การใช้ Acid Volatile Sulfide-Simultaneous Extracted Metals เป็นเครื่องมือสำหรับประเมินความเสี่ยงของมลภาวะโลหะในตะกอนดินอ่าวไทยตอนบน

นางสาวจุฑามาศ สิริรัตน์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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USING ACID VOLATILE SULFIDE–SIMULTANEOUS EXTRACTED METALS AS AN ASSESSMENT TOOL FOR METAL POLLUTION RISK IN THE UPPER GULF OF THAILAND

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จุฑามาศ สิริรัตน์: การใช้ Acid Volatile Sulfide-Simultaneous Extracted Metals เป็นเครื่องมือสำหรับประเมินความเสี่ยงของมลภาวะโลหะในตะกอนดินอ่าวไทยตอนบน (USING ACID VOLATILE SULFIDE–SIMULTANEOUS EXTRACTED METALS AS AN ASSESSMENT TOOL FOR METAL POLLUTION RISK IN THE UPPER GULF OF THAILAND) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร. ศิริชัย ธรรมวานิช, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม: ผศ. ดร. เพ็ญใจ สมพงษ์ชัยกุล, 94 หน้า.

ตัวอย่างตะกอนจากอ่าวไทยตอนบน 30 สถานี และปากแม่น้ำเจ้าพระยา 16 สถานี จากการสำรวจในเดือนสิงหาคม พ.ศ. 2553 และ เดือน มีนาคม พ.ศ. 2554 ตามลำดับ ทำการวิเคราะห์ปริมาณ Acid Volatile Sulfide (AVS) ด้วยเทคนิค purge and trap (colorimetric) และ Simultaneous Extracted Metals (SEM) ตรวจวัดด้วยเทคนิคอะตอมมิคแอบซอบชั่น ผลการศึกษาพบว่า ปริมาณ AVS ในตะกอนอ่าวไทยตอนบน อยู่ในช่วง 0.008-1.367 ไมโครโมลต่อกรัมน้ำหนักแห้ง และมีค่าเฉลี่ย 0.188±0.303 ไมโครโมลต่อกรัมน้ำหนักแห้ง ปริมาณ AVS ในตะกอนปากแม่น้ำเจ้าพระยา อยู่ในช่วง 0.011-3.339 ไมโครโมลต่อกรัมน้ำหนักแห้ง และมีค่าเฉลี่ย 1.753±1.070 ไมโครโมลต่อกรัมน้ำหนักแห้ง ปริมาณผลรวมโลหะ (ΣSEM) ในตะกอนอ่าวไทยตอนบนอยู่ในช่วง 0.30–2.48 ไมโครโมลต่อกรัมน้ำหนักแห้ง และในตะกอนปากแม่น้ำเจ้าพระยา อยู่ในช่วง 1.4–3.17 ไมโครโมลต่อกรัมน้ำหนักแห้ง จากการหาค่าความเป็นพิษที่อาจจะเกิดขึ้นของโลหะ โดยใช้เกณฑ์ความสัมพันธ์ของ SEM และ AVS 3 แบบ คือ (ก) สัดส่วน ΣSEM / AVS (ข) ความแตกต่างของ ΣSEM – AVS และ (ค) สัดส่วน (ΣSEM – AVS)f_{oc} พบว่า มีบางสถานีในปากแม่น้ำเจ้าพระยาและอ่าวไทยตอนบน มีความเสี่ยงที่จะเกิดมลพิษของโลหะ และยังพบอีกว่าสองสถานีบริเวณปากแม่น้ำเจ้าพระยาที่มีความเสี่ยง มีสภาวะเป็น suboxic และมีค่า AVS ต่ำ เพื่อให้การประเมินมลภาวะโลหะในอ่าวไทยตอนบนให้ถูกต้องยิ่งขึ้น ในการศึกษาต่อไปควรศึกษาด้วยวิธีสกัดตามลำดับขั้นและศึกษาปัจจัยที่ควบคุมพฤติกรรมของ AVS ในตะกอน

สาขาวิชา การจัดการสิ่งแวดล้อม ลายมือชื่อนิสิต..
ปีการศึกษา 2554 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก..
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JUTHAMAS SIRIRAT: USING ACID VOLATILE SULFIDE–SIMULTANEOUS EXTRACTED METALS AS AN ASSESSMENT TOOL FOR METAL POLLUTION RISK IN THE UPPER GULF OF THAILAND. ADVISOR: ASST. PROF. SIRICHAI DHARMVANIJ, Ph.D., CO-ADVISOR ASST. PROF. PENJAI SOMPONGCHAIYAKUL, Ph.D., 94 pp.

Surface sediment samples from 30 station in the upper Gulf of Thailand (U-GOT) and 16 stations at the Chao Phraya river mouth collected in August 2010 and March 2011, respectively. The sediment samples were analyzed for Acid Volatile Sulfide (AVS) by purge and trap (colorimetric) technique. Simultaneous Extracted Metals (SEM) was determined by atomic absorption spectrophotometer. The study revealed that the concentrations of AVS in the U-GOT were in the range of 0.008-1.367 µmol/g dry weight, average of 0.188±0.303 µmol/g dry weight. The concentrations of AVS in sediments at the Chao Phraya river mouth were in the range of 0.011-3.339 µmol/g dried weight, average 1.753±1.070 µmol/g dry weight). The summation of metals (∑SEM) in the U-GOT and Chao Phraya river mouth sediments were in the range of 0.30-2.48 and 1.4-3.17 µmol/g dried weight, respectively. Possible toxicity related to these metals was examined using (i) ∑SEM/AVS ratios, (ii) ∑SEM – AVS difference, and (iii) ∑SEM – AVS/f_{oc} criteria. According to the criteria, some stations in the Chao Phraya river mouth and the U-GOT have shown a potential risk of metal pollution. However, two stations from the Chao Phraya river mouth showing metal pollution risk were being suboxic condition with low concentration of AVS in the sediments. For more accuracy assessment of metal risk in the upper Gulf of Thailand, sequential extraction procedure and factors controlling AVS behavior should be further investigated.

Field of Study: Environmental Management	Student's Signature ....
Academic Year: 2011	Advisor's Signature ....
	Co-advisor's Signature ....

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CHAPTER I

Introduction

1.1 Introduction

Anthropogenic activities are important origin of metal contamination in near-shore environments. Most metals discharged into a river are found to end up in nearshore sediment via complex physical, chemical, and biological processes. Therefore, bottom sediments become an important sink as many metals are accumulated therein (Dassenakis *et al.*, 1995).

Near-shore sediments compose of a number of different components which may, or may not have different sources. Thus, near-shore sediments are very heterogeneous and represent the entire range of sediment presently being delivered to the ocean. It has been suggested that near-shore environments are important removal sites of several elements from seawater because the accumulation rates are very much higher and the physicochemical conditions are different from those found in open ocean.

Metals are introduced into estuaries in two principle forms, namely those associated with solid and colloidal materials, and those dissolved in solution. Trace metals associated with solid materials can be subdivided into those elements held in lattice position (within detrital minerals) and those held in surface and inter-sheet (i.e. non-lattice) position (Förstner and Wittman, 1981; Salomons and Förstner, 1984)

The metals held in the non-lattice position of sediment are not being held permanently and can be released by the change in physicochemical conditions of the surrounding environment. The non-lattice held metals may be partitioned into five sub-fractions of different bonding strength: dissolved, exchangeable, carbonate, iron-manganese oxide (Fe-Mn oxide), and organic (Förstner and Wittman, 1981; Salomons and Förstner, 1984). Metals in exchangeable, carbonate-bound, and Fe-Mn oxide-bound speciation, which are contributed by anthropogenic pollution, are considered to be more mobile, dangerous and bioavailable, while organic matter/ sulfide-bound and residual metals are more stable and non-bioavailable (Förstner and Wittman, 1981; Salomons and Förstner, 1984; Lin *et al.*, 2003).

Since metals are not necessarily fixed permanently in sediment, they may be recycled via biological and chemical agents between sediments and water column (Fig. 1-1). Released metals can be potentially dangerous to biota or might cause other damaging effect on people utilizing them.

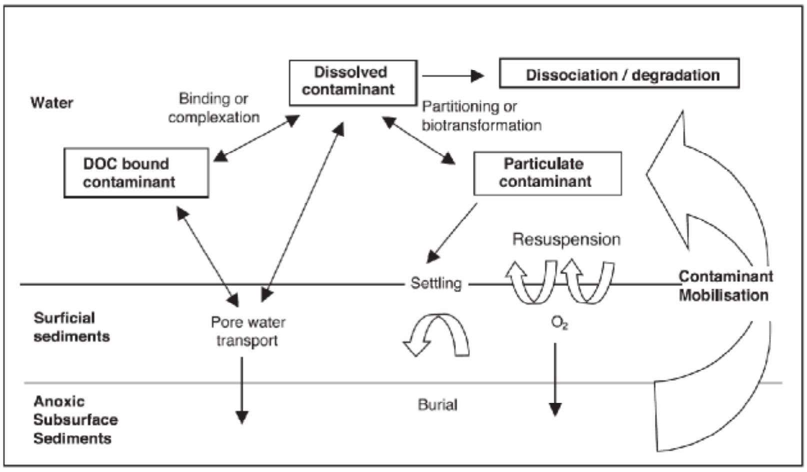

Figure 1-1 Transport and transformation of contaminations in sediments (after Eggleton and Thomas, 2004)

Sediment quality can be assessed with various approaches or using some combination of these approaches to evaluate sediment quality. These approached include the assessment of: (1) benthic community health; (2) sediment toxicity; (3) bio-accumulation of compounds from sediment; (4) toxicity identification evaluations; (5) sediment chemistry; or (6) integrated sediment quality assessments (McCauley *et al.*, 2000). However, one should understand that a single approach alone will hardly elucidate the complex and dynamic nature of interaction that exist between the physical, chemical and biological components, and the binding of metals in sediments.

The sediment chemistry, total metal contents in sediment which are used for studies of spatial and temporal distribution, or identification of pollution sources either of which is not sufficient to get information on the potential availability of metals (whether toxic or essential) to biota under various environmental conditions, whereas extractable forms are determined for assessing their mobility (Quevauviller *et al.*, 1996).

Sequential extraction procedures are also useful in obtaining information on the phases that effect metal leachability the most, thereby distinguishing among easily remobilized elements (e.g. Cd and Zn), elements highly affected by reduction processes (e.g. Pb), elements released by oxidation of organic matters or sulfurs (e.g. Cu and Cr), and metals that basically remain in the residual fraction (e.g. Cr). However, they reflects ‘potential available’ metal fraction by excluding metal forms which unavailable for bioaccumulation but are not limited to, and also metal forms that affect bioaccumulation. It is well established that such approaches cannot specifically extracted only metals from the desired fraction without interfering with the other fractions (Luoma, 1989).

Thus, making the usefulness of total metal contents data from single and sequential chemical extraction in predicting long-term adverse effect of metal from sediment doubtful (Rauret, 1998). Two decades ago, a series of bioassessment techniques were developed to identify the types of stress being exerted, their severity, and the bioavailability of the contaminants present in the ecosystems. Over the past 20 years, a variety of methods have been described for evaluating the geochemical controls on the bioavailability and the toxicity of sediment-associated contaminants to marine benthic invertebrates (Wang *et al.*, 2002). However, only a limited number of methods are currently available for assessing bioaccumulation of contaminants from field-collected or laboratory spiked sediments.

Unfortunately, the link between bioaccumulation and toxicity, acute and chronic, in aquatic organisms is unclear because the residue-effects concentrations. They are the residue concentrations from chemical analyses of such contaminants in the sediments in sufficient concentrations to accumulate in aquatic organisms which cannot provide insight the substances causing the effect, are largely unknown. It is very difficult to use bioaccumulation test to determine causality, or to link the test with other measures of toxicity (McCauley *et al.*, 2000).

Many of the assessment tools tend to be precise or accurate, but not both. For example, chemical analyses are quite precise, but the analytical results are not good enough to estimate contaminant bioavailability. On the other hand, biological measurements and bioassays while they are accurate predictors or assessors of effects to biological communities, but they are not precise because of differences parameters at each site (Dexter, 1995). Chapman *et al.* (1992) described that the various components of an integrated sediment assessment. These include sediment chemistry, sediment toxicity, tissue chemistry, pathology, and community structure. These five areas provide a sufficiently broad description of the general types of tools available for conducting sediment assessment.

Over the last two decades a considerable amount of research effort has been put into investigating sediment toxic threshold levels (Abrahim *et al.*, 2007). US-EPA has developed an Agency-wide Contaminated Sediment Strategy to address the problem of contaminated sediments. One key feature of this strategy is the development of Sediment Quality Guidelines (SQGs) (McCauley *et al.*, 2000), which describe the level of contaminants in sediment associated with various categories of adverse effects and are often used to interpret sediment chemistry data (USEPA, 2000)

1.2 Objective

To assess risk of cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn) pollution in the upper Gulf of Thailand (U-GOT) and the Chao Phraya river mouth sediments using Acid Volatile Sulfide with Simultaneous Extracted Metals (AVS-SEM) technique.

1.3 Hypothesis

Acid volatile sulfide (AVS) together with simultaneous extracted metals (SEM) can be used in conducting risk assessment of metal pollution in estuarine sediments.

1.4 Scope of the study

Most of the metals associated with sediments are in the size range of <63µm (Queralt *et al.*, 1999). Therefore, sediment samples were sieved through 63 µm-sieve. The sediments that passed through the 63 µm-sieve were used for metal analysis except AVS-SEM analysis which using whole wet sediment samples.

Geochemical properties of sediment such as pH and redox potential (Eh), organic matter, carbonates, non-lattice held metal fraction and total metals were analyzed in order to establish the trend of metal partitioning occurred in the sediment samples. The relationship between metals and each geochemical property was used in validating the AVS-SEM technique. However, it is not possible that every metals present in marine environment were tested in this study. Only Cd, Cu, Pb and Zn were chosen to be studied.

Sediment samples in this study were collected from 30 stations in the U-GOT and 16 stations at the Chao Phraya river mouth.

1.5 Study sites

1.5.1 The upper Gulf of Thailand

The upper Gulf of Thailand (U-GOT) is a semi-enclosed square bay situates between latitudes 12° 30' N and 13° 30' N and longitudes 100°E and 101°E. The total area is approximately 100×100 km^2 with the average depth of about 20 m. Water exchange with the lower Gulf is limited. There are high inflows from five rivers, namely Chao Phraya, Thachin, Bangpakong, Maeklong and Phetchaburi, carrying high suspended solids, municipal wastes and industrial wastes.

1.5.2 The Chao Phraya river

The Chao Phraya river is the second longest watercourse in Southeast Asia after the Mekong river, and is by far the largest of the Thai rivers. It has the highest discharge into the U-GOT with the 55-year average of 482 m^3/s (Burnett *et al.*, 2007). It drains an area of about 21,725 km^2, including Bangkok (the most heavily populated and industrialized city in Thailand). There are many activities along the river; 2.1% of forest, 92.7% of agriculture and urban areas and 5.2% of water resource (Tachikawa *et al.*, 2004). There is an increasing amount of heavy industries, especially extending eastwards from Bangkok along the lower reaches of the Chao Phraya River. The Port of Bangkok, near the mouth of the Chao Phraya river, serves as the main point for agricultural export products as well as access for raw materials such as fertilizer, grain, steel and oil products (Burnett *et al.*, 2007).

The average annual precipitation is 1,487.3 mm. Flow rates average is greater than 1000 m^3/s. High flows (>3000 m^3/s) occur from August to October. Low flows (about 100 m^3/s) from January to May (Hungspreugs *et al.*, 1987). The dissolved oxygen concentration was reported at 1.63 mg/l (PCD, 2007)

1.6 Expected results

The AVS-SEM technique can be applied to use as a tool for conducting risk assessment of metal pollutions in the U-GOT and the Chao Phraya river mouth sediments.

CHAPTER II

Theoretical background and literature review

2.1 Estuarine sediment

The estuarine sediments represent the final repository of most contaminants and elements carried to the oceans by rivers, but also play a key role in estuarine systems as potential sources and sinks for these substances. The fate of these substances in sediments is related to the nature and extent of biogeochemical transformations as well as their relative mobility or degradation under varying redox conditions (Mucci *et al.*, 2000).

The transportation of metal binding forms in sediments includes the following main processes: sorption and desorption, formation and dissolution of carbonate bound metals, formation and decomposition of soluble and insoluble metal organic complex compounds, formation and dissolution of hydroxides and oxyhydrates, sorption and coprecipitation of metal by Fe/Mn oxides, particularly in oxidic environments at neutral pH; precipitation of metal sulfides in strong reducing environments and dissolution as sulfates under oxic condition. Relative mobility and availability of metals in these processes are summarized by Salomons (1995) (Table 2-1).

Table 2-1 Relative mobility and availability of trace metals in sediments (modified from Salomons, 1995)

Metal species and association	Mobility
Exchangeable/ Dissolved cations	High. Changes in major cationic composition such as in the estuarine may cause a release due to ion exchange
Fe/Mn oxides associated metals	Medium. Changes in redox conditions may cause a release but some metals precipitate if sulfide mineral present is insoluble
Organic matter associated metals	Medium/High. Decomposition/oxidation of organic matter occurs through time
Sulfide minerals associated metals	Strongly dependent on environmental conditions. Oxidation of sulfide minerals, under oxygen-rich conditions, leads to release of metals
Metals fixed in crystalline phase	Low. Only available after weathering or decomposition

In recent organic carbon-rich sediments, trapped porewater can commonly form a strongly reducing (anoxic) environment. Low redox potential in this environment can promote sulfate reduction and sulfide mineral deposition. Much of the non-silicate-bound fraction of potentially toxic metals (such as As, Cd, Cu, Hg, Pb, and Zn) can be co-precipitated with pyrite, form of insoluble sulfides during diagenesis, and become unavailable to biota (Morse, 1994). As such the major changes that occur in redox conditions between oxic waters and anoxic sediments can have profound influences on the speciation and bioavailability of many trace metals (Petersen *et al*., 1997). The inducing an influx of oxygenated seawater can result in rapid reaction of this anoxic sediment and thereby release significant proportions of these metals. Pyritization and (or) de-pyritization of trace metals can be probably an important process in controlling bioavailability of many trace metals, especially in the marine environment

Anoxic conditions in sediments often result in the microbially mediated production of major amounts of hydrogen sulfide (H_2S) in marine and estuarine environments. Although most of the H_2S is usually reoxidized, a significant fraction generally reacts to form metal sulfides with pyrite (FeS_2) being the most abundant reaction product. However, there is also the potential of formation for other metal sulfide minerals, and subsequently for minor and trace metals to coprecipitate and adsorb on iron sulfides. In deeper layers of the sediments where anoxic conditions prevail, some metals are immobilized very efficiently by the formation of sulfide minerals. However, reoxidation may occur, if these anoxic sediments are exposed to an oxic environment the sulfidic minerals may be reoxidized resulting in the release of trace elements to the aqueous phase or the transformation at the solid phase to more bioavailable phase (Petersen *et al*., 1997).

Therefore, it is important to understand the behavior of anoxic sediment. Although dissolved metal concentration in anoxic sediment are principally governed by equilibrium solubility of metals, the potential for oxidative release are significantly greater. This process might occur during resuspension induced by physical disturbution such as strong currents or by the introduction of oxic water at depth by burrowing organism or dredging. In estuarine sediments, it is likely that the oxidation of sulfide phases represents the major source of metals to oxic overlying waters (Simpson *et al*., 1998)

Sulfides are considered the predominant solid phases, in most anoxic sediments, controlling the concentrations of metals (such as Cu, Cd, Fe, Mn, Ni, Pb, and Zn). The low solubility of metal sulfides results in low concentrations in porewater. During resuspension of a sediment into an oxic overlying water, these metal sulfides may be oxidized, giving oxidized sulfur species (i.e., SO_4^{2-}, S^0), and release the associated metal to the water column. The released metals may in turn be quickly scavenged by or coprecipitated with iron and manganese hydroxides or complexed by organic matter (OM) (Simpson *et al*., 1998). However during the oxidation of S^{2-}, a small portion of metals is available on the OM's surface and the OM structure becomes less. At the same time, the metals associated with OM can be released from sediment and increases their availability to biota. Oxidation of S^{2-} (to SO_4^{2-}) and OM taking place in the sediment disposed from dredging activities can also release metals bound to the oxidizable fraction (Stephens *et al*., 2001).

Table 2.2 Dominant metals by adsorbed or complexed phase in oxic and anoxic sediments (modified from Brown and Neff, 1993)

Metal	Associations in oxic sediment	Associations in Anoxic sediment
Cadmium	Fe/MnO, OM/s, $-CO_3$	CdS
Copper	OM, Fe/MnO	Cu_2S, CuS, FeCuS
Lead	Fe/MnO	PbS
Zinc	Fe/MnO, OM	ZnOM/S

CO_3 = carbonates.
Fe/MnO = iron and manganese oxyhydroxides
OM = organic matter
S = sulfide (dominant species given)

2.2 Sediment quality guidelines

Sediment quality guidelines (SQGs) are an important tool for the assessment of contamination in marine and estuarine sediments. Although such guidelines are not definitive indicators of toxicity, they can have a high predictive ability and are a vital tool in identifying areas with potentially adverse biological effects. In the present study, 15 sets of common SQGs have been compared, including values for Australia/New Zealand, Canada, Hong Kong, Norway, the Netherlands, the USA and regions within the USA (Puget Sound/Washington, New York and Florida). The majority of these SQGs are based on the weight-of-evidence approach (Hübner *et al.*, 2009).

In response, USEPA has developed an Agency-wide Contaminated Sediment Strategy to address the problem of contaminated sediments. One key feature of this strategy is the development of Sediment Quality Guidelines (SQGs) (McCauley *et al*., 2000). The basis for SQGs is sediment quality assessments that have laboratory, field and theoretical foundations.

Sediment Quality Guidelines (SQGs) describe the level of contaminants in sediment associated with various categories of adverse effects and are often used in interpreting sediment chemistry data (USEPA, 2000). It would be used to assess the extent of sediment contamination, or to implement measures to limit or prevent additional contamination.

