หลักการแบ่งส่วนในสภาวะสมดุลเพื่อกำหนดแนวทางคุณภาพตะกอนของโลหะบางชนิด บริเวณปากแม่น้ำเจ้าพระยา

นาย ธนกร จิวรุ่งเรืองกุล

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EQUILIBRIUM PARTITIONING APPROACH TO DEFINE SEDIMENT QUALITY GUIDELINE OF SOME METALS IN CHAO PHRAYA ESTUARY

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A Thesis Submitted in Partial Fulfillment of the Requirements
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การศึกษาครั้งนี้ มีจุดหมายที่จะกำหนดแนวทางคุณภาพตะกอน (SQG) โดยใช้หลักการแบ่งส่วนในสภาวะสมดุล (EqP) ซึ่งบอกถึงปริมาณโลหะในตะกอนดินปากแม่น้ำเจ้าพระยาที่อยู่ในรูปแบบที่สิ่งมีชีวิตจะนำไปใช้ได้ ค่า SQG คำนวณจากค่าแบ่งส่วนในตะกอน-น้ำระหว่างตะกอน (K_D) ร่วมกับค่ามาตรฐานคุณภาพน้ำทะเลของประเทศไทย นอกจากนี้ ในการคำนวณค่า SQG ยังได้เพิ่มปริมาณโลหะส่วนที่จะจับกับซัลไฟด์ได้ (M_{AVS}) เนื่องจากโลหะในส่วนนี้มีศักยภาพที่จะถูกปล่อยออกสู่น้ำระหว่างตะกอน ขณะเกิดกระบวนการรีออกซิเดชันในตะกอนสภาวะขาดออกซิเจน

ค่า K_D คำนวณได้จากนำค่าความเข้มข้นของโลหะที่สกัดได้ตะกอนในส่วนองค์ประกอบที่เคลื่อนไปสู่วัฏภาคใหม่ได้ (labile phase) ของตะกอน หารด้วยค่าความเข้มข้นของโลหะที่อยู่ในน้ำระหว่างตะกอน การที่นำเฉพาะโลหะใน labile phase มาคำนวณค่า K_D เนื่องจาก โลหะในวัฏภาคนี้มีการเคลื่อนย้ายของโลหะไปมาระหว่างตะกอนและน้ำระหว่างตะกอน เมื่อมีการเปลี่ยนแปลงสภาวะทางกายภาพเคมีเกิดขึ้น โลหะใน labile phase ได้จากการสกัดตะกอนด้วย 25% (v/v) กรดอะซิติก และคำนวณโดยปรับให้อยู่บนฐานของตะกอนขนาดเดียวกันและไร้คาร์บอเนต

ค่า SQG สำหรับ แคดเมียม ทองแดง ตะกั่ว และสังกะสี สำหรับตะกอนขนาด <63µm และไร้คาร์บอเนต มีค่าอยู่ในช่วง 1.2–3.1, 7–105, 23–86 และ 16–125 มล.ก./กก. น้ำหนักแห้ง ตามลำดับ ค่า SQG เหล่านี้แทนระดับความเข้มข้นของโลหะในตะกอนที่อยู่ในรูปแบบที่มีศักยภาพที่จะเข้าสู่สิ่งมีชีวิตได้ อย่างไรก็ตาม เพื่อสนับสนุนค่า SQG ที่คำนวณได้ ควรมีการทดสอบเพิ่มเติมในเรื่องความเป็นพิษของโลหะโดยใช้ตะกอนในพื้นที่เดียวกับการศึกษาในครั้งนี้

ภาควิชา วิทยาศาสตร์ทางทะเล ลายมือชื่อนิสิต

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THANAKORN JIWARUNGRUEANGKUL : EQUILIBRIUM PARTITIONING APPROACH TO DEFINE SEDIMENT QUALITY GUIDELINE OF SOME METALS IN CHAO PHRAYA ESTUARY. ADVISOR : ASST. PROF. SIRICHAI DHARMVANIJ, Ph.D., CO-ADVISOR : ASST. PROF. PENJAI SOMPONGCHAIYAKUL, Ph.D., 119 pp.

This study aims to define numerical sediment quality guideline (SQG) based on equilibrium partitioning approach (EqP approach) that represents availability of metals in Chao Phraya estuarine sediment. The numerical SQG was calculated from the sediment-interstitial water partition coefficient (K_D) in conjunction with Thai coastal water quality standards. In addition, the metals bound with sulfide fraction were taken into account in calculating the SQG because this fraction is potentially available to interstitial water when reoxidation process occurs in anoxic sediment.

The K_D was calculated from dividing metal concentrations extracted from the labile phase of sediment by metal concentrations in the interstitial water. The metals in labile phase were used for calculating the K_D due to remobilization of this fraction in the sediment-interstitial water system as a result of changing physicochemical condition in sediment. The labile metals in sediment were extracted using 25% (v/v) acetic acid and calculated on the basis of size normalization and carbonate free basis.

The SQG values for cadmium, copper, lead and zinc were found in the range of 1.2–3.1, 7–105, 23–86, and 16–125 mg kg^{-1} dry weight in <63µm fraction and $CaCO_3$ free basis, respectively. The SQG values represented concentrations of potentially available metals in sediment. However, in order to support the calculated SQG values, toxicity test for metals using the local sediments should be further studied.

Department : Marine Science	Student's Signature
Field of Study : Marine Science	Advisor's Signature
Acdemic Year : 2012	Co-advisor's Signature

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LIST OF ABBREVIATIONS

AET	Apparent effect threshold
AVS	Acid volatile sulfide
BED	Biological effect data
CCME	Canada Council of Ministers of the Environment
C_{IW}	Metals concentrations in interstitial water
C_S	Metals concentrations in sediment
EqP	Equilibrium partitioning approach
ERL	Effect range low
ERM	Effect range median
FAAS	Flame atomic absorption spectrometric
GFAAS	Graphite furnace atomic absorption spectrometric
ISQGs	Interim sediment quality guidelines
ISQVs	Interim sediment quality values
IUPUI	Indiana University-Purdue University Indianapolis
K_D	Partition coefficient
LEL	Lowest effect level
M_{AVS}	Metals bound with sulfide
M_R	Residual metals
NSTP	National Status and Trends Program
NOAA	National Oceanographic and Atmospheric Administration
NYSDEC	New York State Department of Environmental Conservation
PEL	Probable effect level
SEMs	Simultaneously extracted metals
SEL	Severe effect level
SLC	Screening level concentration
SQG	Sediment quality guideline
TEL	Threshold effect level
US-EPA	U.S. Environmental Protection Agency
WQC	Water quality criteria

CHAPTER I

INTRODUCTION

1.1 Overview

The increase in contaminations of metals, persistent organic pollutants, and polycyclic aromatic hydrocarbons in estuarine environment are the results of anthropogenic activities. These contaminants threaten estuarine ecosystems because of their high toxic effect and non biodegradable property. Major sources of these contaminants to estuarine ecosystems via primary river runoff include domestic sewage, industrial wastewater discharges or agricultural runoff.

Metals are introduced into estuarine environment in two principal forms namely those dissolved in solution (dissolved phase) and those associated with particulate materials (particulate phase). However, metals in dissolved phase can be associated with organic colloids, iron and manganese oxides, and clays (Salomons, 1980; Pokrovsky and Schott, 2002; Dong et al., 2007). The association processes can lead to precipitation of metals to the bottom sediment through coagulation and flocculation of metals. The highest precipitation of metals occurs in the mixing zone of estuary (Karbassi et al., 2008). Therefore, most metals associated with particulate materials are accumulated in the estuarine sediments rather than exporting to the ocean (Zwolsman et al., 1996; Saeedi et al., 2004).

As a result, the estuarine sediments play an important role as a sink of metals. However, metals in the sediments under reducing condition can be released back into dissolved forms *via* interstitial (pore) water, and then diffuse back into overlying water. The extent of releasing and remobilization are thus an important source of dissolved metals in aquatic system (Warren, 1981; Lee and Cundy, 2001). In general, dissolved metals in interstitial water are mainly active divalent metals (Sunda et al., 1978). These metals fraction are known as bioavailable fraction that can be uptaken by organisms (Wenholz and Crunkilton, 1995).

Consequently, benthic organisms can accumulate these metals from interstitial water and sediment by (i) directly absorption through the gills or integument, and (ii) ingestion of sediment, food, or water and following by uptake through gut (James, 1978; Reynoldson, 1987). The accumulation of metals in benthic organism’s body may show either acute or chronic toxic effects on benthos, moreover it leads to accumulation of metals in food chain and increasing in metal concentration along tropic levels of food web or so-called biomagnifications (Pourang, 1995; Wang and Pan, 2004). This problem has negative impacts on biological and estuarine ecosystems.

Therefore, it is essential to establish sediment quality guidelines (SQGs) in order to predict potential adverse biological effects from metals accumulated in the sediments. In many countries, the SQGs have been proposed as informal (non-regulatory) benchmarks to aid in interpretation of sediment quality criteria and in environmental management. The SQGs being used in various countries are based on researches taken in temperate zone (e.g., Hong Kong Special Administrative Region of the People’s Republic of China (Hong Kong S.A.R., People's Republic of China), Canada, United Kingdom, United States of America, etc.). The values setting in these SQGs may not be appropriate for the Thai’s coastal sediments because of the differences in physicochemical properties of sediment among tropical and temperate zones. These physicochemical properties of sediment affect directly on sediment quality assessment. Hence, SQG values should be established specifically for local sediments.

The SQG approaches using worldwide can be grouped into two categories: empirically-based and theoretically-based SQGs. The empirically-based SQG is developed on the basis of a direct measurement of contamination levels in the sediment coupled with laboratory or field biological effects. However, the empirically-based SQG does not regard as bioavailability, since it is based on total concentration of contaminants in the sediment (Burton, 2002). Therefore, SQG values derived upon the empirically-based SQG approaches may be overestimate bioavailability of the contaminants (McCauley et al., 2000).

However, this weakness can be solved using the theoretically-based SQG because this approach does reflect on bioavailable type of contaminants in the sediment. The theoretically-based SQG has been developed using the equilibrium partitioning (EqP) approach. The EqP approach for metals is based preliminary on understanding of metals availability partitioning between sediments and interstitial water. Furthermore, the EqP approach does consider on sediment characteristics that control availability of metals in sediment (Di Toro et al., 1991; U.S. EPA, 2005).

1.2 Purpose of the Study

To establish SQGs for cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn) for Chao Phraya river mouth sediment and/or similar areas using EqP approach.

1.3 Scope of the Study

The study was performed on five core sediment samples collected from the Chao Phraya river mouth, Samut Prakarn province, on March 9, 2011. Only top 20 cm of sediment cores were studied because most of benthic organisms live in the upper 20 cm of sediment (Batley et al., 2005).

Concentration of metals in interstitial water, total metals in sediment, and simultaneously extracted metals (SEMs) from sediment was determined. Sediment characteristics of sediment such as, grain size composition, organic carbon content, calcium carbonate content, and acid volatile sulfide (AVS) were analyzed for metal normalization purpose.

Since, it is not possible to study all metals presented in the estuarine sediment, only Cd, Cu, Pb, and Zn were selected because these metals are commonly used in industries, and are toxic to organisms. Although Cu and Zn at very low concentration are essential micronutrients for organisms, these metals show toxic effects to organisms at high concentration (Driscoll et al., 1994; Mohapatra and Rengarajan, 2000).

1.4. Location and Characteristics of Study Site

The Chao Phraya River, the Thai largest river with a 380 km length, covers a drainage basin area about 19,390 km^2 (Dalai et al., 2005). An annual average flow rate is approximately 400 m^3 s^{-1}, with the average low flow of 75 m^3 s^{-1} in March-April and average high flow of 1,150 m^3 s^{-1} in October (Nozaki et al., 2000). The intrusion of salt water is extending up to about 70 km inland from the river mouth during dry season and about 60 km during rainy season (Sirirattanachai, 2001). Before emptying into the Gulf of Thailand, the Chao Phraya River drains through central floodplain provinces including Phra Nakhon Si Ayutthaya, Pathum Thani, Bangkok metropolitan and Samut Prakarn. These provinces are heavily populated from urban and industrial development. The industries located near the river comprises of food processing facilities, pulp and paper factories, textile, chemical industries, steel manufacturing plants, electroplating, and metal finishing industries (Ratasuk et al., 2003). Moreover, only 992,000 m^3 day^{-1}, or 38.2% of total domestic waste, from Bangkok metropolitan, are treated. The rest are directly discharged into the natural watercourse and to end up in Chao Phraya estuary (PCD, 2007).

CHAPTER II

LITERATURE REVIEW

2.1 Metals in Sediments

2.1.1 Metal Fraction

The metals in sediments are associated with various fractions namely (i) exchangeable (dissolved) cations (exchangeable fraction), (ii) metals associated with iron and manganese oxides (Fe-Mn oxides fraction), (iii) metals associated with organic matter (organic matter fraction), (iv) metals with associated sulfide minerals (sulfide fraction), and (v) metals fixed in crystalline phase (residue fractions) (Salomons and Förstner, 1984; Chester et al., 1985; Salomons, 1995). The metals which associated with these fractions have different mobility in the sediment-interstitial water system, as summarized in Table 2-1.

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

Fractions	Mobility
Exchangeable	- high - changes in major cationic composition such as in the estuarine may cause a release due to ion exchange
Fe-Mn oxides	- medium - changes in redox conditions may cause a release but some metals precipitate if sulfide mineral present is insoluble
Organic matter	- medium or high - decomposition/oxidation of organic matter occurs through time
Sulfide	- strongly dependent on environmental conditions - oxidation of sulfide minerals under oxygen-rich conditions leads to release of metals
Residue	- low - only available after weathering or decomposition

The first four fractions (exchangeable, Fe-Mn oxides, organic matter and sulfide fraction) do not hold metals permanently in the sediment. Thus there fraction are called total-non residue fractions (Salomons and Förstner, 1984; Chester et al., 1985; Cuong and Obbard, 2006; Liu et al., 2011). The fraction of metals that can remobilize in the sediment-interstitial water system is considered as a labile fraction, which is only a part of the non-residue fraction of sediment (Fig. 2-1).

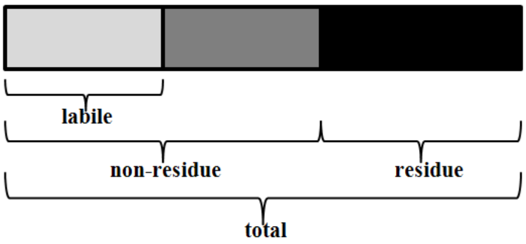


Figure 2-1 Simplified scheme of metals fraction action in the sediments

However, the first three fractions (exchangeable, Fe-Mn oxides and organic matter fraction) are relatively sensitive to physicochemical properties of sediment (Gibbs, 1973). Therefore, these fractions can remobilized in the sediment-interstitial water system by means of the changing in physicochemical properties of sediment such as redox potential, pH, and salinity, etc. (Calmano et al., 1993; Filgueiras et al., 2002; Liu et al., 2011).

Therefore metals in the labile fraction from sediments in this study are based on the assumption that the metals associated in exchangeable, Fe-Mn oxides and organic matter fractions.

2.1.2 Metals in Labile Fraction

In the sediments, metals in solid phase can remobilize into dissolved phase in interstitial water. Theoretically, metals in these two phases can be interexchange within the interstitial water-sediment system. The metal fraction in sediment that can remobilize in the sediment-interstitial water system should be considered as a labile fraction. The metals in labile fraction of sediment are potential availability of metals in sediments (Gupta et al., 1996).

