaminate the river water with toxic including heavy metals from Bangpoo Industrial Estate [113]. Factories in Bang poo industrial estates consist mainly of textiles, food processing, electronic equipment assembly, and the production of building materials [87]. The area of lower metal concentrations was located out of the coastal area and the current flows from the southwestern part to the north along the west coast, also it moves from northeastern part to the central of the lower part of the Gulf.

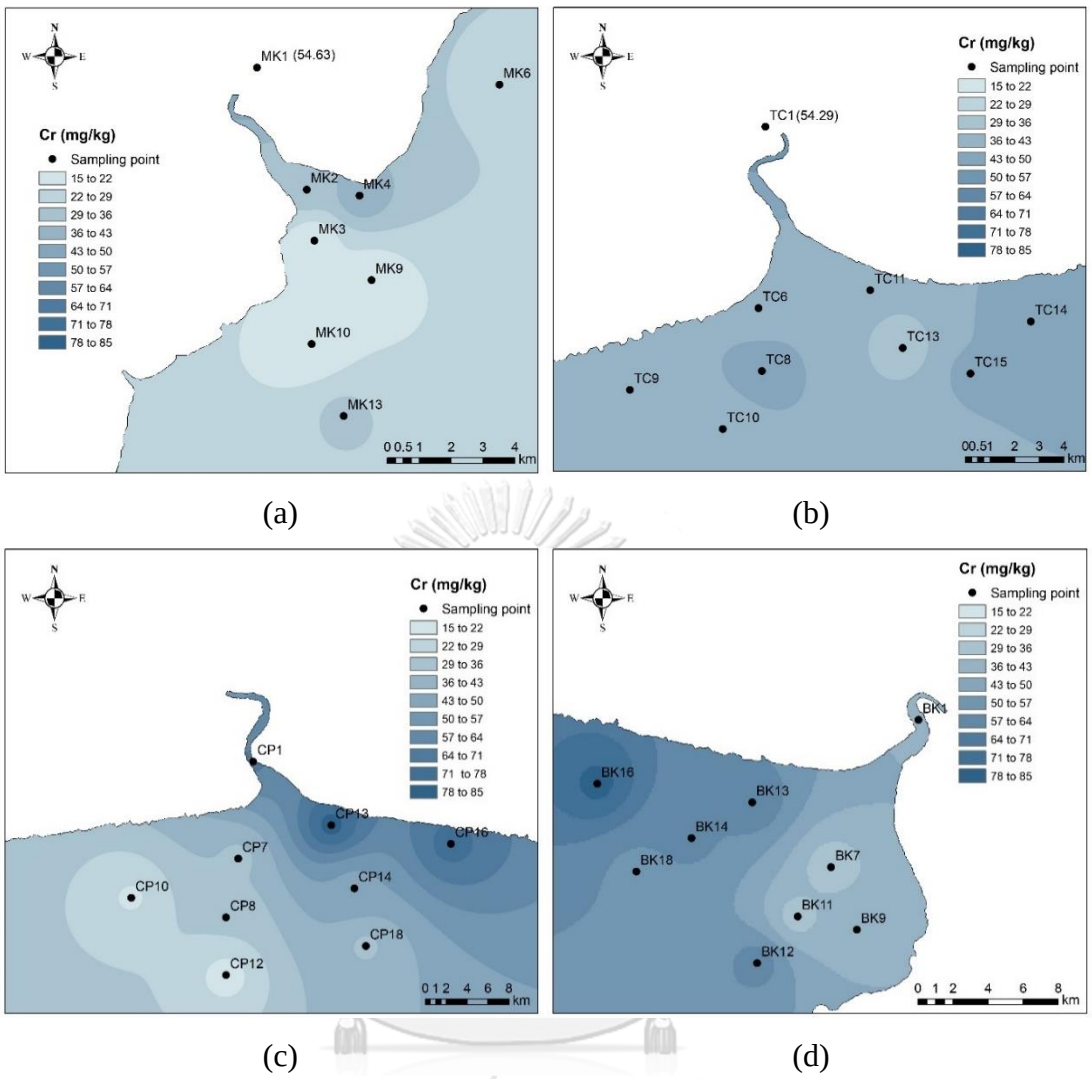
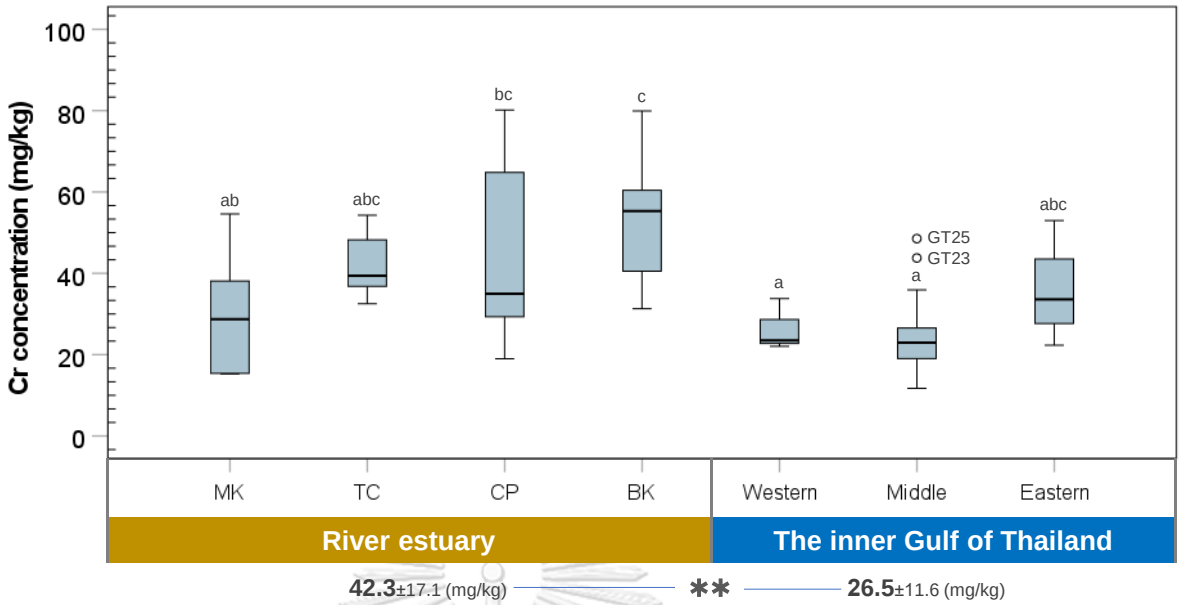


Figure 4.3 Spatial heterogeneity distributions of chromium concentration in the surface sediment entire the Mae Klong (a), the Tha Chin (b), the Chao Phraya (c) and (d) the Bangpakong River estuaries in the southwest monsoon season.



remark: alphabets indicated significant difference at $p<0.05$ using the DMRT analysis

** indicated significant difference at p<0.01 using the T−test

Figure 4.4 A comparison of the chromium concentration in the surface sediment of the Mae Klong (MK), the Tha Chin (TC), the Chao Phraya (CP) the Bangpakong (BK), the western, middle and eastern parts of the inner Gulf of Thailand in the southwest monsoon season. The box shows the 25th and the 75th percentiles, and the whiskers represent the smallest and the largest concentration.

2) Northeast monsoon season

The spatial distribution of Cr in surface sediment of 4 river estuaries are shown in Figure 4.5. The Cr concentrations of the Mae Klong River estuary were ranged from the lowest value of 6.05 mg/kg at MK3, where located at the mouth of the river, while the highest value (41.17 mg/kg at MK13) was found at outside area of the river, which corresponding to an average concentration of 20.23±4.67 mg/kg (Figure 4.5a). For the Tha Chin River estuary, the Cr concentration ranged from 36.53 (TC13) to 57.67 (TC1) mg/kg. The lowest concentration was found at the mouth of the river, while the highest value was occurred at the inner of the river. An average concentration was 47.62±2.27 mg/kg (Figure 4.5b). The Cr concentration of

the Chao Phraya River estuary varied from 51.27 mg/kg at CP12, where located at outside area of the river, to 107.45 mg/kg at CP1, where located at the inner part of the river with an average concentration of 70.58±6.21 mg/kg (Figure 4.5c). The Cr concentrations of the Bangpakong River estuary were in the ranged of 46.95 mg/kg at BK1, where occurred at the inner of the river, while the highest value of 68.24 mg/kg at BK16 was occurred at the mouth of the Bangpakong River with 56.29±4.83 mg/kg of an average concentration (Figure 4.5d).

Comparisons of chromium concentration in the surface sediments of four river estuaries and three parts from the inner Gulf of Thailand are shown in Figure 4.6. In general, mean±SD concentrations of Cr in the surface sediment were ranked, in decreasing order as follows: Chao Phraya (70.58±6.21 mg/kg) > Bangpakong (56.29±2.57 mg/kg) > Tha Chin (47.62±2.27 mg/kg) > Middle of GT (22.30±1.90 mg/kg) > Eastern of GT (21.95±1.73 mg/kg) > Mae Klong (20.23±4.67 mg/kg) > Western of GT (13.05±4.83 mg/kg). Surface sediment profile of chromium concentrations was non-significant difference at Mae Klong, Western of GT, Eastern of GT and Eastern of GT, while chromium concentrations in Tha Chin and Bangpakong were non-significant difference but chromium concentrations in Chao Phraya was significant difference with Mae Klong, Tha Chin, Bangpakong, Western of GT, Middle of GT and Eastern of GT. Sediment quality guidelines are commonly used for the assessment of sediment quality in Thailand, and have been widely applied in environmental studies [110]. Compared with these criteria, the average of Cr concentration in Middle of GT (22.30±1.90 mg/kg), Eastern of GT (21.95±1.73 mg/kg), Mae Klong (20.23±4.67 mg/kg) and Western of GT (13.05±4.83 mg/kg) were low. But the average of Cr concentration in Chao Phraya (70.58±6.21 mg/kg), Bangpakong (56.29±2.57 mg/kg) and Tha Chin (47.62±2.27 mg/kg) were higher than sediment quality guidelines Thailand. The result of Cr concentration was higher than sediment quality guidelines Thailand including TC1 (57.7 mg/kg), TC5 (51.53 mg/kg), TC6 (42.61 mg/kg), TC8 (44.59 mg/kg), TC10 (43.56 mg/kg), TC14 (56.61 mg/kg), TC15 (52.22

mg/kg), All stations of Cr and All stations of BK, where located near coastal area and the emitting source. with frequent anthropogenic activities. Therefore, the results reflect that the high concentrations of the Cr could come from the human activities. The major distribution areas of Cr with higher concentrations were in the Chao Phaya River estuary and with lower concentrations were in the western part area. As a result, the CP is considered major water sources in Chao Phraya River basin, Thailand. Wastes of agrochemicals, urban areas and numerous industries, such as electroplating and electronic equipment, located along the river and large canals connecting the river, either partially treated or without treatment, are discharged into the Chao Phraya River, the Chao Phraya River Mouth and eventually into the Upper Gulf of Thailand causing water quality deterioration with pollutants [2], including heavy metals from Bang poo industrial estates. The area of lower metal concentrations was located out of the coastal area and the current moves counterclockwise along the coastline. The direction of the circulation flows from the east to west and then moves southward to the southwestern part of the Gulf.

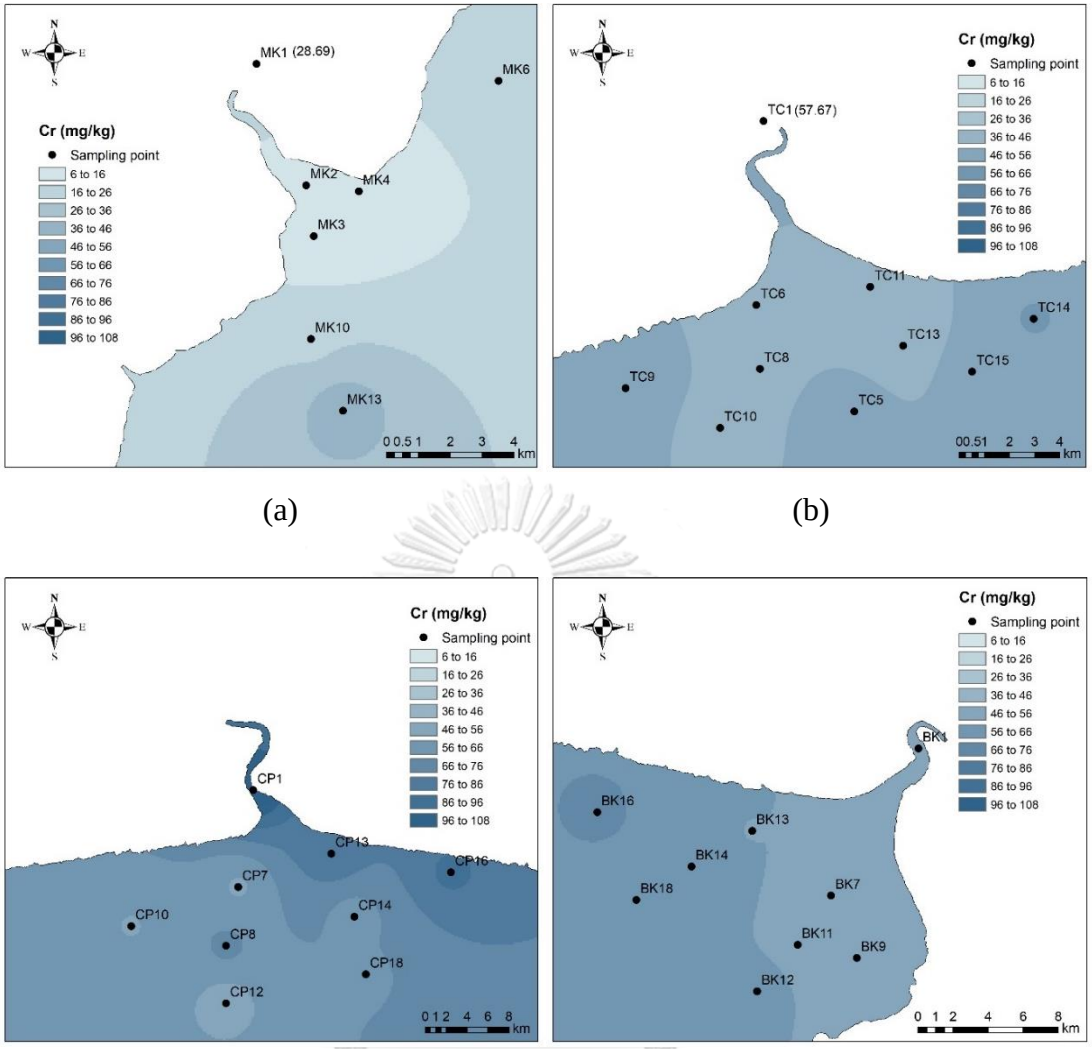
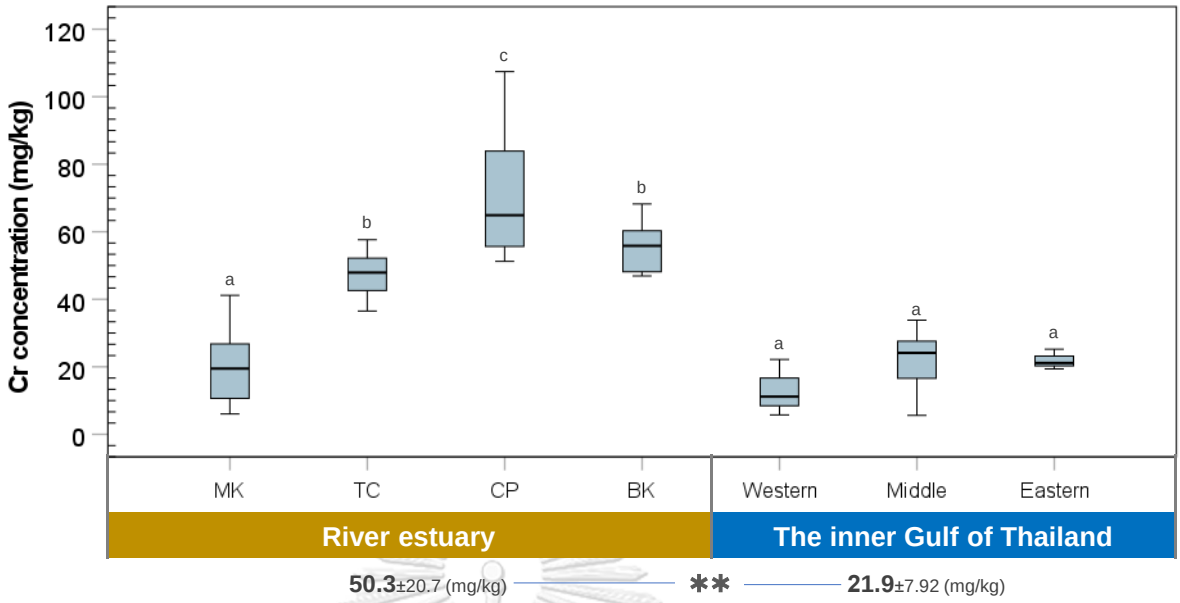


Figure 4.5 Spatial heterogeneity distributions of chromium concentration in the surface sediment entire the Mae Klong (a), the Tha Chin (b), the Chao Phraya (c) and (d) the Bangpakong River estuaries in the northeast monsoon season.



remark: alphabets indicated significant difference at $p<0.05$ using the DMRT analysis

** indicated significant difference at $p<0.01$ using the T−test

Figure 4.6 A comparison of the chromium concentration in the surface sediment of the Mae Klong (MK), the Tha Chin (TC), the Chao Phraya (CP) the Bangpakong (BK), the western, middle, and eastern parts of the inner Gulf of Thailand in the northeast monsoon season. The box shows the 25th and the 75th percentiles, and the whiskers represent the smallest and the largest concentration.

3) Dry season

The spatial distribution of Cr in surface sediment of 4 river estuaries are shown in Figure 4.7. The Cr concentrations of the Mae Klong River estuary were ranged from the lowest value of 10.45 mg/kg at MK6, where located at the mouth of the river, while the highest value (31.28 mg/kg at MK1) was found at inner part of the river, which corresponding to an average concentration of 17.28±3.23 mg/kg (Figure 4.7a). For the Tha Chin River estuary, the Cr concentration ranged from 8.63 (TC13) to 119.47 (TC15) mg/kg. The lowest concentration was found at the mouth of the river, while the highest value was occurred at the inner of the river. An average concentration was 43.35±10.22 mg/kg (Figure 4.7b). The Cr concentration of the Chao Phraya River estuary varied from 40.04 mg/kg at

CP7, where located at mouth of the river, to 68.60 mg/kg at CP18, where located at the outside area of the river with an average concentration of 52.76±3.49 mg/kg (Figure 4.7c). The Cr concentrations of the Bangpakong River estuary were in the ranged of 48.92 mg/kg at BK11, where occurred at the inner of the river, while the highest value of 70.12 mg/kg at BK16 was occurred at the mouth of the Bangpakong River with 55.31±2.12 mg/kg of an average concentration (Figure 4.7d).

Comparisons of chromium concentration in the surface sediments of four river estuaries and three parts from the inner Gulf of Thailand are shown in Figure 4.8. In general, mean±SD concentrations of Cr in the surface sediment were ranked, in decreasing order as follows: Bangpakong (55.31±2.12) > Chao Phraya (52.76±3.49) > Tha Chin (43.35±10.22 mg/kg) > Eastern of GT (31.86±11.18 mg/kg) > Middle of GT (29.98±2.26 mg/kg) > Mae Klong (17.28±3.23 mg/kg) > Western of GT (24.45±5.37 mg/kg). Surface sediment profile of chromium concentrations was non-significant difference at Mae Klong, Western of GT, Middle of GT and Eastern of GT, while chromium concentrations in Tha Chin, Western of GT, Middle of GT and Eastern of GT were non-significant difference and chromium concentrations in Tha Chin was nonsignificant difference with Chao Phraya and Bangpakong. Sediment quality guidelines are commonly used for the assessment of sediment quality in Thailand and have been widely applied in environmental studies [110]. Compared with these criteria, the average of Cr concentration in Eastern of GT (31.86±11.18 mg/kg), Middle of GT (29.98±2.26 mg/kg), Mae Klong (17.28±3.23 mg/kg) and Western of GT (24.45±5.37 mg/kg) were low. But the average of Cr concentration in Bangpakong (55.31±2.12), Chao Phraya (52.76±3.49) and Tha Chin (43.35±10.22 mg/kg) were higher than sediment quality guidelines Thailand. The result of Cr concentration was higher than sediment quality guidelines Thailand including TC9 (44.19 mg/kg), TC14 (46.93 mg/kg), TC15 (119.47 mg/kg), All stations of Cr and All stations of BK, GT17 (43.03 mg/kg), GT24 (42.51 mg/kg) and GT32 (47.46 mg/kg), where located near coastal area and the emitting source. with frequent

anthropogenic activities. Therefore, the results reflect that the high concentrations of the Cr could come from the human activities. The major distribution areas of Cr with higher concentrations were in the Tha Chin River estuary and with lower concentrations were in the western part area. As a result, the TC is located in Thailand's central basin and is the country's second most important waterway. Pollution is released into rivers from both point and non-point sources. The main sources of pollution are household and industrial waste emissions including certain types of agricultural resources such as pigs, ducks, fish, and other types of farms. Although non-point sources are also the main sources of pollution in the basin, but it is often ignored by government agencies and planners. Non−point sources include farmland and orchards, which are the main utilization areas in the basin [90].