2.2.1 Categories of sediment quality guidelines

The SQGs can be classified into two main categories based on the approach used to derive their values: “Empirically-based” and “Theoretically-based” approaches (Burton, 2002).

a) Empirically-based approaches

“Empirically-based” approaches are based on a statistical analysis of large databases of matched sediment chemistry and toxicity data to identify chemical concentrations associated with various levels of biological effects. Although these approaches can be fairly good predictive methods, they do not show causal effects, but rather showing chemical concentrations that are used as an indicator of sediments that may or may not pose risks. Therefore, the approaches may be used in risk-assessing sediments of concern, but must not be used to identify substances of concern. Another disadvantage of these approaches is that they do not resolve the issues of bio-availability because these approaches are based on dry weight concentrations in sediment, and not the biologically available concentrations. While all of these approaches are still commonly used, they tend to be site-specific, and can lead to a wide range of effects data for similar concentrations of contaminants in different sediment types.

b) Theoretically-based” approaches

“Theoretically-based” approaches or theoretically-derived SQGs are based primarily on an understanding of the chemical partitioning of chemicals in the sediment and the toxicity of the dissolved fraction in the sediment porewater (Di Toro *et al.*, 1990; Di Toro *et al.*, 1991). By accounting for variations in bioavailability and mixture effects, theoretically SQGs have a greater ability relative to empirical SQGs to determine the specific contaminant. Theoretically-based guidelines have been developed using the equilibrium-partitioning (EqP) approach.

The EqP is based on the premise that the bio-available fraction of contaminants in sediments cause biological effects and that bio-availability is a function of the partitioning of chemicals between sediments, porewater, and the benthic organisms. As such the EqP is usually understood to refer to (1) the partitioning of non-ionic organic chemicals between sedimentary organic carbon and porewater (Di Toro *et al.*, 1991); and (2) the partitioning of ionic metals between sulfides and porewater, as described by the acid volatile sulphides with simultaneously extracted metals (AVS/SEM) process (Di Toro *et al.*, 1992).

The SQGs using of EqP approach has many advantages including: (1) linked to a large water quality database, (2) its theory is well understood, (3) applied to both ionic and non-ionic compounds, (4) can be applied in a regulatory framework, (5) effects on organisms can be directly measured or estimated, (6) based on toxicological principles, and (7) causality is determined (Di Toro *et al.*, 1991; Ankley *et al.*, 1996). However, the limitations of using this approach are (1) EqP models have only been developed for some non-ionic compounds and five divalent metals, (2) false negatives and positives will occur, (3) analytical measurements are often difficult, (4) does not address additional binding phases, and (5) metal activity is not addressed (McCauley *et al.*, 2000).

One basis for establishing SQG uses equilibrium partitioning between the sediment and porewater phases in sediment. AVS is one of the major chemical components that controls the activities and availability of metals in the interstitial waters of sediments. Sulfide reacts with several divalent transition metal cations (Cd, Cu, Ni, Pb and Zn) to form highly insoluble compounds that are not bioavailable (Allen *et al.*, 1991; Ankley *et al.*, 1996; USEPA, 2004). It has been verified (Di Toro *et al.*,1990) that divalent transition metals do not begin to cause toxicity in sediment until the reservoir of sulfide is used up (i.e. until the molar concentration of metals exceeds the molar concentration of sulfide), typically at relatively high dry-weight metal concentrations. This observation has led to a laboratory measurement technique for calculating the ratio between the SEM concentration and AVS concentration in field samples to determine potential toxicity (Prica *et al*., 2011).

2.3 Acid volatile sulfide and simultaneously extracted metals

Acid volatile sulfide (AVS) is operationally defined as sulfides that form hydrogen sulfide under the condition of mixing sediment with cold dilute HCl. This includes amorphous, moderately crystalline monosulfides, and other sulfides (Allen *et al*., 1991).

Sulfides are produced in estuarine sediments by the coupling of sulfate reduction and oxidation of organics. The diagenetic sulfide formation is a function of porosity, sediment density, mixing intensity, organic matter supply, SO_4 in pore water diffusion coefficient, rate of SO_4 reduction and SO_4 concentration at the water-sediment interface (Garcia *et al*., 2007).

Chemically, the key to the AVS theory is solubility. Iron is one of the most abundant metals in the earth, and the largest reservoir of sulfides in sediments is solid phase iron sulfide. Iron sulfide is more soluble than most other metal sulfides, including those in this study. Because of the worldwide abundance of iron and this unique solubility relationship, iron sulfide has the ability to sorb other metals and convert them to metal sulfides, rendering them nontoxic. This can occur in the pore water of sediment layers like those in Foundry Cove. At equilibrium, the sulfide ion successfully competes with other dissolved or particle-associated ligand for the metal ion to form insoluble metal sulfides. The following are the related chemical equations (Eqs. 2-1, 2-2 and 2-3):

Origination of sulfur:

$$SO_4^{2-} + (CH_20) \quad \leftrightarrow \quad S^{2-} + CO_2 + H_2O \qquad (2\text{-}1)$$

Conversion to iron sulfide:

$$S^{2-} + Fe^{2+} \rightarrow FeS(s) \leftrightarrow FeS^{2+} \text{ (pyrite)} \qquad (2\text{-}2)$$

Conversion to metal sulfide:

$$Me^{2+} + FeS(s) \leftrightarrow MeS + Fe^{2+} \qquad (2\text{-}3)$$

Simultaneously extracted metals (SEM) are operationally defined as metals, commonly Cd, Cu, Pb, Hg, Ni and Zn, that form less soluble sulfides than do Fe and Mn, and which are at least partially soluble under the conditions of this test (Allen *et al.*, 1991).

In the AVS model, it is assumed that the sulfide ligand in anoxic sediment competes effectively with any other ligands, both dissolved or solid-phase, for binding divalent metal ions. Metal ions known to react strongly with sulfide are Cd, Cu, Pb and Zn. The AVS is a major reactive pool of solid-phase ligand in the sediment under equilibrium between dissolved and solid phases (Wenning *et al.*, 2005). Thus, partitioning of metals does occur and sulfides do affect the bioavailability of some metal contaminants (Dexter, 1995). McGrath *et al.* (2002) used AVS to predict the toxicity in sediment of divalent metals, including Cu, Cd, Ni, Pb and Zn.

The potential mobility and toxicity of metal ions could be directly related to the ratio of SEM and AVS for the sediment (USEPA, 2004). A basic principle is that trace metal contaminants in sulfide-rich sediments are predominantly present as metal sulfide phases and that nonsulfidic binding phases (e.g., hydroxide/carbonate phases) are insignificant. It is assumed that the sulfide phases extracted by the AVS procedure are predominantly monosulfides phases (e.g., FeS, MnS, and ZnS) and that for every mole of sulfide measured as AVS there will be a corresponding mole of metal measured in the SEM fraction, and trace metals added to sediments in an ionic form will react to form discrete sulfide phases, MeS (Simpson *et al*., 2000).

Different relationships between AVS and SEM used to establish mechanical models to assess metal toxicity has been widely applied, such as the ∑SEM and AVS ratio (∑SEM/AVS) (Ankley *et al*., 1996), the difference between ∑SEM and AVS (∑SEM

– AVS), or normalization of the difference between ∑SEM and AVS by organic carbon ((∑SEM – AVS)/f_{oc}) (Di Toro *et al.*, 1990; Burton *et al.*, 2005a; Yin *et al.*, 2008).

It was proposed from the ∑SEM and AVS ratio approach to predict toxicity that there should no toxicity occurred if the ∑SEM/AVS ≤ 1, because all available free metals were bound into the AVS phase (e.g., ZnS). Using the ∑SEM – AVS difference approach as an alternative of the ∑SEM/AVS will give concerning the magnitude by which AVS binding has been exceeded. No effects are expected to occur when a molar ∑SEM – AVS difference ≤ 0 (Di Toro *et al.*, 1990; Ankley *et al.*, 1996; Burton *et al.*, 2005a; Yin *et al.*, 2008).

The ∑SEM/AVS ≤ 1 or ∑SEM-AVS ≤ 0 can predict that no occurrence of toxicity with a high degree of certainty. On the other hand, the sediment may be considered potentially toxic when this ratio is > 1. In the absence of other binding phases, metal concentrations in porewater may be high. However, the toxicity may not be accurately predicted if ∑SEM/AVS > 1 or ∑SEMAVS > 0 due to the present of other binding ligands. Organic carbon (OC) is an key partitioning phase for metals in sediment and in water. When using the OC fraction to normalize the excess ∑SEM (f_{oc}; i.e., ∑SEM-AVS/f_{oc}), it has been found in comparisons with toxicity data that a boundary for chronic effects exists when ∑SEM-AVS/f_{oc} is in excess of 100 to 150 mmol/g of OC, allowing the prediction of toxicity (Yin *et al.*, 2011).

The AVS/SEM measurements are being increasingly used in sediment quality studies to predict the absence of toxicity of Cd, Cu, Ni, Pb, and Zn. The using of AVS/SEM as a tool in environmental assessment serves three purposes: (1) hypothesis testing, (2) prioritization, and (3) helping explain observed effects (or lack thereof) (Chapman, 1995).

The concentrations of AVS in sediments can be determined by several methods. The methods to determine AVS include; (i) colorimetric, (ii) gravimetric, (iii) ion selective electrode, and (iv) photoionization detection (PID). Every method starts with using dilute HCl to convert the sulfide in the sample to H_2S, then trapping the evolved H_2S by purging the system with a purified inert gas. Only difference of these methods is the H_2S trapping mechanism and measuring technique; 0.5 M NaOH for colorimetric; 1 M $AgNO_3$ for gravimetric; 0.2 M sulfide antioxidant buffer for ion-selective electrode; and column immersed in liquid nitrogen for photoionization detection. The choice of analytical technique depends on a number of factors including time consuming, reproducibility, waste generation and cost.

The four analytical methods for AVS/SEM analysis performed with similar precision for the same sample. According to the factors previously mentions, colorimetric method is relatively simple, less time consuming, and cost effective particularly for consumables. Although the colorimetric method produced a comparatively large volume of acid waste, it appears to be the best method for determining AVS in sediment and preferable when no specialized equipment available.

2.4 Specific metals of interest

2.4.1 Cadmium

The redox potential of sediment-water systems exerts controlling regulation on the chemical association of particulate cadmium, whereas pH and salinity affect the stability of its various forms. In anoxic environments, nearly all particulate cadmium is complexed by insoluble organic matter or bound to sulfide minerals. Greenockite (CdS) has extremely low solubility under reducing conditions thereby decreasing cadmium bioavailability. Oxidation of reduced sediment or exposure to an acidic environment results in transformation of insoluble sulfide-bound cadmium into more mobile and potentially bioavailable hydroxide, carbonate, and exchangeable forms

2.4.2 Copper

In sediment containing high concentration of organic, copper is associated primary with the organic/sulfide fraction/ with extractable organic matter. Copper is most efficiently scavenged by carbonate minerals and Fe-Mn oxide minerals and coatings and is less mobile than cadmium, lead, and zinc. Sometimes, elemental substitution is more complex; for example, copper toxicity is related to low abundances of zinc, iron, molybdenum, and (or) sulfate. The dominant forms of copper in the solution in the solid phase of sediment include chalcocite (Cu_2S), covelite (CuS), and possibly chalcopyrite ($CuFeS_2$) (Shea and Helz, 1988).

2.4.3 Lead

Most of the lead in sediment is associated with fine grain sediment particles (Krumgalz *et al*., 1992). Both organic and inorganic forms of lead pose serious health risks to all forms of life. Inorganic lead compounds (sulfide, carbonate, and sulfate minerals) are commonly abundant in sediment but have low solubilities in natural water. Soluble lead is little affected by redox potential. Lead is tightly bound under strongly reducing conditions by sulfide mineral precipitation and complexion with insoluble organic matter, and is very effectively immobilized by precipitated iron oxide minerals under well-oxidized conditions (Gambrell *et al*., 1991).

2.4.4 Zinc

In slightly basic, anoxic sediment environments, zinc is effectively immobilized and not bioavailable in residual fraction (Gambrell *et al.*, 1991). The residual zinc is associated with the mineral including chromite, ilmenite, and magnetite (Loring, 1982). Sphalerite (ZnS) and zincite (ZnO) are important carriers of residual zinc in some sediments. Substantial amounts of zinc are released to solution if this sediment is oxidized or exposed to an acidic environment which associated primarily with the reducible Fe-Mn oxide fraction (Rosental *et al.*, 1986).

CHAPTER III

Methodology

3.1 Study sites

Sediment samples were collected from two study sites in the upper Gulf of Thailand (U-GOT) and the Chao Phraya river mouth. The U-GOT site was a collaboration project among (i) Department of Marine Science, Chulalongkorn University, (ii) Department of Marine and Coastal Resources (DMCR), Ministry of Natural Resources, and (iii) the First Institute of Oceanography (FIO) of the State Oceanic Administration (SOA) P.R. China. The Chao Phraya river mouth was a collaboration project between Department of Marine Science and DMCR.

3.1.1 The Upper Gulf of Thailand

Surface sediments were collected from 30 stations in the U-GOT during 23-25 August 2010 using Petersen grab sampler (Fig. 3-1). The sampling stations were accessed by M/V Boonprakob (Fig. 3-2) of DMCR. The sampling locations are shown in Fig. 3-3 and detailed location in Table A-1, Appendix A.

Figure 3-1 Petersen grab sampler

Figure 3-2 M/V Boonprakob (Photo by Prof. Xuefa Shi, FIO)

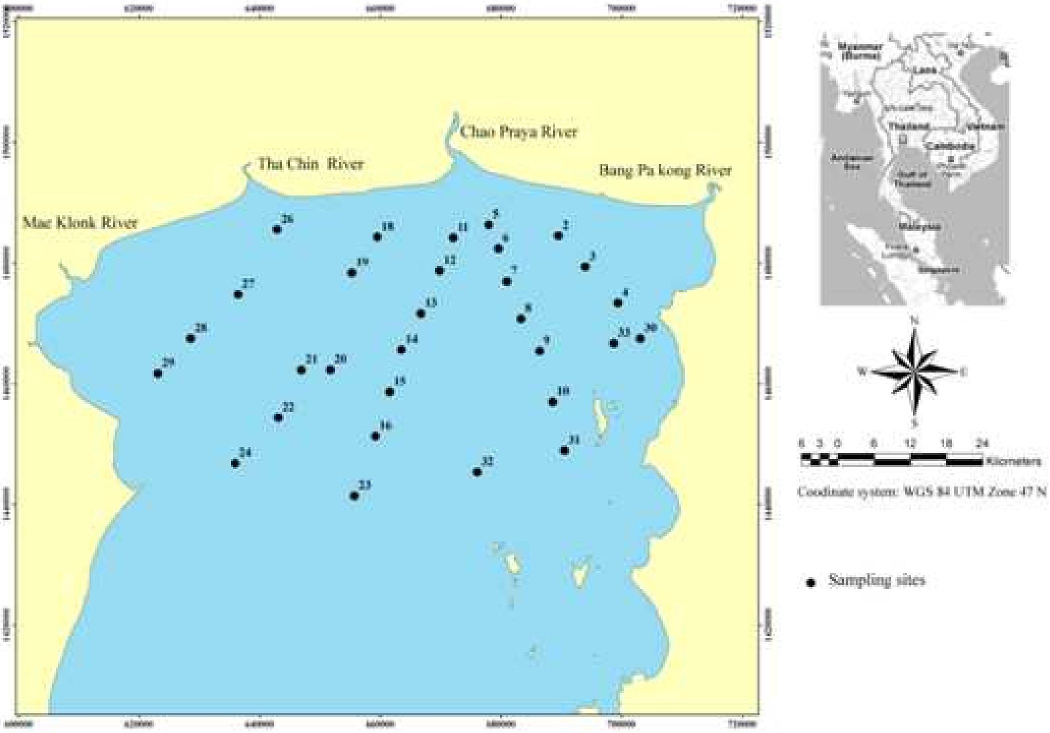

Figure 3-3 Location of sampling sites in the upper Gulf of Thailand

3.1.2 The Chao Phara river mouth

Surface sediments were collected from 16 stations located at the Chao Phraya river mouth on 9 March 2011 using Birge Ekman grab sampler (Fig. 3-4). The sampling stations were accessed by a Thai style speed boat (so-called long-tailed boat) (Fig. 3-5). The sampling locations are shown in Fig. 3-6 and detailed location in Table A-2, Appendix A.

Figure 3-4 Birge Ekman grab sampler

Figure 3-5 A Thai style speed boat (long-tail boat)

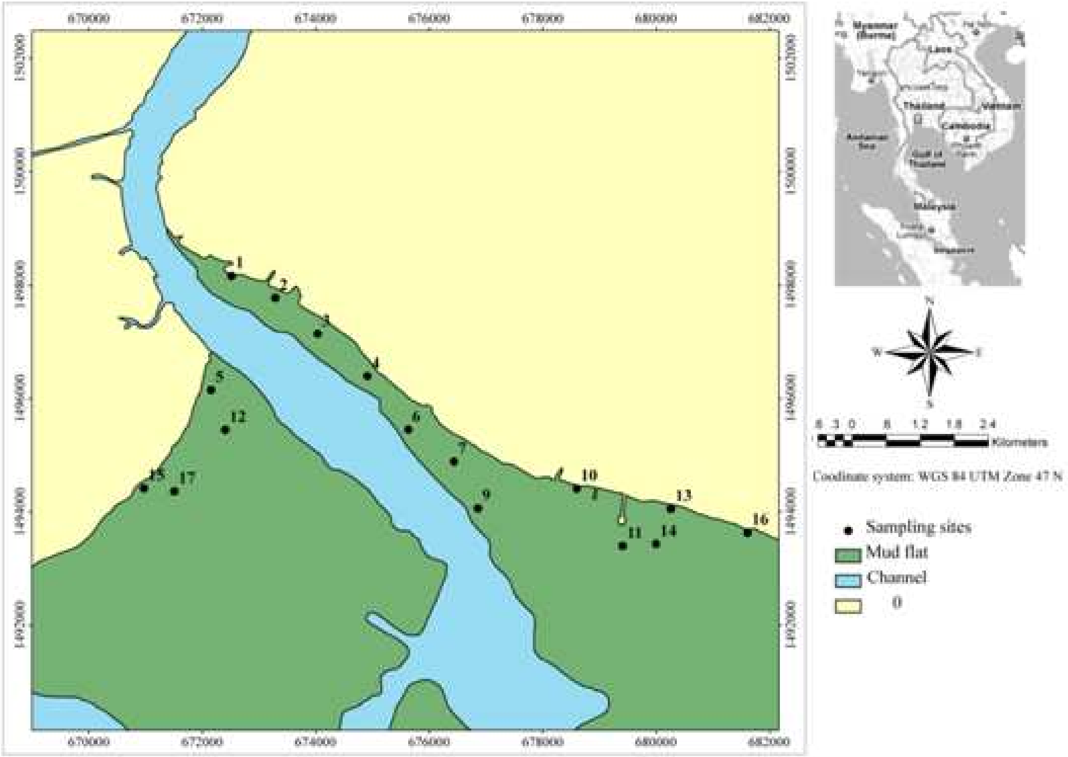

Figure 3-6 Locations of sampling sites at the Chao Phraya river mouth

3.2 Sampling

Once the surface sediments were collected, portions of sediments from the middle of the grab were transferred into 2 labeled cleaned plastic bags using a clean plastic spoon. The U-GOT samples were immediately kept refrigerate on board, while those of Chao Phraya river mouth sediments were kept in ice box, and were transported back to the laboratory at the end of the day to keep properly in the refrigerator until analysis.

For the Chao Phraya river mouth site, redox potential (Eh) of sediment was immediately measured on board after sampling using "Orion" #9678BNWP, Platinum Combination Redox Electrode and a Thermo Orion 290A (Fig. 3-7).

Figure 3-7 Measurement of redox potential (Eh) using Platinum Combination Redox Electrode (Thermo Orion 290A)

Because sulfide ion (S^{2-}) is unstable in the present of oxygen, the first-bag sediment samples for acid volatile sulfide with simultaneous extracted metals, so called AVS-SEM, were intended protected from exposure to oxygen during sample collection and storage. Therefore, the samples were stored cool with no contact to air immediately after sampling. It is noted that holding time of the samples should not exceed 14 days.

The second-bag samples were stored frozen after arrival the laboratory until further analyses of grain size compositions, carbonate contents, organic matter and metals.

3.3 Sample preparation

The first-bag samples (chilled samples) were used immediately for AVS-SEM analysis within 7 days after sampling.

The second-bag samples (frozen samples) were freeze-dried. The dried sediments were subsampled into 2 portions. The first portion was for sedimentological and geochemical analyses. The second portion was sieved through 63 µm non-metallic sieve and kept in plastic zip lock bags until analyses.

3.4 Acid volatile sulfide with simultaneous extracted metals analysis

The AVS-SEM technique is the method that uses the same condition for releasing of both sulfide and metals from the sediment, and thus provides a practical means of assessing the amount of metals associated with sulfides.

The AVS in the wet sediment sample was first converted to hydrogen sulfide (H_2S) gas by acidification with hydrochloric acid (HCl) at room temperature. The H_2S was then purged from the sample and trapped in aqueous solution of sodium hydroxide (NaOH).

The amount of trapped H_2S was determined by colorimetric method. After blue complexes were completely formed, the absorption was measured at the wavelength of 670 nm using 10 mm rectangular spectrophotometric cell.

The metals liberated from the sediments during acidification are called SEM. These include Cd, Cu, Pb and Zn. This study assumed that nickel, antimony, bismuth and chromium, and other metals (which are or are not divalent) that formed insoluble sulfide are not presented in significant concentrations, and mercury has other important factors that play a key role in determining the bioaccumulation in sediment (Prica *et al*., 2008). Sulfides of Fe and Mn are less stable than other trace metals, so these two metals did not take into account in the calculation. As mentioned in Chapter 2, Fe and Mn are one of the most important binding phases for metals in oxidized sediment, therefore Fe and Mn concentrations were determined for this purpose.

These metals were determined, after filtration through GF/C glass fiber filter, by atomic absorption spectrometer (AAS). The AVS-SEM technique is described in Allen *et al.* (1991) and summarized in Appendix B.

3.5 Grain size composition analysis

The freeze-dried sediment samples were pretreated to remove organic matter (OM) using technique slightly modified from Loring and Rantala (1979) by Sompongchaiyakul (1989). After removal of the OM using 10% hydrogen peroxide (H_2O_2), the samples were treated with 10% HCl to remove carbonate materials. The treated sediment samples were then oven dried before using.

Exactly weighed the pretreated sediment, record to 2 decimals, and wet-sieved through a 63-µm sieve. The retained portion on the sieve is called sand fraction. The fraction that passed through the 63-µm sieve was later analyzed for percentages of silt- and clay-sized particles using sedimentation technique as described in Sompongchaiyakul (1989) and detailed in Appendix C. Percentage of fine grain (< 63 µm) particles in the sediments were used for metal data normalization.