2.2 Sediment Quality Guidelines

One of the important tool in assessing of contaminated sediment that affects benthic organisms and for identifying areas with potential for adverse biological effect is a sediment quality guideline (SQG). However, the SQG lacks in ability to indicate toxicity of sediment (Hübner et al., 2009). The numerical SQG is only criteria to help sustaining sediment quality and aquatic ecosystem health in the future (Canada Council of Ministers of the Environment: CCME, 1999; Wenning et al., 2005). The numerical SQGs using worldwide can be grouped into two categories based on the approach used to derive the values establish therein, namely empirically-based and theoretically-based SQGs.

Both empirically-based and theoretically-based SQG approaches are currently being developed and used in several countries, such as Hong Kong S.A.R., People's Republic of China, Australia, New Zealand, United Kingdom, Canada, and United States of America, etc. However, most of the numerical SQGs developed in these countries are empirically-based.

2.2.1 Empirically-based Sediment Quality Guidelines

The empirically-based SQG is based on direct relationship between contaminated levels and observed effects on benthic organism in the sediments. These biological effects can be assessed either in the field *via* benthic community assessments (e.g., species richness, species evenness, diversity index, total abundance, etc.) or in laboratory *via* sediment toxicity tests (e.g., growth rate, reproductive rate, mortality rate, development of life cycle, etc.). There are a number of empirically-based approaches to establish the SQGs. The common uses are (i) a screening level concentration approach (Neff et al., 1988), (ii) an apparent effect threshold approach (MacDonald et al., 2003a), (iii) and an effects range approach (Long and Morgan, 1990).

2.2.1.1 Screening Level Concentration Approach

Neff et al. (1988) had developed the screening level concentration (SLC) approach using field data on the co-occurrence of benthos species and contaminated levels in the sediments. The matching biological and chemical data collected in field surveys is used to calculate the SLC. Therefore, a species screening level concentration (SSLC) can be calculated whenever adequate data are available, by plotting the frequency distribution of the concerned chemicals concentration over all of the sites (at least ten sites) at which the benthos species occurs. The 90th percentile of this distribution is taken as the SSLC for the species being examined. Then, the SSLCs of all examined species are compiled as a frequency distribution to determine the concentration that can be tolerated by a specific proportion of the species. For example, the 5th percentile of the distribution provides an SLC of the concerned chemicals that 95% of the whole benthic organisms in the sediments can tolerate.

A number of authorities had used the SLC approach to derived numerical SQGs. The Quebec Ministry of the Environment derived two SQGs for each concerned chemicals in the St. Lawrence River, including a minimal effect threshold (MET) and a toxic effect threshold (TET) (Environment Canada and Ministere de l'Envionnement du Quebec: EC and MENVIQ 1992). The MET and TET were calculated as the 15th and 90th percentile, respectively, of the SSLC distribution for each substance. Hence, the MET and TET are considered to provide protection for 85% and 10% of the species represented in the database, respectively.

Besides, Environment Ontario established a lowest effect level (LEL) and severe effect level (SEL) for various chemicals using the SLC approach. The LEL and SEL were calculated as the 90th and 15th percentiles, respectively, of the SSLC (Laurent, 1992; Persaud et al. 1993).

2.2.1.2 Apparent Effect Threshold Approach

The apparent effect threshold (AET) approach was developed to be used as the numerical SQG for dredging disposal project in the Puget Sound area of Washington State by Tetra Tech Inc. in 1986 (MacDonald et al., 2003a). The AET approach is based on the relationship between measured concentration of concerned chemicals in sediments and observed biological effects from field measured effects (changes in benthic community structure) or laboratory measured effects (sediment toxicity tests). The AET value is defined as the concentration of concerned chemicals in sediment above which significant ($p \leq 0.05$) biological effects are always observed (Barrick et al. 1988; Washington State Department of Ecology: WDOE 1990; Grices and Walden, 1996).

2.2.1.3 Effects Range Approach

The effects range approach is based on correlating concentration of concerned chemicals in sediments with biological responses from sediment toxicity tests.

The sediment toxicity tests data were obtained from the spiked-sediment toxicity tests and field studies from several sampling sites of both freshwater and estuarine sediment conducted throughout North America as a part of the National Oceanographic and Atmospheric Administration (NOAA); and National Status and Trends Program (NSTP) (Long and Morgan, 1990). The effects range approaches have been developed in based on the values of effect range low (ERL) and effect range median (ERM); and threshold effect level (TEL) and probable effect level (PEL), in order to provide informal tools for assessing the potential for various concerned chemicals tested (Long and Morgan 1991).

The sediment toxicity results used in calculating the ERL and the ERM values were obtained from the acute test endpoint of benthic organisms. The ERL and ERM values were calculated as the lower the 10th and 50th percentiles, respectively, of “biological effect data” (Long and Morgan, 1991; Long et al. 1995).

Since, the ERL and the ERM values of NOAA have large biological effects databases. As a consequent, it was adapted to establish SQGs elsewhere. For example, interim sediment quality values-low (ISQVs-low) and interim sediment quality values-high (ISQVs-high) for sediment in Hong Kong S.A.R., People's Republic of China (Chapman et al., 1999), and interim sediment quality guidelines-low (ISQGs-low) and interim sediment quality guidelines-high (ISQGs-high) for sediment in Australian and New Zealand (McCready et al., 2006).

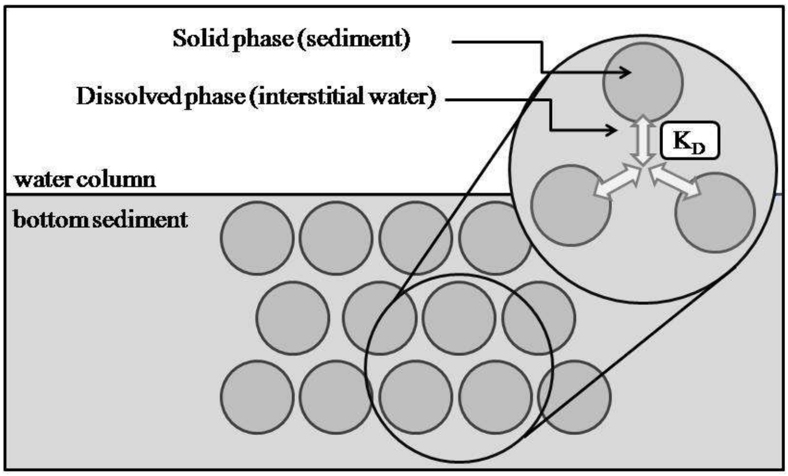
While the TEL and the PEL were developed for Florida coastal waters by MacDonald et al. (1996). Derivation of the TEL and PEL values are similar to the ERL and ERM values. However, the sediment toxicity tests database's NOAA and NSTP to be used to calculate the TEL and PEL values were drawn into two types, namely "biological effect data (BED)" – all observations of adverse biological effect, and "no-biological effect data (no-BED)" – all observations of no adverse biological effect. The TEL value was calculated as the average of the 15th percentile of BED concentration and 50th percentile of no-BED concentration, while the PEL value was calculated as the average of the 50th percentile of BED concentration and the 85th percentile of no-BED concentration (MacDonald et al., 1996).

2.2.2 Theoretically-based Sediment Quality Guidelines

Theoretically-based SQG is derived primarily from partitioning between contaminants in solid phase (sediment) and contaminants in dissolved phase (interstitial water) at the equilibrium, so-called equilibrium partitioning (EqP) approach (Shea, 1988; McCauley et al., 2000). The water-sediment EqP approach is based on the assumption that the distribution of concerned chemicals among different compartments in the sediment matrix (i.e., sediment solids and interstitial water) is predictable based on their physical and chemical properties. The equilibrium exchange between sediment and interstitial water is occurred continuously. It is also assumed that the critical factor controlling sediment toxicity is the concentration of concerned chemicals in the interstitial water. At equilibrium, the partitioning of concerned chemicals between those presented in interstitial water and those presented in sediment is equilibrium can be expressed as the partition coefficient (K_D), as shown in Fig. 2-2.

The EqP approach assumes that the critical factor controlling sediment toxicity is the concentration of contaminants in the interstitial water. The most sensitive benthic and pelagic species have similar sensitivity, then this would be equivalent to requiring that the interstitial water concentration be at the water quality criteria concentration (Di Toro and College 1989).

The procedure to calculate the SQG for prediction potential of adverse effects on benthic organisms in sediments based on the EqP approach, water quality criteria are used in conjunction with the K_D values (i.e., Di Toro et al. 1991; Ankley et al., 1996) (Eq. 2-2).



(modified from Shea, 1988)

Figure 2-2 The partitioning model between sediment and interstitial water

$$SQG = K_D \times WQC \qquad (2\text{-}1)$$

where SQG: sediment quality guideline (mg kg^{-1} dry wt.)
K_D: partition coefficient (L kg^{-1} dry wt.)
WQC: water quality criteria (mg L^{-1})

The Eq. 2-1 is a basic formula which was used to calculate the SQG values for metals (i.e., Cd, Cu, Pb, Zn, Ni, and Ag) (Van Der Kooij et al., 1991; Webster and Ridgway, 1994; U.S. EPA, 2005a), and organic compounds (i.e., PAHs, organochlorine, dieldrin, and endrin) (Webster and Ridgway, 1994; US-EPA, 2003a; 2003b; 2003c).

2.2.3 Advantage and Disadvantage of Empirically-based and Theoretically-based Sediment Quality Guidelines

Most of the numerical SQGs derived from empirically-based approaches are based on total concentration of concerned chemicals per dry weight of sediment (Burton, 2002). Therefore, these numerical SQG for metals are more likely to overestimate availability of metals as the metals in residue fraction were incorporated. Furthermore, several empirically-based SQGs do not show causality of toxic effects on benthic organisms and do not consider chronic effects or sublethal effects on benthic organisms (McCauley et al., 2000; DelValls et al., 2004). In contrast, the EqP approach does consider potentially available metals both in sediment and in interstitial water. Advantages and disadvantages of each empirically-based and EqP approaches are summarized in Table 2-2. The empirically-based SQGs for marine and estuarine sediment currently used worldwide are presented in Table 2-3.

Table 2-2 Summary of the advantages and disadvantages of the common sediment quality guidelines approaches (modified from McCauley et al., 2000; MacDonald et al., 2003b)

	SQG approaches				
	AET	**SLC**	**ERL ERM**	**TEL PEL**	**EqP**
- large database of correlative effects	✓	✓	✓	✓	
- considers effects on benthic invertebrate community structure or sediment toxicity test	✓	✓	✓	✓	
- suitable for all classes of chemicals and most types of sediments	✓	✓	✓	✓	✓
- accounts for the effects of mixtures of contaminants	✓	✓	✓	✓	
- sufficient data to derive SQG are generally available for many chemicals			✓	✓	
- relatively inexpensive and rapid		✓			✓
- common analyses and easily collected		✓			
- fairly good predictive method		✓			
- can be applied in a regulatory framework			✓	✓	✓
- wide geographical application			✓	✓	
- many types of biological effects data are considered			✓	✓	
- provides a weight of evidence			✓	✓	
- linked to a large water quality database					✓
- theory is well understood					✓
- applied to both ionic and non-ionic compounds	✓	✓	✓	✓	✓
- bioavailability is determined					✓
- measure the effects of mixtures	✓				✓
- false negatives and positives will occur	✓	✓	✓	✓	✓

AET: apparent effect threshold
SLC: screening level concentration
ERL: effects range low
ERM: effects range median
TEL: threshold effect level
PEL: probable effect level
EqP: equilibrium partitioning

Table 2-3 Comparison of sediment quality guidelines of marine and estuarine sediment for some metals (modified from Burton 2002; Hübner et al. 2009)

SQGs		**Concentration of metals (mg kg^{-1} dry wt.)**				**References**
Countries	**Approaches**	**Cd**	**Cu**	**Pb**	**Zn**	
USA	ERL	1.2	34	46.7	150	Long et al. (1995)
	ERM	9.6	270	218	410	
Florida	TEL	0.68	18.7	32.2	124	MacDonald et al. (1996)
	PEL	4.21	108	112	271	
Australia	ISQGs-low	1.5	65	50	200	McCready et al. (2006)
	ISQGs-high	10.0	270	220	410	
Hong Kong	ISQVs-low	1.5	65	75	200	Chapman et al. (1999)
	ISQVs-high	9.6	270	218	410	
New York	LEL	0.6	16	31	120	NYSDEC (1999)
	SEL	9	110	110	270	
England	EqP	7.7	34	33	190	Webster and Ridgway (1994)
China	EqP	5.56	53.8	67.8	106.4	Chen et al. (2007)

ERL: effects range low
ERM: effect range median
TEL: threshold effect level
PEL: probable effect level
ISQGs-low: interim sediment quality guidelines-low
ISQGs-high: interim sediment quality guidelines-high
ISQVs-low: interim sediment quality values-low
ISQVs-high: interim sediment quality values-high
LEL: lowest effect level
SEL: severe effect level
EqP: equilibrium partitioning approach

In addition to the advantage as stated in Table 2-2, the EqP-based approach has been chosen to establish the SQG values for metals in this study. Because the approach is making use of Thai coastal water quality standards of metals which already available for Thai's coastline, and this approach does not require intensive toxicity-testing according to the theoretical fact.

2.3 Partition Coefficient for Metals

The K_D values for metals can be directly calculated from metal concentration presented in sediment and in interstitial water (Van Der Kooij et al., 1991; Webster and Ridgway 1994; Chen et al., 2007), or be simulated by surface complex model (Liu and Tang, 1998).

In this study, the first method was chosen for calculating the K_D values because it closely represents real condition of sediment-interstitial water system (US-EPA, 1999a). The formula for calculation of the K_D values is shown in Eq. 2-2. However, the metals in sediment should be considered as a labile fraction because this fraction can remobilize in the sediment-interstitial water system.

$$K_D = \frac{C_S}{C_{IW}} \tag{2-2}$$

where K_D: partition coefficient (L kg^{-1} dry wt.)
C_S: metal concentration in sediment (µg kg^{-1} dry wt.)
C_{IW}: metal concentration in interstitial water (µg L^{-1})

2.4 Sediment Quality Guideline based on Equilibrium Partitioning Approach for metals

At present, less progress has been made with regard to the application of the EqP approach for metals and only few EqP results for metals is currently available (Chen et al., 2007).

Liu and Tang (1998) and Chen et al. (2007) developed the calculation of SQG values based on EqP approach for metals, which it does consider other major binding phases in sediment, namely metal bound with sulfide fraction and in residual fraction, as shown in Eq. 2-3.

$$SQG = K_D \times WQC + M_{AVS} + M_R \tag{2-3}$$

where: SQG: sediment quality guideline (mg kg^{-1} dry wt.)
K_D: partitioning coefficient (L kg^{-1})
WQC: water quality criteria (mg L^{-1})
M_{AVS}: metal bound with sulfide (mg kg^{-1} dry wt.)
M_R: residual metals (mg kg^{-1} dry wt.)

However, metal in residual fraction is that of strongly associated within a crystalline structure of sediment and cannot contribute to sediment-interstitial water system by natural processes (Salomons, 1995). As such, residual metal is not readily available to benthic organisms (Pardo et al., 1990; Perin et al., 1997). Therefore, the SQG values that include residual metals fraction, as Eq. 2-3, should lead to high SQG values, and it may be more likely to overestimate metals availability in sediment.

The SQGs that overestimates metals availability may not be appropriate in setting up sediment quality criteria in predicting potentiality for adverse effects on benthic organisms.