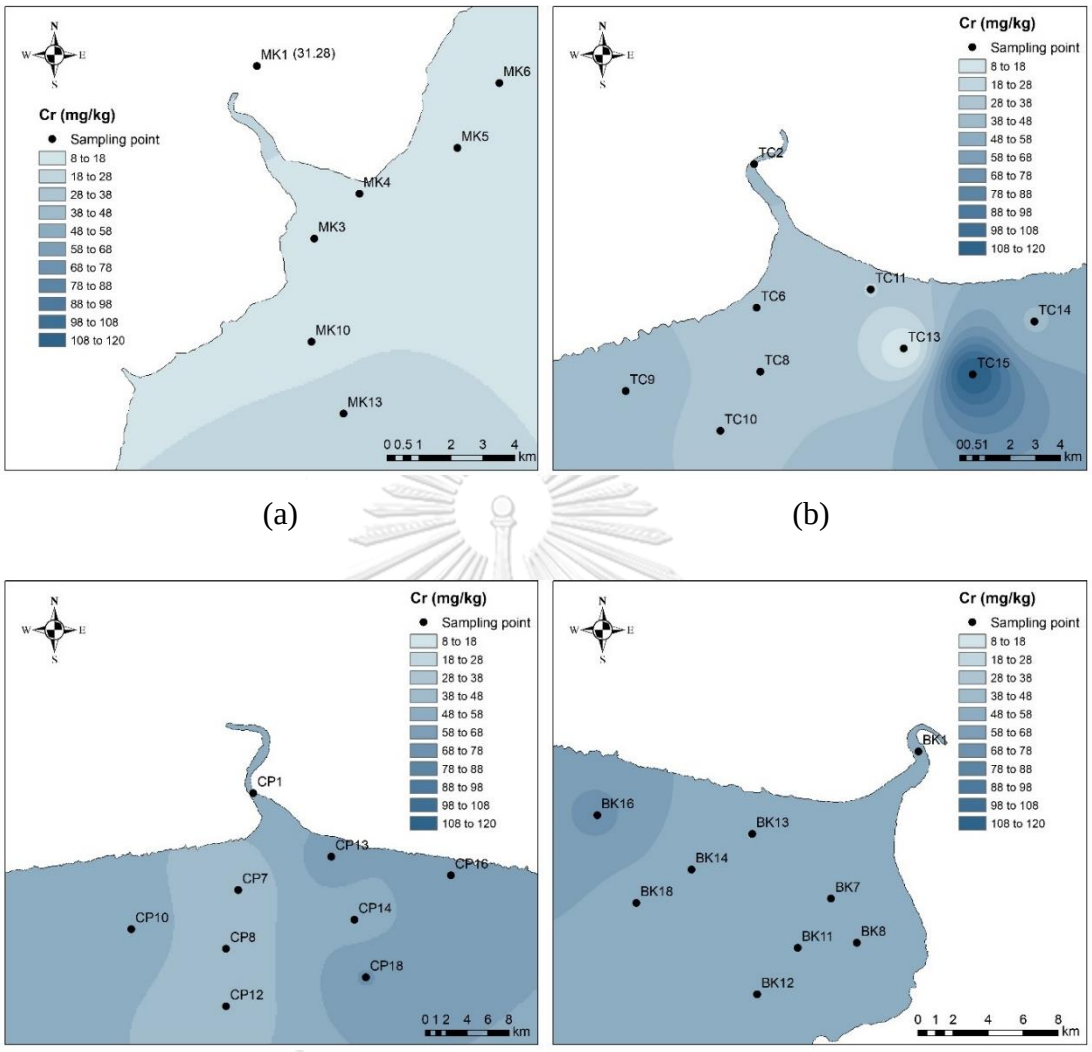
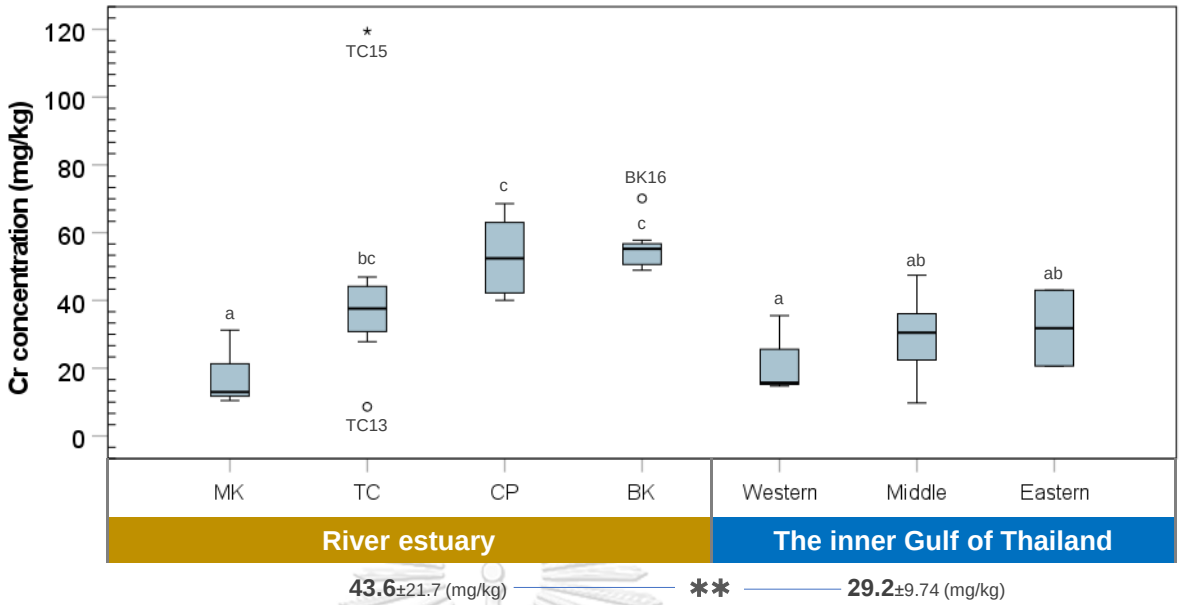


Figure 4.7 Spatial heterogeneity distributions of chromium concentration in the surface sediment entire the Mae Klong (a), the Tha Chin (b), the Chao Phraya (c) and (d) the Bangpakong River estuaries in the dry season.



remark: alphabets indicated significant difference at $p<0.05$ using the DMRT analysis

** indicated significant difference at $p<0.01$ using the T−test

Figure 4.8 A comparison of the chromium concentration in the surface sediment of the Mae Klong (MK), the Tha Chin (TC), the Chao Phraya (CP) the Bangpakong (BK), the western, middle, and eastern parts of the inner Gulf of Thailand in the dry season. The box shows the 25th and the 75th percentiles, and the whiskers represent the smallest and the largest concentration.

4.2 Physicochemical factors

One of the important parameters controlling the accumulation and the availability of Cr concentration in surface sediment are physicochemical factors of the environment including TOM, TOC, TP, AVS and water content. All of the data has been carefully analyzed and reported in detail:

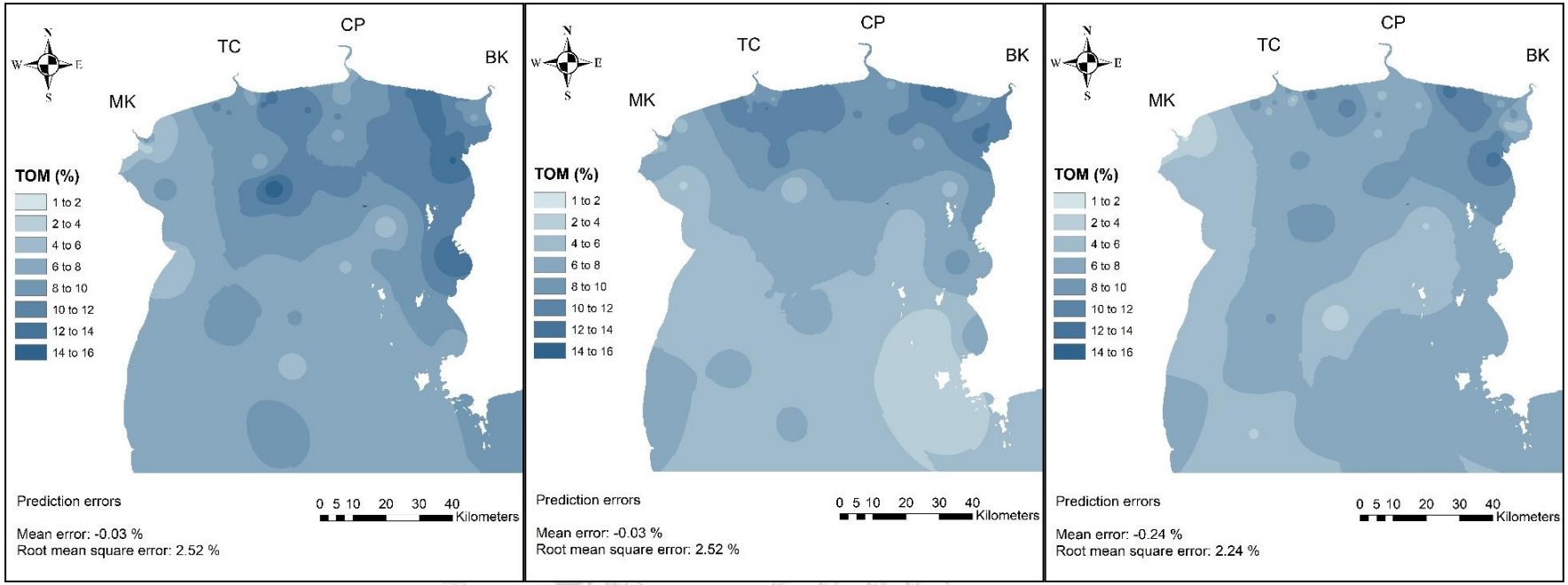
4.2.1 Total organic matter

Percentage of TOM in surface sediment in southwest monsoon season were ranged from 1.86–15.44% (Figure 4.9a) while the highest concentration of TOM was in the middle part of the inner Gulf of Thailand at station GT23 and the lowest concentration of TOM was in the mouth of Mae Klong River at station MK9. The average TOM in surface sediment was 8.87±2.97%. The results demonstrated that spatial distribution decreased from upstream to downstream for TOM.

Percentage of TOM in surface sediment in northeast monsoon season were ranged from 2.28-13.69% (Figure 4.9b) while the highest concentration of TOM was in the mouth of Bangpakong River at station BK16 and the lowest concentration of TOM was in the middle part of the inner Gulf of Thailand at station GT35. The average TOM in surface sediment was 7.98±3.00%. The results demonstrated that spatial distribution decreased from upstream to downstream for TOM.

Percentage of TOM in surface sediment in dry season were ranged from 1.53-13.12% (Figure 4.9c) while the highest concentration of TOM was in the mouth of the Chao Phaya River at station CP16 and the lowest concentration of TOM was in the mouth of the Mae Klong River at station MK4. The average TOM in surface sediment was 7.02±2.70%. The results demonstrated that spatial distribution decreased from upstream to downstream for TOM.

Organic matter (OM) comes from different resources such as plant derivatives, animal waste and their excrement and even artificial organic materials comprising subsurface water systems. The accumulation TOM into coastal waters has been involves the intensive use of agricultural fertilizers, population growth and an increase in urban and domestic sewage of sediments [114].



(a) (b) (c)

Figure 4.9 Spatial heterogeneity distributions of total organic matter (TOM) in the surface sediment and seasonal variations in the southwest monsoon season (a), the northeast monsoon season (b), and the dry season (c) entire the inner Gulf of Thailand

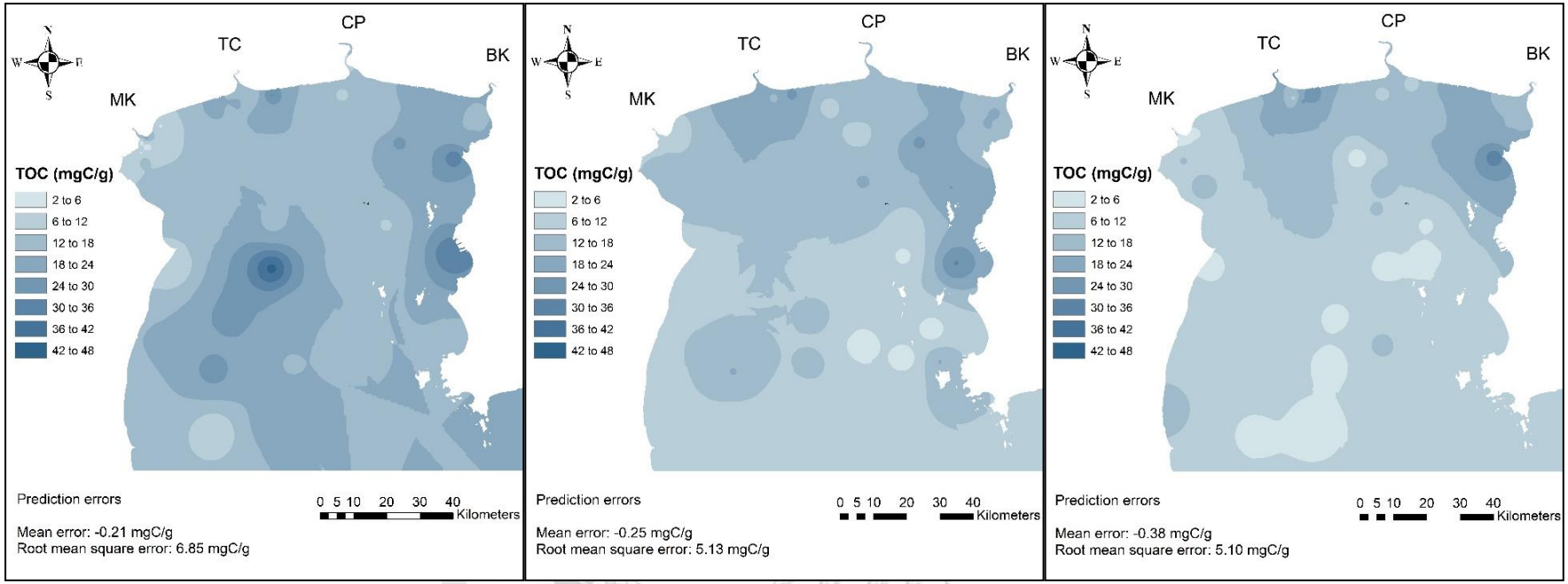
4.2.2 Total organic carbon

The TOC Concentrations in surface sediment in southwest monsoon season were ranged from 2.79-43.17 mg C/g (Figure 4.10a) while the highest concentration of TOC was in the middle part of the inner Gulf of Thailand at station GT35 and the lowest concentration of TOC was in the mouth of the Mae Klong River at station MK9. The average TOC in surface sediment was 17.42±7.23 mg C/g. The results demonstrated that spatial distribution decreased from upstream to downstream for TOC.

The TOC Concentrations in surface sediment in northeast monsoon season were ranged from 3.44-30.22 mg C/g (Figure 4.10b) while the highest concentration of TOC was in the eastern part of the inner Gulf of Thailand at station GT19 and the lowest concentration of TOC was in the middle part of the inner Gulf of Thailand at station GT28. The average TOC in surface sediment was 15.08±6.33 mg C/g. The results demonstrated that spatial distribution decreased from upstream to downstream for TOC.

The TOC Concentrations in surface sediment in dry season were ranged from 2.76-35.50 mg C/g (Figure 4.10c) while the highest concentration of TOC was in the middle part of the inner Gulf of Thailand at station GT6 and the lowest concentration of TOC was in the inner part of the Thachin River at station TC2. The average TOC in surface sediment was 13.72±7.25 mg C/g. The results demonstrated that spatial distribution decreased from upstream to downstream for TOC.

Total organic carbon (TOC) includes all organic carbon compounds present in sediments. The amount of organic matter that can be stored in sediments is influenced by a number of factors, such as types and sources of organic compounds sediment surface grain particle size and precipitation [115].



(a) (b) (c)

Figure 4.10 Spatial heterogeneity distributions of total organic carbon (TOC) in the surface sediment and seasonal variations in the southwest monsoon season (a), the northeast monsoon season (b), and the dry season (c) entire the inner Gulf of Thailand.

4.2.3 Total phosphorus (TP)

The TP concentrations in surface sediment in southwest monsoon season were ranged from 0.19-1.89 g/kg (Figure 4.11a) while the highest concentration of TP was in the inner part of the Chao Phaya River at station CP1 and the lowest concentration of TP was in the mouth of the Mae Klong River at station MK9. The average TP in surface sediment was 0.57±0.30 g/kg. The results demonstrated that spatial distribution decreased from upstream to downstream for TP.

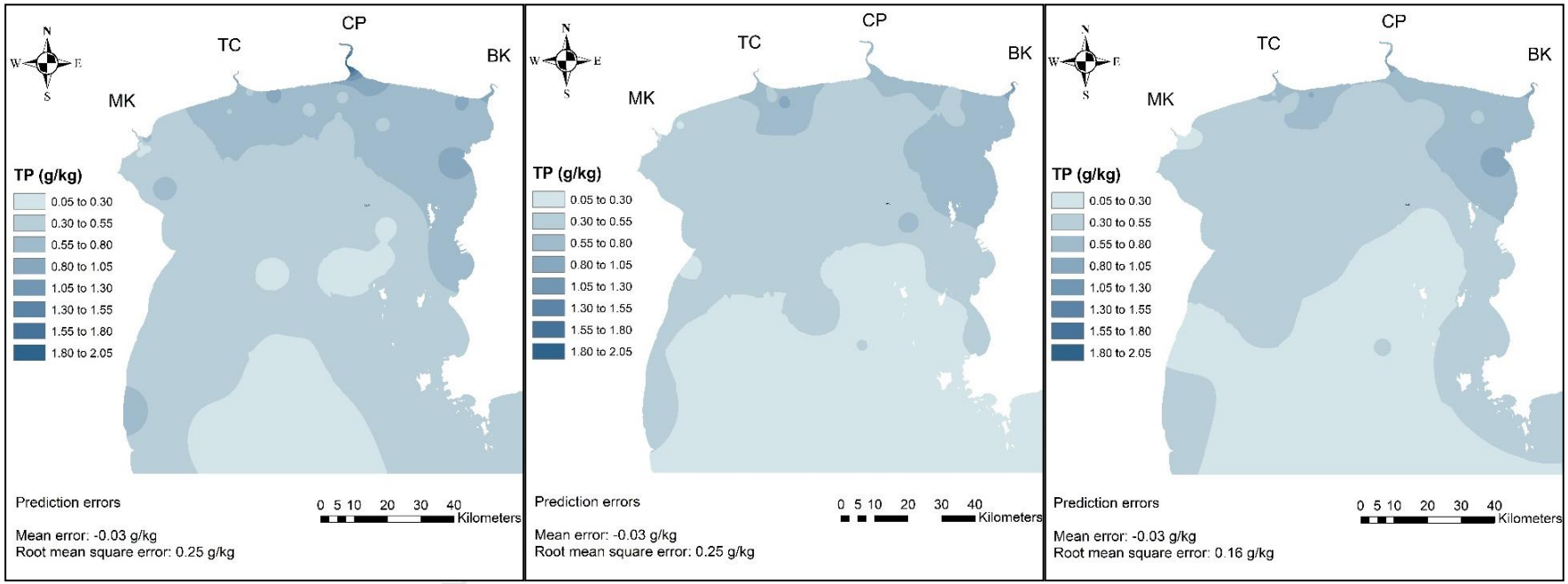
The TP concentrations in surface sediment in northeast monsoon season were ranged from 0.09-1.08 g/kg (Figure 4.11b) while the highest concentration of TP was in the inner part of the Bangpakong River at station BK1 and the lowest concentration of TP was in the middle part of the inner Gulf of Thailand at station GT28. The average TP in surface sediment was 0.46±0.21 g/kg. The results demonstrated that spatial distribution decreased from upstream to downstream for TP.

The TP concentrations in surface sediment in dry season were ranged from 0.15-1.14 g/kg (Figure 4.11c) while the highest concentration of TP was in the inner part of the Thachin River at station TC2 and the lowest concentration of TP was in the mouth of the Mae Klong River at station MK4. The average TP in surface sediment was 0.48±0.22 g/kg. The results demonstrated that spatial distribution decreased from upstream to downstream for TP.

Total phosphorus sources include both point and non−point sources. Excess phosphorus into the river, which are eventually migrates to marine ecosystems usually from industrial emissions, construction site urban areas, wastewater and agricultural runoff [116].