3.6 Carbonate content analysis

Carbonate content in the freeze-dried sediment samples was ground in an agate mortar, pass through 63 µm nylon sieve, and determined by acid-base titration according to Sompongchaiyakul (1989). Carbonate materials in the sediment reacted with 0.5 N HCl. The unused HCl was back titrated with 0.25 N NaOH. The detailed methodology is described in Appendix D. Percentage of carbonate materials in the sediments were used for metal data normalization.

3.7 Organic matter analysis

The OM in the ground freeze-dried sediment was determined by modified Walkley-Black method, so called chromic acid method (Loring and Rantala, 1992). The sediments were allowed to be oxidized by potassium dichromate ($K_2Cr_2O_7$). The unused $K_2Cr_2O_7$ was determined by back titration with ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2$) solution. Full details are described in Appendix E.

3.8 Extraction of non-lattice held metals

Metals contained in non-lattice fraction were extracted by acetic acid (CH_3COOH) according to Loring and Rantala (1992) (Appendix F). The CH_3COOH method was chosen because it is one of the weakest chemical treatments that can be used to remove effectively the weakly bound part of the total metal concentrations sediments, so called non-lattice held (acid soluble) fraction.

The ground freeze-dried sediment was used in this analysis. The concentration of metals was analyzed by AAS. The metal remaining in the residual fraction is defined as the lattice-held (acid-insoluble) fraction of the sediment. Such fractionation allows some deductions as to the carriers, transport mode and potential bio-availability of metals entering and within these different systems.

3.9 Digestion of total metals

To liberated all metals, sediment was digested using hydrofluoric acid (HF) and aqua regia (HNO_3:HCl, 1:3), a concentrated oxidizing acid, according to Loring and Rantala (1992) (Appendix G). The ground freeze-dried sediment was used in this analysis. The concentrations of total metals were analyzed by AAS.

This method has a certain advantage since HF is the only acid that completely dissolved silicate lattices and releases all associated metals, such as aluminium (Al), iron (Fe) and lithium (Li), which are used for the normalization of the metal data.

3.10 Quality control

In order to validate the results, 10% of samples were performed in duplication for all analyses. Standard deviation (Eq. 3-1) was used to estimate the precision of average value. Standard error of the mean was calculated using Eq. 3-2. The average values of the duplicate samples were report as average ± standard error. The uncertainty or precision of the analyses was calculated using the relative standard deviation expressed in percent (%RSD) (Eq. 3-3).

$$SD = \sqrt{\frac{(X_1 - \mathcal{X})^2 + (X_2 - \mathcal{X})^2}{n-1}} \tag{3-1}$$

$$SE = \frac{SD}{\sqrt{n}} \tag{3-2}$$

$$\%RSD = \frac{SD}{\mathcal{X}} \times 100 \tag{3-3}$$

where SD = standard deviation of the measurement
X_i = individual measurement, $i = 1, 2, \ldots, n$
$\mathcal{X}$ = average value
n = number of measurement
SE = standard error of the average value
$\%RSD$ = relative standard deviation

Usually, acceptable %RSD value of general parameter is < 10% for a good precision. For analysis dealing with many analytical steps and low concentration level which prone to error, satisfactory precision for all analyses in this study were required to be < 20%, or %RSD < 20% (Chen and Ma, 1998).

CHAPTER IV

Results and discussion

4.1 The sedimentological setting

Size composition of sediments of the upper Gulf of Thailand (U-GOT) and the Chao Phraya river mouth are shown in Tables H-1 and H-2, Appendix H. The size compositions in term of percentage by weight of sand, silt and clay were plotted in ternary (or triangular) diagrams proposed by Graham *et al.* (2000). The texture of sediment was categorized based on the Graham's ternary diagram.

4.1.1 Sediment texture of sediments in the upper Gulf of Thailand

Figure 4-1 illustrates a ternary plot of sediment collected from the U-GOT. The sediment from the U-GOT could be classified into 8 types namely silt, silty sand, sandy clay, sandy silt, clayey sand, sand silt clay, clayey silt and silty clay. The amount of each type was found in increasing order of abundance respectively. The distribution pattern of fine grain (< 63 μm) sediment is shown in Fig. 4-2.

According to Dharmvanij (1987) and others, the U-GOT sediments are very much likely to be under the direct influence of the four river namely Chao Phraya, Tha Chin, Mae Klong, and Bangpakong.

4.1.2 Sediment texture of sediments at the Chao Phraya river mouth

The ternary plot of sediment collected from the Chao Phraya river mouth is illustrated in Fig. 4-3. In general, sediments from the Chao Phraya river mouth are finer than those of the U-GOT. The distribution pattern of fine grain (< 63 μm) sediment is shown in Fig. 4-4. For the Chao Phraya river mouth, 5 types of sediments namely sand silt clay, silty sand, sandy silt, clayey silt and silt were classified.

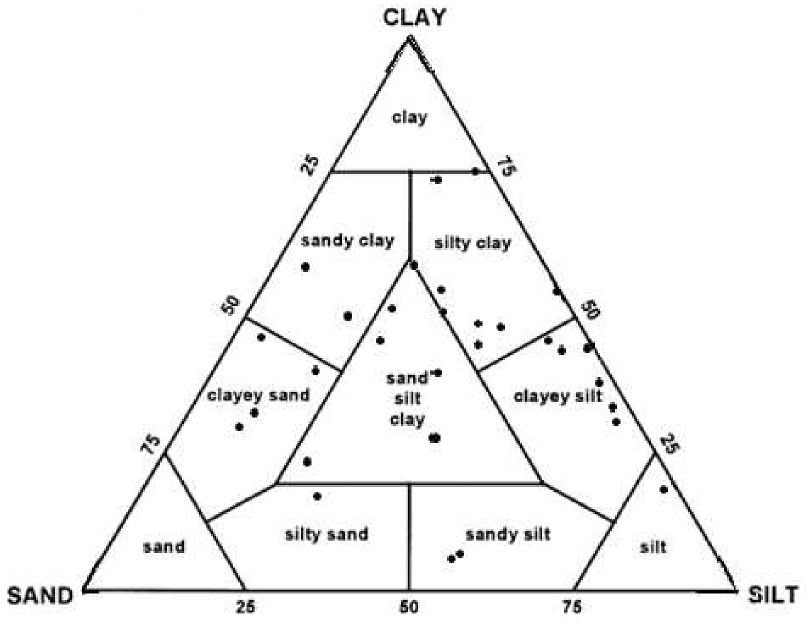

Figure 4-1 Triangular diagram of the sediments in the upper Gulf of Thailand collected during 23-25 August 2010.

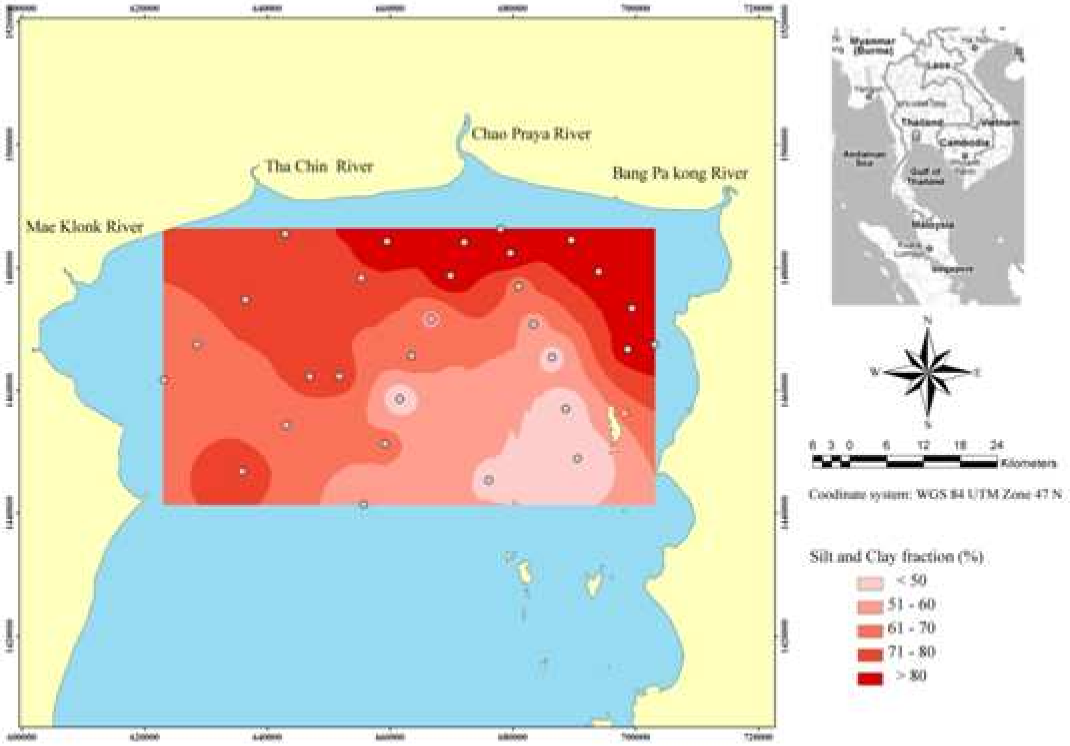

Figure 4-2 Distribution of fine particles (< 63 μm) composition in the sediments of the upper Gulf of Thailand collected during 23-25 August 2011.

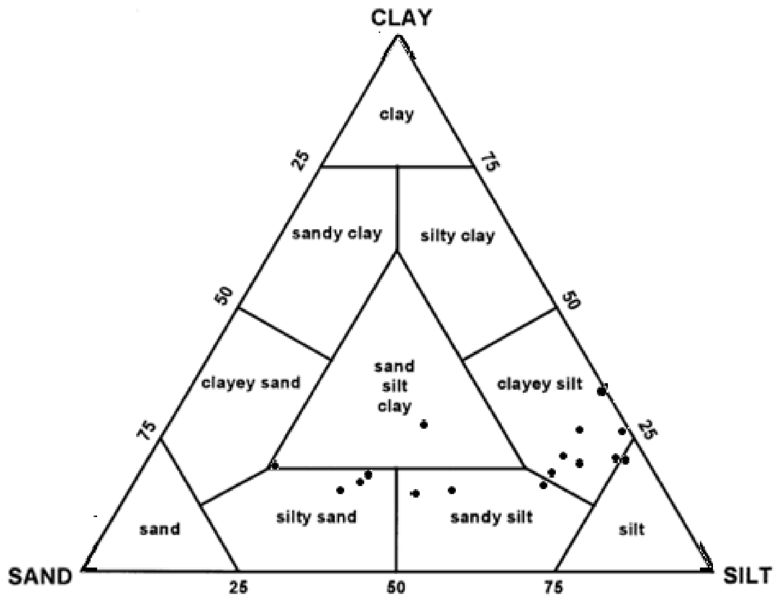

Figure 4-3 Triangular diagram of the sediments from the Chao Phraya river mouth collected on 9 March 2011.

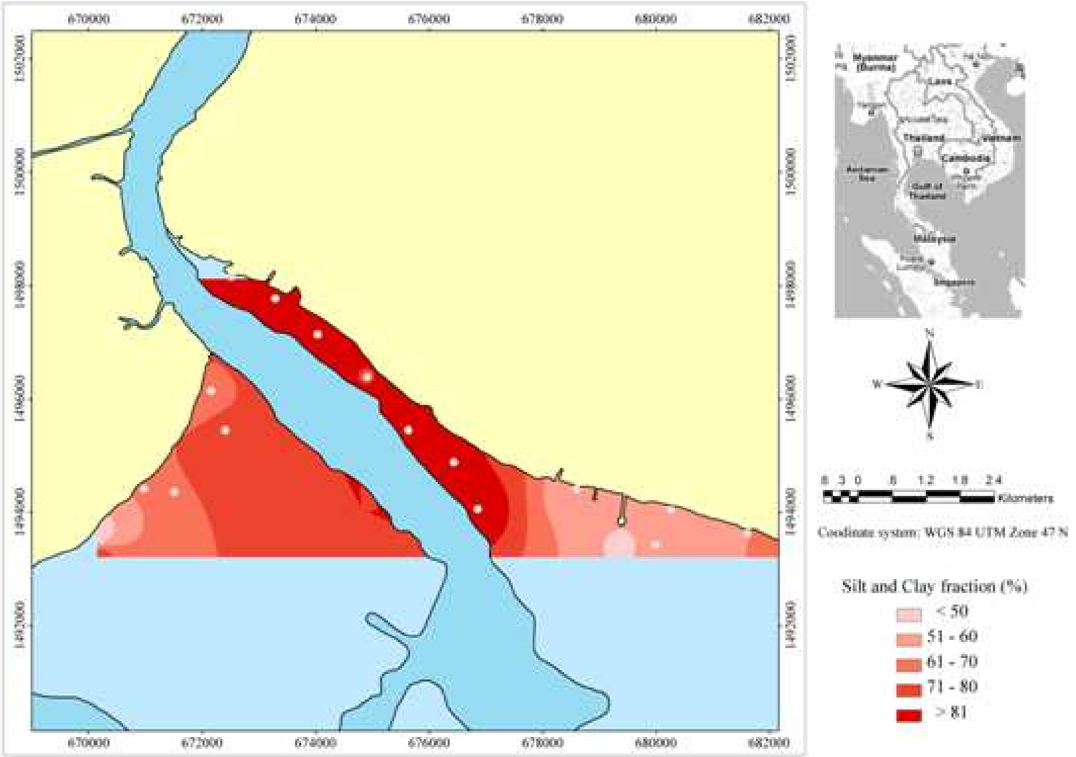

Figure 4-4 Distribution of fine particles (< 63 μm) composition in the sediments of the Chao Phraya river mouth collected on 9 March 2011.

4.2 Calcium carbonate content

Percentage of calcium carbonate in the U-GOT and the Chao Phraya river mouth sediments are presented in Tables H-1 and Table H-2, Appendix H, respectively. Average values, range and median of calcium carbonate in sediments are summarized and compared between two sampling sites in Table 4-1. The distribution pattern of $CaCO_3$ content in the U-GOT and the Chao Phraya river mouth sediment are shown in Fig. 4-5 and Fig. 4-6, respectively. It was found that sediments in the U-GOT contained about five times higher carbonate contents than those of the Chao Phraya river mouth.

Table 4-1 Average, minimum, maximum and median of carbonate content in the sediments of the upper Gulf of Thailand and the Chao Phraya river mouth

SITE	N	Average	Min	Max	Median
The U-GOT (August 2010)	30	11.3 ± 1.3	1.8	21.9	12.1
Chao Phraya river mouth (March 2011)	16	2.1 ± 0.5	0.9	4.24	1.98

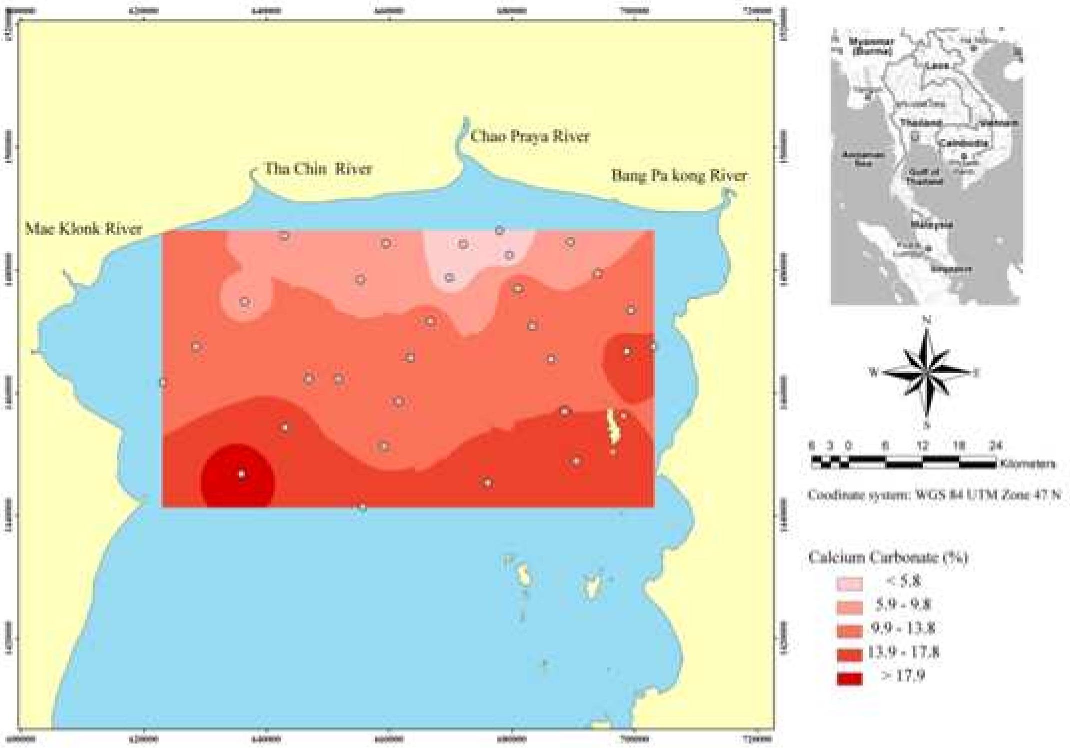

Figure 4-5 Distribution of calcium carbonate ($CaCO_3$) content in the sediments of upper Gulf of Thailand collected during 23-25 August 2010.

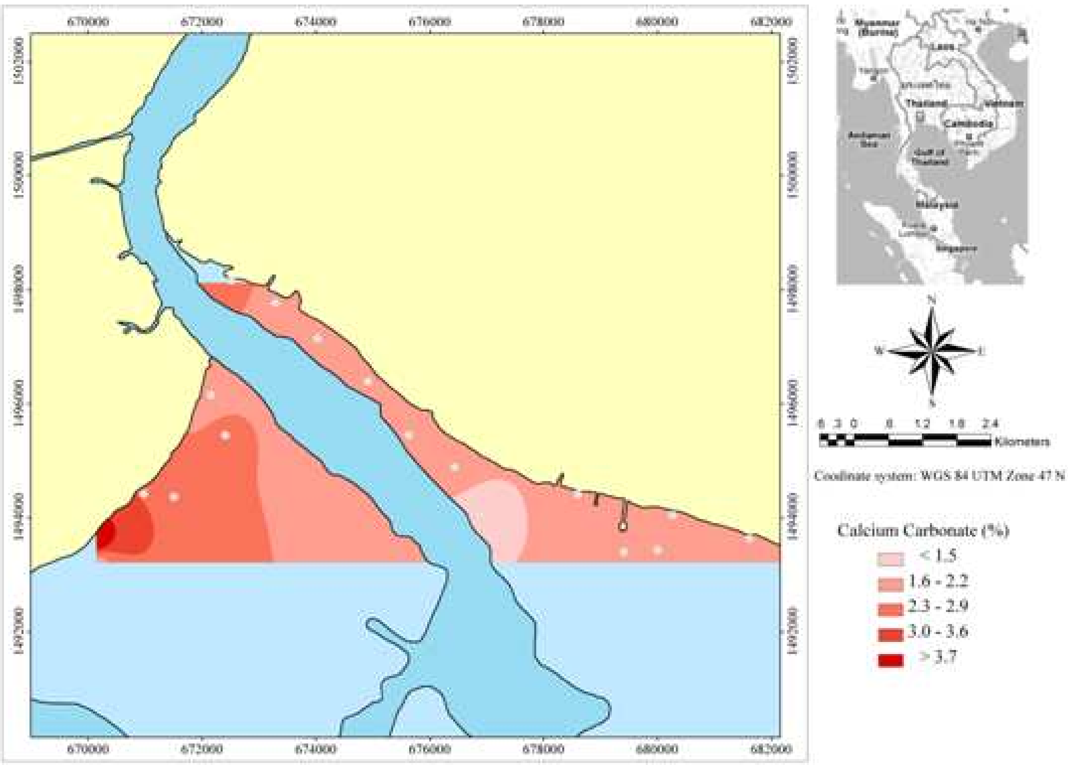

Figure 4-6 Distribution of calcium carbonate ($CaCO_3$) content in the sediments of Chao Phraya river mouth collected on 9 March 2011.

4.3 Readily oxidizable organic carbon content

The values of oxidize organic carbon content analyzed by the chromic acid method are more reliable, and give a better estimation for organic matter (OM) in the sediments (Sompongchaiyakul, 1989). The results of percentage of organic carbon in the U-GOT and the Chao Phraya river mouth sediments were presented in Tables H-1 and H-2, Appendix H.

Average values, range and median of organic carbon expressed as OM in sediments of the U-GOT and the Chao Phraya river mouth are compared in Table 4-2. The distribution patterns of OM in the U-GOT and the Chao Phraya river mouth sediments are shown in Figs. 4-7 and 4-8, respectively the OM in the sediment of both sites were in the same range with the average of 3.02 ± 0.49 and 3.09 ± 0.53 percent for the U-GOT and Chao Phraya river mouth.

The percentage of OM was found to be associated with fine grained sediment (< 63 μm), silt and clay, as shown in Fig. 4-9 since the fine grained sediment has high surface area and contains higher clay minerals (aluminosilicate) composition (Sompongchaiyakul, 1989).

Table 4-2 Average, minimum, maximum and median of organic matter in sediment of the upper Gulf of Thailand and the Chao Phraya river mouth.

Site	N	Average	Min	Max	Median
The U-GOT (August 2010)	30	3.02 ± 0.49	1.62	4.76	3.00
Chao Phraya river mouth (March 2011)	16	3.09 ± 0.53	1.37	4.65	3.17

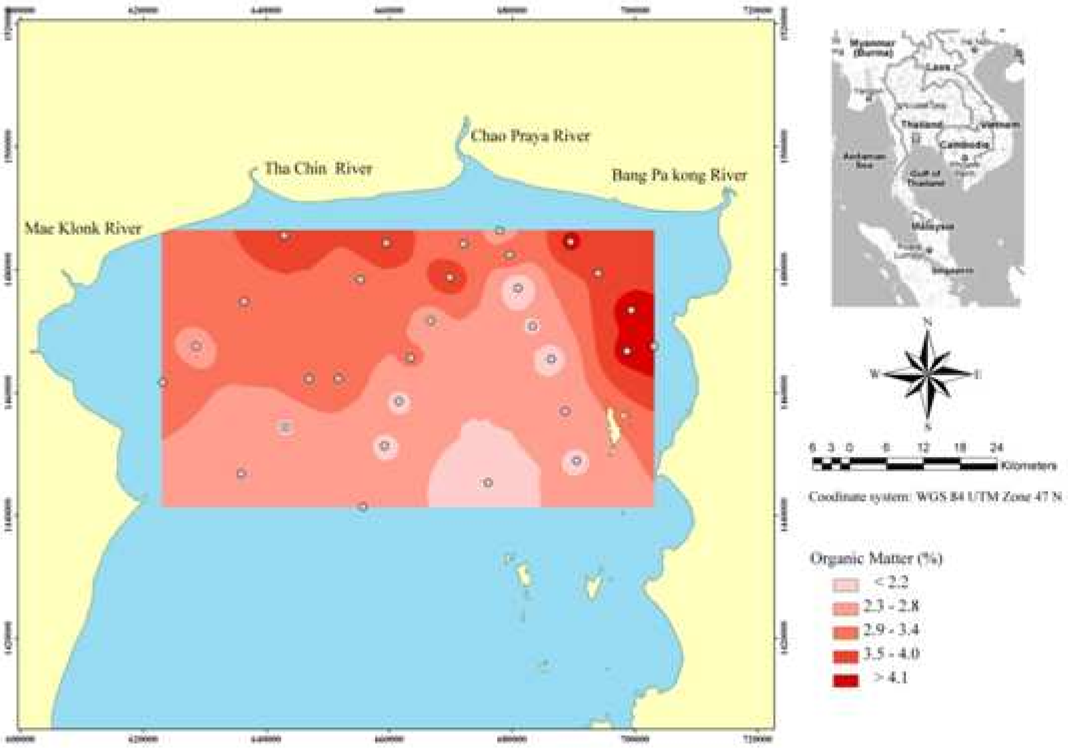

Figure 4-7 Distribution of organic matter in the sediments of upper Gulf of Thailand.