Therefore, calculation of SQG values based on EqP approach for metals in this study did not consider the metals in residual fraction. But the metals bound with sulfide fraction (M_{AVS}) were still included (Eq. 2-4).

$$SQG = K_D \times WQC + M_{AVS} \qquad (2\text{-}4)$$

where SQG: sediment quality guideline (mg kg^{-1} dry wt.)
K_D: partitioning coefficient (L kg^{-1} dry wt.)
WQC: water quality criteria (mg L^{-1})
M_{AVS}: metals bound to sulfide (mg kg^{-1} dry wt.)

The M_{AVS} are potentially released from sediment to interstitial water, and being available for biota. In general, estuarine sediments contain higher concentration of organic matter from river runoff and strong microbial activity (Berner, 1981). Microbial degradation of organic matter in sediments consumes oxygen, resulting anoxic condition in the sediments. An oxic layer of estuarine sediment may present at only few millimeters thick at the upmost layer (Petersen et al., 1997).

Under anoxic condition, other terminal electron acceptors are utilized for the degradation of organic matter in sediments. In estuarine and marine sediments, there are denitrification (nitrate: NO_3^-), manganese oxides (represented by manganese dioxides: MnO_2), iron oxides (represented by ferric oxide: Fe_2O_3), and sulfate reduction (sulfate: SO_4^{2-}) (Fenchel and Jørgensen, 1977) according to the order of electron acceptors, respectively. In general, sulfate in seawater is classified as a major ion, which is found at 7.7% (w/w) of total dissolved ions or 0.0282 mol kg^{-1} of seawater (Libes, 1992). The sulfate is usually important biogeochemical due to it supported from seawater to the estuarine sediments (Kasten and Jørgensen, 1999). The sulfate reduction in anoxic estuarine sediments causes sulfide generatation, as shown in Fig 2-3. Thus, most of anoxic estuarine sediments contain relatively higher concentration of sulfide in sediment (Elderfield and Hepworth, 1975).

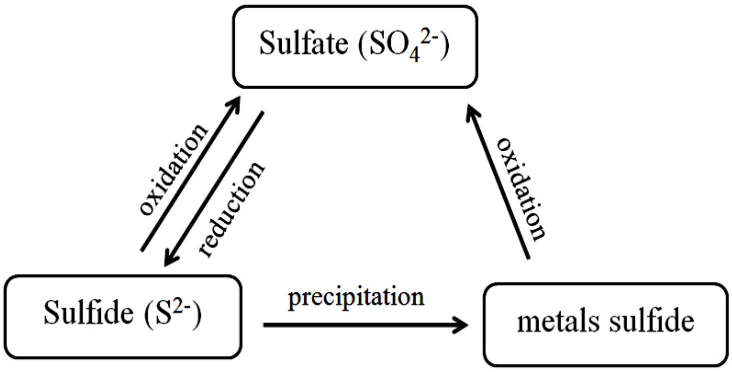


Figure 2-3 Simplified scheme of sulfur cycling in environment (modified from Haaijer, 2007)

It is well known that sulfide plays an important role in controlling speciation of divalent metals in sediment and in interstitial water (Lee et al., 2000), particularly the divalent metals (M^{2+}) in interstitial water. Under anoxic estuarine sediment, sulfide is primarily bound with metals and formed insoluble metal sulfides, such as FeS, CdS, CuS, PbS, ZnS, and NiS (Brown and Neff, 1993), which results in a loss of dissolved metals in interstitial water.

However, reoxidation processes in sediment may occur, if anoxic sediment is exposed and oxidized (Lin and Morse, 1991) through bioturbation, tides, storms, bottom trawling, dredging activities, etc. These processes can induce sediment resuspension resulting in oxidation of sediment. It had been reported that up to 90% of metal sulfide can oxidize within 1 day of exposure to oxic condition, which it leads to release dissolved metals into interstitial water (Cooper and Morse, 1996). Consequently, the reoxidation processes cause the transformation of insoluble metal sulfide to dissolved metals in interstitial water (Petersen et al., 1997; Fang et al., 2005).

However, addition of metals bound with sulfide fraction for calculating the SQG values in Eq. 2-4 is based on the assumption that kinetic of metal sulfide oxidation is rapidly and completely occurs in during reoxidation of anoxic sediment.

2.5 Metals bound with Sulfide

The M_{AVS} in this study are considered from reaction of iron monosulfide (FeS) with various divalent metals (M^{2+}) (e.g., Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} etc.), as shown in Eq. 2-5. The FeS is a large reservoir of sulfide in anoxic sediment (Cornwell and Morse, 1987), which the added M^{2+} displaces FeS to form metal sulfides (MS) (Allen and Unger, 1981; Di Toro et al., 1990).

$$\mathrm{FeS} + \mathrm{M}^{2+} \leftrightarrow \mathrm{Fe}^{2+} + \mathrm{MS} \tag{2-5}$$

Analysis of acid volatile sulfide (AVS) and its simultaneously extracted metals (SEMs) is employed to determinate concentrations of sulfide and metal sulfides in sediment. Consider the following reaction to describe FeS and MS *via* the AVS and SEMs analysis, as shown in Eq. 2-6. Thus, the mole of FeS and M^{2+} can be determined through concentrations of AVS and SEMs.

$$(\mathrm{FeS\ or\ MS}) + 2\mathrm{H}^{+} \quad \leftrightarrow \quad (\mathrm{Fe}^{2+}\ \mathrm{or}\ \mathrm{M}^{2+}) + \mathrm{H_2S} \tag{2-6}$$

where FeS: iron monosulfide
MS: divalent metal sulfide
H_2S: acid volatile sulfide
Fe^{2+}: ferrous iron
M^{2+}: divalent metal ions

The AVS is operationally defined as sulfide that form hydrogen sulfide (H_2S) under the condition of mixing sediment with 1 M HCl, which including FeS and MS (Allen et al., 1991).

As such the SEMs are operationally defined as metals bind mole to mole with sulfides. The SEMs is soluble in acid solution during the extraction of sulfide (acidification step) by 1 M hydrochloric acid (HCl) (Allen et al., 1991). In general, common metals found in SEMs are Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} (Allen, 1993).

2.6 Normalization in Sediment Analyses

Sediments are a heterogeneous mixture of particles ranging from millimeter to micrometer in size. Metal concentration in sediment tends to decrease with increasing grain size in sediment (Förstner and Wittmann, 1981), as shown in Fig. A-1 of Appendix A. Fine grain sediment (<63 µm), silt + clay fraction, adsorbs and transported metals more readily than coarse grain sediment because fine grain sediment has greater surface area which contain more binding sites (Olsen et al., 1982). Therefore, fine grain sediment fraction is recommended as a primary practice for normalization of metal in sediment (Loring, 1991; Szava-Kovats, 2008), which help to reduce the grain size effect on metal concentration in sediment.

For estuarine and marine sediments, calcium carbonate content plays an important role of the “dilution” affecting the metal concentration in sediments (Chester and Voutsinou, 1981; Rubio et al., 2000). Therefore, calcium carbonate content is also recommended to normalize metal concentration in sediment, which it called “free calcium carbonate basis.”

Since the sediment characteristics (e.g., grain size and calcium carbonate) have an influence to metal concentration in sediment. Thus, normalization with sediment characteristics should be included in a calculation of metal concentration in sediment.

In this study, all metal concentrations were normalized by size composition and carbonate contents, in order to reduce effect of size composition and effect of dilution in sediment and help in better inter-comparison of results.

2.7 Validation of Equilibrium Partitioning and Metal Extraction

Before using the EqP approach in establishing the numerical SQG for metals in this study, revision of metals partitioning equilibrium time and appropriate chemicals for metal extraction was carried out.

2.7.1 Equilibrium Time

Chen et al. (2007) applied EqP approach to derive of numerical SQG for metals in Dianchi Lake, PR China, in which the sediment cores for studying partition coefficient were stored at 4°C in the dark for 21 days prior to analysis. However, the study of Chen et al. (2007) did not measure equilibrium time of sediment cores. Therefore, validation of the equilibrium time in this study was studied to ascertain that the equilibrium of metals partitioning between those presented in interstitial water and those presented in core sediment samples is achieved in 21 days after sample collection.

During sampling and transportation from sampling site to laboratory, the equilibrium of metals partitioning between in interstitial water and in sediments might be disturbed. In this study, the equilibrium time for metal partitioning of the collected sediment core samples was studied before further analysis.

At equilibrium the concentration of chemical species in the interstitial water should not change with time (Mackay, 1979; Mayer et al., 2003). However, to make a direct determination of metals in the interstitial water is difficult due to a very small sample size. Since the interstitial water is an interface between sediment and overlying water, changing of metal concentration in the interstitial water will directly effects on metal concentration in the overlying water *via* diffusive flux. Therefore, measuring of changing metal concentration in the overlying water will reflect the changing in metal concentration in the interstitial water. Moreover, the overlying water contains much lower concentration of metals than the interstitial water, thus slightly change of metal concentration in the interstitial water can be easily observed though a slight change of metals concentration in overlying water.

Therefore, the equilibrium time for metal partitioning of sediment core samples in this study was determined by measuring concentration of metals (Cd, Cu, Pb, and Zn) in the overlying water as a function of time. During the experiment, all sediment cores were stored in the dark at 4°C to reduce bacterial activity in the cores (Loring and Rantala, 1992; US-EPA, 2001).

2.7.2 Chemical Extractants

Referring to Eq. 2-2, the K_D was calculated by dividing metal concentration of sediment with metal concentration of interstitial water. Therefore, differences in metal concentration given by difference extraction procedure will lead to the difference in K_D.

Difference chemicals and experimental conditions using to extract metals from sediments will give difference degree of extraction and lead to difference concentration of metals being extracted from sediment. Chemicals that mostly used to extract metals from sediments can be grouped into three categories as following:

(i) Cationic exchange
  - 0.01 M calcium chloride ($CaCl_2$) (Janssen et al., 1997; Peijnenburg et al., 2001)

(ii) Complexation
  - 0.05 M ethylene diamine tetra acetic acid (EDTA) (Degryse et al., 2009)

(iii) Acidification
  - hydrochloric acid (HCl):nitric acid (HNO_3):hydrofluoric acid (HF) (1:3:1 v/v) (Burton et al., 2005; Peng et al., 2005; Ololade et al., 2011)
  - HNO_3+HCl (Chen et al., 2007)
  - 25% (v/v) HNO_3 (Hassan et al., 1996)
  - 25% (v/v) acetic acid (HOAc) (Loring and Rantala, 1992)

In this study, effectiveness of selected types of chemicals using as extractant for the labile fraction in sediment was studied. The appropriate extractant will give the proper concentration of metal using to calculate the accurate K_D.

CHAPTER III

MATERIALS AND METHODS

3.1 Overview

Before using the EqP approach to establish the numerical SQG in this study, the validation of procedures for metal extraction in this study was performed prior to further experiments. The validation was divided into two parts. Firstly, it is important to ensure that equilibrium in the sediment core samples has achieved at 21 days, after sampling, under experiment condition (in the dark at 4°C). Secondly, the most appropriate chemicals have been chosen to extract the metals from labile fraction, which will be used in the calculation of the K_D values of the sediments.

All metals in sediment using in the calculation were carbonate free basis and normalization by the size composition Fig. 3-1 shows a schematic diagram summarizing the consequent and procedures used in this study.

3.2 Sampling Sites and Samples Collection

The sampling site was located at the Chao Phraya river mouth, Samut Prakarn province five stations were selected for sediment core sampling (Fig. 3-2). Prior to sampling, physicochemical properties of water at each sampling site was measured *in situ* using a YSI multi-probe model 620, including temperature, salinity, pH and dissolved oxygen. Immediately after sampling, redox potential (Eh) of surface sediment (~5 cm), was determined using a Platinum Combination Redox Electrode (Thermo Orion 290A).

The sediment samples were collected on March 9, 2011 from five stations using push corer making from Plexiglas® glass (acrylic) with has an inner diameter of 6.4 cm and length of 70 cm (Fig. 3-3). At individual station, one sediment core was carefully collected. For method validation experiment, additional 4 cores were collected at station 4.

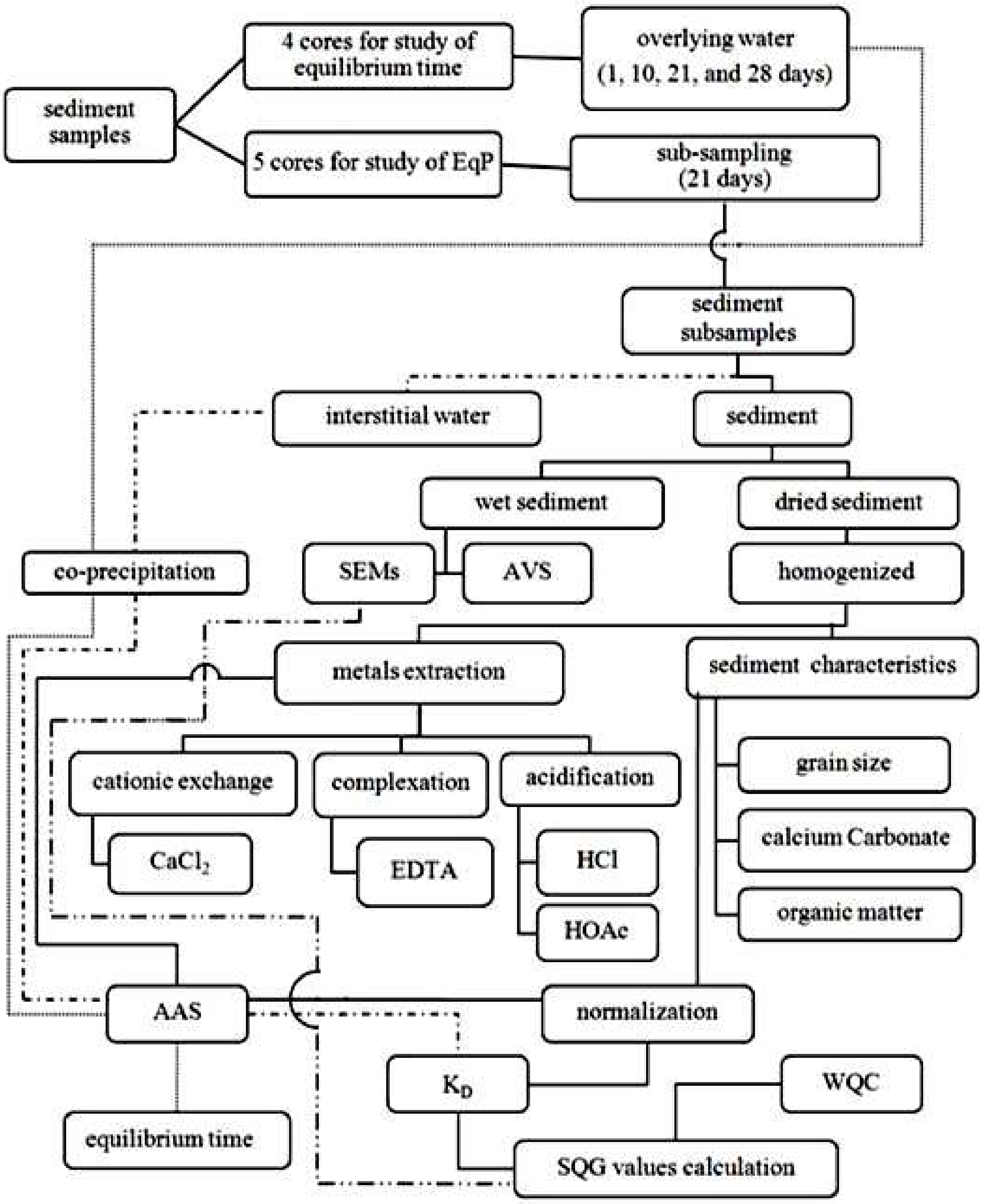


Figure 3-1 Schematic diagram summarizing the consequent and procedures using in evaluation of sediment quality guidelines