Phosphorus is often the limiting nutrient for algal growth in lakes and may limit productivity [117]. phosphorus sources in lakes include phosphorus in runoff from rock conditions and soil transport and agricultural water and sewage directly in the lakes and tributaries. Phosphorus may enter the water system as particles, or dissolved P may be associated with particles as they fall from the

water column. The amount of P in sediment can serve as a good predictor of the eutrophication probability of a water source [118]



(a) (b) (c)

Figure 4.11 Spatial heterogeneity distributions of total phosphorus (TP) in the surface sediment and seasonal variations in the southwest monsoon season (a), the northeast monsoon season (b), and the dry season (c) entire the inner Gulf of Thailand.

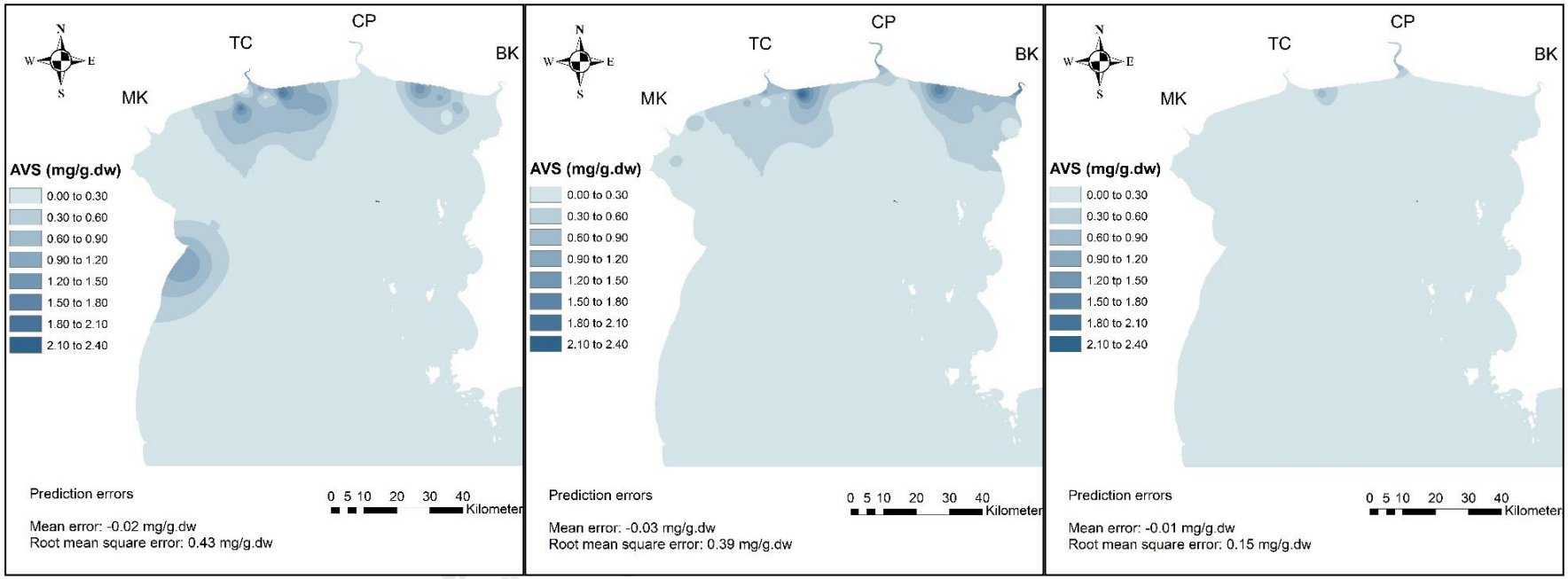
4.2.4 Acid volatile sulfide (AVS)

The AVS concentrations in surface sediment in southwest monsoon season were ranged from 0.00-1.86 mg/g.dw (Figure 4.12a) while the highest concentration of AVS was in the mouth of the Thachin River at station TC14. The average AVS in surface sediment was 0.27±0.48 mg/g.dw. The results demonstrated that spatial distribution decreased from upstream to downstream for AVS.

The AVS concentrations in surface sediment in northeast monsoon season were ranged from 0.00-2.21 mg/g.dw (Figure 4.12b) while the highest concentration of AVS was in the mouth of the Thachin River at station TC14. The average AVS in surface sediment was 0.31±0.48 mg/g.dw. The results demonstrated that spatial distribution decreased from upstream to downstream for AVS.

The AVS concentrations in surface sediment in dry season were ranged from 0.15-1.14 mg/g.dw (Figure 4.12c) while the highest concentration of AVS was in the mouth of the Thachin River at station TC14. The average AVS in surface sediment was 0.06±0.15 mg/g.dw. The results demonstrated that spatial distribution decreased from upstream to downstream for AVS.

Distribution of AVS in sediments is very complex as a result of seasonal and spatial variations in the physical and chemical properties of pores water. The distribution of AVS concentration varies periodically and spatially, and the value of AVS increases with the depth of the sediment. At the surface sediment on the soil surface, its low values may be due to permeation of oxygen from surface water, which causes aerobic oxidation of sulfides and thus lower AVS levels [27].



(a) (b) (c)

Figure 4.12 Spatial heterogeneity distributions of acid volatile sulfide (AVS) in the surface sediment and seasonal variations in the southwest monsoon season (a), the northeast monsoon season (b), and the dry season (c) entire the inner Gulf of Thailand.

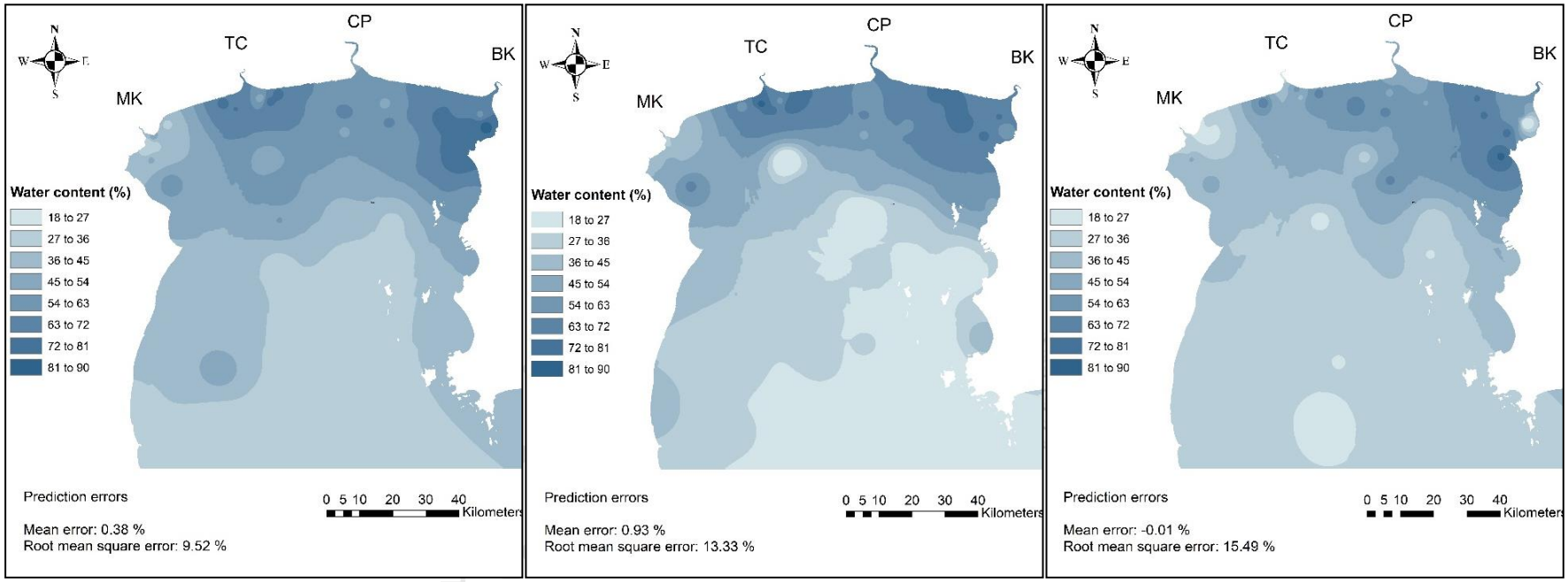
4.2.5 Water content

Percentages of water content in surface sediment in southwest monsoon season were ranged from 26.55-87.93% (Figure 4.13a) while the highest concentration of water content was in the inner of the Bangpakong River at station BK1 and the lowest concentration of water content was in the mouth the Mae Klong River at station MK3. The average water content in surface sediment was 53.22±16.89%. The results demonstrated that spatial distribution decreased from upstream to downstream for water content.

Percentages of water content in surface sediment in northeast monsoon season were ranged from 18.82-87.36% (Figure 4.13b) while the highest concentration of water content was in the mouth of the Tha Chin River at station TC8 and the lowest concentration of water content was in the eastern part of the inner Gulf of Thailand at station GT19. The average water content in surface sediment was 53.31±18.62%. The results demonstrated that spatial distribution decreased from upstream to downstream for water content.

Percentages of water content in surface sediment in dry season were ranged from 22.76-81.83% (Figure 4.13c) while the highest concentration of water content was in the eastern part of the inner Gulf of Thailand at station GT17 and the lowest concentration of water content was in the middle part of the inner Gulf of Thailand at station GT39. The average water content in surface sediment was 47.64±16.06%. The results demonstrated that spatial distribution decreased from upstream to downstream for water content.

Water content in sediment is the physical factor that indicates grain size and abundance of organic matter of sediment. Sediment that has low water content majorly consists of sand and has low organic matter [119].



(a) (b) (c)

Figure 4.13 Spatial heterogeneity distributions of water content (WC) in the surface sediment and seasonal variations in the southwest monsoon season (a), the northeast monsoon season (b), and the dry season (c) entire the inner Gulf of Thailand.

4.3 Regulating Factors of Total Chromium Variation

Correlation matrix between the Cr concentration and related parameters are presented in Table 4.3. The significant correlation could support a common source of Cr contamination in the study.

The correlation between heavy metals and Fe has been used to differentiate between unpolluted and polluted sediments [120]. High positive correlation between Cr and Fe concentrations are identified as un polluted sediment [121]. Positive correlations were show between Cr and Fe (p<0.01), with Pearson's correlation coefficients (r) of 0.783 for southwest monsoon season, 0.831 for northeast monsoon season, and 0.749 for dry season. As a result, the concentration of Cr in the sediments may come from natural source.

Significant positive correlations between Cr and TOM (p<0.01) were established, with Pearson's correlation coefficients (r) of 0.567 for southwest monsoon season, 0.692 for northeast monsoon season, and 0.606 for dry season. These results suggest organic matter has a high affinity to heavy metals in the aquatic environment through adsorption and complexion. The variation in metal solubility depends on the size of the sediment containing TOM. Solubility increases in reduced particle size compared to coarse particles of the sediment sample. As a result of the larger interaction area of particles of lower diameter in fine grains [122]. Total organic matter is one of the most important constituents in Cr ion retention and the presence of TOM can reduce the solubility of the metal. Organic compounds contain several anion functional groups (−OH−, −S−, and −COO−), which have the potential to enhance cation adsorption and result in a decrease in the solubility of metals [123].

Significant positive correlations between Cr and TOC were established, with Pearson's correlation coefficients (r) of 0.294 for southwest monsoon season, 0.483 for northeast monsoon season, and 0.591 for dry season. These results suggest organic carbon has a high affinity for heavy metals by adsorption and complexion in the marine sediments. The impact of aquaculture activities and consequently accumulation of organic matter caused by these activities on metal accumulation in sediment [124].

Significant positive correlations between Cr and TP were established, with Pearson's correlation coefficients (r) of 0.729 for southwest monsoon season, 0.608 for northeast monsoon season, and 0.533 for dry season. These results suggest the metals related to TP productions [116]. Phosphate compounds can immobilize metals in soils by reducing their absorption [29]. Numerous studies have proven that P−induced metal immobilization significantly lowers the bioavailability of heavy metals [121] Phosphates have been shown to be sufficient in immobilizing Cr in contaminated sediment with stable mineral formation. Soluble phosphates such as KH_2PO_4 or H_3PO_4 can be used as existing phosphate sources [122].

Significant positive correlations between Cr and AVS were established, with Pearson's correlation coefficients (r) of 0.0.349 for southwest monsoon season and 0.550 for northeast monsoon season. These results suggest that the sulfide phase has low solubility in anoxic sediment, AVS concentrations are considered high enough to bind positively charged metals and reducing the threshold for final chronic effects on benthic invertebrates [125].

Significant positive correlations between Cr and water content were established, with Pearson's correlation coefficients (r) of 0.663 for southwest monsoon season, 0.755 for northeast monsoon season, and 0.664 for dry season, Cr had strong correlation with water content, suggesting that water carry Cr as part of its source in the sediment [102].

Table 4.3

Results of product–moment correlation analyzes of chromium and physicochemical properties in the surface sediment of the inner Gulf of Thailand during the southwest monsoon season (S1), northeast monsoon season (S2), and dry season (S3).

Factor	Cr (mg/kg)			Fe (mg/kg)			TOM (%)			TOC (mg/g)			TP (mg/g)			AVS (mg/g)		
	S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3
Cr	1.000	1.000	1.000	0.783** n=59	0.831** n=60	0.749** n=58	0.567** n=59	0.692** n=60	0.591** n=58	0.294* n=59	0.483** n=60	0.533** n=58	0.729** n=59	0.608** n=60	0.249 n=58	0.349** n=59	0.550** n=56	0.664** n=55
Fe	0.783**	0.831**	0.749**															
TOM	0.567**	0.692**	0.591**	0.490**	0.706**	0.586**												
TOC	0.294*	0.483**	0.533**	ns	0.465**	0.630**	0.660**	0.531**	0.708**									
TP	0.729**	0.608**	ns	0.615**	0.623**	0.641**	0.341**	0.568**	0.576**	ns	0.653**	0.821**						
AVS	0.349**	0.550**	0.664**	0.362**	0.493**	0.358**	0.274*	0.480**	ns	0.092	0.497**	0.415**	0.295*	0.602**	0.547**			
WC	0.663**	0.755**	0.606**	0.744**	0.766**	0.701**	0.690**	0.732**	0.698**	0.330*	0.566**	0.775**	0.581**	0.724**	0.706**	0.433**	0.594**	0.278*

*p<0.05; ** p<0.01; and ns indicate statistically non−significant relationship

Principal component analysis (*PCA*) reduces data size by isolation of a small number of latent factors (major component) to explore the similarities of distribution behavior between Cr and correlation analysis between observed. To identify and analyze the sources of Cr and physicochemical properties in this region, *PCA* are presented in Table 4.4.

In the southwest monsoon season, the component matrices of the *PCA* are presented in Table 4.4. The Kaiser-Meyer-Olkin (*KMO*) and Bartlett's results were 0.735 and 234.605 (df = 21, Sig < 0.01), respectively, suggesting that *PCA* might be useful in dimensionality reductions. According to these results, Cr, Fe, TOM, TOC, TP, AVS and water content could be grouped into a two-component model, which accounted for 72.55% of all of the data variation. The first principal component (PC1) with high loadings of Cr, Fe, TP, AVS and water content and medium loading of TOM and TOC, accounted for 55.83 % of total variance. These results imply that Cr, Fe, TOM, TP, AVS and water content can be defined as anthropogenic components and may originate from similar pollution sources. The second principal component (PC2) accounted for 16.71% of total variance, with strong loadings on TOM and TOC.

In the northeast monsoon season, the component matrices of the *PCA* are presented in Table 4.4. The Kaiser-Meyer-Olkin (*KMO*) and Bartlett's results were 0.895 and 255.511 (df = 21, Sig < 0.01), respectively, suggesting that *PCA* might be useful in dimensionality reductions. According to these results, Cr, Fe, TOM, TOC, TP, AVS and water content could be grouped into a one-component model, which accounted for 66.65% of all of the data variation. The first principal component (PC1) with high loadings of Cr, Fe, TOM, TOC, TP, AVS and water content, accounted for 66.65% of total variance. These results imply that Fe, TOM, TOC, TP, AVS and water content can be defined as anthropogenic components and may originate from similar pollution sources.

In the dry season, the component matrices of the *PCA* are presented in Table 4.4. The Kaiser-Meyer-Olkin (*KMO*) and Bartlett's results were 0.877 and 252.406 (df = 21, Sig < 0.01), respectively, suggesting that *PCA* might be useful in dimensionality

reductions. According to these results, Cr, Fe, TOM, TOC, TP, AVS and water content could be grouped into a one-component model, which accounted for 65.34% of all of the data variation. The first principal component (PC1) with high loadings of Cr, Fe, TOM, TOC, TP, AVS and water content, accounted for 65.34% of total variance. These results imply that Fe, TOM, TOC, TP, AVS and water content can be defined as anthropogenic components and may originate from similar pollution sources.

Table 4.4 Results of principal component analysis (*PCA*) of chromium and physicochemical properties in the surface sediment of the inner Gulf of Thailand during the southwest monsoon season (S1), northeast monsoon season (S2), and dry season (S3).

Variable	S1		S2	S3
	PC1	PC2	PC1	PC1
Cr	0.865		0.866	0.805
Fe	0.845		0.855	0.841
TOM		0.833	0.822	0.813
TOC		0.930	0.692	0.895
TP	0.804		0.820	0.860
AVS	0.580		0.723	0.502
Water content	0.771		0.913	0.876
Eigen	3.909	1.170	4.666	4.574
% Total variance	55.83	16.71	66.65	65.34
% Cumulative	55.83	72.55	66.65	65.34

Extraction method: principal component analysis

4.4 Sequential Fractions of Chromium

A sequential extraction method proposed by [42]. The major mechanism chromium in sediment leads to existence of five categories including exchangeable, bound to carbonate (acid-soluble), bound to Fe-Mn oxide (reducible), bound to organic matter bond (oxidizable) and residual fraction (silicate). Each difference form respected to bio-availability and remobilization of chromium.

In the southwest monsoon season, Fractional distribution of Cr was mostly bound to organic fraction (Figure 4.14a). The exchangeable fraction of Cr was ranged from the lowest value of 2.86% at BK16, where located at the mouth of the Bangpakong river, while the highest value (11.67% at CP1) was found at the mouth of the Chao Phraya River. The carbonate fraction of Cr varied from 0.92% at BK16, where located at the mouth of the Bangpakong river, to 4.38% at GT3, where located at the western part of the inner Gulf of Thailand. The fraction obtained by exchangeable and bound to carbonate, which are considered to be less bonded, are readily available in the aqueous phase, which is readily biodegradable [8, 126]. The Fe-Mn fraction of Cr ranged from 4.63% at MK1, where found at the inner part of the Mae Klong River, to 21.78% at GT39, where located at the middle part of the inner Gulf of Thailand, these fractions are easily mobile in environmental conditions like low pH and low Eh conditions [136]. The lowest organic fraction of Cr was 33.98% (MK1), where occurred at the inner part of river of the Mae Klong River, while the highest value of 70.90% (CP16) was occurred the mouth of the Chao Phraya River, this fraction may be associated with high molecular weight humic substances. Therefore, it is considered to have low mobility by releasing small amounts of metal into the environment [26]. The Cr content of the residual fraction of the sediments ranged between 1.00% at CP10, where occurred the mouth of the Chao Phraya River, to 51.75% at MK1, where located at the inner part of the Mae Klong River. This fraction includes the residual metals and involves minerals that bind through their crystal structure, immobilize and will not pose a threat to the ecosystem [127].

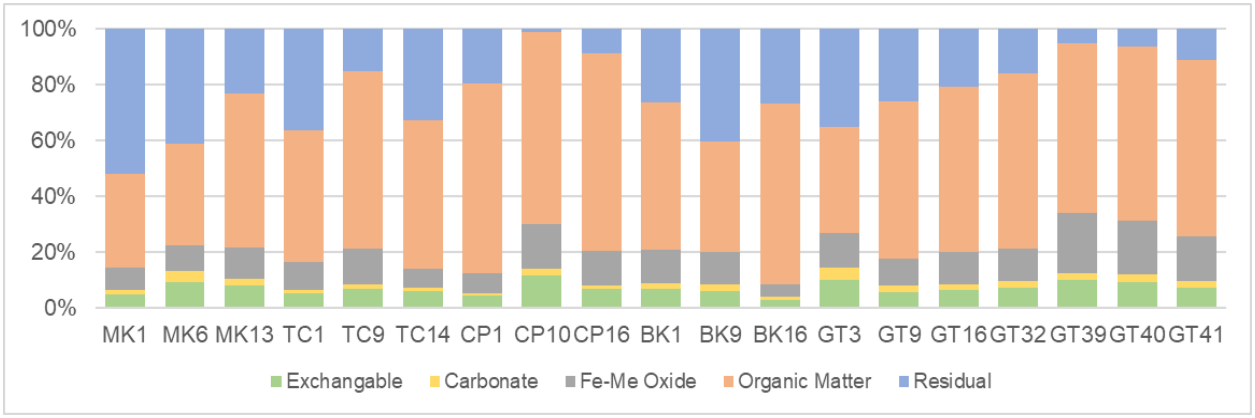
In the northeast monsoon season, Fractional distribution of Cr was mostly residual fraction (Figure 4.14b). The exchangeable fraction of Cr was ranged from the lowest value of 4.14% at CP16, where located at the mouth of the Chao Phraya River, while the highest value (29.75% at GT3) was found at the western part of the inner Gulf of Thailand. The carbonate fraction of Cr varied from 0.35% at CP16, where located at the mouth of the Chao Phraya River, to 15.03% at GT3, where located at the western part of the inner Gulf of Thailand. The fraction obtained by exchangeable and bound to carbonate, which can be released into the environment when conditions become more acidic, negatively affect the environment [128]. The Fe-Mn fraction of Cr ranged from 3.57% at TC14, where found at the mouth of the

Tha Chin River, to 26.73% at CP1, where located at the inner part of the Chao Phraya River, these fractions may be released into environment if conditions become more acidic. The lowest organic fraction of Cr was 15.97% (CP16), where occurred at the mouth of the Chao Phraya River, while the highest value of 68.16% (GT16) was occurred the upper part of the inner Gulf of Thailand, this fraction is considered low mobility by releasing small amounts of metal into the environment. The Cr content of the residual fraction of the sediments ranged between 3.23% at GT16, where occurred the upper part of the inner Gulf of Thailand, to 75.35% at CP16, where located at the mouth of the Chao Phraya River. This fraction characterizes stable compounds in sediments.