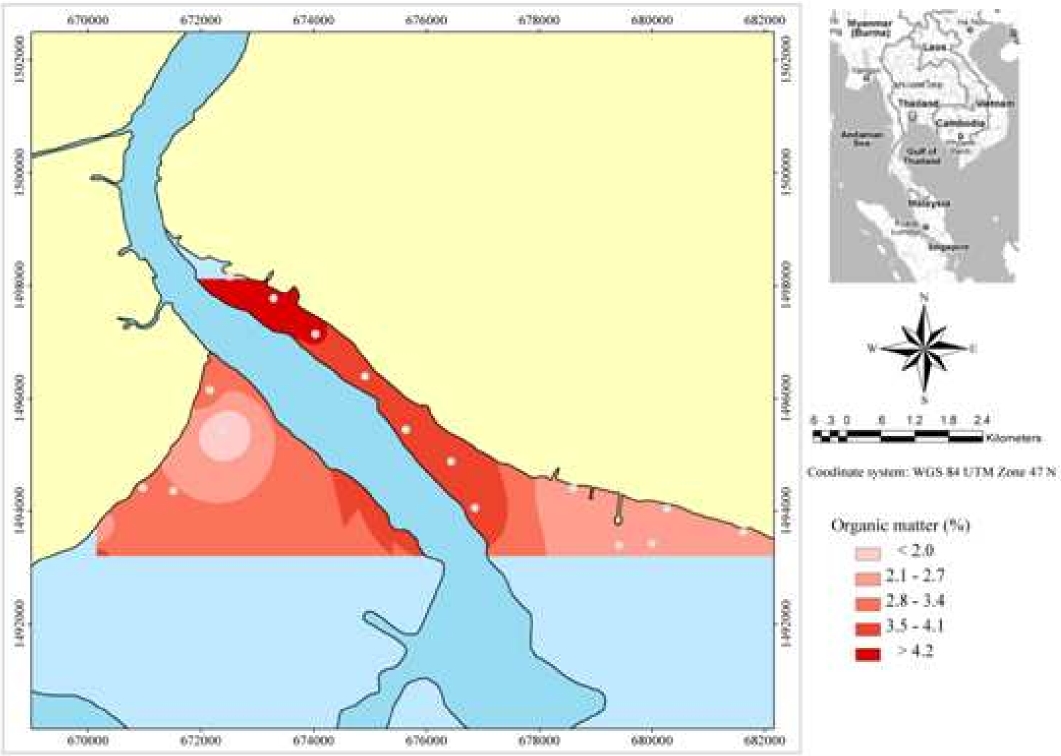

Figure 4-8 Distribution of organic matter in the Chao Phraya river mouth sediments.

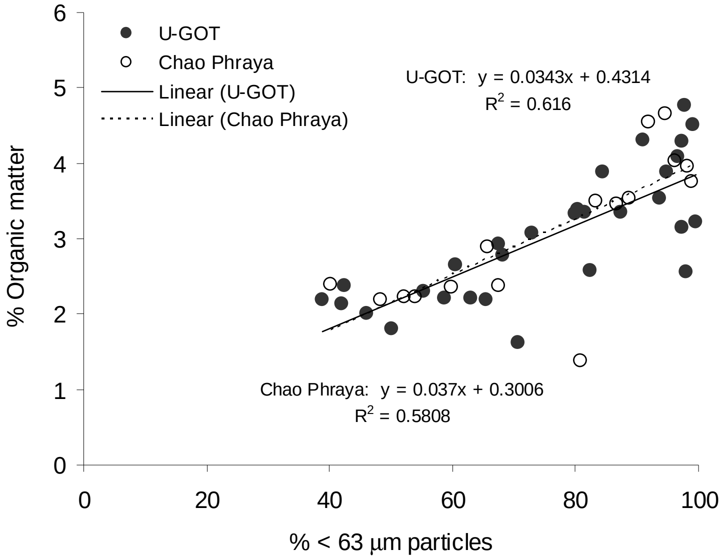

Figure 4-9 Correlation between organic matter and fine-grained fraction determined in 30 surface sediment samples of the upper Gulf of Thailand (U-GOT) and 16 surface sediment samples of the Chao Phraya river mouth.

4.4 Acid volatile sulfide with simultaneous extracted metals

The purpose of this experiment is to illustrate how AVS and SEM can be used to estimate the potential for toxicity of the sediment in the studied sites. In calculating the difference between the SEM and AVS concentrations of the samples, in order to estimate potential toxicity and to evaluate potential effects of metals on benthic species, the molar concentration of AVS was compared to the sum of SEM molar concentrations (∑SEM) for four metals: Cd, Cu, Pb and Zn.

The molar ratio of ∑SEM/AVS < 1 indicated no toxicity (or bioavailability) of the toxic metal ions (i.e., Di Toro *et al.*, 1992; Fang *et al*, 2005). On the other hand, ∑SEM/AVS > 1 suggested the metal may potentially exist as free metal and could cause toxicity.

The amount of AVS and SEM in the surface sediments of the U-GOT and the Chao Phraya river mouth are presented in Tables H-3 and H-4, Appendix H, and summarized in Table 4-3. The limit of detection of the method and instrument, obtained from three times of standard deviation of the blank, is 0.001 µmol/g.

Table 4-3 Average, minimum, maximum and median of AVS (µmol/g dry weight) in sediments of the upper Gulf of Thailand and the Chao Phraya river mouth

Site	N	Average	Min	Max	Median
The U-GOT (August 2010)	30	0.210 ± 0.318	0.008	1.367	0.070
Chao Phraya river mouth (March 2011)	16	1.753 ± 1.070	0.011	3.339	2.071

The AVS in the U-GOT (Table 4-4) was found in the range of 0.008-1.367 µmol/g dry weight, whereas in the Chao Phraya river mouth (Table 4-5) was 0.011-3.339 µmol/g dry weight. The concentrations of Cd, Cu, Pb and Zn in SEM fraction of the sediments ranged from 0.022–0.170, 0.59–8.8, 0.097–3.46 and 18.4-155.9 µg/g dry weight respectively, for the U-GOT, and from 0.049-0.155, 6.4-19.0, 11.7-26.4 and 80.6-187.1 µg/g dry weight, respectively, for the Chao Phraya river mouth. While Fe and Mn ranged from 1.1–19.4 and 0.48–2.36 mg/g dry weight, respectively, for the U-GOT, and from 9.4–70.8 and 0.7–18.8 mg/g dry weight, respectively, for the Chao Phraya river mouth.

The above resulted given the ∑SEM vary between 0.30 to 2.48 and 1.4 to 3.17 μmol/g dry weight in the U-GOT and the Chao Phraya river mouth sediments, respectively (Tables 4-4 and 4-5).

Table 4-4 The AVS, ∑SEM, ∑SEM/AVS ratio, ∑SEM-AVS and (∑SEM-AVS)/f_{oc} of the sediment in the upper Gulf of Thailand

Station	AVS (µmol S^{2-}/g)	∑SEM (µmol/g)	∑SEM/AVS	∑SEM-AVS	(∑SEM-AVS)/f_{oc}
2	0.789	1.89	2.4	1.1	44.0
3	0.613	1.99	3.2	1.4	66.9
4	0.182	1.17	6.4	1.0	37.7
5	1.367	2.36	1.7	1.0	67.1
6	0.021	1.79	87.0	1.8	94.4
7	0.021	1.06	49.4	1.0	110.3
8	0.008	0.53	64.5	0.5	41.0
9	0.015	0.45	29.3	0.4	37.5
10	0.021	0.46	21.5	0.4	31.7
11	0.090	1.60	17.7	1.5	82.1
12	0.038	2.48	65.3	2.4	102.8
13	0.543	0.90	1.7	0.4	23.4
14	0.072	0.56	7.8	0.5	28.5
15	0.120	0.42	3.5	0.3	24.3
16	0.040	0.59	14.7	0.6	43.5
18	0.792	1.23	1.6	0.4	19.5
19	0.255	1.03	4.1	0.8	39.9
20	0.164	0.65	3.9	0.5	24.9
21	0.501	0.67	1.3	0.2	8.8
22	0.067	0.30	4.4	0.2	18.1
23	0.044	0.55	12.5	0.5	38.0
24	0.027	0.44	16.3	0.4	27.7
26	0.160	1.26	7.9	1.1	48.8
27	0.104	1.02	9.8	0.9	47.0
28	0.026	0.50	19.5	0.5	29.6
29	0.077	0.80	10.4	0.7	40.6
30	0.039	1.61	41.5	1.6	56.7
31	0.016	0.51	31.9	0.5	38.9
32	0.013	0.35	27.7	0.3	32.0
33	0.063	1.06	2.4	1.0	39.7

All data was normalized by <63 µm% and % CaCO$_3$
∑SEM (µmol/g) = [Cu$_{SEM}$] + [Cd$_{SEM}$] + [Pb$_{SEM}$] + [Zn$_{SEM}$]
f_{oc} =fraction organic carbon (OC) concentration (according to Loring and Rantala (1992), OC = OM/1.72)

Table 4-5 The AVS, ∑SEM, ∑SEM/AVS ratio, ∑SEM-AVS and ∑SEM-AVS)/f_{oc} of the sediment in the Chao Phraya river mouth

Station	AVS (µmol S^{2-}/g)	∑SEM (µmol/g)	∑SEM/AVS	∑SEM-AVS	∑SEM-AVS)/f_{oc}
1	1.666	2.39	1.4	0.7	27.3
2	3.339	2.76	0.8	-0.6	-21.6
3	1.654	2.32	1.4	0.7	28.5
4	0.323	2.38	7.4	2.1	102.5
5	2.226	1.80	0.8	-0.4	-25.6
6	2.806	2.45	0.9	-0.4	-15.5
7	2.112	2.09	1.0	0.0	-0.9
9	2.397	2.11	0.9	-0.3	-13.1
10	0.012	2.51	202.5	2.5	193.4
11	0.011	3.17	292.1	3.2	247.6
12	3.123	2.04	0.7	-1.1	-136.2
13	0.239	2.03	8.5	1.8	138.3
14	1.162	1.75	1.5	0.6	42.9
15	2.212	2.98	1.3	0.8	55.4
16	2.743	2.40	0.9	-0.3	-24.8
17	2.029	1.44	0.7	-0.6	-29.0

All data was normalized by <63 µm% and % $CaCO_3$
∑SEM (µmol/g) = $[Cu_{SEM}] + [Cd_{SEM}] + [Pb_{SEM}] + [Zn_{SEM}]$
f_{oc} =fraction organic carbon (OC) concentration (according to Loring and Rantala (1992), OC = OM/1.72)

In this study, a trend towards increasing AVS concentration with a decreasing of sediment's Eh values of the Chao Phraya river mouth sediment was observed (Fig. 4-10). Reduction of sulfate (SO_4) to sulfides (S^{2-}) occurs at Eh values less than -120 mV (Bartlett, 1999). At Eh values above +120 mV, which indicate suboxic, moderately reducing conditions, the AVS concentrations were undetectable or negligible (Burton *et al.*, 2005b)

Low AVS concentrations in sediment of this study are possibly due to sulfide reoxidation of iron sulfide (FeS_2) at sediment surface rather than remaining in the form of AVS. The sulfide reoxidation at surface layer is affected by bioturbation, tidal mixing and the negative of redox potential (Holmer *et al.*, 1994; Charriau *et al.*, 2011).

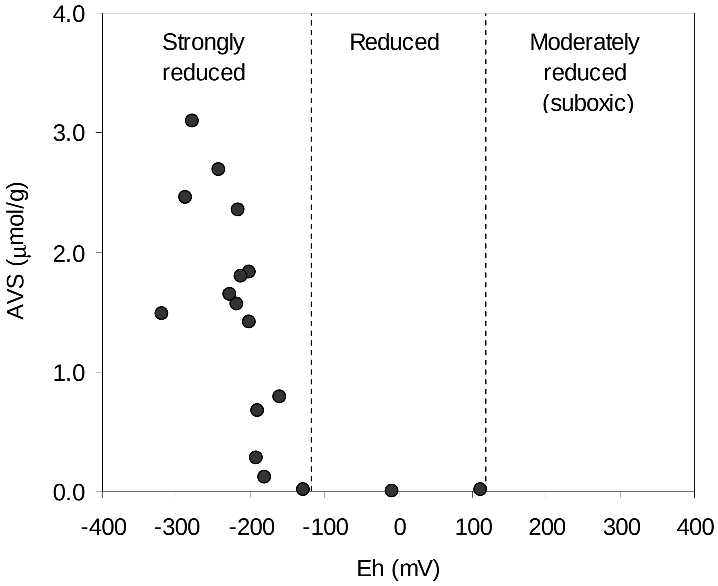

Figure 4-10 Relationship between redox potential (Eh) and acid volatile sulfide (AVS) determined in 16 surface sediment samples of the Chao Phraya river mouth. The three redox zones are based on the redox classification presented by Sposito (1989).

In most deposited sediment, the presence of Fe (III) can cause an underestimation of the AVS concentration. The Fe (III) minerals are fairly insoluble in high pH and high ionic strength like seawater and could be preserved in anoxic sediments along with sulfides. In strong acid medium during analysis, Fe(III) may dissolve and are perhaps allowing soluble Fe (III) to oxidize S^{2-}. Therefore, Fe(III) could interference on AVS analysis of sediments, and may be quite common in samples collected from tropical environment (Hsieh *et al.*, 2002).

Therefore, higher Eh profiles may not contribute to the stability of AVS compounds in the sediments, especially near the water-sediment interface, where partial reoxidation of sulfides occurs (Lesven *et al.*, 2008).

Since diagenetic production of sulfide is a function of porosity, sediment density, mixing intensity, OM loading, SO_4 diffusion coefficient in pore water, rate constant of SO_4 reduction and SO_4 concentration at the water sediment interface (Garcia *et al.*, 2007), the spatial and temporal variability of the AVS concentrations found in this study were probably related to water depth, sediment composition, redox potential and dissolved oxygen in the overlying water (Garcia *et al.*, 2011).

The distribution of AVS (Figs. 4-11 and 4-12) was found in similar pattern as of the pattern of OM (Figs. 4-7 and 4-8). High AVS levels seem to associate with elevated OM inputs both in the U-GOT and the Chao Phraya river mouth (Fig. 4-13). This evidence agrees with previously found in other estuarine regions (Meyer and Gersberg, 1977; Fisher *et al.*, 2004; Peng *et al.*, 2004; Garcia *et al.* 2011), since the presence of OM in large quantity may contribute to the formation of anoxic condition.

The low dissolved oxygen in estuarine water of the Chao Phraya river occurred due to high organics loading, average of 1.0 mg/l was found in A.D. 2009 (PCD, 2010). This could cause the depletion of AVS oxidation in surface sediment, and thus contribute higher values of AVS found in the sediments of the Chao Phraya river mouth in comparison to those of the U-GOT (Fig. 4-13).

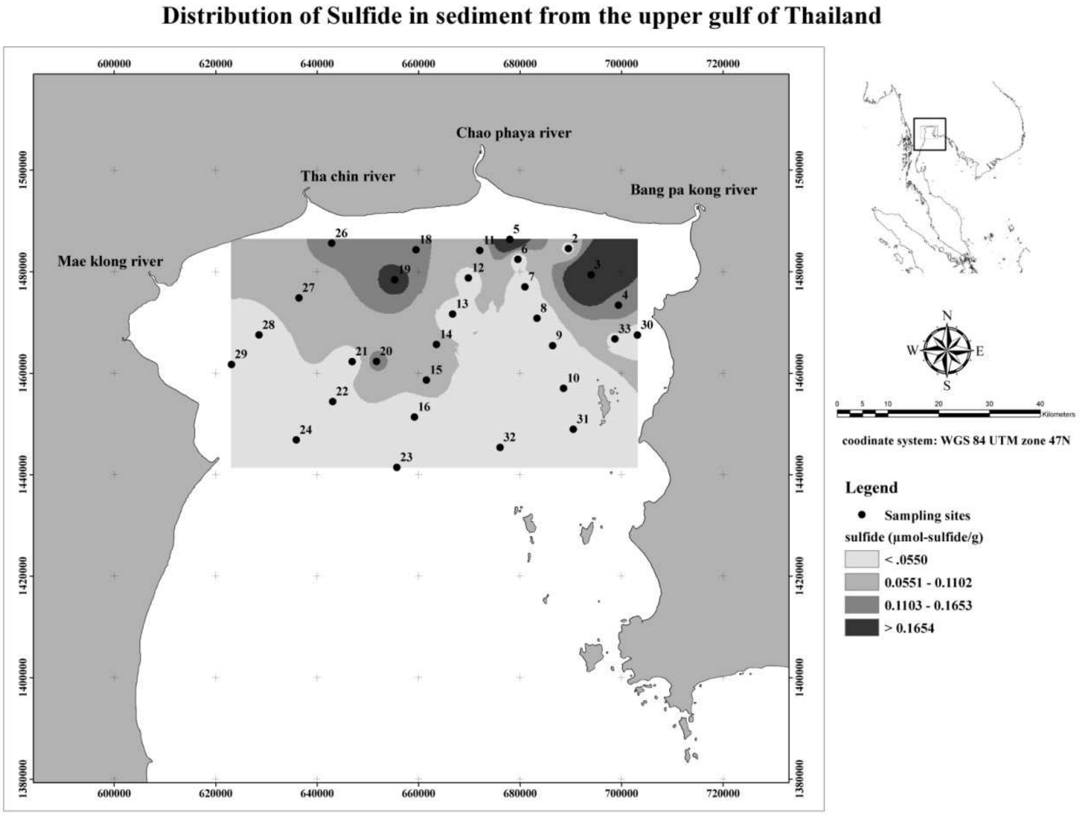

Figure 4-11 Distribution of acid volatiles sulfide (AVS) in the sediments of upper Gulf of Thailand collected during 23-25 August 2010.

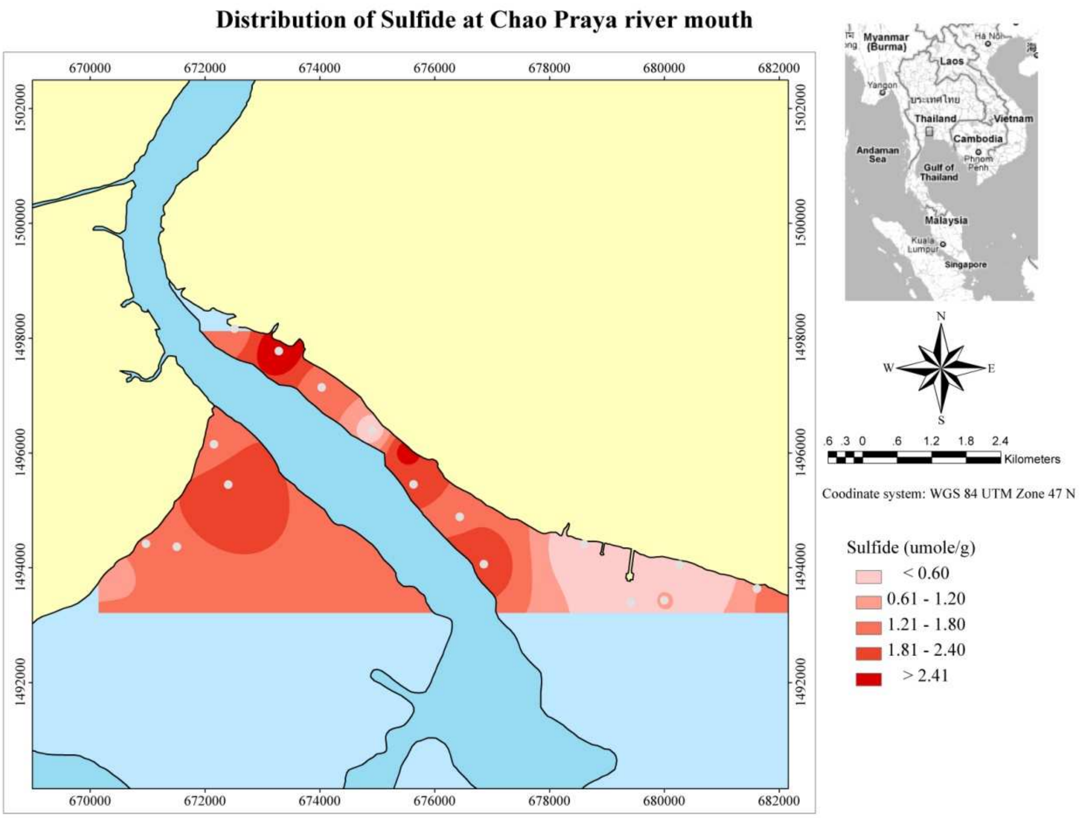

Figure 4-12 Distribution of acid volatiles sulfide (AVS) in the sediments of the Chao Phraya river mouth sediments collected on 9 March 2011.