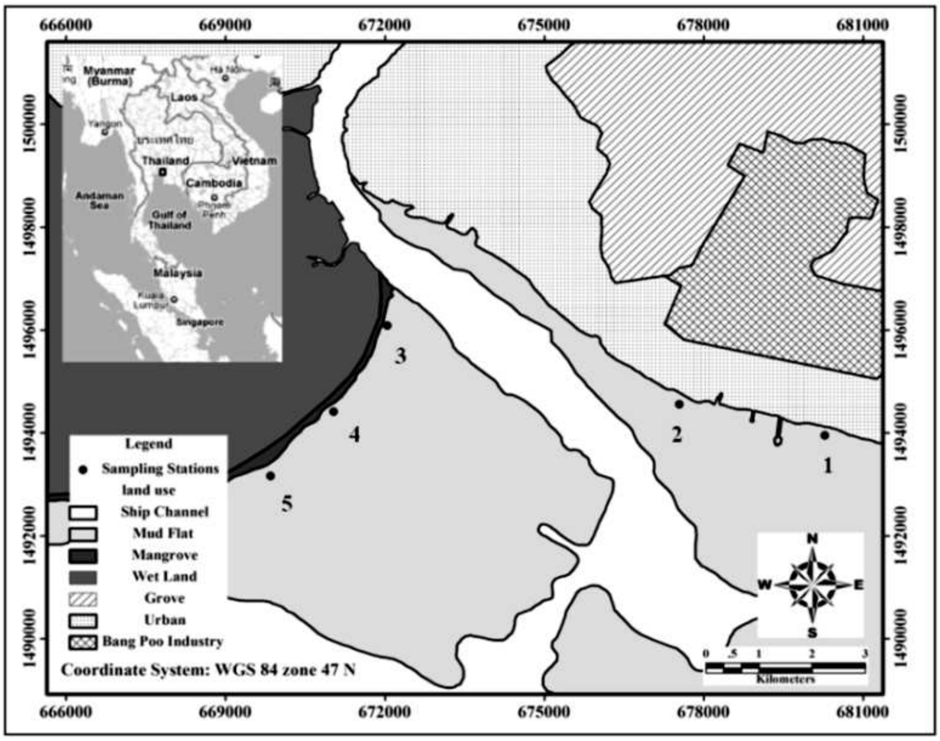
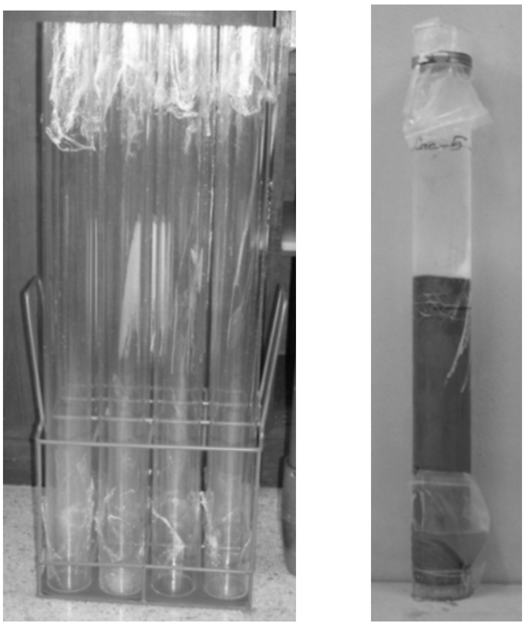


Figure 3-2 Sampling site at the Chao Phraya river mouth, Samut Prakarn province



(a) (b)

Figure 3-3 Push corers (a) Push corers making from Plexiglas®, and (b) Plexiglas containing sediment

Each sediment core sample, a top 30 cm of sediment and a 30 cm water column over the sediment’ surface were collected. The top-end of the corer was immediately sealed with plastic bag. The superlene nylon 6 (polyamide) was inserted to the bottom-end of the core to hold the sediments, as shown in Fig. 3-3(b). The sediment core samples were stored in an ice box. The core should hold up-right in a vertical position after sampling and during transportation back to the laboratory. In laboratory, these sediment core samples were stored in the dark at 4°C in refrigerator to limit biological activities (Loring and Rantala, 1992).

3.3 Equipment and Reagents

3.3.1 Plastic and Glass wares

All the plastic and glass wares using in analysis and storage of samples/reagents were acid-cleaned prior to use. The labwares were soaked in 10% HNO_3 (AR grade) for several days, rinsed with deionized water (DI-water: >18 MΩ·cm) twice, and let them to dry in a laminar flow cabinet. The dried labwares were kept in clean zip-locked plastic bags until using.

The labwares were rinsed twice with 2M high-purity HNO_3 and Milli-Q water (>18 MΩ·cm) before using.

Nuclepore$^{®}$ filter membranes were precleaned by soaking in 5% high-purity HNO_3 for 5 days, rinsing with Milli-Q water several times and kept in Milli-Q water until using.

3.3.2 Reagents

High-purity HNO_3 was propared from 65% HNO_3 AR grade by Teflon$^{®}$ sub-boiling acid distillation system.

Ammonium hydroxide (NH_3OH) was purified using isothermal distillation by placing two beakers in a desiccator. One beaker is filled with Milli-Q water and another is concentrated NH_3OH. The desiccator was sealed and let the samples stayed at room temperature for several days (Armarego and Chriatisa, 2009). The 30% suprapur$^{®}$ HCl was purchased from Merck. All other chemicals were AR grade.

3.4 Subsampling and Sample Collection from Sediment Core Samples

3.4.1 Collection of Overlying water

The overlying water was collected from <5 cm above sediment surface using a polypropylene syringe under oxygen-free condition in a nitrogen glove box (Fig. 3-4). The overlying water was then filtered through a 0.45 µm Nuclepore® filter membrane inside a laminar flow cabinet. The filtrated sample was immediately adjusted to <2 with concentrated high-purity HNO_3 before storing for further analysis in order to prevent adsorption of metal onto the container's surface.

3.4.2 Subsampling of Core sediment

Maintaining of sediment core sample under the nitrogen atmosphere during sub-sampling is important for extraction of interstitial water because of anoxic sediment can be oxidized by oxygen, which will significantly alter metal speciation in interstitial water (Bufflap and Allen, 1995; Mudroch and Azcue, 1995). Therefore, all sediment core samples in this study were subsampled in the nitrogen glove box.

Figure 3-4 Nitrogen glove box for handling sediment samples under oxygen-free (nitrogen) atmosphere

A top 20-cm sediment in the core sample after storing in the dark at 4°C until equilibrated (following the results from section 3.6.1) was subsampled into four layers of 5 cm thickness in nitrogen glove box. Sediment subsample (diameter of 6.4 cm × thickness of 5 cm) gives a sufficient volume of interstitial water for metal analysis. The subsampling of sediment core sample in a nitrogen glove box is shown in Fig. 3-5. Each subsample was divided into two portions. The first portion of sediment (approximate 10-15 g) was kept in a sealed plastic bag and stored at 4°C for AVS and SEMs analyses. The remaining of wet sediment portion was placed into a 50-ml polyethylene centrifuge bottle for extracting of interstitial water.

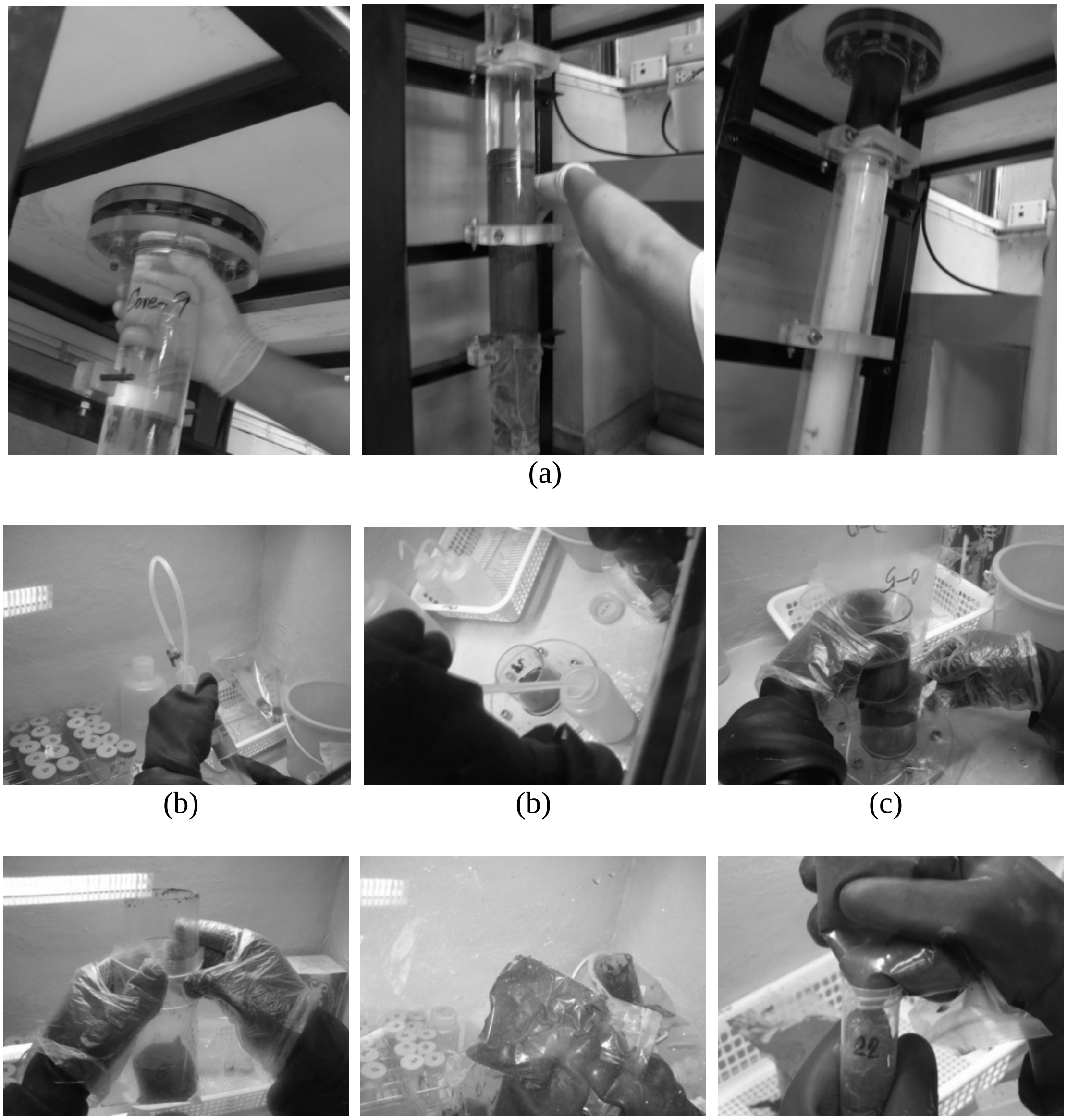
3.4.3 Interstitial water Extraction

The sediment in the centrifuge bottle from section 3.4.2 was centrifuged at 3,500 relative centrifugal force (RCF) (approx. 3,900 round per min) for 30 min at *in situ* temperature (Skrabal et al., 2000). The extracted interstitial water was filtered using the polypropylene syringe through the 0.45 µm Nuclepore® filter membrane under the oxygen-free atmosphere. The filtrated interstitial water was immediately adjusted pH to <2 with concentrated high-purity HNO_3 before storing for further analysis.

After centrifugation, the sediment samples (solid phase) were freeze-dried until dryness (approx. 24 hours) before storing in labeled plastic bag for further analysis.

3.5 Analysis of Overlying water and Interstitial water Samples

In general, overlying water and interstitial water sample from estuary contains higher concentration of saline, organic carbon, free sulfide ions. These matrix interferences were significantly influencing the metal determination of metals by atomic absorption spectrophotometry (AAS), particularly graphite furnace. These matrix interferences can reduce atomic absorption signal (Thompson and Paton, 1991). However, some of these matrix interferences can be minimized through a following preconcentration technique.



(a)

(b) (b) (c)

(c) (d) (e)

Figure 3-5 Sediment sub-sampling steps in a nitrogen glove box: (a) care installation and sediment extruding step, (b) overlying water collection, (c) sub-sampling of sediment, (d) sediment homogenization in plastic ziploc bag, and (e) placing sediment into a polyethylene centrifuge bottle.

Methods of preconcentration prior to the determination of metal in seawater include liquid-liquid extraction, solid-phase extraction, and co-precipitation. One of a widely used method is the co-precipitation due to a relatively fast, less labor intensive, and easily avoid contamination (Komjarova and Blust, 2006). In this study, the co-precipitation method was used to preconcentrate metals in the overlying water and the interstitial water samples prior to AAS analysis.

The filtered samples of both overlying water and interstitial water were preconcentrated with Cobalt-APDC co-precipitation method and redissolved in concentrated high-purity HNO_3 (Boyle and Edmond, 1977). The details for a cleaning step, preparation of reagent solution, and co-precipitation technique are described in Appendix B (B-1).

The concentration of metals (Cd, Cu, Pb, and Zn) in both overlying water and interstitial water samples after preconcentration were determined by graphite furnace atomic absorption spectrophotometer (GFAAS).

3.6 Validation of Procedures for Equilibrium Time and Metal Extraction

3.6.1 Equilibrium Time

The four sediment core samples collected from station 4 were brought out of the refrigerator and let them equilibrate in the dark at 4°C. After day 1, 10, 21 and 28, the overlying water of each core was collected and filtered as described in section 3.4.1. The concentration of metals in the overlying water was preconcentrated and then determined by AAS as described in section 3.5.

3.6.2 Extraction Chemicals for Labile Metals in Sediment

In this study, three single-chemical extraction techniques, including cationic exchange (0.01 M $CaCl_2$), complexation (0.05 M EDTA), and acidification (25% (v/v) HOAc) were performed to evaluate its suitability in estimating the metals in labile fraction of sediment. It is believed that 1 M HCl provides a total non-residual fraction. Therefore, 1 M HCl will be used as a reference for metals extracted with other single-chemical extractants.

Dried sediment sample was homogenized and grind as described in section 3.8. The dried sediment was weight exactly (to milligram) and placed in a precleaned polyethylene centrifuge tubes. The reagent was added and shaking to allow the chemicals to extract the metals associated in the sediment. After a setting time, the solution was separated from the solid sediment by centrifugation. The supernatant was made to assigned volume prior to determine by GFAAS for Cd, Cu, and Pb and by flame atomic absorption spectrophotometer (FAAS) for Zn. Table 3-1 summarizes the methods for each single-chemical extractant. Detailed procedures were described in Appendix B (B-2).

Table 3-1 Summary of extraction methods for evaluating labile metals in non-residual fraction of sediments

Condition	$CaCl_2$	EDTA	HOAc	HCl
Concentration of the reagent	0.01 M[1]	0.05 M[2]	25% (v/v)[3]	1 M[4]
Sediment (g)	1.0	1.5	0.8	0.5
Volume of solution (ml)	10	10	10	10
Shaking time (hr.)	24	12	6	4
Centrifuge (RCF)	3,500	3,500	3,500	3,500
centrifuge duration (minutes)	30	30	30	30
Add high-purity HNO_3 (µL)*	300	-	-	-
Final volume adjust by Milli-Q water (ml)	10	10	10	10
The solution samples were kept in a freezer before making measurements with GFAAS for Cd, Cu, and Pb; and FAAS for Zn.				