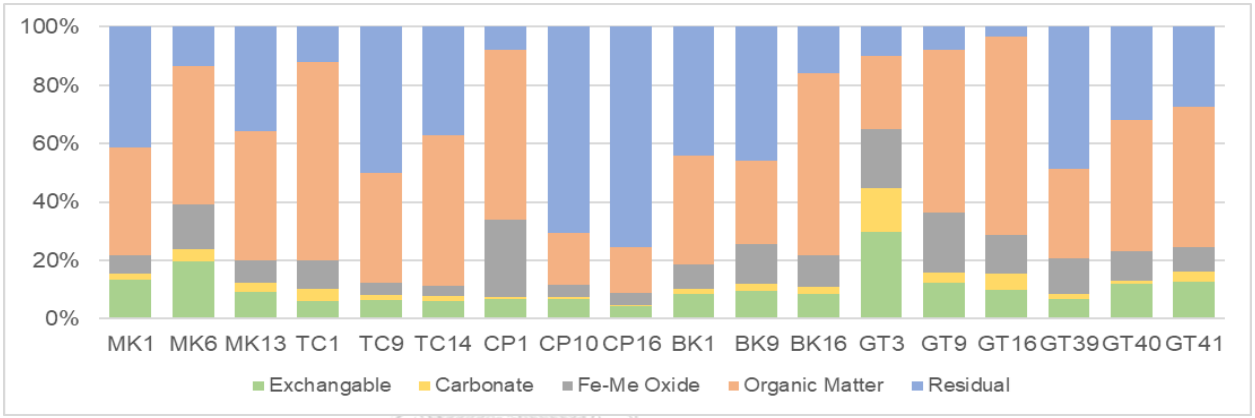
In the dry season, Fractional distribution of Cr was mostly residual fraction (Figure 4.14c). The exchangeable fraction of Cr was ranged from the lowest value of 5.81% at BK16, where located at the mouth of the Bangpakong river, while the highest value (27.75% at GT3) was found at the western part of the inner Gulf of Thailand. The carbonate fraction of Cr varied from 1.99% at CP16, where located at the mouth of the Chao Phraya River, to 12.92% at MK6, where located at the inner part of the Mae Klong River. The fraction obtained by exchangeable and bound to carbonate, includes weakly adsorbed metal forms that are held on the surface of soil and sediment grains by weak electrostatic reactions and ion exchange processes. The Fe-Mn fraction of Cr ranged from 1.17% at BK16, where found at the mouth of the Bangpakong river, to 13.46% at CP1, where located at the inner part of the Chao Phraya River, the release of the Cr from Fe-Mn fraction is most likely to be affected by redox potential and pH. The lowest organic fraction of Cr was 18.95% (CP10), where occurred at the mouth of the Chao Phraya River, while the highest value of 69.36% (GT16) was occurred the upper part of the inner Gulf of Thailand, this fraction considered to be of low mobility, releasing small amounts of metals into the environment. The Cr content of the residual fraction of the sediments ranged between 6.20% at GT3, where occurred the upper part of the inner Gulf of Thailand, to 66.71% at CP10, where located at the mouth of the Chao Phraya River. The residual fraction contains metals that are chemically stable, immobile, and biologically inert.

The fraction of Cr is very important for their toxicity and biological role of the specific constituents varies by chemical form [129]. The toxicity of Cr depends on the

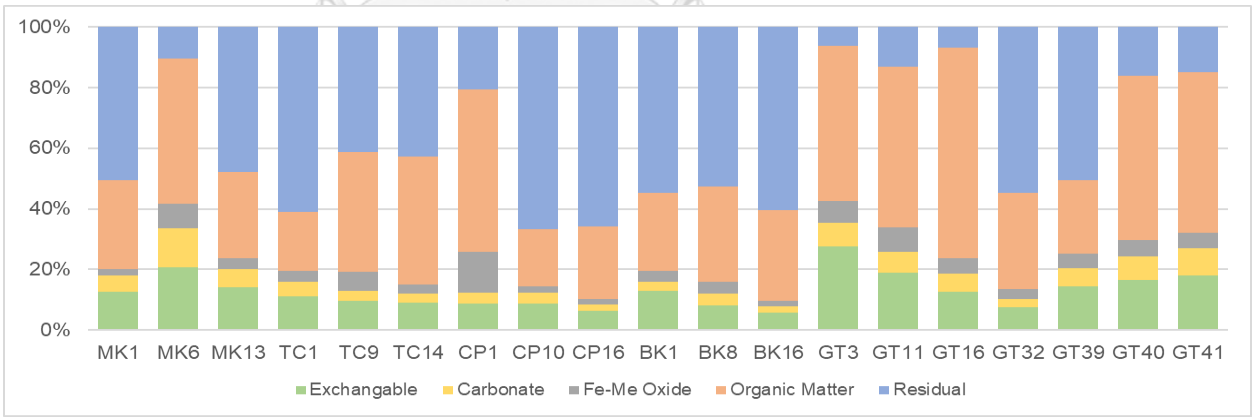
concentration of Cr in the different fractions, some of sediments rather than considering the content of all elements, therefore, the study of fractions is more important. It has been shown that physical properties such as the distribution of a substance are analyzed based on physical properties such as size or solubility. The total physical transport of Cr is controlled, while the dissociation of dissolved Cr is the distribution of the element between a given chemical species [130]. Therefore, the most important process in controlling the effect and fate of Cr in aqueous system is the division between the solid phase and the aqueous phase, when this competition favors the aqueous phase, the uptake of Cr and its toxic potential tends to increase. when the adsorption is greater. The particles act as the primary carriers of Cr, reducing the short-term toxicity of Cr and altering the final fate of these species [25].



(a)



(b)



(c)

Figure 4.14 Sequential fraction of Cr in the surface sediments from the selected sites in the southwest monsoon season (a), the northeast monsoon season (b) and the dry season (c) entire the inner Gulf of Thailand.

4.5 Contamination Status

4.5.1 Sediment quality guidelines

This study, SQG_s reflects the importance of contaminated sediment as adverse impact of heavy metal on aquatic organism [131] US National Oceanic and Atmospheric Administration [60] Canadian and Wisconsin United States sediment quality guidelines were selected to estimate the quality of the collected sediment samples in the inner Gulf of Thailand (Table 4.5).

The chromium contamination compared with US National Oceanic and Atmospheric Administration (NOAA), Canadian SQG_s, National Oceanic Administration of China (NOAC) and Australian and New Zealand Environment and Conservation Council (ANZECC) including effect range low (*ERL*) and effect range median (*ERM)*. The lower 10^{th} percentile of the effects data for each chemical was identified and referred to as the ERL. The median or 50^{th} percentile, of the effects data was identified and referred to as the ERM [61] The level of chemical contamination is classified as 1) the concentrations below *ERL* represent a minimal−effects range which effects would be rarely observed; 2) the concentrations between *ERL* and *ERM* represent a possible−effects range which effects would occasionally occur or 3) the concentrations above *ERM* represent a probable−effects range which effects would frequently occur [60]. In addition, the comparison with Canadian and Wisconsin united states sediment guideline quality and including threshold effect level (*TEL*) was identified to adverse effects only rarely occurred and probable effect level (*PEL*) was identified to adverse effects frequently occurred. the *TEL* and *PEL* were intended to define three concentration ranges as 1) chemical concentrations below *TEL* that rarely associate with adverse effect; 2) chemical concentrations between *TEL* and *PEL* that occasionally associate with adverse effect or 3) chemical concentrations above *PEL* frequently associated with adverse effects (MacDonald et al., 1996). A comparison of SQG_s showed in Table 4.5.

In southwest monsoon season, the SQG_s value for Cr was classified based on *ERL−ERM* compared with NOAA, USA and NOAC, China suggests that mean chromium concentration below *ERL* and 98.31% of sample exceeded the

ERL and 1.69% of sample fall in the range between *ERL* and *ERM*. Comparing with Canadian and ANZECC guideline, there are 100 % less than *ERL* values. The comparability with guideline had found that there are less than *TEL* 69.49% and 30.51% greater than *TEL* but also less than *PEL*. The SQG_s values for Cr were classified based on *TEL−PEL* compared with Canadian SQG_s suggest that mean chromium concentration is lower than *TEL* and 81.36% of sample exceeded *TEL* and 18.64% of sample fall in the range between *TEL* and *PEL*. As a result, indicated that most of the area has minimal effect range within which adverse effects rarely occur and some area has the possible effect range within which adverse effects occasionally occur. Compared with PCD, Thailand suggests that mean chromium concentration is lower than SQG_T and 69.49 % of sample exceeded SQG_T and 30.51% of sample fall in the higher than SQG_T.

In northeast monsoon season, Cr concentration was below *ERL* value and 95% of sample exceeds the *ERL* and 5% of sample fall in the range between *ERL* and *ERM* of Canadian and ANZECC guideline, indicated that biological effects are rarely observed. The comparability with NOAA, USA and NOAC, China guideline had found that there are less than *ERL* 95% and 5% greater than *ERL* but also less than *ERM* indicated that most of the area had rarely observed of biological effects, but some area had occasionally observed of biological effects. Comparing with Wisconsin guidelines, there are 65.52% less than *TEL* and 34.48% greater than *TEL* value but less than *PEL*. The SQG_s values for Cr compared with Canadian suggested that mean chromium concentration less than *TEL* and 73.33% of sample exceeded *TEL* and 26.67% of sample fall in the range between *TEL* and *PEL* indicated that most of the area has minimal effect range within which adverse effects rarely occur and some area has the possible effect range within which adverse effects occasionally occur. Cr concentration also compared with SQG_T from the PCD, Thailand. The result shows that there are 56.67% less than SQG_T values and 43.33% greater than SQG_T.

In dry season, the comparability with NOAA, Canadian, ANZECC and NOAC guideline had found that there are less than *ERL* 98.28% and 1.72% greater than *ERL* but also less than *ERM* indicated that most of the area had rarely observed of biological effects, but some area had occasionally observed of

biological effects. Comparing with Wisconsin guidelines, there are 58.33% less than *TEL* values, 32.76% greater than *TEL* but less than *PEL* and 8.91% more than *PEL*. The SQG_s values for Cr was classified based on *TEL−PEL* compared with Canadian suggested that mean chromium concentration less than *TEL* and 81.03% of sample exceeded *TEL* and 18.97% of sample fall in the range between *TEL* and PEL indicated that most of the area has minimal effect range within which adverse effects rarely occur and some area has the possible effect range within which adverse effects occasionally occur. In comparison to the PCD, Thailand, a mean Cr concentration are lower than SQG_T and 58.62% of sample exceeded SQG_T, 41.38% of sample fall in the higher than SQG_T.

The result from the chromium contamination compared with US National Oceanic and Atmospheric Administration (NOAA), Canadian SQG_s, National Oceanic Administration of China (NOAC), Australian and New Zealand Environment, Conservation Council (ANZECC), Canadian, Wisconsin united states sediment guideline quality and the SQG_T of Thailand. As a result, at concentrations of Cr in the surface sediment greater than *TEL*, *ERL* and SQG_T, the toxic effect of long-term exposure to Cr is predictable and risk of Cr is unclear and needs to be examined by other approaches.

Table 4.5 Comparison between chromium concentrations and numerical sediment quality guidelines (*SQGs*) in mg/kg

Values			Southwest monsoon season	Northeast monsoon season	Dry season
Min			11.72	5.61	8.63
Max			80.16	107.45	119.47
Average			36.04	38.14	37.67
SD			16.72	22.19	19.29
NOAA, USA	*ERL* = 80 *ERM* = 145	% < *ERL*	98.31	95.00	98.28
		% *ERL*−*ERM*	1.69	5.00	1.72
		% > *ERM*			
Canadian	*ERL* = 81 *ERM* = 370	% < *ERL*	100	95	98.28
		% *ERL*−*ERM*		5	1.72
		% > *ERM*			
NOAA, China	*ERL* = 80 *ERM* = 270	% < *ERL*	98.31	95.00	98.28
		% *ERL*−*ERM*	1.69	5.00	1.72
		% > *ERM*			
ANZECC	*ERL* = 81 *ERM* = 370	% < *ERL*	100	95	98.28
		% *ERL*−*ERM*		5	1.72
		% > *ERM*			
Wisconsin	*TEL* = 43 *PEL* = 110	% < *TEL*	69.49	65.52	58.33
		% *TEL*−*PEL*	30.51	34.48	32.76
		% > *PEL*			8.91
Canadian	*TEL* = 52.3 *PEL* = 160	% < *TEL*	81.36	73.33	81.03
		% *TEL*−*PEL*	18.64	26.67	18.97
		% > *PEL*			
PCD, Thailand	SQG_T = 42	% ≤ SQG_T	69.49	56.67	58.62
		% > SQG_T	30.51	43.33	41.38

4.5.2 Enrichment factor

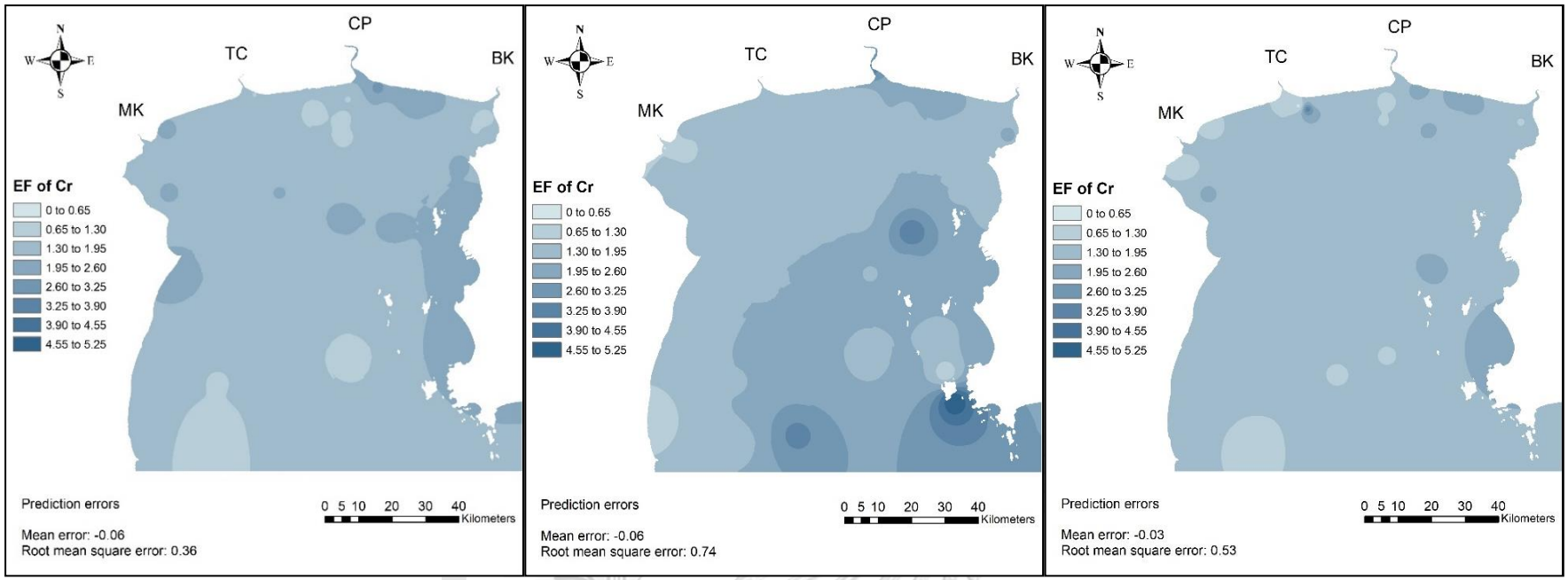
The *EF* in metals is indicators used to assess the presence and intensity of anthropogenic contaminant deposition on surface sediment. These indexes of potential contamination are calculated by the normalization of one metal concentration in the top-sediment with respect to the concentration of a reference element. The values of *EF* for Cr are presented in Figure 4.15.

In southwest monsoon season, the *EF* values of Cr were ranged from lowest value of 0.72 at GT29, where located in the middle part of the inner Gulf of Thailand, suggesting no enrichment. The highest *EF* value (2.78 at CP13) was occurred at the mouth of the Chao Phraya River, suggesting minor enrichment. An average *EF* values was 1.69±0.42 (Figure 4.15a). There are two stations (0.82 for BK7 and 0.72 for GT29) have $1 < EF$ as deficiency to no enrichment and fifty-seven stations have $1 \leq EF < 3$ as deficiency to minor enrichment.

In northeast monsoon season, the *EF* values of Cr were ranged from lowest value of 0.56 at MK3, where located at the mouth of the Mae Klong River, suggesting no enrichment. The highest *EF* value (5.24 at GT38) was occurred at the middle part of the inner Gulf of Thailand, suggesting moderately severe enrichment. An average *EF* value was 1.86±0.72 (Figure 4.15b). There are four stations have $1 < EF$ as deficiency to no enrichment, fifty-two stations have $1 \leq EF < 3$ as deficiency to minor enrichment, three stations have $3 \leq EF < 5$ as deficiency to moderate enrichment and highest value was found at GT38 ($EF>5$), was associated with moderately severe enrichment. Because classification of Cr contamination levels depending on the reference material and the quantitative index used.

In dry season, the *EF* values of Cr were ranged from lowest value of 0.48 at TC13, where located at the mouth of the Tha Chin River, suggesting no enrichment. The highest *EF* value (3.63 at TC15) was occurred the mouth of the Tha Chin River, suggesting moderate enrichment. An average *EF* value was 1.60±0.43 (Figure 4.15c). There are five stations have $1 < EF$ as deficiency to no enrichment, fifty-two stations have $1 \leq EF < 3$ as deficiency to minor enrichment and one stations have $3 \leq EF < 5$ as deficiency to moderate enrichment.

Comparisons of the *EF* values of the Cr concentration in surface sediments of the inner Gulf of Thailand in all seasons are shown in Figure 4.16. The mean *EF* values of Cr concentration in the southwest monsoon season were non-significant difference with the northeast monsoon season and the dry season, while the *EF* values of Cr in the northeast monsoon season and the dry season were significant difference. In other words, the average concentration of *EF* values of Cr in surface sediments in southwest monsoon and dry season is lower than that in northeast monsoon season. The *EF* values varied seasonally as follows: northeast monsoon season > southwest monsoon season > dry season. The mean *EF* values of the River estuary and the inner Gulf of Thailand in all seasons are shown in Figure 4.17, varied seasonally as follows: the inner Gulf of Thailand (1.85±0.63) > River estuary (1.63±0.48), the high value was occurred at the middle part of the inner Gulf of Thailand in the northeast monsoon season (GT26, GT38 and GT39) because the background concentration of Fe was much lower than the other sites and classification of Cr contamination levels depending on the reference material and the quantitative index used. As a result, the average of *EF* values shows significant fluctuations across all sampling sites. Our results indicate that Cr accumulation is both natural and human−caused. It is also reported that high *EF* values reflect man-made sources of Cr, mostly from activities such as industrialization and collecting.



(a) (b) (c)

Figure 4.15 Spatial heterogeneity distributions of enrichment factor (*EF*) in the surface sediment and seasonal variations in the southwest monsoon season (a), the northeast monsoon season (b), and the dry season (c) entire the inner Gulf of Thailand.