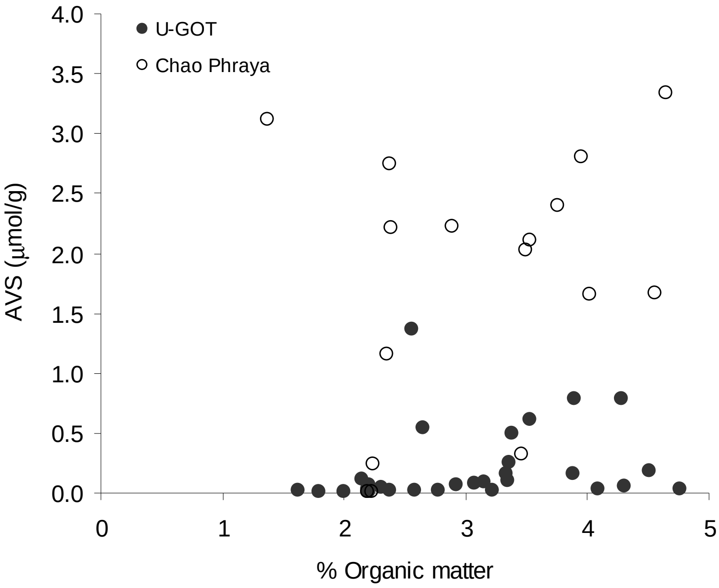

Figure 4-13 Correlation between organic matter (OM) contents and acid volatile sulfide (AVS) determined in 30 surface sediment samples of the upper Gulf of Thailand (U-GOT) and 16 surface sediment samples of the Chao Phraya river mouth

It was reported that the OM plays a major role in the accumulation heavy metals through both ion exchange and chelation. Organic matter is also important in the bacterial formation of biogenic sulfides and provides the reducing capacity necessary for many redox reactions to proceed.

In this study, all stations in the U-GOT and 8 stations at the Chao Phraya river mouth (Stations 1, 3, 4, 10, 11, 13, 14 and 15) having ∑SEM/AVS in sediment > 1 (Tables 4-4 and 4-5) because the AVS at the surface sediment was less than ∑SEM in all stations.

Although the AVS plays an important role in influencing bioavailability of trace metals by removing metals from biologically available chemical species into insoluble sulfides, the sedimentary sulfide system is considering a highly dynamic nature (Yin *et al*., 2008). The reactions between H_2S and oxides, in addition to bioturbation and bioirrigation can cause an oxidation of reduced sulfides in anoxic sediments for over 90% (Lin and Morse, 1991). Accordingly, oxidation processes within sediments can liberate metals that immobilized by the AVS in forms of sulfide minerals. Bottom trawling, dredging activities and storms are the processes that can induce sediment resuspension of which resulting in rapid oxidation in sediment and released metals associated to AVS (Fang *et al.*, 2005).

The incorporation of transition metals into the pyrite phase is influenced by the presence of other competing mineral phases. The adsorbing surfaces of these phases (e.g. clays, Fe/Mn oxyhydroxides) may increase significant amount of metals presented outside a sulfide phase even under conditions where metal sulfide precipitation is favorable (Oakley *et al.*, 1980).

For the group of divalent metals, the sum of the SEM (∑SEM) must be considered, with the assumption that the metal with the lowest solubility product constant (K_{sp}) values will be the first to incorporate with AVS. The K_{sp} of sulfide is in the order of HgS < CuS < PbS < CdS < ZnS < NiS < FeS. As such ZnS can dissolve more easily than Pb and Cd. If excess metal remains, then the most soluble metal, Zn, will appear as free ion species and make the toxicity become possible (Di Toro *et al.*, 1992).

According to Henson *et al.* (1996) (Table 4-6), when ∑SEM/AVS ≤ 1, there was an almost complete absence of toxicity in both spiked sediments and field sediments where metals were the only know source of contamination.

Table 4-6 Toxicity of sediments from saltwater lab spiked sediment test, field locations, and combined lab-spiked and field sediment tests as a function of the molar concentrations of SEM and AVS (SEM/AVS)

Study Type/Parameter		Value	n	Percent of sediments	
				Nontoxic[a]	Toxic[b]
Laboratory Spike :					
	SEM/AVS[c]	≤ 1.0	101	98.0	2.0
	SEM/AVS[c]	> 1.0	95	26.3	73.7
Field :					
	SEM/AVS[c]	≤ 1.0	57	98.2	1.8
	SEM/AVS[c]	> 1.0	79	59.5	40.5
Lab-Spike and Field :					
	SEM/AVS[c]	≤ 1.0	158	98.1	1.9
	SEM/AVS[c]	> 1.0	174	42.0	58.0

Sources: Hansen e*t al.* (1996)

[a] Nontoxic sediment ≤ 24% mortality

[b] Toxic > 24% mortality; sources

[c] An SEM/AVS ratio of ≤ 1.0 indicates an excess of sulfide and probable nontoxic sediment. An SEM/AVS ratio of > 1.0 indicates an excess of metal and potentially toxic sediments.

However, many researchers found toxicity still not occur even the ∑SEM /AVS in the sediment was higher than 1 (Di Toro *et al.*, 1992; Allen *et al.*, 1993; Ankely *et al.*, 1996; Burton *et al.*, 2005a)

Di Toro *et al.* (1992) reported the case of Foundry Cove that the metals concentration ranged from 0.1 to 28 µmol SEM/g were not toxic in some sediments, whereas metals concentrations range of 0.2–1,000 µmol SEM/g in some sediments were toxic. The results of Di Toro *et al.* (1992) indicated that bioavailable fraction of metals in sediments could vary from sediment to sediment. In their studies, there was a clearly distinguish of mortality-concentration relationship. They observed no mortality exceed 50% when ∑SEM/AVS = 1, although, theoretically, mortality should begin to occur at this value. The mortality increased dramatically when ∑SEM/AVS > 1–3. And 80-100% of individuals from all test species died if ∑SEM/AVS in sediment was > 10.

If ∑SEM/AVS > 10 is used for consideration in this study, 16 stations in the U-GOT (Stations 6-12, 16, 23, 24, 27-32) and 2 stations at the Chao Phraya river mouth (Stations 10 and 11) have the ∑SEM/AVS > 10 (Tables 4-4 and 4-5). The sediments of these 2 stations contained low concentrations of AVS (0.011 and 0.012 µmol/g dry weight). Coincidently, these 2 stations are located on the east-side of the river mouth, near Bang Pu Industrial Estate, established since A.D. 1977, where industrial activities have been intense (Fig. 4-14). The AVS in these 2 stations were very low in comparison to other stations. It is suspected that the OM load in this area is low while metal loading remaining high, or the bottom sediment of which high organic matters has been dredged off to clear the area while building the new wharf and jetty during the renovation of QM. Bangpu Recreation Center of Royal Thai Army in A.D. 2000.

Burton *et al.* (2005a) carried out a long period field toxicity experiment and concluded that sediments with a ∑SEM/AVS ≥ 8.32 would result in high toxicity to macroinvertebrate. The ratios of ∑SEM/AVS between 2.0 to 8.32 are occasionally toxic, while ∑SEM/AVS < 2.0 are not toxic.

Using the ratios proposed by Burton *et al.* (2005a) for consideration in this study, there are 26 station of the U-GOT (all stations excluding Stations 5, 13, 18 and 21) and 4 stations at the Chao Phraya river mouth (Stations 4, 10, 11 and 13) having the ∑SEM/AVS > 2. Although the ∑SEM/AVS ≥ 8.32, there are 16 stations of the U-GOT (Stations 6-12, 16, 23, 24, 27-32) and 3 stations of the Chao Phraya river mouth (Stations 10, 11 and 13) fall into this category (Tables 4-4 and 4-5), which is similar to using ∑SEM/AVS > 10 presented in Di Toro *et al.* (1992).

Another approach for interpretation of SEM and AVS results is the use of the ∑SEM – AVS difference instead of using the SEM to AVS ratio (Burton *et al.*, 2005a). This approach regards the magnitude by which AVS binding has been exceeded. At a molar ∑SEM – AVS ≤ 0, no effects are expected to occur but it cannot whether toxicity will occur if ∑SEM – AVS > 0. Using this approach for consideration in this study, all stations in the U-GOT (Table 4-4) and 8 stations at the Chao Phraya river (Stations 1, 3, 4, 10, 11, 13, 14 and 15) (Table 4-5) having ∑SEM – AVS > 0.

Figure 4-14 The sampling stations 10 and 11 of the Chao Phraya river mouth, where $\sum SEM_2/AVS > 10$, locate near Banpu wharf and jetty of QM. Bangpu Recreation Center of Royal Thai Army. There is an industrials estate nearby on shore.

According to the USEPA (2004), when $\sum$SEM – AVS is between 0-5, the sampling site will likely cause toxicity to benthic biota. Additionally, if $\sum$SEM – AVS > 5, metals at sampling site cause adverse effects on aquatic life. No station in the U-GOT and the Chao Phraya river mouth having the $\sum$SEM – AVS > 5.

Since organic carbon (OC) is an important partitioning phase for metals both in sediment and water, Burton *et al*. (2005a) used the fraction of OC (f_{oc}) to normalize the excess $\sum$SEM. It was found in comparisons with toxicity data that a boundary for chronic effects exists when $\sum$SEM – AVS/f_{oc} is in excess of 100-150 µmol/g of OC, allowing the prediction of toxicity (Burton *et al*., 2005a). Using this category for consideration in this study, there are only 2 stations in the U-GOT (Stations 7 and 12) and 4 stations at the Chao Phraya river mouth (Stations 4, 10, 11 and 13) having $\sum$SEM – AVS/f_{oc} > 100 (Tables 4-4 and 4-5).

From all approaches above, Stations 7 and 12 in the U-GOT and Stations 4, 10, 11 and 13 were fall into all categories, this reveals that metals containing in the sediments of these areas may occasionally cause toxic to the benthic biota. However, Stations 10 and 11 may be an exceptable case as aforementioned.

Fang *et al.* (2005) suggested that AVS may not be the major metal-binding phase in the surface sediments or the sediments of the river outlet area. They explained that after SEM being fully incorporated into the sulfide phase, the remaining SEM may be selectively bound with other components of sediments or remobilized into porewater. Table 4-7 shows correlation coefficients between SEM, AVS, organic matter (OM) and percentage of fine grain particles (< 63 µm) in sediments.

In the U-GOT, OM, AVS and all SEM were correlated with fine particles at different significant levels. Fe and Mn show a high relationship to each other. As grain size decreases, trace element concentrations increase, reflecting changes in physical and chemical factors which affect trace elements (Horowitz and Elrick, 1987). Cd was associated with OM and fine particles. Cu associated with fine particles > OM > AVS > Mn. Pb associated with Cu > AVS > Mn. While, Zn related to fine particles > Cu > Fe > Mn > OM > Pb. Only Cu and Pb show a high relation with AVS, while Zn show high relation with Fe and Mn. Cd, Cu and Zn are related with OM, but not Pb.

In the Chao Phraya river mouth, only OM and Cd show positive correlated with fine grain particles. Fe and Mn have a very high correlation to each other. At the river mouth, under normal oxic condition of seawater, along with high pH and high ionic strength, Fe and Mn are mainly presented in the forms of insoluble species. Dissolved Fe and Mn released into the overlying oxic water are immediately precipitated out of the water column, and inducing co-precipitation of other dissolved trace metals (Salomons and Förstner, 1984). They are inversely trend with the percentage of fine grain particles.

Table 4-7 Correlation coefficient values between simultaneously extracted metals, organic matter, acid volatile sulfide and percentage of fine grain particles (< 63 μm) in sediments.

a) The upper Gulf of Thailand

	< 63 μm	OM	AVS	Fe_{SEM}	Mn_{SEM}	Cd_{SEM}	Cu_{SEM}	Pb_{SEM}	Zn_{SEM}
<63 μm	1	0.786^{**}	0.414^{*}	0.453^{*}	0.414^{*}	0.421^{*}	0.706^{**}	0.395^{*}	0.779^{**}
OM		1	0.231	0.125	0.101	0.543^{**}	0.666^{**}	0.259	0.573^{**}
AVS			1	0.231	0.125	0.101	0.543^{**}	0.666^{**}	0.259
Fe_{SEM}				1	0.653^{**}	0.180	0.241	0.160	0.662^{**}
Mn_{SEM}					1	0.276	0.474^{**}	0.586^{**}	0.650^{**}
Cd_{SEM}						1	0.398^{*}	0.410^{*}	0.442^{*}
Cu_{SEM}							1	0.726^{**}	0.748^{**}
Pb_{SEM}								1	0.507^{**}
Zns_{SEM}									1

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

b) The Chao Phraya river mouth

	< 63 μm	OM	AVS	Fe_{SEM}	Mn_{SEM}	Cd_{SEM}	Cu_{SEM}	Pb_{SEM}	Zn_{SEM}
<63 μm	1	0.762^{**}	0.502^{*}	-0.730^{**}	-0.745^{**}	0.671^{**}	0.220	-0.325	-0.272
OM		1	0.291	-0.441	-0.572^{*}	0.632^{**}	0.246	-0.299	0.001
AVS			1	-0.189	-0.102	0.337	-0.439	-0.642^{**}	-0.056
Fe_{SEM}				1	0.929^{**}	-0.332	-0.282	-0.074	0.580^{*}
Mn_{SEM}					1	-0.546^{*}	-0.418	-0.084	0.501^{*}
Cd_{SEM}						1	0.396	-0.195	0.133
Cu_{SEM}							1	0.573^{*}	0.020
Pb_{SEM}								1	-0.043
Zns_{SEM}									1

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

The adsorbing capacity of heavy metals, are linked with the surface area and surface properties of the particles. In this way, the clay minerals and other components like quartz and feldspar grains are usually coated with hydrous Mn and Fe oxides, and by organic substances. These coatings additionally regulate metal concentration in solution (Salomons and Stigliani, 1995). Thus, SEM and AVS cannot be used alone to predict toxicity of sediments contaminated with toxic concentration of other contaminants. However, SEM and AVS have been used in sediment assessment to rule out metal as probable causative agents of toxicity (Wolfe *et al.*, 1994).

Also the use of SEM and AVS to predict bioavailability and toxicity of Cd, Cu, Pb, and Zn is applicable only to anaerobic sediments that contain AVS; binding factors other than AVS control bioavailability in aerobic sediment (Tessier *et al*., 1993).

Although ∑SEM and AVS in different approaches are useful tools for assessment the quality of sediment and can predict the availability of various metals for difference organisms to a certain extent (Di Toro *et al.*, 1992; Tessier *et al.*, 1993; Wolfe *et al.*, 1994; USEPA, 2004; Burton *et al*., 2005a; Fang *et al.*, 2005; Hübner *et al*., 2009), using of the AVS-SEM relationship alone as a primarily tool for assessing metal risk for surface sediment is limited. However, it is good to use as a screening tool.

4.5 Non-lattice held fraction and total metals in sediments

The metals in non-lattice held and total fraction of sediments are used as quality control in this study. The SEM concentration should not be more than total metal or should be nearly the concentration of non-lattice held metal. The concentrations of SEM, non-lattice and total metals in studied sediment are presented in Fig. 4-15. The concentration of total fraction is generally higher than the concentrations of SEM and non-lattice fraction. Not all metals in total metal fraction are the bioavailable concentration because a proportion of may not incorporate in the labile fraction. Weimin *et al.* (1992) found total metal concentration had no correlation coefficients of metal uptake by organism. The bioavailability, mobility or toxicity these properties basically depend on different chemical forms of binding between trace metals and solid phases of the sample (Ghaedi *et al.,* 2007). As such the total metals content in polluted environmental samples is a poor indicator. For the non lattice fractionation allows some deductions as to the carriers, transport mode and potential bioavailability of metals entering and with in different systems (Loring, 1981) The concentration of SEM and that of non lattice held fraction should, therefore, be concerned for bioavailability of metals.

In Fig. 4-17, most metal values in the Chao Phraya river mouth sediment were higher than those of in the U-GOT sediment. The distribution of trace metal concentrations in sediment, descending towards the sea, is similar to that observed in other rivers and estuaries with point sources of pollution (Förstner *et al.*, 1990).

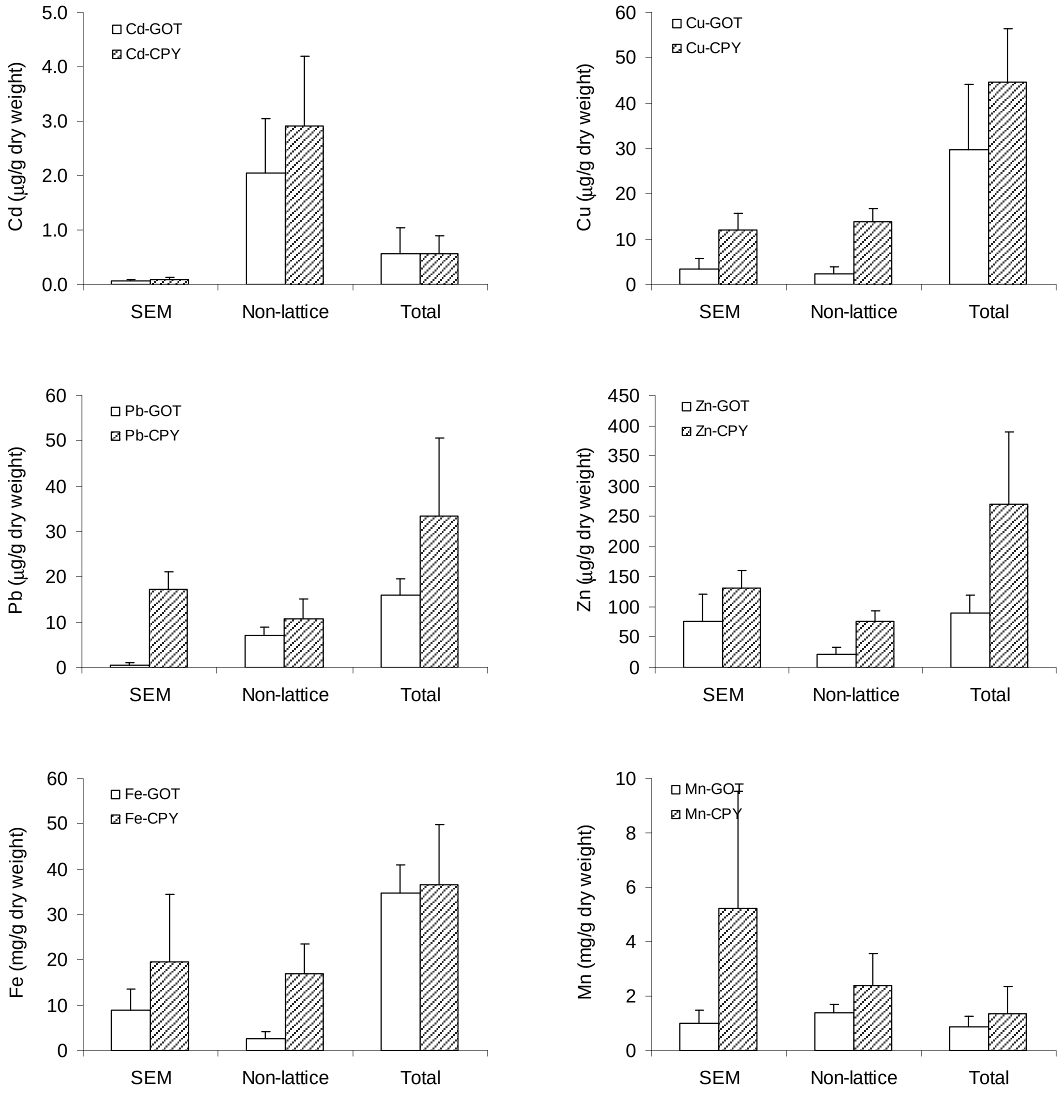

Figure 4-15 Comparison of average values of metal concentration in three fractions; simultaneous extracted metals (SEM), non-lattice held metals and total metals of 30 surface sediment samples of the upper Gulf of Thailand (GOT) and 16 surface sediment samples of the Chao Phraya river mouth (CPY).

4.6 Quality control of analytical results

Since the possibility of analytical replication for all samples is tough and tedious to perform under the restriction of time and funding, as well as collecting more samples from the same site would not represent the true replication, a quality control approach was devised.

Approximately 10% of the number of total samples for each batch of sample was randomly sampled and undergone replicated analysis. Relative standard deviation of the replicated analyses was calculated.

As has been stated in Chapter 3, the %RSD of the replicated analyses of environmental samples that varied between 2- 20% is acceptable as a result of denpendcy on the samples' matrix, concentration range, combined instrument performance, and analytical techniques.

The results of our quality control is shown in Table H-7 to H-12 in Appendix H and are all still in the acceptable range of the above criteria.

CHAPTER V

Conclusion

Between the two study sites, the Chao Phraya river mouth sediments contain higher proportion of fine grain particles than those of the upper Gulf of Thailand (U-GOT). High concentration of organic matter (OM) was found near the river mouth, and was related to proportion of fine grain particles. Calcium carbonate content was low at the Chao Phraya river mouth and increasing seawards.

The level of acid volatile sulfide (AVS), as well as its variation, was higher towards the river mouth. This trends was likely resulted from high OM loading and strong reducing conditions in the sediments (as shown by their reduction potential).

To estimate the potential toxicity of Cd, Cu, Pb and Zn in the estuarine sediments of Thailand, particularly the Chao Phraya river mouth, the U-GOT, the simultaneously extracted metals (SEM) and acid volatile sulfides (AVS) method was employed. Various approaches dealing with the sum of SEM in molar concentrations (∑SEM, µmol/g) and the molar concentration of AVS ([AVS], µmol/g) were considered. The results are summarized in Table 5-1.

Table 5-1 Stations in the upper Gulf of Thailand and at the Chao Phraya river mouth that have higher values than criteria.

Approach	U-GOT[1]	Chao Phraya river[2]	Criteria taken from
∑SEM/AVS > 1	all station	8 stations: 1, 3, 4, 10, 11, 13, 14, 15	Di Toro *et al.* (1992) Ankley *et al.* (1996)
∑SEM/AVS > 10	16 stations: 6, 7, 8, 9, 10, 11, 12, 16, 23, 24, 27, 28, 29, 30, 31, 32	2 stations: 10, 11	Di Toro *et al.* (1992)
∑SEM/AVS > 2	26 stations: 2, 3, 4, 6, 7, 8, 9, 10, 11, 12, 14, 15, 16, 19, 20, 22, 23, 24, 26, 27, 28, 29, 30, 31, 32, 33	4 stations: 4, 10, 11, 13	Burton *et al.* (2005a)
∑SEM/AVS > 8.32	16 stations: 6, 7, 8, 9, 10, 11, 12, 16, 23, 24, 27, 28, 29, 30, 31, 32	3 stations: 10, 11, 13	
∑SEM – AVS > 0	all station	8 stations: 1, 3, 4, 10, 11, 13, 14, 15	
∑SEM – AVS/f_{oc} > 100	2 stations: 7, 12	4 stations: 4, 10, 11, 13	
∑SEM – AVS > 5	none	none	USEPA (2004)

[1] No sample from stations 1, 17 and 25 in the upper Gulf of Thailand (U-GOT)

[2] No sample from stations 8 from the Chao Phraya river mouth

Three types of criteria were being used in evaluation here; (i) $\sum$SEM/AVS ration, (ii) $\sum$SEM – AVS difference, and (iii) $\sum$SEM – AVS/f_{oc} > 100. According to the criteria in several literatures (i.e Di Toro *et al*., 1990; Ankley *et al*., 1996), the concentration of metals in the sediment porewater will be generally below toxic levels because of the low solubility of the metal sulfides if $\sum$SEM/AVS ratios is < 1. On the other hand, the sediment may be considered potentially toxic when this ratio is > 1. Although, theoretically mortality should begin to occur at this value but a long period toxicity study carried out by many researchers revealed that not all sediments with $\sum$SEM/AVS ratios > 1 can cause increasing in toxicity. Because there are many other metal-binding phases in sediments such as organic matter and Fe/Mn oxides (i.e. Ankley *et al*., 1996; Leonard *et al*., 1996; Chapman *et al*., 1999). Therefore, bioavailable fraction of metals in sediments can vary from sediment to sediment (Di Toro *et al.*, 1992).