* To prevent metal adsorb on the bottle and growth of bacteria (Houba et al., 2000)

[1] Houba et al. (2000) [2] Fangueiro (2002)

[3] Loring and Rantala (1992) [4] Snape et al. (2004)

3.7 Acid Volatile Sulfide and Simultaneously Extracted Metals Analysis

The AVS and SEMs method uses the acidification to release both sulfide and metal from the sediment and thus provides a useful means of assessing the amount of metal associated with sulfide (US-EPA, 1997). Approximately 10 g of wet sediment, subsampling from sediment cores as described in section 3.4.2, that stored in sealed plastic bag were analyzed for AVS and SEMs using a method expressed in Allen et al. (1991). Detailed methodology is described in Appendix B (B-3).

The sulfide (AVS) in the wet sediment was converted to hydrogen sulfide (H_2S) by acidification with 1 M HCl at room temperature. The H_2S was purged from the sample by nitrogen gas and trapped in an aqueous solution of 0.5 M sodium hydroxide (NaOH). The amount of AVS was determined by colorimetric method.

After releasing H_2S, the acidified sediment sample was filtered through GF/C filter. The metals solubilized from the sediments during acidification step are called SEMs. The concentration of metals in SEMs fraction was determined by GFAAS for Cd, Cu, and Pb and by FAAS for Zn.

3.8 Homogenization of Sediment Samples

Freeze dried sediments were analyzed for their sediment characteristics (i.e., grain size composition, organic matter, and calcium carbonates) and were extracted for metals in sediment. To ensure that a portion taken for analysis represents the sediment sample, the dried sediments should be homogenized before using. The dried sediment samples were homogenized using coning and quartering technique, as illustrated in Fig. 3-6.

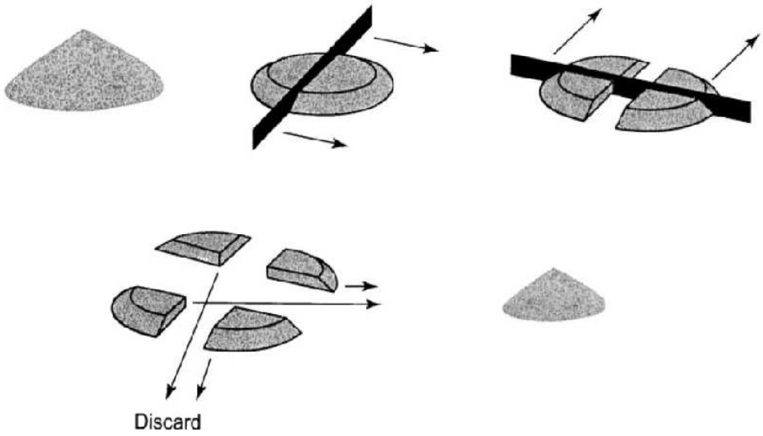


Figure 3-6 Coning and quartering technique (Gerlach et al., 1990)

The procedure is described as the followings: (i) mix the dried sediment by a clean polypropylene spoon and form into a cone; (ii) flatten the cone by pressing the top without further mixing; (iii) divide the flat circular pile into equal quarters by cutting or scraping out 2 diameters at right angles, discard 2 opposite quarters and thoroughly mix the 2 remaining quarters; (iv) use a clean polypropylene spoon to put them into a cone and repeat the procedure several times. The procedure is stopped, when sample homogeneity is achieved.

The homogenized sediment was used for grain size composition analysis with out grinding. One portion was grind to fineness using agate mortar and pestle for all chemical analyses including organic carbon, carcium carbonate, and metals.

3.9 Grain Size Composition Analysis

Analysis of grain size composition of sediment was performed by wet sieving coupled with sedimentation-pipette method after pre-treatment to remove organic matter and calcium carbonate. The amount of organic matter and calcium carbonate presented in the sediment sample are significantly influenced grain size distribution during pipette method.

The wet sieving of pretreated sediment through the 63 µm opening sieve will separate the sand fraction (> 63µm fraction) to remain on the seive. The passing through slurry was collected and allowed to settle and subsampling by pipette method based on Stokes' law to determine silt (2–63 µm) and clay (<2 µm) fractions (Beuselinck et al., 1998). The detailed methodology is described in Appendix B (B-4).

3.10 Organic Carbon Analysis

Determination of organic carbon contents is based on the Walkley-Black method, as described in Loring and Rantala (1992). This method can only determine humus matter but not the graphite and coal fractions of organic materials.

The Walkley-Black method utilized exothermic heating and oxidation with 1 N potassium dichromate ($K_2Cr_2O_7$) in acid condition, followed by the titration of excess dichromate with 0.5 N ferrous ammonium sulfate ($Fe(NH_2)(SO_4)_2 \cdot 6H_2O$) solutions to end point. Silver sulphate (Ag_2SO_4) was added to oxidation of Cl^- to reduce interference. The detailed methodology is described in Appendix B (B-5).

3.11 Calcium Carbonates Analysis

Determination of calcium carbonate contents is based on the acid-base titration method, as described in Sompongchaiyakul (1989). Dried sediment sample was treated with excess of HCl, as shown in Eq. 3-1 and 3-2.

$$\mathrm{CaCO_3 + 2HCl \leftrightarrow CaCl_2 + H_2CO_3} \tag{3-1}$$

$$\mathrm{NaOH + HCl \leftrightarrow NaCl + H_2O} \tag{3-2}$$

The reaction between HCl and carbonate is completed with heating. The unreacted acid was back titrated with NaOH solution. The detailed methodology is described in Appendix B (B-6).

3.12 Atomic Absorption Spectrophotometry

Prior to any determination of metals by AAS, optimal condition of the equipment had to be verified. In GFAAS, the pyrolysis and atomization temperature for metals should be optimized according to the solution sample. The optimization of pyrolysis and atomization temperature for GFAAS of the PERKIN ELMER Zeeman Atomic Absorption Spectrometer 4100 ZL for the determination of Cd, Cu, Pb and Zn in each solution sample is reported in Table C-1 to C-6 of Appendix C.

The optimal condition for FAAS of Flame VARIAN SpectA 220 FS Atomic Absorption Spectrometer for the determination of Zn in sediment is reported in Table C-7 of Appendix C.

However, solution samples may contain unknown components that interfere with the analyst signal causing inaccuracy in the determined concentration. In this study, standard addition method was used to make standard addition curves in order to correct the matrix suppression in the unknown composition samples (May and Brumbaugh, 1982). The calibration curves and standard addition curves in this study are shown in Appendix D.

3.13 Quality Control

The quality control was conducted as part of preparation and analysis of samples. The analytical performance characteristics evaluated include detection limit, laboratory reagent blank, sample replicates (precision) and spikes (recovery).

3.13.1 Detection Limit

Detection limit (DL) is expressed as the lowest concentration that can be detected with a certainty of more than 90%. Calculation of the DL was performed by taking 10 replicates of Milli-Q water, and calculating standard deviation (SD). The calculation of DL is given in Eq. 3-3 and Eq. 3-4.

$$\mathrm{DL} = \frac{3\mathrm{SD}}{\mathrm{m}} \tag{3-3}$$

$$\mathrm{SD} = \sqrt{\sum_{i=1}^{n} \frac{(x_i - \overline{x})^2}{(n-1)}} \tag{3-4}$$

where
SD : standard deviation
m : slope of detections
x_i : each individual value used to calculate mean
$\overline{x}$: mean
n : total number of values

3.13.2 Laboratory Reagent blank

Laboratory reagent blank (LRB) was used to assess contamination from reagents and during the analytical procedures by replacing a sample with Milli-Q water and treating the reagent blank like the sample. The LRB should gives a similar value as the DL.

3.13.3 Precision

The precision is the measurement of the correction degree of analytical method. Normally it is expressed as a percentage of relative standard deviation (%RSD). The %RSD calculation is shown in Eq. 3-5.

$$\%\mathrm{RSD} = \frac{\mathrm{SD}}{\overline{\mathrm{X}}} \times 100 \qquad (3\text{-}5)$$

where SD : standard deviation
$\overline{\mathrm{X}}$: mean

Typically, an acceptable the %RSD value of general parameter is <10% for a good precision. However, a satisfactory precision for low concentration level of measurement, which is prone to error. The %RSD value is required to be <20% (Chen and Ma, 1998).

3.13.4 Recovery

The percent recovery (%R) is used to indicate the yield of analytical in pre-concentration method. The percent recovery was performed by using estuarine water from sampling site, spiked with known concentration metals. The calculation of the %R is followed in Eq. 3-6. Normally, the %R value is 100±20%.

$$\%\mathrm{R} = \frac{(\mathrm{C_{sp}} - \mathrm{C_s})}{\mathrm{C_r}} \times 100 \qquad (3\text{-}6)$$

where $\mathrm{C_{sp}}$: concentration of spiked sample
$\mathrm{C_s}$: concentration of non-spiked sample
$\mathrm{C_r}$: concentration of real concentration

CHAPTER IV

RESULTS

4.1 Physicochemical Quality of Seawater and Surface Sediment at Sampling Sites

Physicochemical condition of seawater at the Chao Phraya river mouth prior to sampling, on 9 March 2011, was measured using the YSI multi-probe model 620. The parameter included temperature, salinity, pH and dissolved oxygen. Redox potential of the top 5-cm surface sediment was measured by the HANA instrument combined with redox potential probe. The physicochemical condition of seawater and surface sediment in each sampling station were reported in Table 4.1

Table 4-1 Physicochemical condition of seawater and surface sediment at the Chao Phraya River mouth on 9 March 2011

Stations	Latitude (N)	Longitude (E)	Temp	S	pH	DO	Eh
1	13° 30′ 32.6″	100° 40′ 09.5″	29.1	24.0	7.89	5.71	-157.0
2	13° 31′ 02.8″	100° 38′ 29.7″	29.2	23.5	7.75	4.98	-150.9
3	13° 30′ 36.9″	100° 33′ 23.2″	29.2	24.6	7.93	3.73	- 105.3
4	13° 31′ 27.1″	100° 35′ 18.4″	29.9	21.4	7.69	4.00	-
5	13° 30′ 50.7″	100° 38′ 35.9″	29.2	22.3	7.82	4.96	-159.9

Temp:	temperature (°C)
S:	salinity (psu)
DO:	dissolved oxygen (mg L^{-1})
Eh:	redox potential (mV)

4.2 Dissolved Metals Concentration in Overlying water

In the validation of equilibrium time after sampling, the overlying water in the four sediment cores from station 4 were collected at day 1, 10, 21, and 28, after incubation at 4°C in the dark, to determine dissolved Cd, Cu, Pb and Zn concentration. The results were reported in Table 4-2. The achieved equilibrium time was used to incubate all sediment cores prior to extract interstitial water.

Table 4-2 Concentrations of dissolved metals in overlying water during equilibration experiment

Days	Metals in overlying water (µg L^{-1})			
	Cd	Cu	Pb	Zn
1	0.46	4.11	53.5	43.3
10	0.19	2.43	0.65	27.6
21	0.09	2.13	0.92	15.2
28	0.13	1.67	0.60	22.0

4.3 Dissolved Metals Concentration in Interstitial water

After incubation at 4°C in the dark for 21 days according to the results from section 4.2, dissolved Cd, Cu, Pb and Zn concentration in interstitial water extracted from four sections of the sediment cores collected from five stations were determined. The results were reported in Table 4-3. These dissolved metals concentration were used to the calculation of K_D which reported in section 5.4 in Chapter V.

Table 4-3 Concentrations of dissolved metals in interstitial water at various depth of the core sediments

Stations	Layers (cm)	Metals in interstitial water (µg L^{-1})			
		Cd	Cu	Pb	Zn
1	0 – 5	0.12	2.51	0.67	42.6
	5 – 10	0.15	2.51	0.55	87.5
	10 – 15	0.18	1.64	0.48	76.7
	15 – 20	0.16	0.75	0.40	49.2
2	0 – 5	0.19	2.29	0.86	75.5
	5 – 10	0.13	0.93	1.28	37.8
	10 – 15	0.17	0.94	1.53	62.9
	15 – 20	0.13	1.95	0.58	87.7
3	0 – 5	0.18	3.17	1.30	65.2
	5 – 10	0.15	0.78	0.63	68.1
	10 – 15	0.23	1.38	1.29	88.9
	15 – 20	0.13	2.46	1.02	52.7
4	0 – 5	0.19	1.53	1.90	63.5
	5 – 10	0.10	0.68	0.41	68.3
	10 – 15	0.13	0.93	1.27	50.1
	15 – 20	0.11	3.42	2.24	51.6
5	0 – 5	0.17	3.36	0.83	33.3
	5 – 10	0.14	1.11	0.60	30.8
	10 – 15	0.34	1.20	0.69	50.5
	15 – 20	0.11	4.12	1.13	82.1

4.4 Concentration of Acid Volatile Sulfide and Simultaneously Extracted Metals

The wet sediments of five sediment core samples from five sites were stored in the dark at 4 ºC for days 21. The AVS and SEMs (i.e., Cd, Cu, Pb, and Zn) concentration in vertical sediment were reported in Table 4.4. These AVS and SEMs concentration in sediment be used to the calculation of M_{AVS} which reported in section 5.5 in Chapter V. The AVS and SEMs values on the basis of weight and carbonate free were calculated using moisture and carbonate contents reported in section 4.5.

Table 4-4 Concentrations of acid volatile sulfide and simultaneously extracted metals at various depths of the core sediments

Stations	Layers (cm)	AVS (µ mols-S^{2-} g^{-1} dry wt)	SEM in <63 µm fraction ($CaCO_3$ free)			
			Cd (nmols g^{-1} dry wt)	Cu (µmols g^{-1} dry wt)	Pb (µmols g^{-1} dry wt)	Zn (µmols g^{-1} dry wt)
1	0 – 5	0.67	0.71	0.51	0.12	3.82
	5 – 10	0.66	0.69	0.47	0.19	4.69
	10 – 15	1.35	0.59	0.30	0.13	2.96
	15 – 20	1.32	0.55	0.35	0.14	2.72
2	0 – 5	0.87	0.32	0.07	0.04	1.05
	5 – 10	1.50	0.74	0.23	0.08	2.55
	10 – 15	1.24	0.92	0.35	0.08	2.58
	15 – 20	1.42	0.86	0.40	0.08	3.49
3	0 – 5	0.04	0.68	0.49	0.10	1.56
	5 – 10	1.74	0.80	0.27	0.08	1.52
	10 – 15	1.14	0.84	0.21	0.11	1.88
	15 – 20	1.51	0.77	0.12	0.07	1.82
4	0 – 5	0.09	0.96	0.26	0.15	6.20
	5 – 10	0.67	0.92	0.45	0.11	3.73
	10 – 15	0.69	0.70	0.29	0.09	1.92
	15 – 20	0.95	0.83	0.25	0.10	1.57
5	0 – 5	0.03	1.07	0.33	0.10	1.43
	5 – 10	2.21	1.30	0.19	0.07	1.27
	10 – 15	0.53	0.61	0.21	0.08	1.12
	15 – 20	1.08	0.63	0.41	0.08	1.21

AVS: Acid volatile sulfide
SEMs: simultaneously extracted metals

4.5 Sedimentological and Geochemical Characteristics of Sediments

After subsampling of sediment core samples, redox potential (Eh) was determined immediately. Moisture value was taken from the difference of the weight before and after freeze dried. The characteristics of sediment include grain size composition, organic carbon (OC), and calcium carbonate ($CaCO_3$) was reported in Table 4.5.