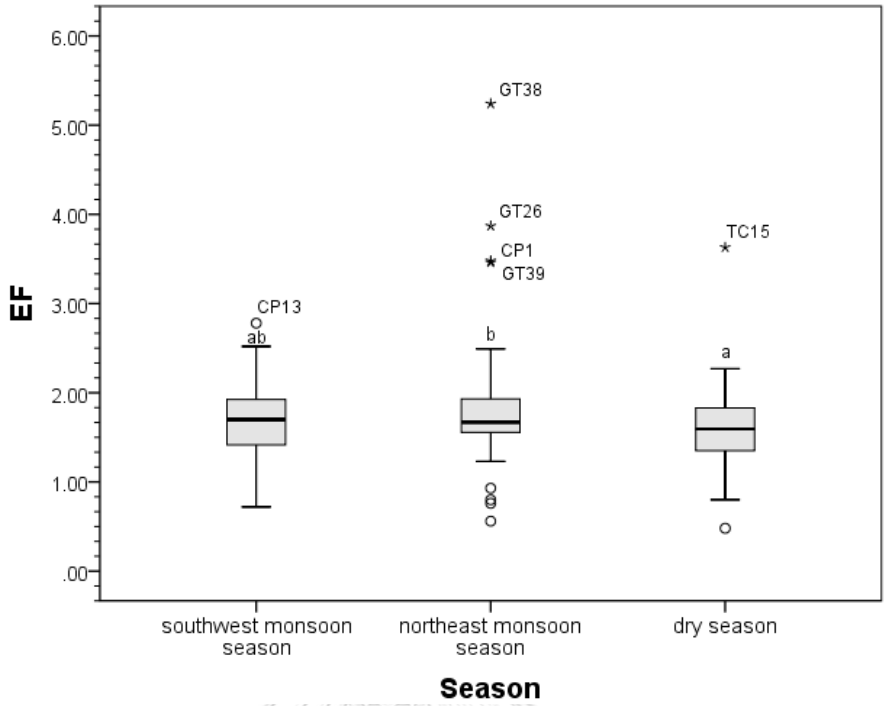


Figure 4.16 A comparison of the enrichment factor (*EF*) in surface sediments of the inner Gulf of Thailand between southwest monsoon season, northeast monsoon season and dry season. The box shows the 25th and the 75th percentiles, and the whiskers represent the smallest and the largest concentration. (alphabet indicated significant difference at p<0.05 using the DMRT analysis).

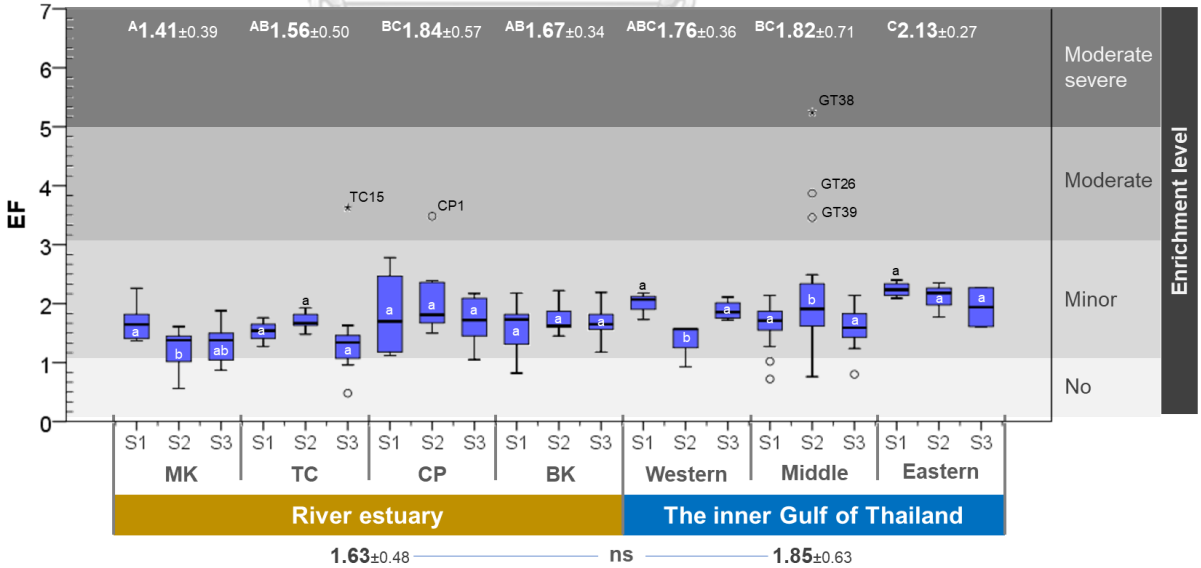


Figure 4.17 Box-Whisker plots compares the *EF* of Cr contamination in surface sediments of four river estuaries and three parts from the inner Gulf of Thailand (southwest monsoon season (a), northeast monsoon season (b) and dry season (c). The box shows the 25th and the 75th percentiles, and the whiskers represent the smallest and the largest concentration.

4.5.3 Geo-accumulation index

A common method for estimating the concentration of metal concentrations above background or baseline concentrations is to calculate the geo-accumulation index (I_{geo}) as proposed by Müller (1969). The metal pollution in terms of seven enrichment levels is determined by the increasing numerical value of the index. The values of I_{geo} for Cr are presented in Figure 4.18.

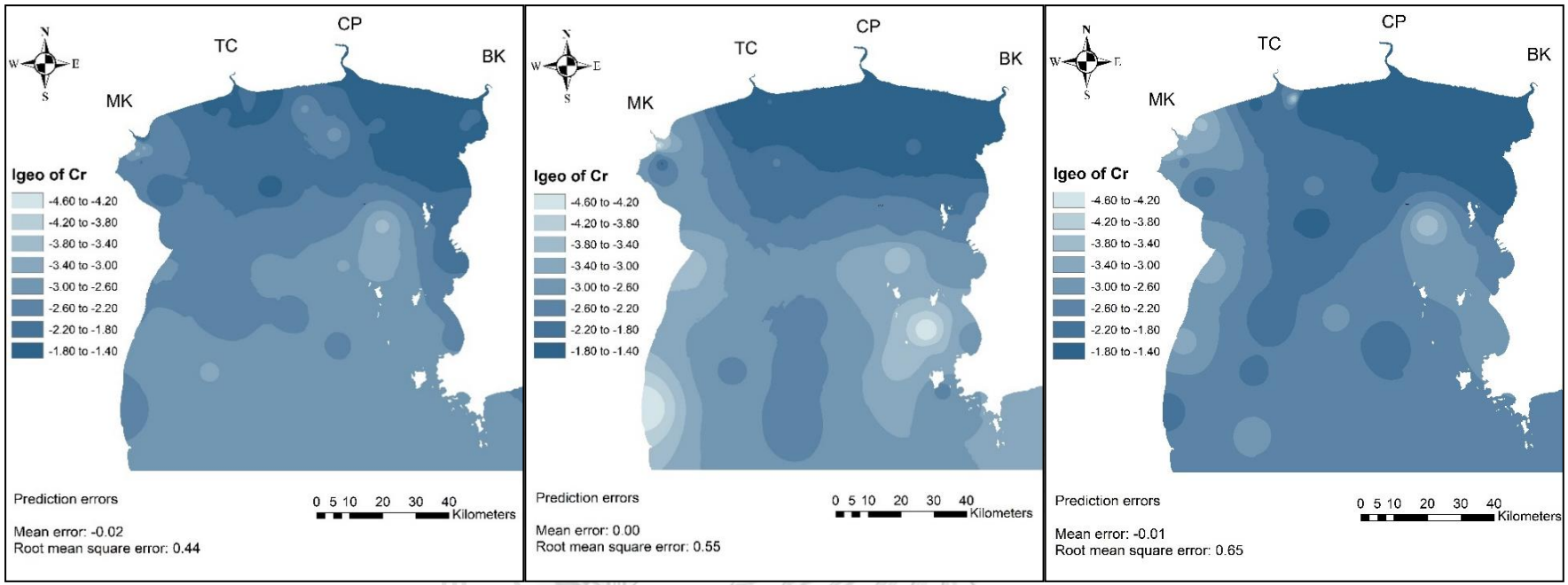
In southwest monsoon season, The I_{geo} values of Cr varied from -3.53 at GT26, where located at the middle part of the inner Gulf of Thailand, to -0.75 at CP13, where located at the mouth of the Chao Phraya River with an average I_{geo} values of -2.06±0.68 (Figure 4.18a). The calculated I_{geo} values indicated that Cr has negative I_{geo} value. All stations were categorized as practically uncontaminated.

In northeast monsoon season, The I_{geo} values of Cr varied from -4.05 at GT28, where located at the middle part of the inner Gulf of Thailand, to -0.33 at CP1, where located at the inner part of the Chao Phraya River with an average I_{geo} values of -2.12±1.01 (Figure 4.18b). The calculated I_{geo} values indicated that Cr has negative I_{geo} value. All stations were categorized as practically uncontaminated.

In dry season, The I_{geo} values of Cr varied from -3.97 at TC13, where located at the the mouth of the Tha Chin River, to -0.18 at TC15, where located at the the mouth of the Tha Chin River with an average I_{geo} values of -2.04±0.81 (Figure 4.18c). The calculated I_{geo} values indicated that Cr has negative I_{geo} value. All stations were categorized as practically uncontaminated.

Comparisons of the I_{geo} values of the Cr concentration in surface sediments of the inner Gulf of Thailand in all seasons are shown in Figure 4.19. The mean difference of I_{geo} values between the seasonal variation did not vary significantly (p>0.05). In other words, the average concentration of I_{geo} values of Cr in surface sediments in southwest monsoon and dry season is lower than that in northeast monsoon season. The I_{geo} values varied seasonally as follows: northeast monsoon season > southwest monsoon season > dry season. The mean I_{geo} values of the river estuary and the inner Gulf of Thailand in all seasons are shown in Figure

4.20, varied seasonally as follows: River estuary (-1.76±0.81) > the inner Gulf of Thailand (-2.52±0.65). As a results, the I_{geo} values were negative at all stations. Therefore, the result indicated unpolluted.



(a) (b) (c)

Figure 4.18 Spatial heterogeneity distributions of geo−accumulation (I_{geo}) in the surface sediment and seasonal variations in the southwest monsoon season (a), the northeast monsoon season (b), and the dry season (c) entire the inner Gulf of Thailand.

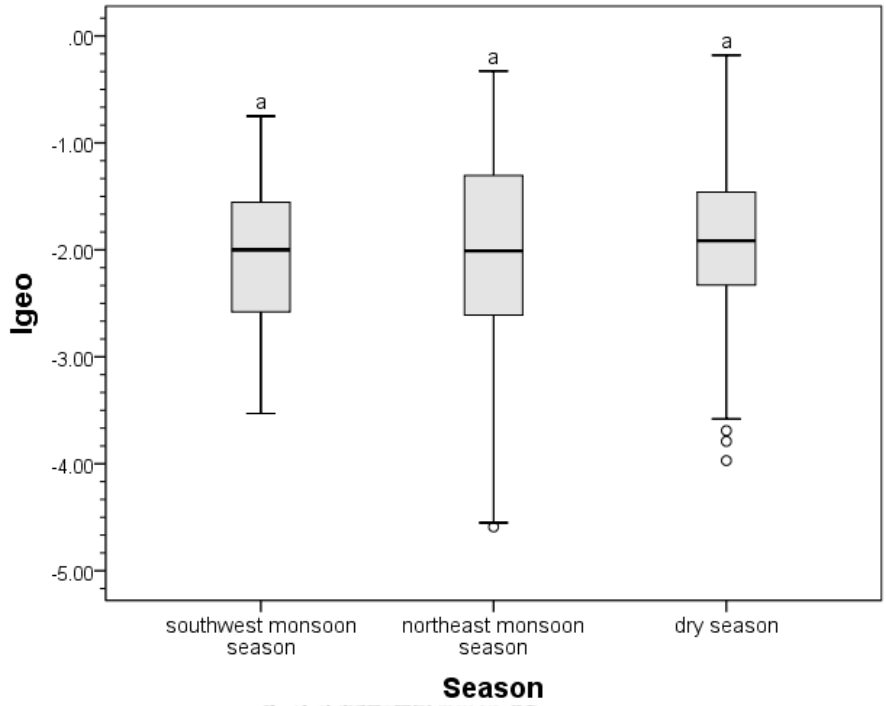


Figure 4.19 A comparison of the geo−accumulation (I_{geo}) in surface sediments of the inner Gulf of Thailand between southwest monsoon season, northeast monsoon season and dry season. The box shows the 25th and the 75th percentiles, and the whiskers represent the smallest and the largest concentration. (alphabet indicated significant difference at p<0.05 using the DMRT analysis).

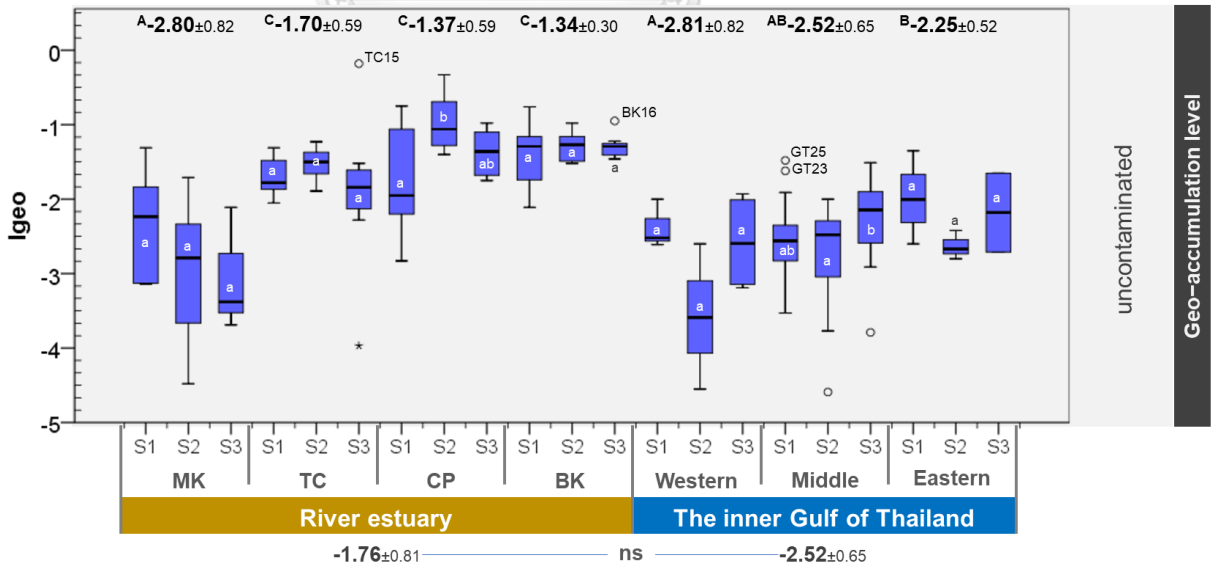


Figure 4.20 Box-Whisker plots compares the I_{geo} of Cr contamination in surface sediments of four river estuaries and three parts from the inner Gulf of Thailand (southwest monsoon season (a), northeast monsoon season (b) and dry season (c). The box shows the 25th and the 75th percentiles, and the whiskers represent the smallest and the largest concentration.

4.6 Potential Risk of Chromium in the Surface Sediment

4.6.1 Ecological risk assessment

The ecological risk index was used to evaluate the potential ecological risk of heavy metals. This method considers the synergy toxic level, the concentration of the heavy metals and ecological sensitivity of heavy metals. The E_r value of all station shows in Figure 4.21.

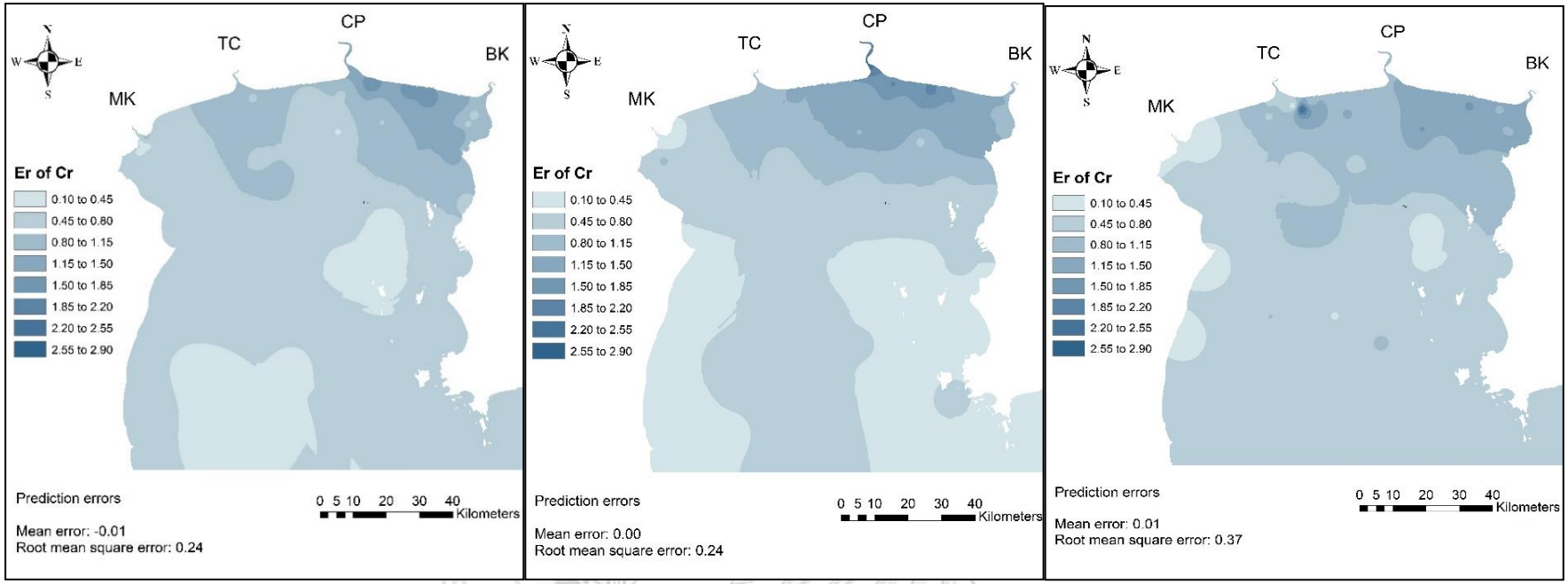
In southwest monsoon season, the lowest E_r value was 0.25 (GT28), where occurred at middle part of the inner Gulf of Thailand, while the highest value of 1.78 (CP13) was occurred at the mouth of the Chao Phraya River (Figure 4.21a). The average E_r values was 0.80±0.37, all stations were classified as low potential ecological risk (E_r <40). The highest was found at CP13 that is subjected to natural and anthropogenic processes.

In northeast monsoon season, the lowest E_r value was 0.12 (GT28), where occurred at middle part of the inner Gulf of Thailand, while the highest value of 2.39 (CP1) was occurred at the inner part of the Chao Phraya River (Figure 4.21b). The average E_r values was 0.85±0.49, all stations were classified as low potential ecological risk (E_r<40). The highest was found at CP1 that is subjected to natural and anthropogenic processes.

In dry season, the lowest E_r value was 0.12 (TC13), where occurred at the mouth of the Tha Chin River, while the highest value of 2.65 (TC15) was occurred at the mouth of the Tha Chin River (Figure 4.21c). The average E_r values was 0.83±0.43, all stations were classified as low potential ecological risk (E_r<40). The highest was found at TC15 that is subjected to natural and anthropogenic processes.

Comparisons of the E_r values of the Cr concentration in surface sediments of the inner Gulf of Thailand in all seasons are shown in Figure 4.22. The mean difference of E_r values between the seasonal variation did not vary significantly (p>0.05). In other words, the average concentration of E_r values of Cr in surface sediments in southwest monsoon and dry season is lower than that in northeast monsoon season. The E_r values varied seasonally as follows: northeast monsoon season > dry season > southwest monsoon season. The mean E_r values of the

river estuary and the inner Gulf of Thailand in all seasons are shown in Figure 4.23, varied seasonally as follows: the inner Gulf of Thailand (1.18±0.63) > River estuary (1.10±0.45). As a result, the E_r values indicate the sensitivity of various biological communities to toxic substances and indicates the potential ecological risk of heavy metals. All areas are at low ecological risk, the highest being at CP13 in southwest monsoon, CP1 in northeast monsoon and TC15 in dry season, which is under the influence of river runoff. The E_r values were clearly related to the degree of anthropogenic disturbance. The sources of heavy metal pollution in rivers are influenced by many factors, both natural and man-made.



(a) (b) (c)

Figure 4.21 Spatial heterogeneity distributions of ecological risk (E_r) in the surface sediment and seasonal variations in the southwest monsoon season (a), the northeast monsoon season (b), and the dry season (c) entire the inner Gulf of Thailand.