The $\sum$SEM – AVS difference approach regards the magnitude by which AVS binding has been exceeded by the amount of metals extracted. At a molar $\sum$SEM – AVS ≤ 0, no effects are expected to occur but it cannot predict whether toxicity will occur if $\sum$SEM – AVS > 0. According to the USEPA (2004), no toxicity will occur when $\sum$SEM – AVS = 0-5, if $\sum$SEM – AVS > 5, metals at sampling site can cause toxic to aquatic life.

Taking quatity of organic carbon (OC) into account by normalizing the excess $\sum$SEM with the fraction of OC (f_{oc}), the boundary for chronic effects exists when $\sum$SEM – AVS/f_{oc} is in excess of 100-150 µmol/g of OC, thus allowing the toxicity to be predicted (Burton *et al*., 2005a).

According to USEPA (2004), none of the station in the study area falls in the category of toxic condition to the aquatic life. However, most criteria in Table 5-1 indicate that a few stations are likely to have a potential risk of metal pollution. This include Station 7 and 12 in the U-GOT and Stations 4, 10, 11, 13 at the Chao Phraya river mouth.

However, Stations 10 and 11 may be an exceptional case. These 2 stations contained very low concentrations of AVS (0.011 and 0.012 µmol/g dry weight) and were suboxic sediment (the redox potential (Eh); 112.0 and -9.2 mV respectively). Coincidently, they are located near Bang Pu Industrial Estate, where industrial activities have been intense. It is suspected that the OM load in this area is low while metal loading remaining high, or the bottom sediment of which high organic matters has been dredged off to clear the area while building the new wharf and jetty during the renovation of QM. Bangpu Recreation Center of Royal Thai Army in A.D. 2000.

In the USA, sediment quality criteria already account for the AVS. There are many researches on spiked and field-contaminated sediments demonstrated that the ∑SEM and AVS method is successful at predicting potential metal availability (Poot *et al*., 2009). The AVS, therefore, should be used primarily of a risk assessment as a screening and prioritization tool to focus expertise and resources (Chapman, 1995; US-EPA, 2005).

However, to use the AVS-SEM as the tool to predict metal availability and assess metal risk in the area that highly dynamic such as in estuarine region, it is necessary to evaluate factors controlling AVS behavior. Such factors include OM levels, redox potential (Eh), and probably other metal-binding phases.

Meanwhile, it would be suggested that sequential extraction procedure could be used as an additional tool with the AVS method for assessing the potential bioavailability and toxicity of metals in sediment of Thai’s river mouth and the Gulf of Thailand.

However, Sediment Quality Guidelines (SQGs) should not use any of these approaches alone when making decisions or taking management actions to migrate or remediate toxic effects from sediment heavy metals.

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APPENDICES

APPENDIX A

Sampling locations

Table A-1 Location of sampling stations in the upper Gulf of Thailand during 23-25 August 2010.

Stations	Latitude (°N)	Longitude (°E)	Water Depth (m)	Sampling date
2	13° 25' 20.460"	100° 45' 02.088"	9.8	25/08/2010
3	13° 22' 32.520"	100° 47' 29.220"	13.1	25/08/2010
4	13° 19' 15.888"	100° 50' 27.672"	12.2	25/08/2010
5	13° 26' 23.028"	100° 38' 38.472"	4.8	24/08/2010
6	13° 24' 14.832"	100° 39' 31.068"	11.8	24/08/2010
7	13° 21' 17.136"	100° 40' 15.312"	16.5	24/08/2010
8	13° 17' 55.284"	100° 41' 33.324"	20	24/08/2010
9	13° 14' 59.856"	100° 43' 13.872"	18.9	24/08/2010
10	13° 10' 25.356"	100° 44' 24.072"	21.9	24/08/2010
11	13° 25' 13.188"	100° 35' 21.480"	6.7	24/08/2010
12	13° 22' 16.536"	100° 34' 05.844"	9.8	24/08/2010
13	13° 18' 26.460"	100° 32' 20.256"	13.5	24/08/2010
14	13° 15' 11.772"	100° 30' 33.264"	14.3	24/08/2010
15	13° 11' 24.324"	100° 29' 26.124"	15.4	24/08/2010
16	13° 07' 27.120"	100° 28' 06.600"	16.9	24/08/2010
18	13° 25' 19.812"	100° 28' 23.412"	8.2	24/08/2010
19	13° 22' 07.788"	100° 26' 02.688"	10.2	24/08/2010
20	13° 13' 25.212"	100° 24' 00.612"	12.2	24/08/2010
21	13° 13' 25.212"	100° 21' 20.988"	14.7	24/08/2010
22	13° 09' 09.720"	100° 19' 12.072"	18.1	24/08/2010
23	13° 02' 05.100"	100° 26' 09.456"	20.1	24/08/2010
24	13° 05' 04.560"	100° 15' 12.528"	17.6	24/08/2010
26	13° 29' 56.652"	100° 19' 26.004"	6	23/08/2010
27	13° 20' 15.360"	100° 15' 34.632"	8.1	23/08/2010
28	13° 16' 18.840"	100° 11' 12.012"	11.1	23/08/2010
29	13° 13' 10.812"	100° 08' 10.428"	13.3	23/08/2010
30	13° 16' 03.828"	100° 52' 29.532"	9.5	25/08/2010
31	13° 06' 02.412"	100° 45' 25.992"	27.5	24/08/2010
32	13° 04' 09.552"	100° 37' 26.040"	18.9	24/08/2010
33	13° 15' 39.204"	100° 50' 02.796"	11.9	25/08/2010

Table A-2 Location of sampling stations at the Chao Phraya river mouth on 9 March 2011.

Stations	**Latitude (°N)**	**Longitude (°E)**	**Water Depth (m)**	**Eh (mV)**
1	13° 32' 50.400"	100° 35' 39.600"	2.0	-319.0
2	13° 32' 35.484"	100° 36' 04.788"	2.2	-277.6
3	13° 32' 14.784"	100° 36' 29.484"	3.1	-217.8
4	13° 31' 50.304"	100° 36' 58.500"	3.0	-192.0
5	13° 31' 47.100"	100° 35' 13.812"	0.8	-202.3
6	13° 31' 19.488"	100° 37' 22.296"	3.5	-241.8
7	13° 31' 00.912"	100° 37' 48.900"	3.1	-200.6
9	13° 30' 33.912"	100° 38' 02.796"	3.9	-216.7
10	13° 30' 45.000"	100° 39' 00.792"	2.0	112.0
11	13° 30' 13.896"	100° 38' 55.116"	3.5	-9.2
12	13° 31' 19.992"	100° 35' 35.016"	3.1	-288.5
13	13° 30' 36.000"	100° 39' 56.484"	1.3	-181.7
14	13° 30' 12.816"	100° 39' 47.088"	3.1	-189.6
15	13° 30' 50.688"	100° 34' 35.904"	1.0	-159.9
16	13° 30' 24.300"	100° 40' 41.808"	1.3	-212.1
17	13° 30' 45.000"	100° 35' 04.992"	2.5	-227.8

APPENDIX B

Acid volatile sulfide with simultaneous extracted metals

This method describes procedures for the determination of acid volatile sulfide (AVS) and for selected metals that are solubilized during the acidification step (simultaneously extracted metal; SEM) using the same conditions for releasing of both sulfide and metal from the sediment. The AVS analysed procedure is fully discribed in Allen *et al.* (1991).

B.1 Reagents

All chemicals used in this study are analytical reagent grade. Approximately 50 µmoles/ml stock sulfide standard solution is prepared by dissolving 12 g sodium sulfide ($Na_2S.9H_2O$) in 1 l of deionized water (DI water; >18 MΩ cm^{-1}). Standard 0.025 N is prepared by dissolving 2.25 g potassium iodide (KI) and 3.2 g iodine crystal (I_2) in 1 l of DI water. Thiosulfate solution is prepared by dissolving 6.2 g sodium thiosulfate ($Na_2S_2O_3.5H_2O$) and 0.1 g sodium carbonate (Na_2CO_3) in 1 l of DI water. Other reagents included 6 M HCl, 0.5 M NaOH, 1.0 M H_2SO_4, 99% nitrogen gas (N_2), starch indicator (1 g starch power in 100 ml DI water, boiled to dissolve) and mixed diamine reagent (MDR).

The MDR is prepared by mixing solution A with solution B. The solution A is 2.25g N,N-dimethyl-p-phenylendiamine hydrochloride in a mixture of 660 ml conc. H_2SO_4 in 340 ml DI water. The solution B is ferric chloride ($FeCl_3$) solution prepared by dissolving 5.4 g $FeCl_3.6H_2O$ in 100 ml conc. HCl then dilute to 200 ml with DI water.

B.2 Generation of hydrogen sulfide

The system to generate hydrogen sulfide (H_2S) gas (so-called AVS) from sediments is set up as seen in Fig. B-1.

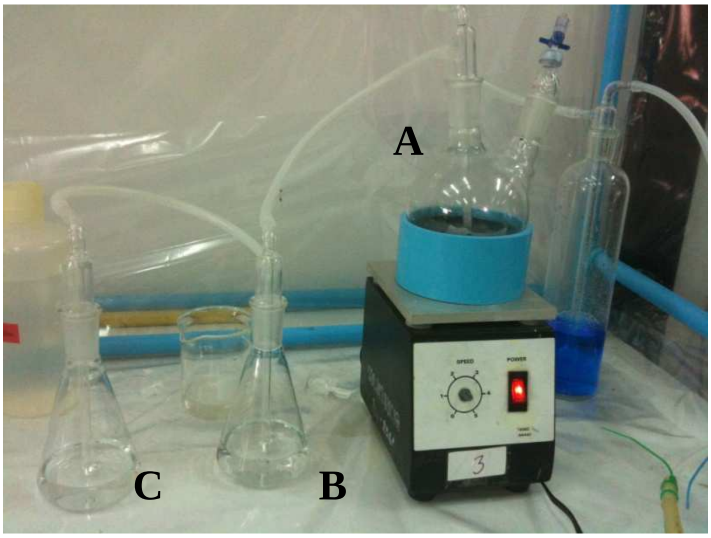

Figure B-1 The system sets up for generation acid volatile sulfide

Flask A is a round bottom flask filled with 100 mL DI water. Flasks B and C are erlenmayer flasks with ground glass joints, each is filled with 80 mL 0.5 M NaOH. Purge the system with N_2 gas at the flow rate of 100 cm^3/min for 10 minutes. Add 10 g of wet sediment, record weight at 4 decimals, into the flask A, then purge with N_2 gas at the flow rate of 40 cm^3/min for 10 minutes. Stop the gas flow prior to inject 20 ml of 6 M HCl into the flask A. Bubbling N_2 gas through the sample for 1 hour at the flow rate of 20 cm^3/min and magnetically stir the sample at the same time.

B.3 Analysis of sulfide

After stop the gas flow, 10 ml of MDR is directly added to the flasks B and C each in order to develop color. Transfer this solution to 100 ml volumetric flask. Adjust the volume of solutions to 100 ml using DI water. Stand for 30 minutes, allowing AVS to completely form blue complexes prior to measure the absorption by spectrophotometry at 670 nm using 10 mm rectangular spectrophotometric cell.

If the solution in the flask C developed blue complex, this means all generated sulfide is not sufficiently trapped in the flask B. The generation of sulfide in section B.2 is needed to be repeated using slower flow rate of N_2 gas in the last step.

B.4 Calculation of AVS concentration in sediment

The dry to wet weight ratio (R) of sediment is determined by drying the wet sediment at 103-105ºC and weight. Calculate the ratio of dry weight to wet weight using Eq. B-1.

$$R = \frac{\mathrm{Wd}}{\mathrm{Ww}} \tag{B-1}$$

where
R = ratio of dry weight to wet weight
W_d = dry weight of sediment sample (g)
W_w = wet weight of sediment sample (g)

The AVS concentration in micromoles per gram dry weight of sediment is calculated using Eq. B-2.

$$\text{AVS (µmoles/g)} = \frac{\mathrm{S}}{\mathrm{R} \times \mathrm{Ww}} \tag{B-2}$$

where
S = the amount of AVS in sediment (µmoles)
R = ratio of dry weight to wet weight
W_w = wet weight of sediment (g) taken for AVS analysis

B.5 Determination of simultaneously extracted metals (SEM)

After the generation of AVS has been completed, filter the sediment suspension remaining in the H_2S generation flask, flask A, through a GF/C glass fiber filter which resistant to acid. The filter apparatus should be presoaked in 0.1 M HNO_3, then rinsed with DI water prior to use. Transfer the solution into a 250 mL volumetric flask. Rinsing the filtering flask with DI water, adding the rinse to the volumetric flask and make to volume.

Determined the concentrations of sulfide binding metals (so-called SEM) by Atomic Absorption Spectrophotometer. Metal concentrations in sediment are reported on a µmole per gram dry weight basis (µmoles/g).

B.6 Calculation the SEM to AVS ratio

The ratio of SEM to AVS is calculated using Eq. B-3.

$$\frac{SEM}{AVS} = \frac{\sum[metal]}{AVS} \tag{B-3}$$

where $\sum$ [metals] = the sum of the concentrations of metals
AVS = the acid volatile sulfide concentration

APPENDIX C

Grain size composition analysis

C.1 Removal of organic matter

Weight 20-30 g of dried homogenized sediment. Treat the sediment with 10% (v/v) hydrogen peroxide (H_2O_2) solution to remove organic matter and help the sediment to disperse. Allow the reaction to progress overnight. Heat at about 60ºC to complete the reaction. Extra amount of H_2O_2 is required for some samples having high organic matter. Remove the excess H_2O_2 by boiling off.

C.2 Removal of carbonate content

After all organic matter in the sediment is removed, the sediment is then treated with 10% (v/v) hydrochloric acid (HCl). Extra HCl solution is required for sediments having large amount of carbonate content. Discard the clear solution above the sediment. Dry the sediment, which free from organic and carbonate contents, at 103-105ºC until dryness.

C.3 Sedimentation technique using pipette method

Determine the composition of sand (> 63 µm), silt (2-63 µm) and clay (< 2 µm) in the sediment using wet sieving and pipette method.

Weight the dry sediment (to nearest 0.0001 g) from section C.2 and record as the total weight of sediment. Separate sand size particle from the sediment by wet sieving through a 63 µm-opening sieve. Dry and weight remaining particles on the sieve to nearest 0.0001 g, result is the amount of sand fraction. The passed through turbid solution contains silt and clay size particles. Transfer the turbid sediment into 1000 ml sedimentation cylinder. Add 10 ml of 10% (w/v) sodium hexametaphosphate, as an dispersing agent, and make up volume to 1000 ml. Stir the solution in the cylinder rigorously using stirring rod as shown in Fig. C-1. Immediately after remove the stirring rod from the cylinder, start timing.

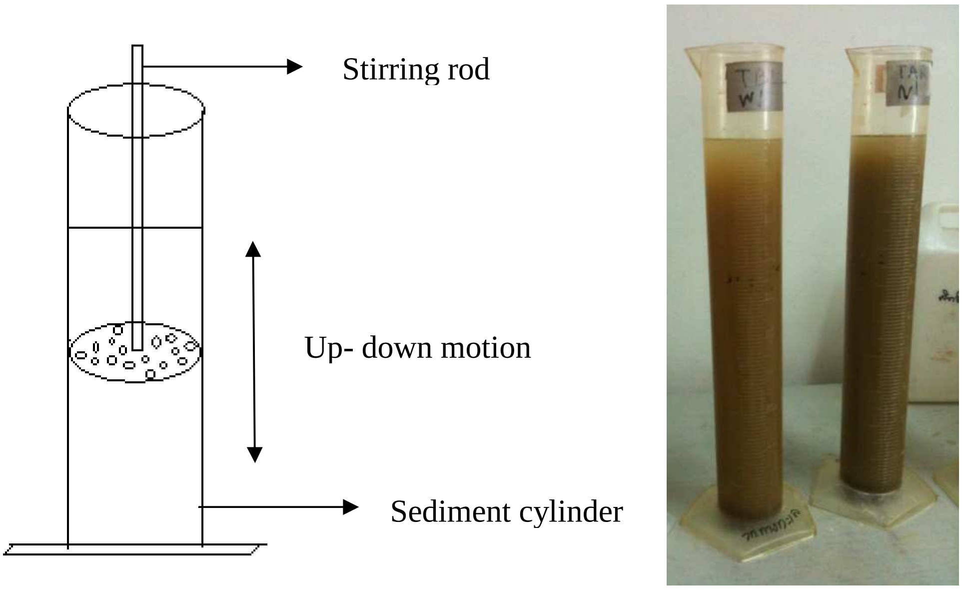

Figure C-1 Stirring turbid sediment prior to allowing sediment to settle and timing.

After 3 hour 52 minutes, according to Stoke’s Law (Box C-1), the aliquot is taken off by pipette at 5 cm depth from water surface to a preweighted container, wash the pipette with distilled water into the same container to ensure that all sediment is transferred from the pipette. Dry at 103-105°C until dryness. Store in a dissector to cool and then weight accurately to nearest 0.0001 g. The amount of clay size fraction is calculated.

Box C-1 Stroke's Law

$$k \quad = \quad 175[\frac{\eta h}{t(\rho k-\rho f)}]1/2 \qquad \text{(C-1)}$$

when η = viscosity of the suspension in poises

ρ_k = specific gravity of substance

ρ_f = specific gravity of the liquid

t = time (minute)

h = cm for surface of the liquid

In this experiment the representative particle for calculate the time required was quartz. At 20ºC for quartz dispersed in water the value of ρk = 2.65, ρf = 0.998 and η = 0.0100.

Equation C-1 is using for calculate a settling time (t) that no particle sized larger than k µm in the layer above the depth h. When k <2 µm and h = 5 cm, the time required for settling is

$$2 \quad = \quad 175[\frac{(0.01)(5)}{t(2.65-0.998)}]1/2$$

t = 231.726695 minutes

= 3 hours and 52 minutes

APPENDIX D

Determination of carbonate content

In this experiment, the acid-base titration technique (Sompongchaiyakul, 1989) is chosen because of its simplicity and suitability to clayey sediment. The sediment sample is treated with excess amount of standardized hydrochloric acid (HCl). Completing the reaction between acid and carbonate by heating, then back titrate the untreated acid with sodium hydroxide (NaOH) solution using phenolphthalein as an indicator.

D.1 Reagents

All chemicals used are analytical reagent grade. 0.5 N HCl and 0.25 N NaOH are prepared. Phenolphthalein indicator is prepared by dissolving 100 mg of solid indicator in 100 ml of 80% ethyl alcohol (equal to 0.1% in ethyl alcohol). Bromocresal green indicator is prepared by dissolving 100 mg of solid indicator with 1.45 ml of 0.1 N NaOH, dilute to 100 ml with distilled water. Other reagents include sodium carbonate (Na_2CO_3) and potassium hydrogen phthalate ($KHC_8H_4O_4$).

D.2 Procedure

Accurately weigh 1 g (4 decimals) of freeze-dried sediment sample, ground in an agate mortar and pass through 63 µm nylon sieve, transfer to 250 ml Erlenmeyer flask. Adding 10 ml of 0.5 N HCl. Heat at about 90ºC for 20 minutes. Test the pH of the solution with pH paper, if the pH was > 2, add another 10 ml of 0.5 N HCl and resume heating for 20 minutes.

When pH < 2, dilute the solution by about 200 ml of distilled water. Back-titrate with 0.25 N NaOH solution using phenolphthalein as an indicator. At end-point, the color of the solution will change sharply from colorless to purple.

Standardization of acid (0.5 N HCl) and base (0.25 N NaOH) solution is made daily.

D.3 Standardization of hydrochloric acid solution

Oven dry sodium carbonate (Na_2CO_3) at 110ºC for 2 hours and cool in a desiccator. Weigh about 0.6-0.7 g portion of Na_2CO_3 to nearest 0.0001 g into a 250 ml erlenmeyer flask. Dissolve the solid with about 25-50 ml distilled water. Add 3-4 drops of bromocresal green. Titrate with prepared 0.5 N HCl solution until the solution just begins to change from blue to green. Boil the solution for 2-3 minutes, cool at room temperature, and complete the titration if the color is changed back from green to blue.three replicates should be performed.

D.4 Standardization of sodium hydroxide solution

Oven dry potassium hydrogen phthalate ($KHC_8H_4O_4$) at 110ºC for 2 hours and cool in a desiccator. Weigh 0.9-1.0 g of $KHC_8H_4O_4$ to nearest 0.0001 g into a 250 ml Erlenmeyer flask. Dissolve in 100 ml of distilled water. Add 3-4 drops of phenolphthalein. Titrate with prepared 0.25 N NaOH solution until the pink color of the indicator persists for 30 seconds. Three replicates should be performed.

D.5 Calculation

The reactions during standardization of sodium hydroxide and hydrochloric acid solutions are shown in Eqs. D-1 and D-2.

$$KHC_8H_4O_4 + NaOH \rightarrow NaK(C_8H_4O_4) + H_2O \qquad (D\text{-}1)$$

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2CO_3 \qquad (D\text{-}2)$$

The results from the acid-base titration for carbonate contents are calculated as Eqs. D-3 and D-4. Eq. D-3 involves no assumptions about the forms of the carbonate phases, and Eq. D-4 assumes that all the carbonate occurs as $CaCO_3$.

$$\%CO_3\text{-}C = [(100)(0.006)(ml_{HCl})(N_{HCl})] - [(ml_{NaOH})(N_{NaOH})] \qquad (D\text{-}3)$$

$$\%CaCO_3 = [(100)(0.05)(ml_{HCl})(N_{HCl})] - [(ml_{NaOH})(N_{NaOH})] \qquad (D\text{-}4)$$

APPENDIX E

Determination of organic matter

The method for determine the organic content in the sediment was first presented by Walkey-Black (1947), which modified by Loring and Rantala (1992).