Table 4-5 Sedimentological and geochemical characteristics at various depths of the core sediments collected from the Chao Phraya River mouth on 9 March 2011

Stations	**Layers (cm)**	**Eh (mV)**	**Moisture (%)**	**Size composition (%)**			**OC (%)**	**$CaCO_3$ (%)**
				Sand (>63 μm)	**Silt** (2-63 μm)	**Clay** (<2 μm)		
1	0 – 5	-96.0	43	27	49	24	0.70	1.12
	5 – 10	-108.0	32	56	27	17	0.40	1.29
	10 – 15	-130.8	32	42	40	18	0.53	1.60
	15 – 20	-151.4	31	41	37	22	0.76	2.06
2	0 – 5	-141.6	34	27	53	20	0.43	1.91
	5 – 10	-188.9	37	35	44	21	0.82	1.57
	10 – 15	-241.6	37	35	48	17	0.83	1.32
	15 – 20	-255.4	31	24	51	25	1.01	1.34
3	0 – 5	-19.9	50	26	52	22	0.95	1.73
	5 – 10	-88.0	45	28	68	4	1.05	2.20
	10 – 15	-76.6	42	33	53	14	0.89	8.61
	15 – 20	-96.0	43	27	50	23	1.03	3.47
4	0 – 5	-94.0	31	3	71	26	0.36	3.23
	5 – 10	-117.3	32	8	69	23	0.58	5.25
	10 – 15	-131.0	38	2	70	28	0.78	4.33
	15 – 20	-189.3	33	2	66	32	0.97	4.39
5	0 – 5	-89.5	73	67	12	21	1.66	3.70
	5 – 10	-79.2	60	56	20	24	1.27	7.76
	10 – 15	-130.1	55	29	43	28	1.23	3.62
	15 – 20	-130.3	56	23	57	20	1.44	3.28

4.6 Metals Concentration in Sediment

The sediment, after interstitial water extraction, was freeze dried and extracted separately with 0.01 M $CaCl_2$, 0.05 M EDTA, 25% (v/v) HOAc, and 1M HCl. The concentrations of Cd, Cu, Pb and Zn in sediment extracted by each individual extractant were reported in Table 4-6, 4-7, 4-8 and 4-9 for 0.01 M CaCl2, 0.05 M EDTA, 25% (v/v) HOAc and 1M HCl, respectively.

Table 4-6 Concentration of metals in the sediment samples extracted by 0.01 M $CaCl_2$ at various depths of the core sediments

Stations	Layers (cm)	Metals in <63 µm fraction of sediments ($CaCO_3$ free basis)			
		Cd (µg kg^{-1} dry wt)	Cu (µg kg^{-1} dry wt)	Pb (µg kg^{-1} dry wt)	Zn (µg kg^{-1} dry wt)
1	0 – 5	13.3	139.3	21.7	531.1
	5 – 10	17.5	165.1	40.1	573.1
	10 – 15	16.2	167.6	39.7	1098.2
	15 – 20	12.6	161.8	27.4	333.0
2	0 – 5	18.4	67.4	17.6	301.3
	5 – 10	15.0	80.7	24.9	272.1
	10 – 15	18.9	68.2	16.3	282.3
	15 – 20	12.9	76.9	19.5	234.8
3	0 – 5	14.7	75.0	13.6	249.4
	5 – 10	14.3	79.1	18.2	283.2
	10 – 15	13.1	99.7	35.0	179.1
	15 – 20	9.7	88.7	15.5	82.4
4	0 – 5	42.6	81.1	67.9	398.8
	5 – 10	16.7	86.5	32.5	253.2
	10 – 15	10.6	88.9	23.4	182.9
	15 – 20	10.4	75.8	16.9	132.5
5	0 – 5	12.3	118.5	9.4	95.2
	5 – 10	14.9	63.8	19.5	193.5
	10 – 15	7.4	66.6	10.0	69.2
	15 – 20	6.5	47.2	11.2	102.6

Table 4-7 Concentration of metals in the sediment samples extracted by 0.05 M EDTA at various depths of the core sediments

Stations	Layers (cm)	Metals in <63 µm fraction of sediments ($CaCO_3$ free basis)			
		Cd (µg kg^{-1} dry wt)	**Cu** (mg kg^{-1} dry wt)	**Pb** (mg kg^{-1} dry wt)	**Zn** (mg kg^{-1} dry wt)
1	0 – 5	45.0	20.8	15.2	97.9
	5 – 10	48.8	26.0	28.5	94.7
	10 – 15	47.9	22.5	31.0	87.0
	15 – 20	59.6	32.0	27.1	63.5
2	0 – 5	37.6	6.5	9.7	28.5
	5 – 10	61.5	13.3	14.8	49.6
	10 – 15	72.4	11.8	14.5	52.9
	15 – 20	58.3	10.7	13.7	48.7
3	0 – 5	50.0	9.6	15.3	21.0
	5 – 10	61.8	8.5	16.8	19.1
	10 – 15	68.3	9.5	20.5	19.9
	15 – 20	65.0	10.1	17.6	14.8
4	0 – 5	62.3	6.2	26.8	34.0
	5 – 10	70.0	9.0	29.1	22.0
	10 – 15	54.1	9.5	20.8	16.5
	15 – 20	63.8	11.0	23.4	19.3
5	0 – 5	69.4	11.6	18.6	10.4
	5 – 10	65.4	8.9	18.5	9.2
	10 – 15	40.4	8.6	18.8	6.0
	15 – 20	46.2	9.3	19.6	6.4

Table 4-8 Concentration of metals in the sediment samples extracted by 25% (v/v) HOAc at various depths of the core sediments

Stations	**Layers (cm)**	**Metals in <63 µm fraction of sediments ($CaCO_3$ free basis)**			
		Cd (µg kg^{-1} dry wt)	**Cu (mg kg^{-1} dry wt)**	**Pb (mg kg^{-1} dry wt)**	**Zn (mg kg^{-1} dry wt)**
1	0 – 5	55.0	11.3	4.8	98.5
	5 – 10	71.8	21.7	9.8	156.0
	10 – 15	57.7	17.9	8.3	116.3
	15 – 20	72.9	23.4	9.5	106.1
2	0 – 5	44.6	4.8	2.7	48.7
	5 – 10	70.0	7.5	3.9	71.7
	10 – 15	81.6	8.3	3.8	77.8
	15 – 20	69.1	6.8	4.0	65.1
3	0 – 5	61.3	3.6	3.3	34.2
	5 – 10	70.9	3.6	4.3	30.4
	10 – 15	69.4	4.0	5.6	33.3
	15 – 20	75.7	3.1	5.7	27.5
4	0 – 5	68.0	4.4	8.3	119.2
	5 – 10	79.1	3.5	9.4	66.9
	10 – 15	66.0	3.0	4.7	30.6
	15 – 20	59.6	3.3	5.1	27.9
5	0 – 5	68.1	2.9	3.4	14.4
	5 – 10	72.3	1.9	5.0	15.0
	10 – 15	95.7	1.8	5.0	8.9
	15 – 20	42.5	1.7	5.2	10.3

Table 4-9 Concentration of metals in the sediment samples extracted by 1 M HCl at various depths of the core sediments

Stations	Layers (cm)	Metals in <63 µm fraction of sediments ($CaCO_3$ free basis)			
		Cd (µg kg^{-1} dry wt)	**Cu** (mg kg^{-1} dry wt)	**Pb** (mg kg^{-1} dry wt)	**Zn** (mg kg^{-1} dry wt)
1	0 – 5	71.0	31.8	21.0	219.4
	5 – 10	81.8	44.1	40.8	361.1
	10 – 15	76.5	41.2	32.9	237.3
	15 – 20	89.7	60.1	40.2	216.2
2	0 – 5	61.5	12.7	11.6	105.3
	5 – 10	97.0	23.1	15.5	154.5
	10 – 15	118.0	22.7	20.3	179.8
	15 – 20	100.4	24.8	20.3	146.2
3	0 – 5	87.5	16.8	22.1	86.8
	5 – 10	86.5	15.4	23.4	75.7
	10 – 15	149.5	18.0	28.0	99.4
	15 – 20	106.1	15.1	24.2	78.0
4	0 – 5	152.8	11.7	41.4	266.3
	5 – 10	150.4	13.9	37.7	157.3
	10 – 15	104.7	13.7	26.9	80.5
	15 – 20	119.7	17.6	23.3	72.6
5	0 – 5	96.8	12.7	25.9	58.1
	5 – 10	105.1	15.3	25.9	57.9
	10 – 15	79.8	14.4	22.5	38.7
	15 – 20	71.3	14.4	24.3	38.0

4.7 Quality Control

Approximately 10% of the total samples, for each batch, were randomly sampled and undergone replicated analyses. Relative standard deviation (%RSD) of the replicated analyses was calculated. The %RSD of the replicated analyses of environmental samples that varied between 2-20% is an acceptable result, depending on the samples matrix, concentration range, and instrument performance.

The results of quality control of the metal analyses in overlying water, interstitial water, and sediment were reported in Appendix E and these were all in the acceptable range of the above criteria.

CHAPTER V

DISCUSSIONS AND RECOMMENDATIONS

5.1 Controlling Process of Available Dissolved Metals in Seawater

In general, concentration of dissolved metals in overlying water above sediment-water interface was likely to be controlled by two processes; (i) removal of dissolved metals in overlying water by adsorption onto suspended particles and complexation with humic substances, and (ii) diffusion of dissolved metals from interstitial water into overlying water.

5.1.1 Removal of Dissolved Metals in Overlying Water by Adsorption onto Suspended Particles and Complexation with Humic Substances

The rapid removal of dissolved metals from overlying water occurred during the first 10 days (Fig 5-1). The removal of dissolved Pb, Cd, Cu and Zn from overlying water was 99%, 58%, 38% and 36%, respectively, for the first 10 days.

Adsorption of dissolved metals onto suspended particles in overlying water was believed to remove the dissolved metals in overlying water. The removal efficiency of dissolved Pb, Cd, Cu and Zn found in this study follows the affinity series of metals toward clay particle. Mitchell (1954) cited in Förstner and Wittmann (1981) established the following empirical-sequence for the affinity series of metals toward clay particle, namely Pb > Ni > Cu > Zn. The affinity series refers to ability of competition of each metal absorbed onto clay particle. Pb has the greatest affinity of metals toward clay particle. Therefore, Pb was absorbed with clay particle in overlying water faster than other metals.

In addition, dissolved metals in the overlying water can be absorbed onto organic compounds. In natural aquatic system, humic substances (both dissolved and particulate) were common organic compounds. These humic compounds form stable complexes (so-called chelates) with most metal cations (dissolved metals) (Golterman et al., 1983).

Therefore, adsorption onto clay particle and complexation with organic compounds lead to a transformation of metals in dissolved form to metals in particulate metal form. Eventually, these suspended particles in the overlying water were bought to settle and deposit on the surface sediment by gravity force.

According to Stroke's law (Eq. 5-1), the particles are falling in the viscous fluid by their own weight due to gravity. The Stokes' law is commonly used in calculating a time required for all specific size of particle settle below a specific depth of fluid, as described by Sompongchaiyakul (1989).

$$\upsilon_s = \frac{2}{9}\frac{(\rho_p - \rho_f)}{\mu} g \times R^2 \qquad (5\text{-}1)$$

where: v_s: the particles' settling velocity (m/s) (vertically downwards if $\rho_p > \rho_f$, upwards if $\rho_p < \rho_f$),
g: the gravity acceleration (m/s^2),
ρ_p: the mass density of the particles (kg/m^3),
ρ_f : the mass density of the fluid (kg/m^3)
R: the radius of particle

The Stokes' law can be used to confirm the deposition efficiency of suspended particles from overlying water onto surface sediment during the experiment. In this study, sediment core was collected by retaining a 30-cm water column over the sediment surface. If allow the particles in the water column to settle for 10 days at 4°C salinity 20, the particles of the size of 0.048 µm were all reached the sediment surface (Wood and Ayers, 1977). Therefore, the suspended clay particles (<2 µm) in the overlying water should be all removed from the overlying water.

As such, suspended particles are an important role in the removal of dissolved metals from the water column to accumulate at the sediment surface.

5.1.2 Diffusion of Dissolved Metals from Interstitial water into Overlying water

In turn, diffusion of dissolved metals from interstitial water into overlying water was increase concentrations of metals in the overlying water. The diffusion depends on a difference of dissolved metals concentration between interstitial water and overlying water. However, the magnitude of dissolved metals diffused from interstitial water into overlying water in this study was relatively less significant than dissolved metals removed from overlying water.

5.2 Equilibrium Time

Disturbance of sediment cores during sampling and transportation can cause resuspension of surface sediment into overlying water and lead to a mixing of dissolved metals in interstitial water of the surface sediment and overlying water. Therefore, concentrations of suspended particles and dissolved metals in the overlying water at the day-1 were expected to be relatively high by these disturbances.

The equilibrium condition in this study assumes that the dissolved metals concentrations in overlying water should not change with time. The trend of dissolved Cd, Cu, Pb and Zn removal from the overlying water of the sediment cores after storing at 4°C in the dark, as reported in Table 4-2, is illustrated in Fig. 5-1. The concentrations of all dissolved metals in overlying water decreased rapidly after day-1 and remained constant after day-21 except Pb which was faster equilibrated.

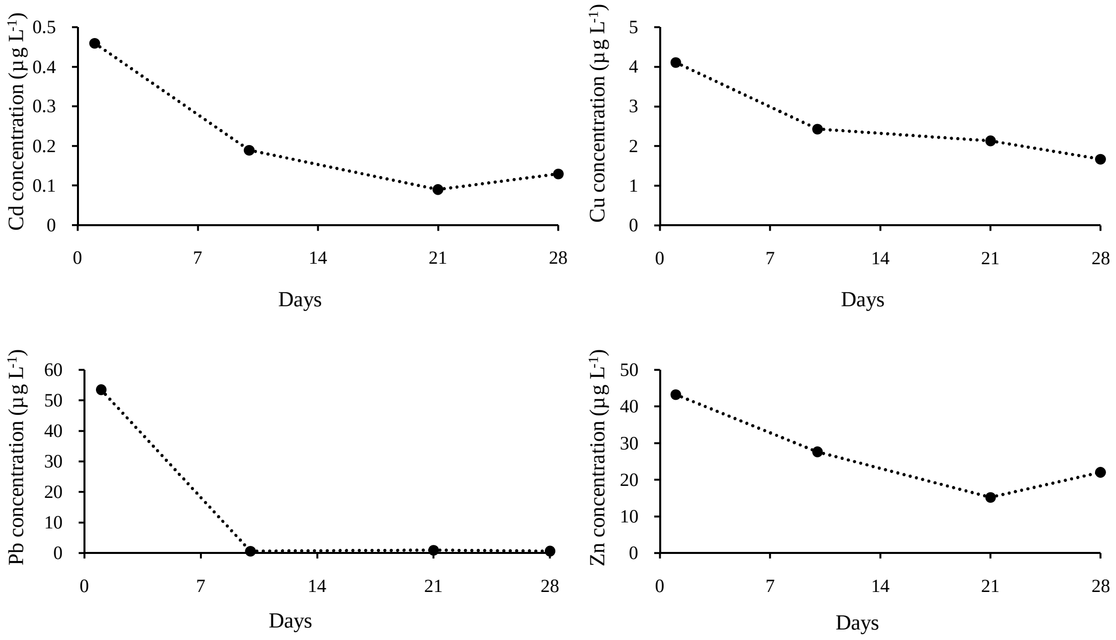


Figure 5-1 Dissolved metals concentrations in the overlying water after incubated at 4°C in the dark for 1, 10, 21 and 28 days.