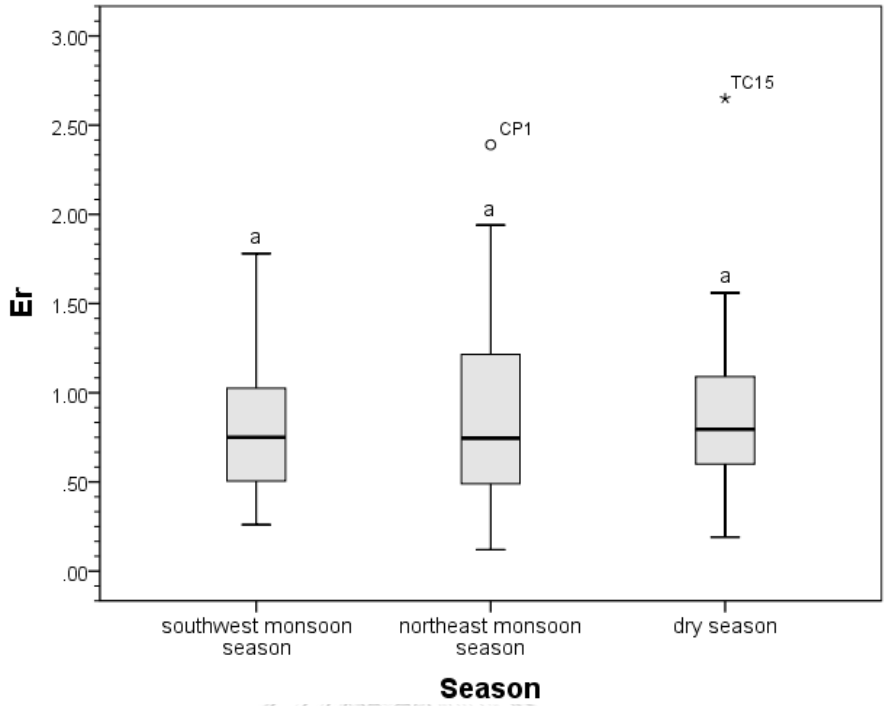


Figure 4.22 A comparison of the ecological risk (E_r) in surface sediments of the inner Gulf of Thailand between southwest monsoon season, northeast monsoon season and dry season. The box shows the 25th and the 75th percentiles, and the whiskers represent the smallest and the largest concentration. (alphabet indicated significant difference at p<0.05 using the DMRT analysis).

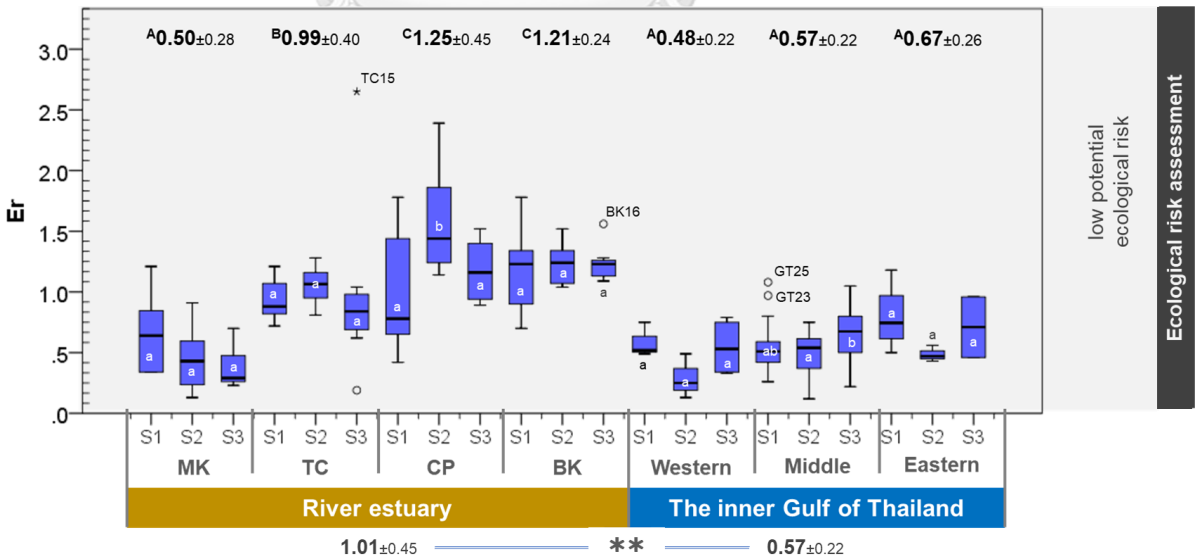


Figure 4.23 Box-Whisker plots compares the E_r of Cr contamination in surface sediments of four river estuaries and three parts from the inner Gulf of Thailand (southwest monsoon season (a), northeast monsoon season (b) and dry season (c). The box shows the 25th and the 75th percentiles, and the whiskers represent the smallest and the largest concentration.

4.6.2 Assessment of mobility and availability of chromium

The potential risk of heavy metals in sediment is partially influenced by the total content of heavy metals, but the chemical classification involved in the mobility of heavy metals determines the potential risk of release into water bodies [132]. It is evident that the metals in sediments are bound to different strengths, this creates inconsistent risks in the aqueous sludge interface [133]. The risk assessment code (*RAC*) proposed by Perin et al. (1985) relies on a continuous extraction method [42] on metal partitioning. Researchers [134-140] proposed that higher amounts of metal contained within the exchangeable and carbonate fractions cause a higher potential release and remobilization risk. suggest that higher metal content within the exchangeable and carbonate fractions creates a higher release and recovery risk. Several studies have looked at metal toxicity factors and chemically bonded states as measures of effect and release potential.

The present study, the mobility and availability of Cr were assessed using the risk assessment code (*RAC)* indices. The *RAC* is defined as follows [141]:

$$\frac{F_{exc}+F_{ca}}{F_t}\times 100 \qquad (4.1)$$

where F_{exc} and F_{ca} are the concentrations of exchangeable and carbonate−bound Cr fractions, respectively, and F_t is the sum of the contents of the five Cr fractions. The sum of the F_{exc} and F_{ca} Cr fractions represents the amount of loosely bound Cr. The risk level classifications of the *RAC* are shown in Table 4.6.

Table 4.6 Classifications of the risk assessment code (*RAC*)

RAC value	Risk level
<1	No risk
1−10	Low risk
11−30	Moderate risk
31−50	High risk
>50	Very high risk

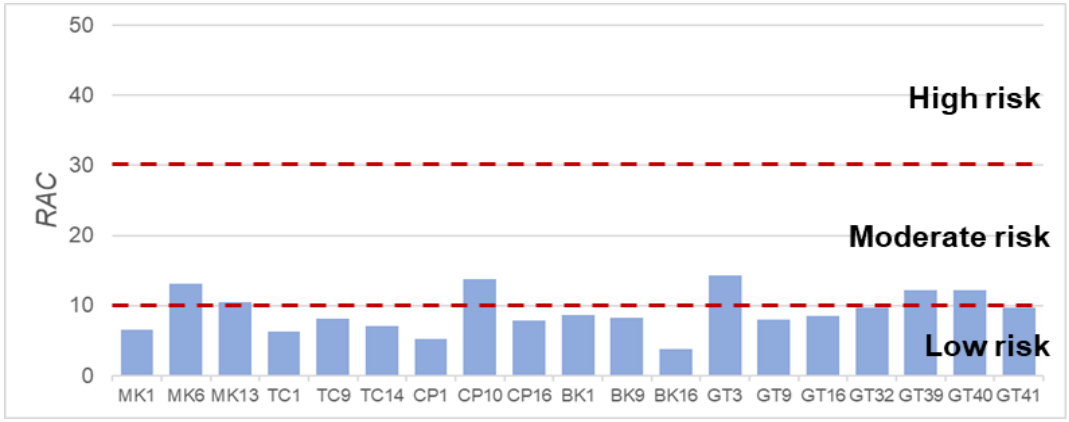
In the southwest monsoon season, the *RAC* of Cr was ranged from the lowest value of 5.23% at CP1, where located at the mouth of the Chao Phraya River, while the highest value (14.24% at GT3) was at the western part of the inner Gulf of Thailand. There are 14 stations (MK1, MK13, TC1, TC9, TC14, CP1, CP16, BK1, BK9, BK16, GT9, GT16, GT32 and GT41) have 1 < *RAC* < 10 as deficiency to low risk and 5 stations (MK6, CP10, GT3, GT39 and GT40) have 11 < *RAC* < 30 as deficiency to moderate risk (Figure 4.24a).

In the northeast monsoon season, the *RAC* of Cr was ranged from the lowest value of 4.49% at CP16, where located at the mouth of the Chao Phraya River, while the highest value (44.78% at GT3) was at the western part of the inner Gulf of Thailand. There are 9 stations (MK1, TC1, TC9, TC14, CP1, CP10, CP16, BK1 and GT39) have 1 < *RAC* < 10 as deficiency to low risk and 8 stations (MK6, MK13, BK9, BK16, GT9, GT16, GT40 and GT41) have 11 < *RAC* < 30 as deficiency to moderate risk. Their highest value was found at GT3, suggesting high risk (Figure 4.24b).

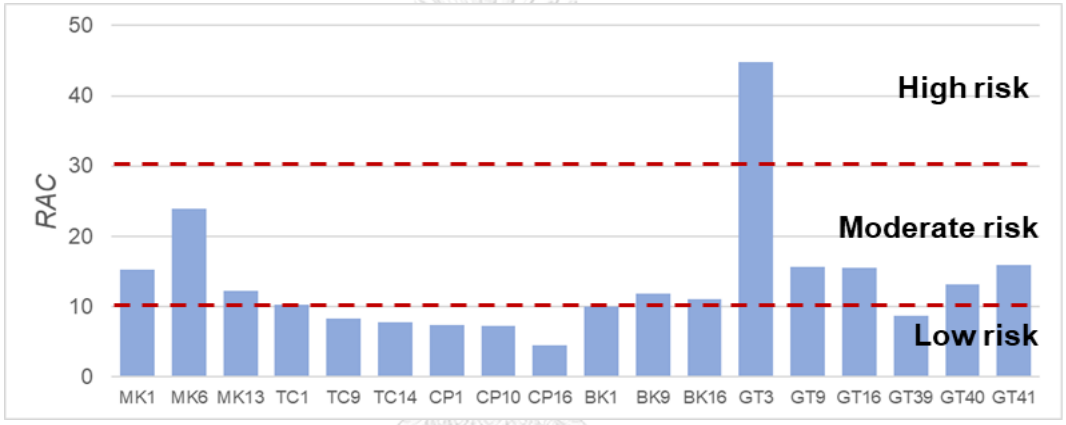
In the dry season, the *RAC* of Cr was ranged from the lowest value of 8.03% at BK16, where located at the mouth of the Bangpakomg River, while the highest value (35.42% at GT3) was at the western part of the inner Gulf of Thailand. There are 3 stations (CP16, BK16 and GT31) have 1 < RAC < 10 as deficiency to low risk and 14 stations (MK1, MK13, TC1, TC9, TC14, CP1, CP10, BK1, BK8, GT11, GT16, GT39, GT40 and GT41) have 11 < *RAC* < 30

as deficiency to moderate risk. Their high value was found at MK6 and GT3, suggesting high risk (Figure 4.24c).

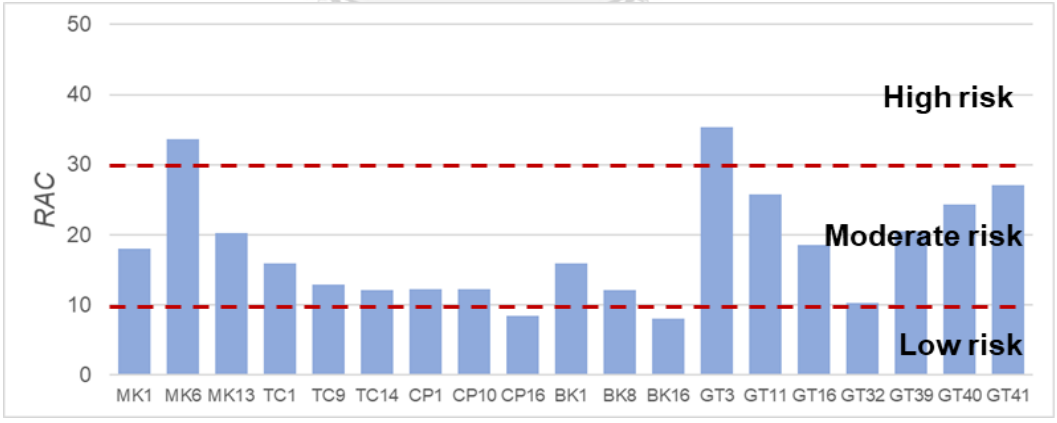
The high amounts of *RAC* in the study area reveal that potential adverse effects Cr in sediments is highly dependent upon either the high risk of release or presence of high concentrations of Cr with higher toxicity in loosely bonded fractions. The exchangeable and bound to carbonate includes weakly adsorbed metal forms that are held on the surface of soil and sediment grains by weak electrostatic reactions and ion exchange processes and can be released into the environment when conditions become more acidic. However, the percentages of GT3 value in all seasons in this *RAC* were high because TOM of GT3 in all seasons were low indicating that higher degradation processes of organic matter can lead to lower pH due to humic acid production, which increases Cr emission, although Cr binding to organic matter is considered stable, but it is necessary to note that these Cr may be depleted over time due to organic degradation. Since the binding characteristics of TOM-containing heavy metals can be clearly altered by modifying the TOM properties, an enhancement or maximum stability of overall absorption within a geographic absorbent medium may be possible [27].



(a)



(b)



(c)

Figure 4.24 Risk assessment code of sequential fraction of Cr in the surface sediments from the selected sites in the southwest monsoon season (a), the northeast monsoon season (b) and the dry season (c) entire the inner Gulf of Thailand

CHAPTER V
CONCLUSIONS

The inner Gulf of Thailand is loaded with heavy metals, particularly Cr from both natural and anthropogenic sources due to runoff of the Mae Klong, the Tha Chin, the Chao Phraya, and the Bangpakong Rivers. The present study was measured of spatial distributions and seasonal variations of total concentration of Cr coupling with physicochemical factors in the surface sediment. Moreover, fractional forms of Cr were additionally analyzed and discussed in different toxic response. Finally, this study was focused to assess ecological risk of Cr contaminations in the in the inner Gulf of Thailand. The summary results are shown as following:

5.1 Conclusion

5.1.1 Spatial distributions and seasonal variations

Chromium contamination in surface sediment was decreased from the river estuaries to the lower of the inner Gulf of Thailand. The average concentration difference of Cr in the surface sediment between the seasonal variation did not vary significantly. The average concentration of Cr in the surface sediments of the inner Gulf of Thailand changes similarly in three seasons. In other words, the average concentration of Cr in surface sediments in the southwest monsoon and dry season is lower than that in northeast monsoon season. The amounts of Cr concentration in surface sediment varied seasonally as follows: northeast monsoon season > dry season > southwest monsoon season. As the result, the average Cr concentration in all seasons in the inner Gulf of Thailand which was relatively low to moderate concentration when compared to another coastal surface sediment. The major distribution areas of Cr with higher concentrations were in the river estuaries and with lower concentrations were in the middle part of the inner Gulf of Thailand.

Physicochemical factor changes, including TOM, TOC, TP, AVS and water content in surface sediment in the inner Gulf of Thailand, affected the abundance of Cr concentration in surface sediment. From the results of related factors, the Cr concentration had a positive correlation with physicochemical factors shows that Cr concentration with higher accumulation of the amount of physicochemical factor.

5.1.2 Sequential Fractions of Chromium

The sequential fraction of chromium in surface sediment in the inner Gulf of Thailand, the residual and organic fraction, was the most abundant fraction for Cr concentration in the sediment studied. Cr associated with the organic fraction can be remobilized and be available to the biota when the pH and redox conditions of water–sediment system change and the residual fraction inferring less risk to the environment.

5.1.3 Contamination status and potential ecological risk of chromium

Base on the *SQG*s, the result from the chromium contamination compared with US National Oceanic and Atmospheric Administration (NOAA), Canadian *SQG*s, National Oceanic Administration of China (NOAC), Australian and New Zealand Environment, Conservation Council (ANZECC), Canadian, Wisconsin united states sediment guideline quality and the SQG_T of Thailand, which suggesting that most of area may not cause any adverse biological effects but some area were occasionally associate with adverse biological effect within the inner Gulf of Thailand. As a result, at concentrations of Cr in the surface sediment greater than *TEL*, *ERL* and SQG_T, the toxic effect of long−term exposure to Cr is predictable and risk of Cr is unclear and needs to be examined by other approaches.

The Cr contamination levels depending on the reference material and the quantitative index used, the *EF* values of Cr were mostly minor enrichment. It is also reported that the high *EF* values reflect an anthropogenic source of the Cr, mostly from activities such as industrialization and deposition. The calculated I_{geo}

values indicated that Cr was negative I_{geo} values entire the inner Gulf of Thailand in all stations, which are evaluated as practically uncontaminated.

The potential ecological risk of individual metal is regarded as an accurate method to assess ecological risk caused by chromium. The E_r of all stations was less than 40, which was indicated that in the inner Gulf of Thailand is not associated ecological risk. The risk assessment code (*RAC*) is based on the sequential extraction method, the percentages of GT3 value in all seasons in this *RAC* were high because the exchangeable and carbonate fraction of Cr were high, indicating that their potential environmental and ecological risks cannot be ignored.

5.2 Future research

Despite the above findings but there are still some questions and work to be done to answer them. In the future, it will be necessary to analysis of speciation and sequential fraction of Cr that should cover in all stations and developing a model for risk assessment of Cr distribution. In particular, it will be important to identify the potential sources of Cr in the surface sediment of the inner Gulf of Thailand and measure the concentration of Cr released from industries and factories, which are anticipated to be high. However, the background values of Cr and Fe in the sediments of the inner Gulf of Thailand should be measured and collect the hydrodynamic forces control the sediment transport, by collecting more measurement data.

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APPENDIX A

Table 1 The concentration of Cr and Fe (mg/kg) in surface sediment in the inner Gulf of Thailand in southeast monsoon season.

Station	E	N	Cr (mg/kg)	Fe (mg/kg)
MK1	607299	1480991	54.63	23731.67
MK2	608860	1477171	33.44	14071.55
MK3	609094	1475578	15.38	6826.73
MK4	610514	1476986	42.83	16073.72
MK6	614896	1480457	26.79	8551.86
MK9	610888	1474340	15.47	8136.87
MK10	609008	1472341	15.31	8011.30
MK13	610011	1470085	30.70	15391.85
TC1	637425	1497650	54.29	22299.90
TC6	637147	1490299	38.45	18897.34
TC8	637292	1487747	48.26	T22349.08
TC9	631938	1486977	39.42	17245.19
TC10	635701	1485395	36.81	18857.14
TC11	641681	1491022	36.34	20592.41
TC13	642989	1488676	32.53	17726.59
TC14	648180	1489753	48.67	22841.22
TC15	645734	1487644	44.38	18970.07
CP1	671069	1499008	64.81	18947.02
CP7	669643	1489744	34.65	19699.63
CP8	668472	1484139	29.32	17890.51
CP10	659422	1486019	21.25	13763.55
CP12	668472	1478641	19.02	12031.36
CP13	678514	1492952	80.16	20846.43
CP14	680716	1486906	47.65	18660.04
CP16	689943	1491163	73.38	20992.36
CP18	681816	1481408	35.00	14857.30
BK1	714374	1491999	41.09	22735.37
BK7	709399	1483594	31.32	27468.77
BK9	710866	1480036	40.52	19987.71
BK11	707501	1480780	32.80	20872.50
BK12	705191	1478135	60.44	22660.80
BK13	704906	1487297	62.69	24859.96
BK14	701446	1485253	58.13	23568.84
BK16	696086	1488355	79.93	26540.97
BK18	698303	1483354	55.35	23127.69
GT1	605098	1395667	23.53	9833.70
GT3	618036	1438402	22.05	7308.88

Station	E	N	Cr (mg/kg)	Fe (mg/kg)
GT4	615876	1462806	33.81	11799.17
GT9	707280	1457559	34.13	10278.51
GT10	702930	1442275	33.07	10909.17
GT11	703947	1416657	22.32	7076.10
GT16	645029	1470301	34.36	15959.93
GT17	703236	1470962	52.98	18341.83
GT23	649099	1462285	43.79	15817.16
GT24	669847	1463573	35.93	13874.59
GT25	686685	1475557	48.55	18720.70
GT26	682810	1450634	11.72	4141.38
GT27	681948	1441398	13.59	5893.28
GT29	631140	1388455	19.26	19262.69
GT30	630824	1406633	16.33	9292.01
GT31	636282	1422993	25.96	10970.30
GT32	648845	1451604	24.10	11154.51
GT33	668073	1455100	26.55	8943.44
GT34	670784	1438746	16.64	7029.87
GT35	648271	1437562	20.89	8567.15
GT36	669358	1414723	22.97	16197.34
GT39	648555	1391124	19.80	7847.64
GT40	654426	1408978	19.04	9686.84
GT41	655601	1423059	23.74	10537.71

Table 2 The concentration of Cr and Fe (mg/kg) in surface sediment in the inner Gulf of Thailand in northwest monsoon season.