Organic carbon in the sediment is oxidized by chromic acid. The oxidation of carbon chromic acid may be represented as Eq. E-1.

$$2Cr_2O_7^{2-} + 3C + 28H^+ \rightarrow 4Cr^{3+} + 3C^{4+} + 14H_2O \qquad \text{(E-1)}$$

The used $Cr_2O_7^{2-}$ in Eq. E-1 is reduced by ferrous solution. The reduction of $Cr_2O_7^{2-}$ by ferrous solution may be given as Eq. E-2.

$$Cr_2O_7^{2-} + 6Fe(NH_4)_2^{4+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe(NH_4)^{4+} + 6NH^{4+} + 7H_2O \qquad \text{(E-2)}$$

Since carbon only constitutes about 58% of the soft organic remain in sediments, the carbon content can be converted to the organic matter content by multiplying the formular with 1.72.

E.1 Reagents

All chemicals using in this study are analytical reagent grade. Concentrated sulfuric acid (H_2SO_4) with silver sulfate ($AgSO_4$) is prepared by dissolving 2.5 g of Ag_2SO_4 in 1 l of conc. H_2SO_4. Diphenylamine indicator is prepared by dissolving 0.5 g of diphenylamine in 20 ml of distilled water and 100 ml of conc. H_2SO_4. Primary standard 0.1 N potassium dichromate solution is prepared by dissolving exactly 49.04 g of $K_2Cr_2O_7$ in 1 l of distilled water. 0.5 N ferrous ammonium sulfate solution is prepared by dissolving 196.1 g of $Fe(NH_2)(SO_4)_2 \cdot 6H_2O$ in 800 ml of distilled water containing 20 ml conc. H_2SO_4 then dilute to 1 l with distilled water. Other reagents include 85% orthophosphoric acid (H_3PO_4) (sp. gr. = 1.71) and sodium fluoride solid (NaF) (sp. gr. = 1.84).

E.2 Analytical procedure

Carefully weigh approximately 0.5 g, to nearest 0.0001 g, of freeze-dried sediment sample which ground in an agate mortar and passed through 63 µm nylon sieve. Place the sample in a 500 ml erlenmeyer flask. Add exactly 10 ml of 0.1 N $K_2Cr_2O_7$ and mixed carefully by gentle swirling. Add 20 ml of conc. H_2SO_4 (with $AgSO_4$), gently mix thoughtfully for 1 minute, and avoid spattering of the sediment onto the side of the flask. Let the reaction to be completed for 30 minutes, dilute the solution to about 200 ml by distilled water. Add 10 ml of 85% H_3PO_4, 0.2 g NaF, and 15 drops (1 ml of indicator), respectively. The sample is then back titrated with 0.5 N ferrous ammonium sulfate solution until the color of the solutions change from dull green to brilliant green.

In the beginning the color of the sample is dull green because of the chromous ions, and then become a turbid as the titration proceeds before change sharply to a brilliant green at the end-point.

If most of dichromate solution is consumed, the analysis should be repeated with smaller amount of sediment sample. Blank is performed by the same manner but without sediment, and should be run daily.

E.3 Standardization of organic carbon determination

Dextrose ($C_6H_{12}O_6$) is used as the standard. It should contain 39.99% carbon. Weight exactly 0.01 g, to nearest 0.0001 g, of dextrose and treat in the same manner as the sediment sample. Three replicates should be done. The carbon in dextrose is calculated using Eq. E-3. The theoretical value is 39.99% C in one gram of dextrose.

$$\%\,C = 10\left(1-\frac{T}{S}\right)\times F \qquad \text{(E-3)}$$

$$F = (1.0\,N)\times\left(\frac{12}{4000}\right)\times\left(\frac{100}{sample\ weight}\right) \qquad \text{(E-4)}$$

$$= 30 \text{ for 0.01 g of dextrose.}$$

E.4 Calculation of results

The volume in ml of used ferrous ammonium sulfate solution is used to calculate the percentage of organic carbon and organic matter by Eqs. E-5 and E-6, respectively.

$$\text{\% organic carbon} = 10\left(1-\frac{T}{S}\right)(1.0)\left(\frac{12}{4000}\right)\left(\frac{100}{sample\ weight}\right) \tag{E-5}$$

$$\text{\% organic matter} = 10\left(1-\frac{T}{S}\right)(1.0)\left(\frac{12}{4000}\right)(1.72)\left(\frac{100}{sample\ weight}\right) \tag{E-6}$$

where S = ml of ferrous ammonium sulfate solution used for titrate blank

T = ml of ferrous ammonium sulfate solution used for titrate sample

1.72 = conversion factor of carbon content to organic carbon

$\frac{12}{4000}$ = milliequivalent weight carbon

APPENDIX F

Determination of metals in non-lattice fraction

The metals held in non-lattice fraction can be determined by selective chemical methods using acetic acid (CH_3COOH) according to Loring and Rantana (1992). Acetic acid, 25% (v/v), is added to remove metals held in ion exchange positions, easily soluble amorphous compounds of iron and manganese, carbonates and those metals weakly held in organic matter. It leaves the silicate lattices intact and does not attack the resistant iron and manganese minerals or organic compounds. The proportion of the total metal concentration removed by the extraction is operationally defined as the non-lattice held (acid soluble) metal fraction of sediment.

F.1 Reagent

25% (v/v) acetic acid (CH_3COOH) is prepared from analytical reagent grade glacial acetic acid diluted with DI water (>18 mΩ cm^{-1}).

F.2 Analytical procedure

Place a portion of freeze-dried sediment sample in an agate mortar. Do not grind it but simply crush the lumps. Weigh 2 g of sample and transfer it into a propylene centrifuge tube. Add 25 ml of 25% (v/v) CH_3COOH. Shake slowly in a mechanical shaker for 6 hours, prior to separate the solution and sediment by centrifuging at 2,500 RPM for 10 minutes. Pour the clear supernatant, CH_3COOH solution, into 50 ml volumetric flask. Wash the sediment with 10 ml of DI water and shake the tube briefly on the shaker. Separated the wash water by centrifuging and add it to the volumetric flask. Make up the solution to a volume of 50 ml.

Dry the tube containing the residue in the oven at 105ºC and place to cool in the desiccator. Keep this sediment for further analysis of lattice-held fraction.

The extracted solution is transfer to polyethylene bottle and left overnight prior to determine metal concentration by atomic absorption spectrophotometer.

APPENDIX G

Determination of total metals in sediments

Total metals in sediment can be released using hydrofluoric acid (HF). To analysis metals held in lattice fraction, HF and aqua regia (HNO_3:HCl, 1:3) are used to decompress sediment in order to release all elements into solution according to the method fully described in Loring and Rantana (1992).

A sealed Teflon bomb is used as a decomposition vessel. The main advantages of the Teflon bomb decomposition are (a) rapid decomposition, (b) reduce risk of contamination (c) small volume of acid required and (e) no loss of volatile elements.

G.1 Special Apparatus

- Teflon decomposition vessels (Teflon bomb)
- Domestic microwave
- Microwave pressure cooker
- Polypropylene and Teflon labware

G.2 Chemicals

All chemicals using in this study are analytical reagent grade. There include hydrofluoric acid (49% HF), nitric acid (70% HNO_3), hydrochloric acid (37% HCl), aqua regia (HNO_3-HCl) (1:3 v/v), boric acid crystal (H_3BO_3), de-ionized water (>18mΩ cm^{-1})

G.3 Procedure

1. Accurately weigh 100-200 mg to nearest 0.0001 g for microwave heating of finely ground sample.
2. Transfer to a Teflon bomb.
3. Add 1 ml of aqua regia (HNO_3-HCl, 1:3 v/v).
4. Add 6 ml of HF very slowly to avoid excessive frothing.

5. Close the bomb tightly and place the bombs in the microwave pressure cooker; place the cooker along with a beaker containing 50 ml water in the microwave oven; heat for 5 min at full power and 10 minute at a half power then keep it for 10 min and repeat heat step.
6. Remove the bomb from the heat source and cool it to room temperature in cold water or an ice bath.
7. Weight 5.6 g of HBO3 and transfer into a 100 ml Polypropylene volumetric flasks.
8. Add 20 ml of De-ionized reverse osmosis water and shake briefly.
9. Remove the bomb from the cooling water and dry it.
10. Open the bomb, (be sure to wipe off any water found on the outside of the sealing area) and transfer the contents into the 100 ml Polypropylene volumetric flasks.
11. Rinse the bomb several times with deionized water and add the rinsing to the flask.
12. Shake the flask to complete the dissolution (black carbon residue may remain but does not contain significant amounts of metal and does not interfere with subsequent metal determinations).
13. Make the solution up to 100 ml with deionized water.
14. Transfer the solution into Polypropylene narrow mouth bottles for storage.
15. Allow solution obtained from 100-500 mg sample size to settle overnight; those from 500-1000 mg sample size should settle for several days in case borosilicate forms.
16. Analyze the solution for metals by graphite furnace AAS.

APPENDIX H

Analytical results

Table H-1 Size composition, calcium carbonate content and organic matter in the sediments collected from the upper Gulf of Thailand during 23-25 August 2010.

Station	%Sand (>63 µm)	%Silt (2-63 µm)	%Clay (<2 µm)	%$CaCO_3$	%OM
2	2.7	59.9	37.4	5.8	4.28
3	6.4	48.6	44.9	9.9	3.53
4	1.0	55.5	43.6	12.1	4.51
5	2.1	80.0	17.9	1.8	2.55
6	0.4	45.4	54.2	4.3	3.22
7	26.5	34.3	39.2	13.0	1.62
8	41.2	53.3	5.5	13.1	2.20
9	53.9	22.5	23.6	11.5	2.00
10	57.6	10.3	32.1	13.9	2.37
11	2.6	64.1	33.3	3.0	3.16
12	3.4	66.1	30.5	4.2	4.08
13	39.4	54.0	6.6	11.6	2.65
14	32.5	39.9	27.6	12.1	2.92
15	55.9	27.2	16.8	13.2	2.14
16	34.5	15.8	49.8	12.7	2.19
18	5.2	51.5	43.3	6.2	3.89
19	12.6	39.8	47.7	9.5	3.36
20	20.2	29.7	50.2	9.8	3.34
21	19.6	21.6	58.8	12.5	3.38
22	37.1	4.7	58.2	15.9	2.20
23	44.6	15.8	39.6	17.8	2.30
24	17.5	38.2	44.3	21.9	2.58
26	15.6	36.1	48.3	9.7	3.88
27	18.5	27.3	54.3	9.1	3.35
28	31.8	23.2	44.9	10.0	2.77
29	27.0	22.0	51.0	12.9	3.08
30	2.3	22.0	75.8	14.2	4.76
31	61.3	9.3	29.4	16.6	2.19
32	49.8	4.4	45.8	15.1	1.79
33	9.0	16.9	74.1	15.9	4.30

Table H-2 Size composition, calcium carbonate content and organic matter in the sediments collected from the river mouth of Chaopraya River on 9 March 2011.

Station	%Sand (>63 µm)	%Silt (2-63 µm)	%Clay (<2 µm)	%$CaCO_3$	%OM
1	8.2	26.2	65.6	2.79	4.55
2	5.5	20.7	73.7	1.70	4.65
3	3.9	20.5	75.6	1.73	4.02
4	13.4	20.9	65.7	1.92	3.46
5	34.3	14.6	51.0	2.08	2.89
6	1.8	25.8	72.4	2.19	3.95
7	11.3	19.9	68.8	2.12	3.53
9	1.2	33.3	65.5	0.89	3.76
10	46.1	17.6	36.2	1.81	2.22
11	51.8	14.8	33.4	1.95	2.20
12	19.1	15.6	65.3	2.31	1.37
13	47.9	16.5	35.6	1.86	2.23
14	40.2	14.0	45.8	2.03	2.35
15	59.9	19.5	20.7	4.24	2.39
16	32.4	27.2	40.4	1.87	2.37
17	16.7	18.2	65.1	2.01	3.50

Table H-3 Concentrations of simultaneously extracted metals (SEM) in the sediments collected from the upper Gulf of Thailand during 23-25 August 2010.

Station	Cd (µg/g)	Cu (µg/g)	Pb (µg/g)	Zn (µg/g)	Fe (mg/g)	Mn (mg/g)
2	0.15	5.59	1.48	116.6	9.47	0.63
3	0.17	8.57	3.46	118.9	11.75	2.36
4	0.04	8.76	1.25	65.8	2.11	0.59
5	0.04	6.00	1.36	147.7	17.17	2.32
6	0.07	4.73	0.32	111.8	12.73	1.09
7	0.04	2.40	0.19	66.3	12.46	0.94
8	0.03	1.47	0.21	32.9	7.04	0.68
9	0.03	1.18	0.21	27.8	2.54	0.48
10	0.02	1.02	0.14	28.3	3.11	0.51
11	0.03	4.84	0.45	99.1	19.35	1.65
12	0.05	5.56	0.20	155.9	19.05	1.64
13	0.04	2.15	0.10	56.3	11.41	1.10
14	0.02	1.43	0.15	34.5	11.92	0.90
15	0.10	0.90	0.17	26.2	8.95	0.88
16	0.02	1.09	0.13	37.4	5.86	0.62
18	0.06	3.32	0.14	76.8	14.08	1.40
19	0.04	2.07	0.12	65.1	11.53	0.87
20	0.09	0.97	0.24	41.0	6.69	0.63
21	0.04	1.70	0.11	41.8	10.00	1.02
22	0.02	0.80	0.16	18.4	6.73	0.81
23	0.03	0.99	0.18	34.6	6.12	0.75
24	0.03	0.73	0.31	27.8	1.06	1.06
26	0.08	1.98	0.16	80.1	7.95	0.77
27	0.09	2.50	0.16	63.6	10.77	1.07
28	0.07	1.54	0.13	31.0	8.19	0.79
29	0.06	1.32	0.13	50.7	7.90	0.89
30	0.10	5.96	0.23	97.8	3.68	0.85
31	0.04	1.19	0.20	31.3	3.12	1.22
32	0.04	0.59	0.16	21.7	6.03	0.89
33	0.12	4.53	0.30	63.3	3.88	0.73

All data was normalized by percentage of < 63 µm and $CaCO_3$

Table H-4 Concentrations of simultaneously extracted metals (SEM) in the sediments collected from the river mouth of Chaopraya River on 9 March 2011.

Station	Cd (µg/g)	Cu (µg/g)	Pb (µg/g)	Zn (µg/g)	Fe (mg/g)	Mn (mg/g)
1	0.13	9.36	13.54	142.3	9.38	0.87
2	0.15	16.60	17.64	157.5	12.07	0.71
3	0.14	16.74	17.23	129.0	12.50	2.83
4	0.11	19.03	17.12	130.7	18.20	2.59
5	0.05	8.21	16.96	103.6	13.03	5.71
6	0.10	10.29	16.79	144.2	11.92	3.08
7	0.10	13.06	17.32	117.9	13.13	3.98
9	0.06	10.62	15.93	122.0	11.48	5.55
10	0.05	13.75	21.72	143.3	26.47	7.84
11	0.07	12.92	21.92	187.1	29.81	7.64
12	0.11	9.48	16.67	118.0	15.05	4.96
13	0.06	16.58	26.44	107.6	21.43	5.80
14	0.07	10.20	18.68	97.8	20.02	4.49
15	0.07	6.41	12.21	184.5	70.80	18.76
16	0.06	9.79	11.67	143.2	18.07	7.43
17	0.08	9.20	12.75	80.6	11.08	1.39

All data was normalized by percentage of < 63 µm and $CaCO_3$

Table H-5 Concentrations of metals in non-lattice and lattice held fractions of the sediments collected from the upper Gulf of Thailand during 23-25 August 2010.

Station	Cd (µg/g)		Cu (µg/g)		Pb (µg/g)		Zn (µg/g)		Fe (mg/g)		Mn (mg/g)	
	non-lattice	total	non-lattice	total	non-lattice	total	non-lattice	total	non-lattice	total	non-lattice	total
2	1.19	1.27	2.74	75.01	8.79	23.54	51.8	156.5	2.50	32.0	2.45	2.59
3	0.71	0.78	2.13	47.27	6.77	15.92	24.8	100.5	1.32	31.1	0.78	1.30
4	0.37	0.42	2.28	38.71	5.36	13.43	25.6	95.2	1.94	23.8	0.64	0.79
5	0.16	0.30	7.84	29.56	6.65	16.02	38.7	130.5	6.99	35.1	1.20	1.37
6	0.22	0.29	5.86	35.34	8.18	10.92	59.0	171.2	4.44	44.2	0.84	1.01
7	0.30	0.45	2.69	25.69	8.82	13.66	21.7	79.2	2.82	41.1	0.44	0.76
8	0.05	0.11	1.43	35.61	8.67	12.94	19.3	62.8	2.30	29.4	0.40	0.52
9	0.04	0.20	2.91	33.00	9.73	13.21	20.1	62.7	1.99	28.0	0.46	0.62
10	0.18	0.31	1.45	44.77	10.54	16.40	17.4	78.2	2.01	34.7	0.36	0.59
11	0.16	0.21	4.77	40.85	7.47	12.34	46.1	108.3	9.02	39.1	0.54	0.67
12	0.36	0.48	4.78	44.48	6.57	16.87	30.7	140.7	4.69	39.3	0.58	0.85
13	0.37	0.48	0.87	33.00	6.52	15.67	15.2	87.0	2.04	34.8	0.46	0.85
14	0.63	0.64	1.05	17.38	9.11	16.73	15.1	73.4	1.65	32.7	0.70	0.89
15	0.57	0.67	1.03	19.81	8.87	19.51	14.0	77.9	1.87	35.4	0.86	0.96
16	0.05	0.11	1.58	17.10	7.64	15.43	11.7	67.4	1.61	30.6	0.66	0.69
18	0.14	0.27	1.57	25.10	6.94	12.82	22.9	70.1	2.21	46.5	0.25	0.60
19	0.36	0.42	1.93	37.02	5.21	14.94	15.2	111.2	2.21	43.6	0.36	0.75
20	0.76	0.78	0.83	60.04	4.62	13.40	10.0	80.9	2.05	36.7	0.70	0.94
21	0.14	0.23	0.85	26.88	6.37	25.19	9.7	83.1	1.89	37.6	0.93	1.02
22	0.17	0.28	1.36	19.63	7.47	14.80	11.2	95.5	2.17	35.1	0.72	0.92
23	2.07	2.19	1.12	20.66	8.40	18.58	11.5	106.5	2.18	40.7	0.77	0.82
24	0.52	0.68	1.66	16.08	8.77	20.58	13.5	81.6	2.35	32.2	0.56	0.85

Table H-5 (cont.)

Station	Cd (µg/g)		Cu (µg/g)		Pb (µg/g)		Zn (µg/g)		Fe (mg/g)		Mn (mg/g)	
	non-lattice	total	non-lattice	total	non-lattice	total	non-lattice	total	non-lattice	total	non-lattice	total
26	0.39	0.56	1.94	16.45	3.05	15.66	19.1	73.0	2.12	40.6	0.58	0.64
27	0.56	0.74	0.85	13.90	4.59	13.55	12.1	65.8	1.80	36.8	0.70	0.84
28	0.10	0.23	3.95	17.17	5.66	13.62	10.7	63.3	1.92	25.0	0.56	0.87
29	0.15	0.24	0.93	18.50	6.10	14.47	11.9	67.0	2.07	35.9	0.19	0.57
30	0.72	0.88	3.40	20.56	6.34	13.38	25.6	65.5	1.12	19.3	0.49	0.62
31	0.73	1.02	1.60	21.93	5.44	23.71	18.3	103.7	1.46	41.3	0.39	0.45
32	1.49	1.66	1.12	23.58	7.49	16.47	12.3	73.9	1.91	32.1	0.46	0.51
33	0.06	0.26	2.17	17.35	5.16	15.22	18.8	54.7	1.01	26.4	0.35	0.64

All data was normalized by percentage of < 63 µm and $CaCO_3$

Table H-6 Concentrations of metals in non-lattice and lattice held fractions of the sediments collected from the river mouth of Chao Phraya on 9 March 2011.