The ratio calculated from a difference of dissolved metals concentrations (C_2-C_1) per unit of time (T_2-T_1) (µg L^{-1} day^{-1}) was used to estimate the equilibrium condition. When the difference was approaching zero, it meant that there was a little difference of dissolved metals concentration between time or called “equilibrium”. The changing ratio of dissolved Cd, Cu, Pb and Zn in overlying water during prolonged incubation was reported in Table 5-1.

Table 5-1 The difference of dissolved metals concentrations per unit of time during the equilibration period of sediment core at 4°C in the dark

Time (days)	**Ratio values (µg L^{-1} day^{-1})**			
	Cd	**Cu**	**Pb**	**Zn**
1 to 10	0.03	0.17	5.87	1.74
10 to 21	0.01	0.04	0.02	1.13
21 to 28	0.01	0.06	0.05	0.76

During the Day-21 to Day-28, there was a little change in dissolved metals concentration making the ratio approaching zero. It can be summarized that the sediment cores stored in at 4°C in the dark for 21 days after sampling were sufficient to achieve equilibrium.

5.3 Chemical Extractants

The partition coefficient (K_D) was obtained by dividing metal concentration in labile fraction of sediment with metal concentration in interstitial water (Eq. 2-2 in Chapter II). In this study, metals in labile fraction, a potentially remobilize in sediment-interstitial water system, was based on the assumption that the metals associated in exchangeable, Fe-Mn oxides and organic matter fractions.

In general, there are three categories of single-extraction procedure: (i) cationic exchange, most often use are $CaCl_2$ and $NaNO_3$, (ii) organic complexation, most often use are EDTA and DTPA, and (iii) acidification, most often use is CH_3COOH (HOAc) (Sahuquillo et al., 2003). The fraction of metal extracted from sediment depends on the chemicals using and extraction conditions. In this study, the fraction emphasized was labile fraction which subjected to be remobilized in sediment-interstitial water system when physicochemical condition is changed.

To date, the standard procedure for extraction of metals from the labile phase of sediment is not yet available. Therefore, it is important to evaluate whether the strength of selected chemicals are sufficient to extract only the labile fraction from the sediments.

In this study, the 0.05 M EDTA (complexation) and 25% (v/v) HOAc (acidification) were selected to extract total labile metals from the sediments without disturbing silicate lattices. It was reported that 0.05 M EDTA extracts only metals from exchangeable, Fe-Mn oxides and organic matter fractions (Pickering, 1981). Whereas 25% (v/v) HOAc was reported to extract metals from exchangeable, easily amorphous of Fe-Mn oxides, carbonate and metals weakly held in organic matter. The 25% (v/v) HOAc do not disturb silicate lattices, resistant Fe and Mn minerals, and organic compounds (Loring and Rantala, 1992; UNEP, 1995).

In order to ensure that selected chemicals for extraction were sufficient enough to extract metals from the labile fraction. Extraction efficiency of 0.05 M EDTA and 25% (v/v) HOAc was studied comparing with 0.01 $CaCl_2$ and 1 M HCl, which reported to extract metals from exchangeable and total non-residue fractions, respectively.

The 0.01 $CaCl_2$ was referred as the low level benchmark of extraction efficiency, and was commonly used to extract metals associated in exchangeable fraction in sediment and soil (Sahuquillo et al., 2003). Sediment extraction using 0.05 M EDTA and 25% (v/v) HOAc should give higher metal concentration than those of using 0.01 $CaCl_2$.

While the 1 M HCl was referred as the high level benchmark of extraction efficiency as it was believed to provide the “total non-residual” fraction. The 1 M HCl was reported to extract metals from exchangeable, carbonates, Fe-Mn oxides, organic matter and sulfide fractions (Hall, 1997; Basaham, 2010). Therefore, sediment extraction using 0.05 M EDTA and 25% (v/v) HOAc should give lower metal concentration than those of using 1 M HCl.

The extraction efficiency of the selected chemicals was calculated as a percentage of the total non-residual fraction (extracted by 1 M HCl) (%$E_{1\ M\ HCl}$). The formula for calculating the % $E_{1\ M\ HCl}$ is shown in Eq. 5-2.

$$\%\, E_{1M\_HCl} = \frac{C_E}{C_{1M\_HCl}} \times 100 \qquad (5\text{-}2)$$

where; $E_{1\ M\ HCl}$: extraction efficiency (%)
S_E: metals concentration in sediment extracted by chemical extractants (mg kg^{-1})
S_{HCl}: metals concentration in sediment extracted by 1 M HCl extractants (mg kg^{-1})

The concentration of metals in sediments extracted by 0.01 M $CaCl_2$, 0.05 M EDTA, 25% (v/v) HOAc and 1 M HCl was reported in Chapter IV (Tables 4-6 to 4-9). The extraction efficiency of 0.01 M $CaCl_2$, 0.05 M EDTA, 25% (v/v) HOAc in comparison to 1 M HCl (%$E_{1\ M\ HCl}$) was reported in Table 5-2.

Table 5-2 Extraction efficiency of the others chemical extractants compared with 1 M HCl

Chemical extractants	**Extraction efficiencies (%)***			
	Cd	**Cu**	**Pb**	**Zn**
0.01 M $CaCl_2$	9 - 30	~ 0 - 1	~ 0	~ 0
0.05 M EDTA	41 - 72	43 - 69	65 - 100	13 - 45
25% (v/v) HOAc	45 - 88	12 - 49	13 - 25	23 - 49

*exclude the outlier and far-outlier values

The most appropriate chemicals for extracting metals from labile fraction of sediments should gave a higher %$E_{1\ M\ HCl}$ than those given from 0.01 $CaCl_2$, and should be lower than 100% $E_{1\ M\ HCl}$.

Both 0.05 M EDTA and 25% (v/v) HOAc, for all metals, gave %$E_{1\ M\ HCl}$ higher than those given from 0.01 $CaCl_2$, and lower than 100% $E_{1\ M\ HCl}$. These results confirm that both 0.05 M EDTA and 25% (v/v) HOAc extractants be able to extract metals from the labile fraction of sediment.

In comparison, Cu and Pb had much higher %$E_{1\ M\ HCl}$ when extracted by 0.05 M EDTA than those by 25% (v/v) HOAc, particularly for the Pb. The reason may due to Cu and Pb preferable to complex with EDTA, but less sensitive to the acidification by 25% (v/v) HOAc) (Wu et al., 2011). In Pb case, the % $E_{1\ M\ HCl}$ of 0.05 M EDTA was ranging from 65% to100%. Thus one can clearly see that Pb is highly mobilized with 0.05 M EDTA in the sediments, which it is consistent with the high value of the complexation constant of Pb with EDTA (log K= 18.3) (Sahuquillo et al., 2002; Labanowski et al., 2008). Moreover, the study of Gismerab et al. (2004) found that Pb associated with crystalline hydrous oxides can be extracted by EDTA. However, this fraction cannot remobilize in sediment-interstitial water system by natural processes. Therefore, extraction of metals (Pb) with 0.05 M EDTA extractant may overestimate metals (Pb) in labile fractions (Sahuquillo et al., 2003; Gismerab et al., 2004).

For this study, it can be concluded that 25% (v/v) HOAc is more appropriate than 0.05 M EDTA for extracting metals in labile fraction of sediment. Consequently, metals concentrations in sediment extracted by 25% (v/v) HOAc are chosen for the calculation of the K_D in this study.

5.4 Calculation of Partition Coefficients for Metals

Only the upper 20 cm of sediment were emphasized because most benthic organisms living therein (Batley et al., 2005). The interstitial water extracted from each layer of 5-cm thickness subsampling from the top 20 cm section of the sediment core (6.4 cm diameter × 5 cm thick), after achieving equilibrium, were analyzed for metals and calculated for the K_D. The results were shown in Chapter IV (Table 4-4).

In order to reduce the effect of some sediment characteristics (i.e., grain size and calcium carbonate), the metal concentration in sediment should be reported by mean of size normalization and calcium carbonate free basis. Fine grain sediment contains higher active site for metals to bind with, while the high carbonate in sediment gives a dilution effect. The normalization will provide the better inter-comparison of the results, as describe in Chapter II. Sedimentological and geochemical characteristics of the core sediment presented in Table 4-5.

The K_D of each layer of sediment was calculated separately due to the different in sediment characteristics of each layer. As sediment characteristics play an important role in controlling metal concentrations in both sediment and interstitial water, thereby sediment characteristics do have the greatest influence on the magnitude K_D (US-EPA, 2005b). The K_D, in L kg^{-1}, to be used to evaluate numerical SQG for metals in this study was calculated from labile metals extracted by 25% (v/v) HOAc after size normalization (<63µm fraction) and calcium carbonate free basis (Table 4-8), and dissolved metals concentrations in interstitial water (µg L^{-1}) (Table 4-3). The K_D results were reported in Table F-2 of Appendix F, and summarized in Table 5-3.

Table 5-3 The partition coefficients (K_D) for the metals of the sediment samples

Metals	**Partition coefficients** (L kg^{-1} dry wt. in <63 µm fraction of sediments ($CaCO_3$ free basis))
Cd	237 – 797
Cu	419 – 31,092
Pb	2,292 – 23,758
Zn	125 – 2,314

In general, the variation of the K_D can often be found within data groups because the natural variability in sediment characteristics, the results in variation of the K_D (Otte et al., 2001). US-EPA (2005b) reported that within the data group of K_D may have values in different orders of magnitude, even for a single metal.

In summary, the K_D reported in Table 5-3 should be appropriate to be used to evaluate the numerical SQG, because these K_D were calculated from in the concentrations of metals in labile fraction of sediments and did consider only top 20 cm of the sediments, which is habitat of most benthic organisms.

5.5 Calculation of Metal bound with Sulfides

One of the important parameter for the numerical SQG calculation is metal bound with sulfides. The calculation is based on the assumption that oxidation kinetics of M_{AVS} in anoxic sediment is rapid and complete as described in Chapter II. And the molar of individual metal that be able to bind to sulfides was calculated based on an assumption that the affinity of all metals bound with sulfide is similar.

From the molar concentration of AVS and SEMs (Table 4-4 in Chapter IV), the mole available of AVS for each metal was calculated from the total molar concentration of AVS divided by the number of metals bound with sulfides. According to Di Toro et al. (1992) and US-EPA (2005a), Cd, Cu, Ni, Pb and Zn are common metals that bound with sulfides in the sediment. Thus, available sulfide for individual metal was the total molar concentration of AVS divided by five.

For example, it was found that the molar concentration of AVS in station 1 (layer I), was 0.67 µmols-S^{2-} kg^{-1} dry wt. The available sulfide for individual metal equals to AVS concentration divide by 5 (= 0.13 µmols-S^{2-} kg^{-1} dry wt.). It means there is 0.13 µmols-S^{2-} kg^{-1} dry wt. in the sediment available to bind with each individual metal.

The examples for calculation of M_{AVS} for Cd and Zn are demonstrated as following. From the results in Table 4-4, SEM_{Cd} and SEM_{Zn} are 0.0007 and 3.82 µmols kg^{-1} dry wt., respectively.

For Cd case, the available mole of sulfides for Cd was 0.13 µmols-S^{2-} kg^{-1} dry wt. which was higher than SEM_{Cd} (0.0007 µmols-S^{2-} kg^{-1} dry wt.). It means that M_{AVS} for Cd is limited by the mole of SEM_{Cd}, as expressed in Eq. 5-2. Therefore, the M_{AVS} for Cd in station 1 (layer I) is 0.0007 µmols kg^{-1} dry wt. or equivalent to 0.08 mg-Cd kg^{-1} dry wt.

$$0.0007\ SEM_{Cd} + 0.13\ AVS \leftrightarrow 0.0007\ MS_{Cd} \qquad (5\text{-}2)$$

In contrast, SEM_{Zn} is 3.82 µmols kg^{-1} dry wt. which is higher than 0.13 µmols-S^{2-} kg^{-1} dry wt. of sulfide. In this case, the M_{AVS} for Zn is limited by the mole of available sulfides, as expressed in Eq. 5-3. Therefore, the M_{AVS} for Zn in station 1 (layer I) is 0.13 µmols kg^{-1} dry wt. or equivalent to 8.7 mg-Zn kg^{-1} dry wt.

$$3.82\ SEM_{Zn} + 0.13\ AVS \leftrightarrow 0.13\ MS_{Zn} \qquad (5\text{-}3)$$

Based on the above principle, the M_{AVS} for Cd, Cu, Pb and Zn was calculated using the AVS and SEMs results in Table 4-4. The M_{AVS} for Cd, Cu, Pb and Zn is presented in Table F-3 in Appendix F, and summarized in Table 5-4.

Table 5-4 The metal bound with sulfides (M_{AVS}) of the sediment samples

Metals	**Metal bound with sulfide** (mg kg^{-1} dry wt. in <63 µm fraction of sediments ($CaCO_3$ free basis))
Cd	~ 0 - 0.1
Cu	~ 0 - 28
Pb	1 - 28
Zn	~ 0 - 29

5.6 Calculation of Sediment Quality Guideline for Metals

The numerical SQG for Cd, Cu, Pb and Zn in this study was calculated follow Eq. 2-4 in Chapter II using K_D, WQC and M_{AVS}.

- K_D taken from the results of section 5.4 which presented in Table F-2 of Appendix F
- WQC using the Thai coastal water quality standards (Thai Royal Government Gazette, 2007). For Cd, Cu, Pb and Zn are 5, 8, 8.5 and 50 µg L^{-1}, respectively, as described in Table F-1 in Appendix F
- M_{AVS} taken from the results of section 5.5 which presented in Table F-3 of Appendix F

The SQG values of Cd, Cu, Pb and Zn calculated using Eq. 2-4 for individual subsamples is reported in Table F-4 of Appendix F. As the box plot is an exploratory chart used to extract meaningful information from groups of numerical data at a quick glance, which can be easily explained to non-statisticians (Benjamini, 1988), the data in Table F-4 was illustrated using the box-plot as seen in Fig 5-2.

The SQG values of Cd, Cu, Pb and Zn were found in a range of 1.2–4.1, 7–265, 23–230 and 16–125 mg kg^{-1} dry wt., respectively. However, some of the data were clustered to outlier and far-outlier of data groups (Fig. 5-2). However, the outlier and far-outlier values may represent contamination or source of pollutants in the study sites (Rawlins et al., 2005; Reimann et al., 2005). In general, the established SQG values should represented most the data group. Therefore, it is necessary to remove the outlier and far-outlier values of the individual SQG data. Table 5-5 summarized the general ranges of SQG values for Cd, Cu, Pb and Zn for the Chao Praya river mouth sediment.