Station	E	N	Cr (mg/kg)	Fe (mg/kg)
MK1	607299	1480991	28.69	13972.97
MK2	608860	1477171	10.95	6450.72
MK3	609094	1475578	6.05	7829.32
MK4	610514	1476986	10.35	9362.51
MK6	614896	1480457	19.48	9917.11
MK10	609008	1472341	24.91	13019.66
MK13	610011	1470085	41.17	18472.47
TC1	637425	1497650	57.67	22357.68
TC5	641041	1486056	51.53	22778.87
TC6	637147	1490299	42.61	18372.63
TC8	637292	1487747	44.59	17676.90
TC9	631938	1486977	51.30	19235.69
TC10	635701	1485395	43.56	18809.53
TC11	641681	1491022	39.56	19268.04
TC13	642989	1488676	36.53	15767.79
TC14	648180	1489753	56.61	24847.05
TC15	645734	1487644	52.22	24487.48
CP1	671069	1499008	107.45	22280.86
CP7	669643	1489744	54.86	26368.58
CP8	668472	1484139	67.47	28213.26
CP10	659422	1486019	55.66	24456.89
CP12	668472	1478641	51.27	22119.49
CP13	678514	1492952	83.90	25658.66
CP14	680716	1486906	62.21	24887.10
CP16	689943	1491163	87.49	26395.10
CP18	681816	1481408	64.93	25039.81
BK1	714374	1491999	46.95	21208.70
BK7	709399	1483594	48.00	23913.16
BK9	710866	1480036	48.17	15672.60
BK11	707501	1480780	54.56	24563.79
BK12	705191	1478135	58.92	26198.34
BK13	704906	1487297	55.85	26425.20
BK14	701446	1485253	65.55	25363.78
BK16	696086	1488355	68.24	22457.58
BK18	698303	1483354	60.33	24818.86
GT1	605098	1395667	5.77	4496.01
GT3	618036	1438402	11.19	5157.32
GT4	615876	1462806	22.20	10238.48
GT9	707280	1457559	25.26	10278.28
GT11	703947	1416657	19.42	5961.76
GT16	645029	1470301	28.71	13808.48
GT18	696353	1461870	31.43	11852.48

Station	E	N	Cr (mg/kg)	Fe (mg/kg)
GT19	697903	1439187	21.17	7024.40
GT20	692990	1409569	13.24	12531.02
GT23	649099	1462285	30.25	13732.83
GT24	669847	1463573	33.82	14772.23
GT25	686685	1475557	33.40	13331.33
GT26	682810	1450634	24.80	4626.08
GT27	681948	1441398	10.08	2926.08
GT28	690762	1419103	5.61	2551.00
GT29	631140	1388455	19.41	8062.11
GT30	630824	1406633	23.30	8726.10
GT33	668073	1455100	22.58	8881.72
GT34	670784	1438746	13.82	5235.11
GT36	669358	1414723	21.98	11002.45
GT37	682471	1410575	9.89	3358.75
GT38	695566	1400950	24.14	3324.75
GT39	648555	1391124	26.50	5529.11
GT40	654426	1408978	25.72	7683.14
GT41	655601	1423059	25.06	7998.79

Table 3 The concentration of Cr and Fe (mg/kg) in surface sediment in the inner Gulf of Thailand in dry season.

Station	E	N	Cr (mg/kg)	Fe (mg/kg)
MK1	607299	1480991	31.28	16352.74
MK3	609094	1475578	12.98	6724.14
MK4	610514	1476986	12.22	5481.86
MK5	613583	1478424	14.91	5718.98
MK6	614896	1480457	10.45	8662.28
MK10	609008	1472341	11.28	9307.29
MK13	610011	1470085	27.81	16596.79
TC2	637048	1496024	39.56	21190.43
TC6	637147	1490299	30.85	20770.72
TC8	637292	1487747	37.62	22894.45
TC9	631938	1486977	44.19	19608.15
TC10	635701	1485395	35.07	18959.92
TC11	641681	1491022	27.85	21051.32
TC13	642989	1488676	8.63	13106.40
TC14	648180	1489753	46.93	23267.71
TC15	645734	1487644	119.47	23787.60
CP1	671069	1499008	48.69	24179.05
CP7	669643	1489744	40.04	27561.34
CP8	668472	1484139	42.25	25038.73
CP10	659422	1486019	52.42	22012.55
CP12	668472	1478641	42.05	18972.04
CP13	678514	1492952	63.02	20956.48
CP14	680716	1486906	54.31	22791.14
CP16	689943	1491163	63.47	21856.86
CP18	681816	1481408	68.60	23697.56
BK1	714374	1491999	50.65	23463.60
BK7	709399	1483594	56.77	34883.65
BK8	710864	1481069	52.02	23964.72
BK11	707501	1480780	48.92	20498.70
BK12	705191	1478135	57.82	23001.29
BK13	704906	1487297	50.54	26345.94
BK14	701446	1485253	55.74	21439.44
BK16	696086	1488355	70.12	23122.07
BK18	698303	1483354	55.24	24215.62
GT1	605098	1395667	31.78	13311.96
GT2	610228	1415626	15.74	5927.90
GT3	618036	1438402	14.76	5941.82
GT4	615876	1462806	35.52	12163.54
GT6	662200	1470718	32.76	13216.55
GT11	703947	1416657	20.68	6565.55
GT16	645029	1470301	29.76	15013.82
GT17	703236	1470962	43.03	19321.50

Station	E	N	Cr (mg/kg)	Fe (mg/kg)
GT23	649099	1462285	26.89	13674.08
GT24	669847	1463573	42.51	16004.78
GT25	686685	1475557	42.05	19095.07
GT26	682810	1450634	9.77	4569.19
GT27	681948	1441398	17.90	6029.18
GT29	631140	1388455	20.60	18653.43
GT30	630824	1406633	31.21	14162.05
GT31	636282	1422993	36.09	14279.18
GT32	648845	1451604	47.46	19304.63
GT33	668073	1455100	35.09	13202.20
GT34	670784	1438746	28.04	13136.53
GT35	648271	1437562	33.25	13385.48
GT36	669358	1414723	36.99	21150.35
GT39	648555	1391124	26.97	10118.27
GT40	654426	1408978	22.44	13040.95
GT41	655601	1423059	19.87	9099.70

APPENDIX B

Table 1 The *EF*, I_{geo} and E_r values of Cr in surface sediment in the inner Gulf of Thailand in southeast monsoon season.

Station	*EF*	I_{geo}	E_r
MK1	1.66	-1.31	1.21
MK2	1.72	-2.01	0.74
MK3	1.63	-3.13	0.34
MK4	1.92	-1.66	0.95
MK6	2.26	-2.33	0.60
MK9	1.37	-3.13	0.34
MK10	1.38	-3.14	0.34
MK13	1.44	-2.14	0.68
TC1	1.76	-1.31	1.21
TC6	1.47	-1.81	0.85
TC8	1.56	-1.48	1.07
TC9	1.65	-1.78	0.88
TC10	1.41	-1.87	0.82
TC11	1.27	-1.89	0.81
TC13	1.33	-2.05	0.72
TC14	1.54	-1.47	1.08
TC15	1.69	-1.61	0.99
CP1	2.47	-1.06	1.44
CP7	1.27	-1.96	0.77
CP8	1.18	-2.20	0.65
CP10	1.12	-2.67	0.47
CP12	1.14	-2.83	0.42
CP13	2.78	-0.75	1.78
CP14	1.84	-1.50	1.06
CP16	2.52	-0.88	1.63
CP18	1.70	-1.95	0.78
BK1	1.31	-1.72	0.91
BK7	0.82	-2.11	0.70
BK9	1.46	-1.74	0.90
BK11	1.14	-2.04	0.73
BK12	1.93	-1.16	1.34
BK13	1.82	-1.11	1.39
BK14	1.78	-1.22	1.29
BK16	2.18	-0.76	1.78
BK18	1.73	-1.29	1.23
GT1	1.73	-2.52	0.52
GT3	2.18	-2.61	0.49

Station	EF	I_{geo}	E_r
GT4	2.07	-2.00	0.75
GT9	2.40	-1.98	0.76
GT10	2.19	-2.03	0.73
GT16	1.55	-1.97	0.76
GT17	2.09	-1.35	1.18
GT23	2.00	-1.62	0.97
GT24	1.87	-1.91	0.80
GT25	1.87	-1.48	1.08
GT26	2.04	-3.53	0.26
GT27	1.67	-3.31	0.30
GT29	0.72	-2.81	0.43
GT30	1.27	-3.05	0.36
GT31	1.71	-2.38	0.58
GT32	1.56	-2.49	0.54
GT33	2.14	-2.35	0.59
GT34	1.71	-3.02	0.37
GT35	1.76	-2.69	0.46
GT36	1.02	-2.56	0.51
GT39	1.82	-2.77	0.44
GT40	1.42	-2.83	0.42
GT41	1.63	-2.51	0.53

Table 2 The *EF*, I_{geo} and E_r values of Cr in surface sediment in the inner Gulf of Thailand in in northwest monsoon season.

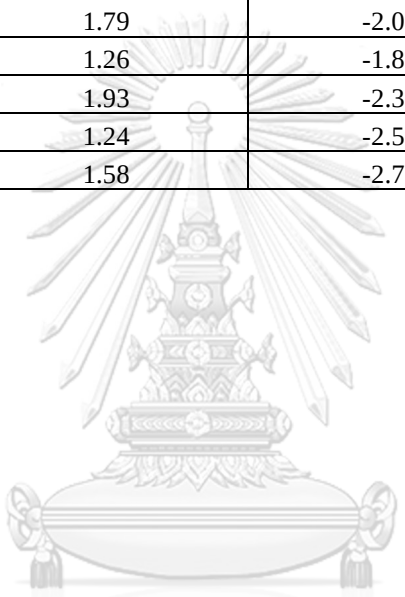
Station	*EF*	I_{geo}	E_r
MK1	1.48	-2.23	0.64
MK2	1.23	-3.62	0.24
MK3	0.56	-4.48	0.13
MK4	0.80	-3.71	0.23
MK6	1.42	-2.79	0.43
MK10	1.38	-2.44	0.55
MK13	1.61	-1.71	0.91
TC1	1.86	-1.23	1.28
TC5	1.63	-1.39	1.15
TC6	1.67	-1.66	0.95
TC8	1.82	-1.60	0.99
TC9	1.93	-1.40	1.14
TC10	1.67	-1.63	0.97
TC11	1.48	-1.77	0.88
TC13	1.67	-1.89	0.81
TC14	1.65	-1.25	1.26
TC15	1.54	-1.37	1.16
CP1	3.48	-0.33	2.39
CP7	1.50	-1.30	1.22
CP8	1.73	-1.00	1.50
CP10	1.64	-1.28	1.24
CP12	1.67	-1.40	1.14
CP13	2.36	-0.69	1.86
CP14	1.81	-1.12	1.38
CP16	2.39	-0.63	1.94
CP18	1.87	-1.06	1.44
BK1	1.60	-1.52	1.04
BK7	1.45	-1.49	1.07
BK9	2.22	-1.49	1.07
BK11	1.60	-1.31	1.21
BK12	1.62	-1.20	1.31
BK13	1.53	-1.27	1.24
BK14	1.87	-1.04	1.46
BK16	2.19	-0.98	1.52
BK18	1.76	-1.16	1.34
GT1	0.93	-4.55	0.13
GT3	1.57	-3.59	0.25
GT4	1.57	-2.60	0.49
GT9	1.77	-2.42	0.56
GT11	2.35	-2.80	0.43
GT16	1.50	-2.23	0.64

Station	EF	I_{geo}	E_r
GT18	1.92	-2.10	0.70
GT19	2.18	-2.67	0.47
GT23	1.59	-2.16	0.67
GT24	1.65	-2.00	0.75
GT25	1.81	-2.02	0.74
GT26	3.87	-2.44	0.55
GT27	2.49	-3.74	0.22
GT28	1.59	-4.59	0.12
GT29	1.74	-2.80	0.43
GT30	1.93	-2.53	0.52
GT33	1.84	-2.58	0.50
GT34	1.91	-3.29	0.31
GT36	1.44	-2.62	0.49
GT37	2.13	-3.77	0.22
GT38	5.24	-2.48	0.54
GT39	3.46	-2.35	0.59
GT40	2.42	-2.39	0.57
GT41	2.26	-2.43	0.56

Table 3 The *EF*, I_{geo} and E_r values of Cr in surface sediment in the inner Gulf of Thailand in dry season.

Station	*EF*	I_{geo}	E_r
MK1	1.38	-2.11	0.70
MK3	1.39	-3.38	0.29
MK4	1.61	-3.47	0.27
MK5	1.88	-3.18	0.33
MK6	0.87	-3.69	0.23
MK10	0.88	-3.58	0.25
MK13	1.21	-2.28	0.62
TC2	1.35	-1.77	0.88
TC6	1.07	-2.13	0.69
TC8	1.19	-1.84	0.84
TC9	1.63	-1.61	0.98
TC10	1.34	-1.94	0.78
TC11	0.96	-2.28	0.62
TC13	0.48	-3.97	0.19
TC14	1.46	-1.52	1.04
TC15	3.63	-0.18	2.65
CP1	1.45	-1.47	1.08
CP7	1.05	-1.75	0.89
CP8	1.22	-1.68	0.94
CP10	1.72	-1.36	1.16
CP12	1.60	-1.68	0.93
CP13	2.17	-1.10	1.40
CP14	1.72	-1.31	1.21
CP16	2.10	-1.09	1.41
CP18	2.09	-0.98	1.52
BK1	1.56	-1.41	1.13
BK7	1.18	-1.25	1.26
BK8	1.57	-1.38	1.16
BK11	1.72	-1.46	1.09
BK12	1.82	-1.22	1.28
BK13	1.39	-1.42	1.12
BK14	1.88	-1.28	1.24
BK16	2.19	-0.95	1.56
BK18	1.65	-1.29	1.23
GT1	1.72	-2.09	0.71
GT2	1.92	-3.10	0.35
GT3	1.79	-3.19	0.33
GT4	2.11	-1.93	0.79
GT6	1.79	-2.04	0.73
GT11	2.27	-2.71	0.46
GT16	1.43	-2.18	0.66
GT17	1.61	-1.65	0.96

Station	*EF*	I_{geo}	*ER*
GT23	1.42	-2.33	0.60
GT24	1.92	-1.67	0.94
GT25	1.59	-1.68	0.93
GT26	1.54	-3.79	0.22
GT27	2.14	-2.91	0.40
GT29	0.80	-2.71	0.46
GT30	1.59	-2.11	0.69
GT31	1.83	-1.90	0.80
GT32	1.78	-1.51	1.05
GT33	1.92	-1.94	0.78
GT34	1.54	-2.27	0.62
GT35	1.79	-2.02	0.74
GT36	1.26	-1.87	0.82
GT39	1.93	-2.32	0.60
GT40	1.24	-2.59	0.50
GT41	1.58	-2.76	0.44



APPENDIX C

Table 1 The concentration of physicochemical factors including TOM, TOC, TP, AVS and water content in surface sediment in the inner Gulf of Thailand in southeast monsoon season.

Station	TOM %	TOC (mg/g)	TP (mg/kg)	AVS (mg/g. dw)	water content (%)
MK1	9.5535	22.280	0.8089	0.0025	51.43
MK2	6.6705	12.473	0.4457	0.0456	38.10
MK3	2.2342	3.871	0.2170	0.0019	26.55
MK4	9.8092	21.537	0.8231	0.1993	56.42
MK6	3.9703	5.615	0.3150	0.0859	33.67
MK9	1.8623	2.790	0.1943	0.0000	28.31
MK10	4.4453	5.486	0.2420	0.0020	29.81
MK13	7.9586	14.417	0.4851	0.2209	47.96
TC1	8.7363	14.199	1.3433	1.7377	73.15
TC6	7.9773	15.667	0.6831	0.1120	68.27
TC8	9.5852	19.563	0.7731	0.6343	67.73
TC9	10.2508	20.967	0.6308	0.3319	74.36
TC10	10.1478	17.116	0.5184	1.7111	72.74
TC11	7.1626	13.494	0.4863	1.0008	61.70
TC13	6.7982	13.486	0.5722	0.1835	44.58
TC14	13.1449	30.486	0.9351	1.8609	74.84
TC15	12.5968	23.305	0.6744	0.4692	76.70
CP1	5.1935	10.745	1.8937	0.1314	50.34
CP7	6.8272	11.006	0.4887	0.0197	61.64
CP8	10.2010	14.376	0.5446	0.0117	66.06
CP10	12.2096	16.322	0.5195	1.1690	62.21
CP12	7.4396	12.823	0.4371	0.0103	52.58
CP13	9.1498	15.838	1.0023	0.0803	59.77
CP14	8.9959	13.518	0.5759	0.1195	51.56
CP16	12.1700	20.052	0.7193	1.3521	63.79
CP18	11.0936	15.294	0.4943	0.0053	64.23
BK1	9.2412	19.255	0.9940	0.0107	70.18
BK7	7.0566	14.827	0.6978	0.1952	59.60
BK9	10.3727	17.849	0.6070	0.0000	87.93
BK11	10.5664	16.438	0.7080	0.2206	74.64
BK12	12.8474	22.960	0.7153	0.2100	75.06
BK13	9.6283	19.107	0.8879	0.0462	68.75
BK14	11.8731	19.106	0.6536	0.8617	70.42
BK16	13.4129	22.762	0.6909	0.9551	67.67
BK18	13.5802	21.716	0.5520	0.1289	78.09
GT1	6.0530	13.305	0.6251	0.0289	34.85

Station	TOM %	TOC (mg/g)	TP (mg/kg)	AVS (mg/g. dw)	water content (%)
GT3	4.4011	7.421	0.3393	1.1688	44.99
GT4	8.9615	17.262	0.6245	0.1205	60.17
GT9	11.2108	19.368	0.7423	0.0854	57.29
GT11	7.8915	16.584	0.4685	0.0614	41.61
GT16	7.1526	14.800	0.4443	0.0268	45.94
GT17	14.2201	33.806	0.9795	0.2084	79.79
GT23	15.4439	17.694	0.4261	0.0383	58.45
GT24	11.0484	17.987	0.5039	0.0285	50.14
GT25	11.0627	25.241	0.7569	0.0090	55.59
GT26	4.7488	11.326	0.2522	0.0069	32.46
GT27	8.4539	15.039	0.2694	0.0019	28.37
GT29	6.4085	7.367	0.2499	0.0012	27.31
GT30	7.9061	25.572	0.3181	0.0000	50.42
GT31	9.0223	25.777	0.3602	0.0216	40.01
GT32	9.3700	16.723	0.4772	0.0541	54.21
GT33	9.0927	16.082	0.3997	0.0497	42.45
GT34	5.7681	15.221	0.2158	0.0032	29.71
GT35	7.2695	43.174	0.2600	0.0028	31.47
GT36	6.0996	14.492	0.3695	0.0013	28.38
GT39	9.4400	20.701	0.2228	0.0022	27.14
GT40	5.4196	17.645	0.2008	0.0000	32.55
GT41	8.0986	18.465	0.3295	0.0025	30.21

Table 2 The concentration of physicochemical factors including TOM, TOC, TP, AVS and water content in surface sediment in the inner Gulf of Thailand in northwest monsoon season.

Station	TOM %	TOC (mg/g)	TP (mg/kg)	AVS (mg/g. dw)	water content (%)
MK1	5.61	14.60	0.53	0.07	54.07
MK2	6.78	6.15	0.26	0.01	32.66
MK3	2.47	5.82	0.30	0.07	34.05
MK4	10.16	10.88	0.37	0.01	37.91
MK6	5.42	11.07	0.28	0.40	38.93
MK10	6.11	10.80	0.39	0.12	44.68
MK13	6.77	17.50	0.50	0.44	46.98
TC1	10.38	27.94	0.83	0.74	72.20
TC5	12.34	22.50	0.57	0.35	73.36
TC6	7.76	22.55	0.66	1.02	74.69
TC8	10.10	23.64	0.60		87.36
TC9	11.84	23.93	0.54	0.63	60.24
TC10	9.95	18.25	0.43	0.33	67.57
TC11	8.46	18.71	0.53	0.73	66.91
TC13	7.38	15.48	0.42	0.23	58.32
TC14	11.02	26.10	0.70	2.21	77.74
TC15	11.14	21.58	1.05	0.72	78.28
CP1	9.26	17.92	0.70	1.00	63.06
CP7	9.03	12.91	0.41	0.05	57.95
CP8	10.12	13.70	0.42	0.04	63.78
CP10	11.31	9.61	0.41	0.06	67.76
CP12	8.84	8.20	0.39	0.04	53.11
CP13	7.68	17.17	0.80	0.25	66.66
CP14	9.61	12.18	0.42	0.00	65.31
CP16	13.12	20.49	0.65	1.70	74.24
CP18	10.95	14.91	0.40	0.02	62.14
BK1	10.13	18.09	1.08	1.69	65.79
BK7	11.73	18.70	0.77	0.31	73.40
BK9	10.81	14.16	0.54	0.03	55.13
BK11	12.25	19.34	0.58	0.34	66.82
BK12	13.11	13.52	0.57	0.51	73.92
BK13	7.73	17.10	0.60	0.85	70.74
BK14	9.02	16.34	0.67	0.56	70.70
BK16	13.69	19.24	0.45	0.83	73.11
BK18	9.74	19.64	0.48	0.63	78.77
GT1	7.37	7.41	0.35	0.03	39.53
GT3	4.21	7.78	0.29	0.04	37.32
GT4	3.79	14.86	0.49	0.04	65.35
GT9	9.89	18.70	0.66	0.08	53.59
GT11	7.58	10.13	0.41	0.01	42.15

Station	TOM %	TOC (mg/g)	TP (mg/kg)	AVS (mg/g. dw)	water content (%)
GT16	10.68	14.81	0.37		
GT18	5.34	24.07	0.67	0.07	60.61
GT19	8.64	30.22	0.46	0.00	18.82
GT20	2.39	18.20	0.14	0.00	22.03
GT23	4.22	14.00	0.41	0.03	41.69
GT24	9.94	18.74	0.43	0.06	51.14
GT25	7.55	25.42	0.68	0.04	63.06
GT26	4.42	7.93	0.62	0.00	27.61
GT27	5.37	4.65	0.12	0.08	24.62
GT28	2.28	3.44	0.09	0.00	25.02
GT29	4.50	8.25	0.20	0.06	29.99
GT30	6.22	18.12	0.27	0.00	30.81
GT33	7.62	13.71	0.30		
GT34	6.13	9.60	0.22	0.00	29.95
GT36	4.71	3.67	0.31	0.00	28.61
GT37	2.36	3.87	0.16	0.00	
GT38	3.23	13.22	0.15	0.00	23.32
GT39	6.30	7.18	0.17		
GT40	5.44	13.04	0.20	0.00	31.63
GT41	6.62	13.34	0.36	0.01	29.98

Table 3 The concentration of physicochemical factors including TOM, TOC, TP, AVS and water content in surface sediment in the inner Gulf of Thailand in in dry season.