Station	Cd (µg/g)		Cu (µg/g)		Pb (µg/g)		Zn (µg/g)		Fe (mg/g)		Mn (mg/g)	
	non-lattice	total	non-lattice	total	non-lattice	total	non-lattice	total	non-lattice	total	non-lattice	total
1	3.02	0.47	11.4	46.7	7.90	28.6	85.5	233.4	10.2	23.1	0.88	0.30
2	3.52	0.54	15.8	53.6	7.21	37.9	89.8	244.2	10.0	25.2	0.71	0.22
3	3.55	0.59	14.1	46.6	7.07	30.2	68.8	239.2	10.3	26.0	1.88	1.22
4	2.46	0.26	14.7	38.8	7.22	19.3	66.5	193.3	15.1	31.9	1.82	0.91
5	2.12	0.42	11.2	56.6	9.02	34.1	106.4	188.0	19.6	37.2	2.66	1.74
6	3.01	0.41	13.9	38.4	9.03	7.4	65.4	190.7	10.0	27.5	1.93	1.05
7	2.09	0.51	11.7	26.8	6.87	26.8	56.7	242.7	12.4	33.0	1.86	0.86
9	1.90	0.42	15.3	41.6	8.4	23.2	56.1	224.4	9.9	30.9	3.22	1.36
10	1.89	0.94	14.5	42.5	17.5	36.5	88.1	230.2	27.8	40.8	3.79	0.87
11	2.46	0.60	13.5	48.7	16.0	45.0	89.0	311.4	29.4	46.0	3.23	0.71
12	2.30	0.53	10.8	32.2	11.0	22.2	57.0	187.0	13.1	32.7	2.07	1.25
13	2.94	0.73	20.1	43.2	21.7	39.2	84.9	513.3	21.8	37.6	2.42	1.62
14	7.33	0.43	11.4	41.4	14.7	13.5	67.4	215.1	22.5	35.6	2.34	1.68
15	3.27	1.61	19.8	78.5	6.84	17.0	102.9	602.7	24.0	79.5	5.59	4.33
16	2.02	0.38	12.8	32.1	11.6	3.53	85.2	282.6	19.8	46.9	2.09	2.62
17	2.56	0.36	8.5	44.8	10.2	20.1	51.1	224.3	14.1	30.0	1.47	0.85

All data was normalized by percentage of < 63 µm and $CaCO_3$

Table H-7 Precision of acid volatile sulfide and simultaneous extracted metals analysis

(a) Acid volatile sulfide (AVS) (µmol/g dry weight)

Station	Rep. 1	Rep. 2	Rep. 3	Average ± SE	SD	%RSD
U-GOT 9	0.012	0.012		0.012 ± 0.000	0.000	0.6
U-GOT 10	0.015	0.014		0.014 ± 0.001	0.001	5.1
U-GOT 16	0.050	0.015		0.033 ± 0.018	0.025	76.5
U-GOT 21	0.512	0.334		0.423 ± 0.089	0.125	29.6
U-GOT 23	0.024	0.056	0.010	0.030 ± 0.014	0.023	78.0
U-GOT 31	0.009	0.009		0.009 ± 0.000	0.000	1.3
U-GOT 32	0.006	0.011		0.009 ± 0.003	0.004	43.5
CPY 4	0.192	0.354		0.273 ± 0.081	0.114	41.9
					Average	34.6

(b) Simultaneous extracted cadmium (Cd) (µg/g dry weight)

Station	Rep. 1	Rep. 2	Rep. 3	Average ± SE	SD	%RSD
U-GOT 9	0.016	0.031		0.023 ± 0.008	0.011	46.4
U-GOT 10	0.017	0.014		0.016 ± 0.002	0.002	15.7
U-GOT 16	0.016	0.020		0.018 ± 0.002	0.003	17.6
U-GOT 21	0.035	0.032		0.033 ± 0.001	0.002	6.4
U-GOT 23	0.019	0.018	0.02	0.019 ± 0.001	0.001	4.6
U-GOT 31	0.028	0.023		0.025 ± 0.002	0.003	12.6
U-GOT 32	0.025	0.030		0.027 ± 0.003	0.004	13.1
CPY 4	0.094	0.100		0.097 ± 0.003	0.004	4.1
					Average	15.1

(c) Simultaneous extracted copper (Cu) (µg/g dry weight)

Station	Rep. 1	Rep. 2	Rep. 3	Average ± SE	SD	%RSD
U-GOT 9	0.996	1.370		1.183 ± 0.187	0.264	22.3
U-GOT 10	1.067	0.981		1.024 ± 0.043	0.061	5.9
U-GOT 16	0.914	1.269		1.091 ± 0.177	0.251	23.0
U-GOT 21	1.577	1.813		1.695 ± 0.118	0.167	9.8
U-GOT 23	0.952	1.028	0.977	0.986 ± 0.022	0.039	3.9
U-GOT 31	1.093	1.281		1.187 ± 0.094	0.133	11.2
U-GOT 32	0.596	0.580		0.588 ± 0.008	0.011	1.9
CPY 4	12.84	19.39		16.11 ± 3.28	4.63	28.8
					Average	13.4

(d) Simultaneous extracted lead (Pb) (µg/g dry weight)

Station	Rep. 1	Rep. 2	Rep. 3	Average ± SE	SD	%RSD
U-GOT 9	0.151	0.162		0.157 ± 0.005	0.007	4.8
U-GOT 10	0.073	0.118		0.096 ± 0.022	0.032	33.1
U-GOT 16	0.091	0.123		0.107 ± 0.016	0.023	21.1
U-GOT 21	0.070	0.108		0.089 ± 0.019	0.027	30.2
U-GOT 23	0.100	0.146	0.122	0.123 ± 0.013	0.023	18.9
U-GOT 31	0.110	0.122		0.116 ± 0.006	0.008	7.1
U-GOT 32	0.095	0.130		0.112 ± 0.018	0.025	22.1
CPY 4	14.68	14.33		14.50 ± 0.17	0.25	1.7
					Average	17.4

(e) Simultaneous extracted zinc (Zn) (µg/g dry weight)

Station	Rep. 1	Rep. 2	Rep. 3	Average ± SE	SD	%RSD
U-GOT 9	23.1	18.7		20.9 ± 2.21	3.12	14.9
U-GOT 10	17.9	20.3		19.1 ± 1.21	1.71	8.9
U-GOT 16	36.4	23.9		30.1 ± 6.22	8.80	29.2
U-GOT 21	36.8	33.9		35.4 ± 1.48	2.09	5.9
U-GOT 23	21.2	29.1	20.2	23.5 ± 2.82	4.89	20.8
U-GOT 31	13.2	22.5		17.8 ± 4.63	6.55	36.8
U-GOT 32	16.0	14.4		15.2 ± 0.77	1.09	7.2
CPY 4	113.8	107.6		110.7 ± 3.11	4.40	4.0
					Average	16.0

(f) Simultaneous extracted iron (Fe) (mg/g dry weight)

Station	Rep. 1	Rep. 2	Rep. 3	Average ± SE	SD	%RSD
U-GOT 9	1.69	2.13		1.91 ± 0.22	0.31	16.2
U-GOT 10	3.20	0.99		2.09 ± 1.10	1.56	74.5
U-GOT 16	4.30	5.14		4.72 ± 0.42	0.60	12.6
U-GOT 21	8.52	8.39		8.45 ± 0.06	0.09	1.1
U-GOT 23	5.06	3.68	3.73	4.16 ± 0.45	0.78	18.8
U-GOT 31	2.30	1.26		1.78 ± 0.52	0.74	41.4
U-GOT 32	4.42	4.02		4.22 ± 0.20	0.28	6.6
CPY 4	16.2	14.7		15.4 ± 0.74	1.04	6.8
					Average	22.2

(g) Simultaneous extracted managnese (Mn) (mg/g dry weight)

Station	Rep. 1	Rep. 2	Rep. 3	Average ± SE	SD	%RSD
U-GOT 9	0.335	0.382		0.358 ± 0.024	0.034	9.4
U-GOT 10	0.433	0.256		0.344 ± 0.088	0.125	36.3
U-GOT 16	0.422	0.584		0.503 ± 0.081	0.115	22.8
U-GOT 21	0.835	0.889		0.862 ± 0.027	0.038	4.4
U-GOT 23	0.550	0.493	0.49	0.511 ± 0.020	0.034	6.7
U-GOT 31	0.772	0.621		0.696 ± 0.075	0.107	15.3
U-GOT 32	0.657	0.584		0.621 ± 0.037	0.052	8.4
CPY 4	2.59	1.80		2.19 ± 0.39	0.56	25.4
					Average	16.1

Table H-8 Precision of the analysis of sediment size composition

(a) Sand percentage (%)

Station	Rep. 1	Rep. 2	Average ± SE	SD	%RSD
U-GOT 5	34.3	38.7	36.5 ± 2.2	3.1	8.5
U-GOT 16	32.4	49.5	41.0 ± 8.5	12.1	29.4
CPY 7	26.5	32.4	29.4 ± 2.9	4.1	14.1
CPY 15	55.9	60.0	58.0 ± 2.1	2.9	5.0
				Average	14.3

(b) Silt percentage (%)

Station	Rep. 1	Rep. 2	Average ± SE	SD	%RSD
U-GOT 5	51.0	41.5	46.3 ± 4.7	6.7	14.5
U-GOT 16	40.4	39.7	40.1 ± 0.3	0.5	1.2
CPY 7	34.3	27.3	30.8 ± 3.5	5.0	16.3
CPY 15	22.7	27.2	25.0 ± 2.3	3.2	12.7
				Average	11.2

(c) Clay percentage (%)

Station	Rep. 1	Rep. 2	Average ± SE	SD	%RSD
U-GOT 5	14.6	19.7	17.2 ± 2.5	3.6	20.9
U-GOT 16	27.2	10.8	19.0 ± 8.2	11.6	61.0
CPY 7	39.2	40.4	39.8 ± 0.6	0.9	2.2
CPY 15	17.2	16.8	17.0 ± 0.2	0.3	1.7
				Average	21.5

Table H-9 Precision of the analysis of carbonate material (%) in the sediments

Station	Rep. 1	Rep. 2	Average ± SE	SD	%RSD
U-GOT 2	6.2	5.4	5.8 ± 0.4	0.5	9.3
U-GOT 3	10.1	9.7	9.9 ± 0.2	0.3	2.6
U-GOT 4	12.0	12.1	12.1 ± 0.0	0.1	0.6
U-GOT 6	4.5	4.1	4.3 ± 0.2	0.3	5.9
U-GOT 7	13.1	12.8	13.0 ± 0.1	0.2	1.6
U-GOT 8	13.5	12.8	13.1 ± 0.4	0.5	4.1
U-GOT 9	11.5	11.4	11.5 ± 0.0	0.1	0.6
U-GOT 10	15.5	12.2	13.9 ± 1.7	2.4	17.0
U-GOT 11	3.1	3.0	3.0 ± 0.1	0.1	2.9
U-GOT 12	3.5	4.8	4.2 ± 0.6	0.9	20.7
U-GOT 13	11.5	11.6	11.6 ± 0.0	0.1	0.6
U-GOT 14	12.1	12.1	12.1 ± 0.0	0.0	0.1
U-GOT 15	13.5	13.0	13.2 ± 0.3	0.4	2.8
U-GOT 16	13.1	12.4	12.7 ± 0.3	0.5	3.7
U-GOT 18	6.6	5.9	6.2 ± 0.4	0.5	7.9
U-GOT 19	9.7	9.3	9.5 ± 0.2	0.3	2.8
U-GOT 20	9.4	10.2	9.8 ± 0.4	0.5	5.5
U-GOT 21	12.0	12.9	12.5 ± 0.4	0.6	4.9
U-GOT 22	16.0	15.9	15.9 ± 0.1	0.1	0.5
U-GOT 23	17.8	17.8	17.8 ± 0.0	0.0	0.1
U-GOT 24	21.2	22.5	21.9 ± 0.7	0.9	4.3
U-GOT 26	10.0	9.5	9.7 ± 0.2	0.4	3.6
U-GOT 27	9.0	9.3	9.1 ± 0.2	0.3	2.8
U-GOT 28	10.1	9.8	10.0 ± 0.2	0.2	2.5
U-GOT 29	12.7	13.1	12.9 ± 0.2	0.3	2.1
U-GOT 30	14.1	14.4	14.2 ± 0.2	0.3	1.9
U-GOT 31	16.5	16.8	16.6 ± 0.1	0.2	1.2
U-GOT 32	15.0	15.2	15.1 ± 0.1	0.2	1.1
U-GOT 33	15.6	16.1	15.9 ± 0.2	0.3	2.0
CYP 1	2.7	2.9	2.8 ± 0.1	0.1	3.2
CYP 2	1.6	1.8	1.7 ± 0.1	0.2	10.0
CYP 3	1.6	1.9	1.7 ± 0.2	0.2	13.4
CYP 4	2.0	1.9	1.9 ± 0.0	0.0	2.4
CYP 5	2.3	1.9	2.1 ± 0.2	0.3	12.6
CYP 6	1.8	2.6	2.2 ± 0.4	0.5	23.4
CYP 7	2.2	2.1	2.1 ± 0.1	0.1	4.3
CYP 9	2.2	1.7	2.0 ± 0.2	0.3	15.1
CYP 10	1.9	1.8	1.9 ± 0.1	0.1	5.7
CYP 11	1.9	2.0	2.0 ± 0.0	0.0	2.5
CYP 12	2.5	2.1	2.3 ± 0.2	0.2	10.4
CYP 13	1.9	1.9	1.9 ± 0.0	0.0	0.5
CYP 14	2.2	1.9	2.0 ± 0.2	0.2	11.2
CYP 15	4.0	4.5	4.2 ± 0.2	0.3	8.2
CYP 16	2.0	1.8	1.9 ± 0.1	0.2	8.7
CYP 17	2.0	2.1	2.0 ± 0.0	0.1	2.9
				Average	5.6

Table H-10 Precision of the analysis of organic matter (%) in the sediments

Station	Rep. 1	Rep. 2	Rep. 3	Average ± SE	SD	%RSD
U-GOT 2	4.12	4.16	4.57	4.28 ± 0.14	0.25	5.8
U-GOT 3	3.64	3.67	3.29	3.53 ± 0.12	0.21	5.9
U-GOT 4	4.44	4.54	4.54	4.51 ± 0.03	0.06	1.3
U-GOT 5	2.71	2.27	2.68	2.55 ± 0.14	0.24	9.5
U-GOT 6	3.39	3.12	3.16	3.22 ± 0.05	0.15	4.6
U-GOT 7	1.64	1.60		1.62 ± 0.02	0.03	2.0
U-GOT 8	2.14	2.21	2.26	2.20 ± 0.04	0.06	2.8
U-GOT 9	1.94	1.89	2.18	2.00 ± 0.09	0.16	7.8
U-GOT 10	2.26	2.38	2.48	2.37 ± 0.06	0.11	4.7
U-GOT 11	3.18	3.10	3.18	3.16 ± 0.03	0.04	1.4
U-GOT 12	3.69	3.92	4.64	4.08 ± 0.28	0.49	12.1
U-GOT 13	2.41	2.78	2.76	2.65 ± 0.12	0.21	7.8
U-GOT 14	2.85	2.94	2.97	2.92 ± 0.04	0.06	2.1
U-GOT 15	2.13	2.16	2.13	2.14 ± 0.01	0.02	1.0
U-GOT 16	2.29	2.09		2.19 ± 0.10	0.14	6.4
U-GOT 18	3.85	3.93		3.89 ± 0.04	0.06	1.5
U-GOT 19	3.48	3.23		3.36 ± 0.13	0.18	5.4
U-GOT 20	3.42	3.26		3.34 ± 0.08	0.11	3.4
U-GOT 21	3.38	3.38		3.38 ± 0.00	0.00	0.1
U-GOT 22	2.19	2.21		2.20 ± 0.01	0.02	0.8
U-GOT 23	2.18	2.42		2.30 ± 0.12	0.17	7.2
U-GOT 24	2.48	2.68		2.58 ± 0.10	0.14	5.6
U-GOT 26	3.91	3.85		3.88 ± 0.03	0.05	1.2
U-GOT 27	3.38	3.32		3.35 ± 0.03	0.04	1.2
U-GOT 28	2.77	2.78		2.77 ± 0.01	0.01	0.3
U-GOT 29	3.10	3.05		3.08 ± 0.03	0.04	1.2
U-GOT 30	4.74	4.79		4.76 ± 0.02	0.03	0.7
U-GOT 31	2.24	2.15		2.19 ± 0.05	0.07	3.0
U-GOT 32	1.79	1.80		1.79 ± 0.00	0.01	0.4
U-GOT 33	4.33	4.27		4.30 ± 0.03	0.05	1.0
CYP 1	4.65	4.46		4.55 ± 0.10	0.14	3.0
CYP 2	4.73	4.57		4.65 ± 0.08	0.11	2.5
CYP 3	4.06	3.98		4.02 ± 0.04	0.05	1.3
CYP 4	3.50	3.41		3.46 ± 0.05	0.06	1.9
CYP 5	2.90	2.88		2.89 ± 0.01	0.01	0.3
CYP 6	3.98	3.91		3.95 ± 0.04	0.05	1.3
CYP 7	3.52	3.54		3.53 ± 0.01	0.02	0.5
CYP 9	3.80	3.72		3.76 ± 0.04	0.06	1.5
CYP 10	2.26	2.18		2.22 ± 0.04	0.06	2.5
CYP 11	2.18	2.21		2.20 ± 0.02	0.02	1.1
CYP 12	1.43	1.32		1.37 ± 0.06	0.08	5.9
CYP 13	2.24	2.22		2.23 ± 0.01	0.01	0.6
CYP 14	2.35	2.34		2.35 ± 0.00	0.00	0.2
CYP 15	2.37	2.40		2.39 ± 0.01	0.02	0.8
CYP 16	2.34	2.40		2.37 ± 0.03	0.05	2.0
CYP 17	3.48	3.51		3.50 ± 0.01	0.02	0.6
					Average	2.9

Table H-11 Precision of non-lattice held metals analysis

(a) Non-lattice held cadmium (Cd) (µg/g dry weight)

Station	Rep. 1	Rep. 2	Average ± SE	SD	%RSD
U-GOT 10	1.07	1.16	1.11 ± 0.05	0.07	6.0
U-GOT 13	1.09	1.14	1.12 ± 0.03	0.04	3.5
CPY 3	3.12	3.59	3.35 ± 0.24	0.33	10.0
CPY 9	1.77	1.95	1.86 ± 0.09	0.13	6.8
CPY 17	1.88	2.28	2.08 ± 0.20	0.28	13.5
				Average	8.0

(b) Non-lattice held copper (Cu) (µg/g dry weight)

Station	Rep. 1	Rep. 2	Average ± SE	SD	%RSD
U-GOT 10	0.95	1.00	0.98 ± 0.02	0.03	3.1
U-GOT 13	0.75	0.66	0.71 ± 0.04	0.06	8.8
CPY 3	13.5	13.0	13.3 ± 0.26	0.37	2.8
CPY 9	14.0	15.9	14.9 ± 0.94	1.33	8.9
CPY 17	6.88	7.00	6.94 ± 0.06	0.08	1.2
				Average	5.0

(c) Non-lattice held lead (Pb) (µg/g dry weight)

Station	Rep. 1	Rep. 2	Average ± SE	SD	%RSD
U-GOT 10	7.03	7.14	7.09 ± 0.05	0.07	1.0
U-GOT 13	5.16	5.40	5.28 ± 0.12	0.17	3.2
CPY 3	6.53	6.81	6.67 ± 0.14	0.20	3.0
CPY 9	7.63	8.83	8.23 ± 0.06	0.85	10.4
CPY 17	8.26	8.33	8.30 ± 0.04	0.05	0.6
				Average	3.7

(d) Non-lattice held lead (Zn) (µg/g dry weight)

Station	Rep. 1	Rep. 2	Average ± SE	SD	%RSD
U-GOT 10	11.2	12.2	11.7 ± 0.5	0.7	5.8
U-GOT 13	12.1	12.5	12.3 ± 0.2	0.3	2.2
CPY 3	125.7	128.2	127.0 ± 1.2	1.8	1.4
CPY 9	112.0	113.2	112.6 ± 0.6	0.8	0.7
CPY 17	95.9	89.8	92.8 ± 3.0	4.3	4.6
				Average	2.9

(e) Non-lattice held iron (Fe) (mg/g dry weight)

Station	Rep. 1	Rep. 2	Average ± SE	SD	%RSD
U-GOT 10	1.31	1.39	1.35 ± 0.04	0.05	3.9
U-GOT 13	1.62	1.68	1.65 ± 0.03	0.04	2.5
CPY 3	9.66	9.77	9.71 ± 0.05	0.07	0.8
CPY 9	9.84	9.49	9.67 ± 0.17	0.24	2.5
CPY 17	12.1	10.8	11.5 ± 0.68	0.96	8.3
				Average	3.6

(f) Non-lattice held manganese (Mn) (mg/g dry weight)

Station	Rep. 1	Rep. 2	Average ± SE	SD	%RSD
U-GOT 10	0.87	0.76	0.82 ± 0.06	0.08	9.9
U-GOT 13	0.94	1.23	1.08 ± 0.14	0.20	18.7
CPY 3	1.67	1.87	1.77 ± 0.10	0.14	7.9
CPY 9	3.15	3.17	3.16 ± 0.01	0.01	0.3
CPY 17	1.19	1.19	1.19 ± 0.00	0.00	0.0
				Average	7.4

Table H-12 Precision of total metals analysis

(a) Total cadmium (Cd) (µg/g dry weight)

Station	Rep. 1	Rep. 2	Rep. 3	Average ± SE	SD	%RSD
U-GOT 3	0.96	0.44	0.40	0.70 ± 0.19	0.33	47.8
U-GOT 13	0.56	0.23		0.39 ± 0.17	0.23	59.9
CPY 1	0.45	0.39		0.42 ± 0.03	0.04	9.2
CPY 9	0.41	0.41		0.41 ± 0.00	0.00	0.0
CPY 14	0.18	0.32		0.25 ± 0.07	0.10	39.5
					Average	31.3

(b) Total copper (Cu) (µg/g dry weight)

Station	Rep. 1	Rep. 2	Rep. 3	Average ± SE	SD	%RSD
U-GOT 3	55.0	29.6	33.3	42.3 ± 8.2	14.2	33.5
U-GOT 13	31.8	21.5		26.7 ± 5.1	7.3	27.3
CPY 1	40.9	42.3		41.6 ± 0.7	1.0	2.4
CPY 9	40.7	40.7		40.7 ± 0.0	0.0	0.0
CPY 14	24.4	23.5		23.9 ± 0.5	0.7	2.9
					Average	13.2

(c) Total lead (Pb) (µg/g dry weight)

Station	Rep. 1	Rep. 2	Rep. 3	Average ± SE	SD	%RSD
U-GOT 3	14.1	14.4	11.7	14.2 ± 1.0	1.8	12.6
U-GOT 13	13.9	11.5		12.7 ± 1.2	1.7	13.5
CPY 1	17.6	33.4		25.5 ± 7.9	11.2	43.9
CPY 9	18.6	27.0		22.8 ± 4.2	6.0	26.2
CPY 14	7.6	8.0		7.8 ± 0.2	0.3	4.0
					Average	20.0

(d) Total zinc (Zn) (µg/g dry weight)

Station	Rep. 1	Rep. 2	Rep. 3	Average ± SE	SD	%RSD
U-GOT 3	93.3	86.5	93.3	91.0 ± 2.3	4.0	4.3
U-GOT 13	73.7	67.1		70.4 ± 3.3	4.7	6.6
CPY 1	196.2	219.5		207.8 ± 11.7	16.5	7.9
CPY 9	226.4	213.3		219.8 ± 6.5	9.3	4.2
CPY 14	127.1	121.6		124.3 ± 2.8	3.9	3.1
					Average	5.3

(e) Total iron (Fe) (mg/g dry weight)

Station	Rep. 1	Rep. 2	Rep. 3	Average ± SE	SD	%RSD
U-GOT 3	20.8	34.9	34.4	27.9 ± 4.9	8.4	30.2
U-GOT 13	29.1	27.1		28.1 ± 1.0	1.4	5.0
CPY 1	20.5	20.5		20.5 ± 0.0	0.0	0.1
CPY 9	30.3	30.3		30.3 ± 0.0	0.0	0.0
CPY 14	20.3	20.8		20.6 ± 0.2	0.4	1.7
					Average	7.4

(f) Total manganese (Mn) (mg/g dry weight)

Station	Rep. 1	Rep. 2	Rep. 3	Average ± SE	SD	%RSD
U-GOT 3	1.16	1.16	1.12	1.16 ± 0.02	0.03	2.3
U-GOT 13	0.48	0.89		0.69 ± 0.21	0.29	43.0
CPY 1	0.19	0.34		0.26 ± 0.07	0.10	38.9
CPY 9	1.43	1.23		1.33 ± 0.10	0.14	10.6
CPY 14	0.98	0.96		0.97 ± 0.01	0.01	1.2
					Average	19.2

BIOGRAPHY

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