Station	TOM %	TOC (mg/g)	TP (mg/kg)	AVS (mg/g. dw)	water content (%)
MK1	5.75	15.33	0.63	0.01	50.36
MK3	2.47	3.25	0.20	0.00	32.85
MK4	1.53	3.15	0.15	0.00	26.62
MK5	2.68	4.73	0.22		
MK6	3.67	7.32	0.38	0.05	30.70
MK10	3.59	10.55	0.32	0.00	34.77
MK13	5.35	12.77	0.47	0.00	46.57
TC2	9.29	35.50	1.14		
TC6	7.76	18.66	0.54	0.02	39.79
TC8	8.26	22.01	0.55	0.11	44.43
TC9	8.62	14.32	0.53	0.06	69.64
TC10	5.26	19.86	0.52	0.04	52.82
TC11	8.46	16.89	0.59	0.04	56.62
TC13	3.49	10.33	0.40	0.03	42.39
TC14	11.05	29.26	0.84	0.78	66.50
TC15	7.64	24.53	0.59	0.05	60.77
CP1	6.41	18.02	0.94	0.80	44.80
CP7	5.61	10.93	0.39	0.00	53.55
CP8	8.13	14.07	0.42	0.00	65.26
CP10	11.31	13.94	0.47	0.11	67.71
CP12	5.69	14.59	0.44	0.00	52.71
CP13	7.68	10.74	0.72	0.01	50.75
CP14	5.69	12.00	0.54	0.01	53.69
CP16	13.12	21.48	0.55	0.13	70.28
CP18	7.92	13.93	0.43	0.00	57.81
BK1	7.83	13.48	1.01	0.20	64.77
BK7	8.66	15.68	0.72	0.08	59.61
BK8	4.21	17.32	0.59		
BK11	4.20	17.30	0.64	0.08	63.09
BK12	11.40	23.64	0.64	0.11	76.16
BK13	7.73	14.40	0.55	0.27	58.63
BK14	10.64	20.29	0.63	0.15	63.77
BK16	11.52	22.95	0.59	0.17	72.91
BK18	10.94	20.30	0.49	0.04	73.90
GT1	7.32	14.08	0.50	0.01	29.40
GT2	4.81	10.48	0.22	0.00	29.98
GT3	4.21	4.90	0.30	0.05	36.90
GT4	5.91	13.32	0.48	0.00	47.61
GT6	6.88	2.76	0.41	0.00	32.96
GT11	7.59	11.36	0.49	0.00	36.52
GT16	8.15	14.10	0.41	0.01	45.18

Station	TOM %	TOC (mg/g)	TP (mg/kg)	AVS (mg/g. dw)	water content (%)
GT17	13.00	33.69	1.02	0.00	82.83
GT23	7.03	12.42	0.41	0.00	42.92
GT24	9.94	13.43	0.45	0.00	64.68
GT25	10.01	18.72	0.61	0.00	61.80
GT26	3.89	5.42	0.19	0.00	27.96
GT27	5.37	4.32	0.17	0.00	26.41
GT29	3.93	5.04	0.18	0.00	29.71
GT30	6.49	8.92	0.30	0.00	35.65
GT31	8.10	9.80	0.34	0.01	30.65
GT32	9.71	13.86	0.46	0.00	23.67
GT33	6.93	12.25	0.33	0.00	48.55
GT34	4.62	4.67	0.20	0.00	37.55
GT35	6.76	10.22	0.32	0.01	32.71
GT36	7.63	13.01	0.31	0.00	34.38
GT39	6.30	4.54	0.17	0.00	22.76
GT40	6.09	4.76	0.25	0.00	26.71
GT41	2.97	4.92	0.22	0.00	28.62

APPENDIX D

Table 1 The fraction of Cr in surface sediment in the inner Gulf of Thailand in southeast monsoon season.

Station	Exchangeable	Carbonate	Fe-Me Oxide	Organic Matter	Residual
MK1	4.72	1.80	7.75	33.98	51.75
MK6	9.35	3.82	9.13	36.64	41.07
MK13	8.08	2.35	11.15	55.40	23.01
TC1	5.34	0.94	10.23	47.22	36.27
TC9	6.85	1.32	13.11	63.63	15.09
TC14	6.10	0.95	6.80	53.41	32.73
CP1	4.53	0.69	6.96	68.38	19.43
CP10	11.67	2.14	16.15	69.05	1.00
CP16	6.72	1.19	12.40	70.90	8.79
BK1	6.60	2.10	12.19	52.66	26.45
BK9	6.16	2.08	11.66	39.91	40.19
BK16	2.86	0.92	4.63	64.85	26.73
GT3	9.87	4.38	12.54	38.26	34.97
GT9	5.69	2.35	9.47	56.44	26.05
GT16	6.37	2.16	11.40	59.22	20.85
GT32	7.26	2.41	11.50	62.82	16.00
GT39	10.16	2.09	21.78	60.92	5.04
GT40	9.35	2.81	19.17	62.42	6.25
GT41	7.26	2.47	16.02	63.03	11.22

Table 2 The fraction of Cr in surface sediment in the inner Gulf of Thailand in in northwest monsoon season.

Station	Exchangeable	Carbonate	Fe-Me Oxide	Organic Matter	Residual
MK1	13.33	1.96	6.59	36.93	41.18
MK6	19.60	4.38	15.27	47.25	13.50
MK13	9.16	3.11	7.78	44.29	35.67
TC1	6.22	4.01	9.90	67.92	11.94
TC9	6.54	1.74	4.08	37.66	49.98
TC14	6.19	1.67	3.57	51.43	37.13
CP1	6.65	0.70	26.73	58.14	7.78
CP10	6.62	0.68	4.30	17.93	70.47
CP16	4.14	0.35	4.19	15.97	75.35
BK1	8.65	1.41	8.70	37.21	44.02
BK9	9.38	2.50	13.85	28.39	45.88
BK16	8.65	2.38	10.61	62.37	16.00
GT3	29.75	15.03	20.07	25.22	9.93
GT9	12.16	3.55	20.72	55.63	7.94
GT16	9.79	5.80	13.02	68.16	3.23
GT39	6.88	1.78	11.88	30.80	48.67
GT40	11.92	1.26	9.94	44.80	32.08
GT41	12.81	3.19	8.64	47.88	27.48

Table 3 The fraction of Cr in surface sediment in the inner Gulf of Thailand in in in dry season.

Station	Exchangeable	Carbonate	Fe-Me Oxide	Organic Matter	Residual
MK1	12.59	5.42	2.22	29.34	50.43
MK6	20.75	12.92	8.01	47.76	10.57
MK13	14.14	6.11	3.61	28.15	47.98
TC1	11.06	4.89	3.58	19.43	61.04
TC9	9.63	3.34	6.41	39.31	41.31
TC14	9.03	3.17	2.96	41.94	42.90
CP1	8.90	3.39	13.46	53.48	20.77
CP10	8.92	3.36	2.03	18.98	66.71
CP16	6.49	1.99	1.87	23.98	65.66
BK1	12.85	3.06	3.61	25.82	54.66
BK8	8.27	3.82	3.75	31.41	52.75
BK16	5.81	2.22	1.71	29.87	60.40
GT3	27.75	7.67	7.18	51.19	6.20
GT11	19.05	6.71	8.07	53.14	13.03
GT16	12.61	5.91	5.14	69.36	6.98
GT32	7.60	2.66	3.32	31.56	54.85
GT39	14.43	6.12	4.71	24.04	50.69
GT40	16.43	7.94	5.34	54.16	16.13
GT41	17.96	9.08	4.92	52.94	15.10

APPENDIX E

Table 1 Test of normality of concentration of Cr in surface sediment in the inner Gulf of Thailand.

Case Processing Summary

		Cases					
		Valid		Missing		Total	
	Station	N	Percent	N	Percent	N	Percent
Cr	July	59	100.0%	0	0.0%	59	100.0%
	December	60	100.0%	0	0.0%	60	100.0%
	April	58	100.0%	0	0.0%	58	100.0%

Tests of Normality

		Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Station	Statistic	df	Sig.	Statistic	df	Sig.
Cr	July	.109	59	.080	.938	59	.005
	December	.117	60	.041	.950	60	.015
	April	.066	58	.200*	.916	58	.001

*. This is a lower bound of the true significance.

a. Lilliefors Significance Correction

Table 2 One-way ANOVA of concentration of Cr in surface sediment in the inner Gulf of Thailand.

Test of Homogeneity of Variances

Cr

Levene Statistic	df1	df2	Sig.
3.387	2	174	.036

ANOVA

Cr

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	143.961	2	71.980	.188	.828
Within Groups	66475.871	174	382.045		
Total	66619.832	176			

Cr

Duncan[a,b]

Station	N	Subset for alpha = 0.05
		1
July	59	36.0393
April	58	37.6712
December	60	38.1390
Sig.		.587

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 58.989.

b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.

Table 3 One-way ANOVA of concentration of Cr in surface sediment in the inner Gulf of Thailand in southwest monsoon season.

Test of Homogeneity of Variances

Cr

Levene Statistic	df1	df2	Sig.
3.669	6	52	.004

ANOVA

Cr

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	5922.336	6	987.056	4.989	.000
Within Groups	10287.390	52	197.834		
Total	16209.726	58			

Cr

Duncan[a,b]

Station	N	Subset for alpha = 0.05		
		1	2	3
MiddleGT	17	24.8953		
WestGT	3	26.4633		
MK	8	29.3187	29.3187	
EastGT	4	35.6250	35.6250	35.6250
TC	9	42.1278	42.1278	42.1278
CP	9		45.0267	45.0267
BK	9			51.3633
Sig.		.055	.073	.073

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 6.361.

b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.

Table 4 One-way ANOVA of concentration of Cr in surface sediment in the inner Gulf of Thailand in northeast monsoon season.

Test of Homogeneity of Variances

Cr

Levene Statistic	df1	df2	Sig.
3.442	6	53	.006

ANOVA

Cr

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	23020.201	6	3836.700	33.692	.000
Within Groups	6035.466	53	113.877		
Total	29055.667	59			

Cr

Duncan[a,b]

Station	N	Subset for alpha = 0.05		
		1	2	3
WestGT	3	13.0533		
MK	7	20.2286		
EastGT	3	21.9500		
MiddleGT	19	22.3021		
TC	10		47.6180	
BK	9		56.2856	
CP	9			70.5822
Sig.		.181	.168	1.000

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 5.910.

b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.

Table 5 One-way ANOVA of concentration of Cr in surface sediment in the inner Gulf of Thailand in dry season.

Test of Homogeneity of Variances

Cr

Levene Statistic	df1	df2	Sig.
1.487	6	51	.201

ANOVA

Cr

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	9884.335	6	1647.389	7.418	.000
Within Groups	11326.144	51	222.081		
Total	21210.479	57			

Cr

Duncan[a,b]

Station	N	Subset for alpha = 0.05		
		1	2	3
MK	7	17.2757		
WestGT	4	24.4500	24.4500	
MiddleGT	18	29.9806	29.9806	
EastGT	2	31.8550	31.8550	
TC	9		43.3522	43.3522
CP	9			52.7611
BK	9			55.3133
Sig.		.147	.060	.217

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 5.461.

b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.

Table 6 Correlation analyzes of chromium and physicochemical properties in the surface sediment of the inner Gulf of Thailand during the southwest monsoon season

Correlations

		Cr	Fe	TOM	TOC	TP	AVS	Water
Cr	Pearson Correlation	1	.783**	.567**	.294*	.729**	.349**	.663**
	Sig. (2-tailed)		.000	.000	.024	.000	.007	.000
	N	59	59	59	59	59	59	59
Fe	Pearson Correlation	.783**	1	.490**	.195	.615**	.362**	.744**
	Sig. (2-tailed)	.000		.000	.139	.000	.005	.000
	N	59	59	59	59	59	59	59
TOM	Pearson Correlation	.567**	.490**	1	.660**	.341**	.274*	.690**
	Sig. (2-tailed)	.000	.000		.000	.008	.036	.000
	N	59	59	59	59	59	59	59
TOC	Pearson Correlation	.294*	.195	.660**	1	.211	.092	.330*
	Sig. (2-tailed)	.024	.139	.000		.109	.487	.011
	N	59	59	59	59	59	59	59
TP	Pearson Correlation	.729**	.615**	.341**	.211	1	.295*	.581**
	Sig. (2-tailed)	.000	.000	.008	.109		.023	.000
	N	59	59	59	59	59	59	59
AVS	Pearson Correlation	.349**	.362**	.274*	.092	.295*	1	.433**
	Sig. (2-tailed)	.007	.005	.036	.487	.023		.001
	N	59	59	59	59	59	59	59
Water	Pearson Correlation	.663**	.744**	.690**	.330*	.581**	.433**	1
	Sig. (2-tailed)	.000	.000	.000	.011	.000	.001	
	N	59	59	59	59	59	59	59

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

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

Table 7 Correlation analyzes of chromium and physicochemical properties in the surface sediment of the inner Gulf of Thailand during the northeast monsoon season

Correlations

		Cr	Fe	TOM	TOC	TP	AVS	Water
Cr	Pearson Correlation	1	.831**	.692**	.483**	.608**	.550**	.755**
	Sig. (2-tailed)		.000	.000	.000	.000	.000	.000
	N	60	60	60	60	60	56	56
Fe	Pearson Correlation	.831**	1	.706**	.465**	.623**	.493**	.766**
	Sig. (2-tailed)	.000		.000	.000	.000	.000	.000
	N	60	60	60	60	60	56	56
TOM	Pearson Correlation	.692**	.706**	1	.531**	.568**	.480**	.732**
	Sig. (2-tailed)	.000	.000		.000	.000	.000	.000
	N	60	60	60	60	60	56	56
TOC	Pearson Correlation	.483**	.465**	.531**	1	.653**	.497**	.566**
	Sig. (2-tailed)	.000	.000	.000		.000	.000	.000
	N	60	60	60	60	60	56	56
TP	Pearson Correlation	.608**	.623**	.568**	.653**	1	.602**	.724**
	Sig. (2-tailed)	.000	.000	.000	.000		.000	.000
	N	60	60	60	60	60	56	56
AVS	Pearson Correlation	.550**	.493**	.480**	.497**	.602**	1	.594**
	Sig. (2-tailed)	.000	.000	.000	.000	.000		.000
	N	56	56	56	56	56	56	55
Water	Pearson Correlation	.755**	.766**	.732**	.566**	.724**	.594**	1
	Sig. (2-tailed)	.000	.000	.000	.000	.000	.000	
	N	56	56	56	56	56	55	56

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

Table 8 Correlation analyzes of chromium and physicochemical properties in the surface sediment of the inner Gulf of Thailand during the dry season

Correlations

		Cr	Fe	TOM	TOC	TP	AVS	Water
Cr	Pearson Correlation	1	.749**	.606**	.591**	.533**	.249	.664**
	Sig. (2-tailed)		.000	.000	.000	.000	.066	.000
	N	58	58	58	58	58	55	55
Fe	Pearson Correlation	.749**	1	.586**	.630**	.641**	.358**	.701**
	Sig. (2-tailed)	.000		.000	.000	.000	.007	.000
	N	58	58	58	58	58	55	55
TOM	Pearson Correlation	.606**	.586**	1	.708**	.576**	.255	.698**
	Sig. (2-tailed)	.000	.000		.000	.000	.060	.000
	N	58	58	58	58	58	55	55
TOC	Pearson Correlation	.591**	.630**	.708**	1	.821**	.415**	.775**
	Sig. (2-tailed)	.000	.000	.000		.000	.002	.000
	N	58	58	58	58	58	55	55
TP	Pearson Correlation	.533**	.641**	.576**	.821**	1	.547**	.706**
	Sig. (2-tailed)	.000	.000	.000	.000		.000	.000
	N	58	58	58	58	58	55	55
AVS	Pearson Correlation	.249	.358**	.255	.415**	.547**	1	.278*
	Sig. (2-tailed)	.066	.007	.060	.002	.000		.040
	N	55	55	55	55	55	55	55
Water	Pearson Correlation	.664**	.701**	.698**	.775**	.706**	.278*	1
	Sig. (2-tailed)	.000	.000	.000	.000	.000	.040	
	N	55	55	55	55	55	55	55

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

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

Table 9 Principal component analysis (PCA) of chromium and physicochemical properties in the surface sediment of the inner Gulf of Thailand during the southwest monsoon season

KMO and Bartlett's Test

Kaiser-Meyer-Olkin Measure of Sampling Adequacy.		.735
Bartlett's Test of Sphericity	Approx. Chi-Square	234.605
	df	21
	Sig.	.000

Communalities

	Initial	Extraction
Cr	1.000	.800
Fe	1.000	.787
TOM	1.000	.856
TOC	1.000	.865
TP	1.000	.660
AVS	1.000	.336
Water	1.000	.774

Extraction Method: Principal Component Analysis.

Total Variance Explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	3.909	55.837	55.837	3.909	55.837	55.837
2	1.170	16.710	72.547	1.170	16.710	72.547
3	.796	11.376	83.923			
4	.484	6.910	90.833			
5	.292	4.170	95.002			
6	.235	3.359	98.361			
7	.115	1.639	100.000			

Extraction Method: Principal Component Analysis.

Component Matrix[a]

	Component	
	1	2
Water	.880	-.027
Cr	.877	-.177
Fe	.845	-.269
TOM	.769	.514
TP	.751	-.309
AVS	.505	-.284
TOC	.490	.791

Extraction Method: Principal Component Analysis.

a. 2 components extracted.

Table 10 Principal component analysis (PCA) of chromium and physicochemical properties in the surface sediment of the inner Gulf of Thailand during the northeast monsoon season

KMO and Bartlett's Test

Kaiser-Meyer-Olkin Measure of Sampling Adequacy.		.895
Bartlett's Test of Sphericity	Approx. Chi-Square	255.511
	df	21
	Sig.	.000

Communalities

	Initial	Extraction
Cr	1.000	.750
Fe	1.000	.731
TOM	1.000	.676
TOC	1.000	.479
TP	1.000	.672
AVS	1.000	.523
Water	1.000	.834

Extraction Method: Principal Component Analysis.

Total Variance Explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	4.666	66.651	66.651	4.666	66.651	66.651
2	.791	11.297	77.948			
3	.518	7.394	85.342			
4	.367	5.247	90.589			
5	.313	4.465	95.054			
6	.179	2.559	97.613			
7	.167	2.387	100.000			

Extraction Method: Principal Component Analysis.

Component Matrix[a]

	Component
	1
Cr	.866
Fe	.855
TOM	.822
TOC	.692
TP	.820
AVS	.723
Water	.913

Extraction Method: Principal Component Analysis.

a. 1 components extracted.

Table 11 Principal component analysis (PCA) of chromium and physicochemical properties in the surface sediment of the inner Gulf of Thailand during the dry season

KMO and Bartlett's Test

Kaiser-Meyer-Olkin Measure of Sampling Adequacy.		.877
Bartlett's Test of Sphericity	Approx. Chi-Square	252.406
	df	21
	Sig.	.000

Communalities

	Initial	Extraction
Cr	1.000	.648
Fe	1.000	.707
TOM	1.000	.661
TOC	1.000	.801
TP	1.000	.739
AVS	1.000	.252
Water	1.000	.767

Extraction Method: Principal Component Analysis.

Total Variance Explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	4.574	65.344	65.344	4.574	65.344	65.344
2	.921	13.153	78.497			
3	.519	7.416	85.913			
4	.354	5.063	90.976			
5	.246	3.520	94.497			
6	.217	3.093	97.590			
7	.169	2.410	100.000			

Extraction Method: Principal Component Analysis.

Component Matrix[a]

	Component
	1
Cr	.805
Fe	.841
TOM	.813
TOC	.895
TP	.860
AVS	.502
Water	.876

Extraction Method: Principal Component Analysis.

a. 1 components extracted.

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