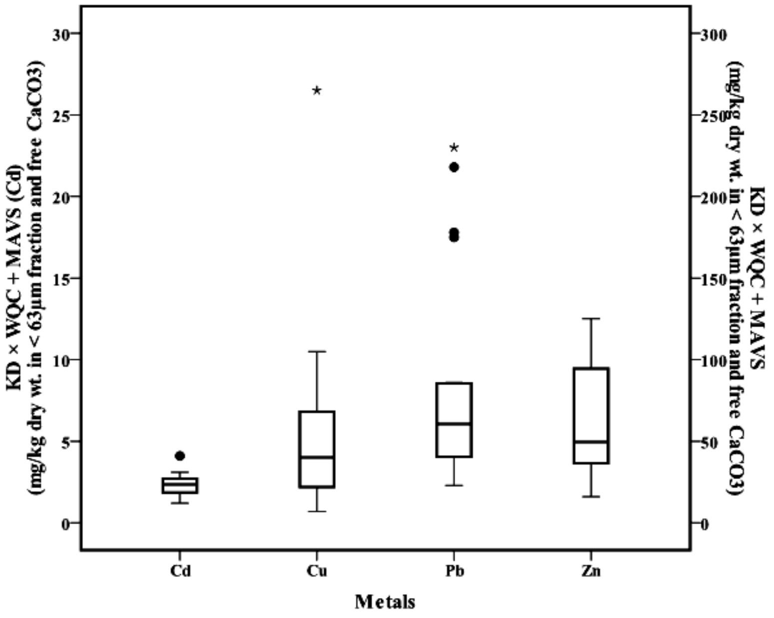


Figure 5-2 Sediment quality guideline for Cd, Cu, Pb and Zn for Chao Praya river mouth sediment showing a box-plot comparison of median and range among metals (the horizontal line in the box means median (or 50th percentile), the upper and lower lines outside the box refer to 75th and 25th percentiles (so-called interquartile range; IQR), filled circle and star refer to outlier (1.5 IQR) and far-outlier (3 IQR) of data)

Table 5-5 The sediment quality guideline values for the metals of the sediment samples

Metals	**Sediment quality guideline values** (mg^{-1} dry wt. in <63 µm fraction of sediments (CaCO$_3$ free basis))
Cd	1.2 - 3.1
Cu	7 - 105
Pb	23 - 86
Zn	16 - 125

It is noted that the outlier and far-outlier values of the SQG values for Cu, Pb and Zn were found at station 1, while for Cd was at station 4 (Table F-4 in Appendix F). These outlier high SQG values implied a possibility to have a potential for adverse biological effects over the other stations.

Station 1 is located near the QM Bang Poo Recreation Center of Royal Thai Army. Most of the SQG value for individual subsamples ion this station were higher than other stations. Sirirat (2011) using the ΣSEMs/AVS molar ratio to assess metals toxicity risk at the Chao Phraya river mouth, and also reported a potential risk for metal pollution in the station near Bang Poo wharf and jetty of the QM Bang Poo Recreation Center of Royal Thai Army.

The obtained SQG values represented metals in the labile fraction and metals bound with sulfide fraction. Both fractions can be potentially remobilize to interstitial water (refer to sections 2.1 and 2.4 in Chapter II). It was reported that concentrations of dissolved metals in the interstitial water are correlated with observed biological effects (Swartz et al., 1985; Kemp and Swartz, 1986; Ankley, et al., 1994). Therefore, the dissolved metals in interstitial water were supposed to be potential bioavailable, of which related to sediment toxicity (Chapman et al., 1998; Ciutat and Boudou, 2003). Accordingly, the SQG values represented concentrations of potentially available metals in sediment.

5.7 Comparison of Sediment Toxicity

In order to estimate adverse biological effects for benthic organism, it is necessary to compare the maximum SQG value (in Table 5-5) with toxicity levels on the benthic organism. To date, there is no sediment toxicity data established for the benthic organism in Thailand. The frequent used animal in most toxicity test for estuarine sediment are amphipod and polychaete due to their high sensitivity to common sediment contaminants, relatively easily cultured in the laboratory; and commonly found in marine sediments (Bat, 2005). In this study, the toxicity data of amphipod (*Melita plumulosa*) and polychaete (*Nephtys australiensis*) were chosen to compare with the maximum SQG value (in Table 5-5). Both species can be found in sediments of the tropical zone (Dean, 2008; Campana et al., 2012).

M. plumulosa (Family Melitidae) is a common amphipod found in freshwater and marine sediments. It is an epibenthic deposit feeder living in close association with sediments (Adams and Stauber, 2008). It has two major pathways to exposure contaminants: by direct diffusion of contaminants *via* its gills or by ingestion of particles to which toxicants may be adsorbed (major pathway for metal uptake) (King et al. 2006).

N. australiensis (Family Nephytyidae) is common and widespread polychaete found in estuarine sediment, burrows to at least 20-cm depth. It tolerates to a wide range of sediment grain sizes and salinity (5 to 34‰). High sulfide content in sediments may cause toxicity, more than 300 µmol g^{-1} AVS causing complete mortality of the polychaete after 10 days (King et al., 2004).

The sensitivity of these two species to spiked contaminant was presented in Table 5-6. The levels of toxicity on *M. plumulosa* and *N. australiensis* include lethal concentration fifty (LC_{50}), no observable effect concentrations (NOECs), effective concentration fifty (EC_{50}) and effective concentration ten (EC_{10}).

In comparison of the maximum SQG values from this study (Table 5-5) with the sensitivity to metals of *M. plumulosa* and *N. australiensis* (Table 5-6), it was found that the maximum SQG values were about 10 to 50-fold lower than the levels that cause toxic to *M. plumulosa* and *N. australiensis*. This may due to two reasons.

Firstly, sediment toxicity testing for metals were likely to be overestimated due to metal-spiked in sediments were strongly bound with sediments. This process leads to a loss of metal toxicity (Simpson et al., 2004).

Secondly, the WQC values for calculation of the SQGs may not reflect toxicity on benthic organism. Moreover, different country established different WQC. For example, recommended water quality criteria of chronic toxic for seawater in USA for Cd, Cu, Pb and Zn were 8.8, 3.1, 8.1 and 81 µg L^{-1}, respectively (US-EPA, 2009), while in Thailand was Cd, Cu, Pb and Zn are 5, 8, 8.5 and 50 µg L^{-1}, respectively (Thai Royal Government Gazette, 2007). The WQC value that not reflects toxicity on benthic organism or the difference of WQC value can lead to under or over estimation of sediment toxicity. This is may be a disadvantage of the EqP approach in calculating SQG value.

In order to make in order to support the EqP approach to calculated SQG values or sediment quality standard, sediments toxicity test in sediment should be studied in local sediment as the benthic organism in each area may different sensitivity to toxic effect.

Table 5-6 Sensitivity of amphipod (*Melita plumulosa*) and polychaete (*Nephtys australiensis*) to contaminant-spiked silty sediments (modified from Adams and Stauber, 2008)

Life stage	Test	Metals	Effect	Concentration*	Reference
Amphipod (*Melita plumulosa*)					
Adult	acute	Cd	LC_{50}	> 260	King et al. (2006)
			NOEC	260	
		Cu	LC_{50}	1310	
			NOEC	520	
		Pb	LC_{50}	> 3560	
			NOEC	3560	
		Zn	LC_{50}	> 9040	
			NOEC	2290	
Juvenile (no feeding)	acute	Cd	LC_{50}	1630	King et al. (2006)
			NOEC	620	
		Cu	LC_{50}	790	
			NOEC	460	
		Pb	LC_{50}	1980	
			NOEC	580	
		Zn	LC_{50}	1790	
			NOEC	< 2290	
Adult	chronic	Cd	LC_{50}	> 630	Gale et al. (2006)
		Cu	LC_{50}	800	
		Zn	LC_{50}	> 1770	
	fertility	Cd	EC_{50}	> 630	
		Cu	EC_{50}	290-330	
		Zn	EC_{50}	< 630	
	growth	Cd	EC_{50}	> 630	
		Cu	EC_{50}	420	
		Zn	EC_{50}	> 1770	
	fecundity	Cu	NOEC	200	Mann et al. (2008)
		Pb	NOEC	300	
		Zn	NOEC	500	
Adult	chronic	Cu	EC_{10}	5200	Campana et al. (2012)
Polychaete (*Nephtys australiensis*)					
40-50 mm	acute	Cu	NOEC	1400	King et al. (2004)
		Zn	NOEC	3900	

* mg kg^{-1} dry wt.

LC_{50}: lethal concentration fifty

NOECs: no observable effect concentrations

EC_{50}: effective concentration fifty

EC_{10}: effective concentration ten

5.8 Conclusions and Recommendations

During sampling and transportation of sediment cores, the interstitial water and sediment system was disturbed. Prior to further analysis, the equilibrium of an interstitial water-sediment system should be achieved. After setting the sediment cores at 4°C in the dark, dissolved Cd, Cu, Pb and Zn were rapidly removed from the overlying water in the first day. The adsorption of dissolved metals onto suspended particles and organic compounds in overlying water may be a controlling process of dissolved metals concentrations. The highest removal of dissolved Pb, Cd, Cu and Zn in overlying water was found during the first 10 days, with the percentage of 99%, 58%, 38% and 36%, respectively. This is following to the affinity series of metals toward clay particle. In conclusion, leaving the sediment core at 4°C in the dark for 21 days after sampling is sufficient to achieve equilibrium of the interstitial water-sediment system.

In the study of chemicals strength for labile phase (exchangeable, Fe-Mn oxides and organic matter fractions) extraction, the efficiency of 0.01 $CaCl_2$, 0.05 M EDTA and 25% (v/v) HOAc were evaluated in comparison with 1 M HCl which believe to extract total residue fraction. The results revealed that extraction efficiency 0.05 M EDTA and 25% (v/v) HOAc were possible to be used for extracting metals from labile fraction of sediments. However, Pb had a high complexation constant with EDTA. As a result, remobilization of Pb with 0.05 M EDTA gave an overestimate of Pb in labile fraction. In conclusion, 25% (v/v) HOAc is most appropriate chemicals for extracting metals in the labile phase of sediments for using in partition coefficient (K_D) calculation.

The K_D of Cd, Cu, Pb and Zn were calculated from dividing metal concentrations extracted from the labile phase of sediment with metal concentrations in the interstitial water. The concentrations of labile Cd, Cu, Pb and Zn in sediment were extracted using 25% (v/v) HOAc and calculated on the basis of size normalization and carbonate free. The concentrations of Cd, Cu, Pb and Zn in the interstitial water were assessed after the interstitial water-sediment system was in equilibrium.

The SQG values for Cd, Cu, Pb and Zn based on the EqP approach in this study were calculated from the K_D in conjunction with Thai coastal water quality standards and M_{AVS}. The M_{AVS} is a potentially available metal to interstitial water, when anoxic sediment occurring in reoxidation processes. The SQG values (size normalization and carbonate free basis) for the Chao Praya river mouth sediment were found in the range of 1.2–3.1 mg kg^{-1} dry wt. for Cd, 7–105 mg kg^{-1} dry wt. for Cu, 23–86 mg kg^{-1} dry wt. for Pb, and 16–125 mg kg^{-1} dry wt. for Zn.

Since the ranges of the SQG values represent concentrations of potential availability of metals in sediment, a comparison of the SQG values with sediment toxicity was evaluated. Unfortunately, no sediment toxicity test in tropical benthic animals has been found in the literatures. The best comparison, therefore, have been done with the common found benthic animals both in temperate and tropical zones. In comparison of the SQG values with, the toxicity test with the toxicity levels of metals on amphipod (*M. plumulosa*) and polychaete (*N. australiensis*). It was found that sediment of Chao Phraya river mouth is not likely to have a potential risk of adverse biological effects on amphipod and polychaete.

However, the sediments toxicity test should be further studied to predict toxic effect on benthos in the local sediments since animals in different area may adapt to tolerant to different toxicity levels. In addition, it would suggest that sequential extraction that extract metals in each different fraction of sediment namely exchangeable, Fe-Mn oxides, organic matter, sulfides and residual fractions, should be considerably for further validation in order to extract metals precisely from in the labile fraction.

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APPENDICES

APPENDIX A

A-1 Concentration of Metals with Grain Size in Sediment

The metals concentrations in sediment tend to decrease with increasing grain size in sediment, which show in Fig. A-1. Consequently, fine grain sediment (silt and clay fraction: < 63 µm) can adsorbs metals more readily and more carries than coarse grained sediment because they have greater surface areas per weight are enriched in layered aluminosilicate minerals but coarse grained sediment is generally enriched in quartz, which is relatively un-reactive to binding metals (Olsen et al., 1982).

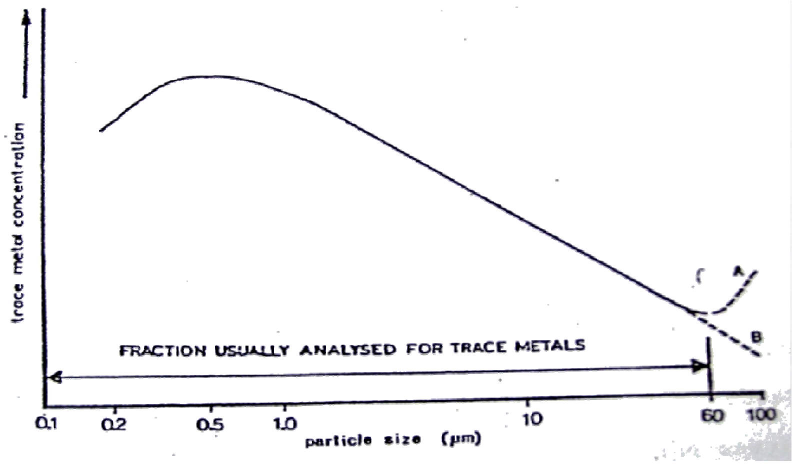


Figure A-1 Generalized profile of the variation of the concentration of metals with grain size in sediment (Förstner and Wittmann, 1981)

APPENDIX B

Procedures of Laboratory Analysis

The procedures of laboratory analysis in this study are described in below.

B-1 Cobalt-APDC co-precipitation Technique

I. Reagents

(i) 2% ammonium pyrrolidine dithiocarbamate (APDC)

Weight approximately 5.4 g of APCD dissolved with Milli-Q water and made up to 200 ml, shake 5 min, then stand 30 min, and pour the clear solution into a Teflon® separatory funnel. Solution purified with three times extraction with methyl isobutyl ketone (MIBK). The pure APDC solution was stored frozen when not use.

(ii) Cobalt solution

Weight approximately 0.425 g of Cobalt chloride ($CoCl_2 \cdot 6H_2O$) dissolved with 150 ml of 9 M HCl suprapur®. Cobalt solution purified with Dowex column

(iii) Dowex column

Weight approximately 10 g of Dowex 1-X8 resin (100-200 mesh) was clean up with 30 ml of 0.01 M HCl suprapur® and added to column (Ø 1 cm × 22 cm). Dowex rasin column was pre-condition with 5 ml of 9 M HCl suprapur®. Volume 150 ml of Cobalt solution was added to column and clean up with 20 ml of 9 M HCl suprapur®. Elute with 4 M HCl suprapur® and keep pink solution about 8 ml. The pink solution was makes volume to 500 ml with Milli-Q water.

II. Analytical procedure

Overlying water (40 ml) or interstitial water (5 ml + Milli-Q water 35 ml) was volume accurately into polypropylene centrifuge tube in 50 ml. High-purify NH_3OH solution was added (about 80 µl) to adjust pH ~ 3. After the addition of the cobalt 2 ml and 2% APDC 2 ml, shaken for 1 minute and stand at room temperature for minimum of 30 minute. Samples were centrifuged at 3,500 RCF for 30 minutes at in situ temperature, decanted sample, wash the sediment with 30 ml of Milli-Q water, centrifuged at 3500 RCF at in situ temperature for 30 minutes, decanted a Milli-Q water. The concerted high-purify HNO_3 was added 300 µl to redissolved a precipitate colloids and make volume to 5 ml by Milli-Q water. Samples were kept for 24 hours before determination by GFAAS.

B-2 Extraction Chemicals for Labile Metals in Sediment

1. 0.01 M $CaCl_2$ extraction

I. Reagents

0.01 M $CaCl_2$ is prepared from $CaCl_2$ (AR grade) diluted with Milli-Q water.

II. Analytical procedure

Weigh 1.0 g of dried sediments and transfer it into a propylene centrifuge tube. Add 10 ml of 0.01 M $CaCl_2$. Shake slowly in a mechanical shaker for 24 hours, prior to separate the solution and sediment by centrifuging at 3,500 RCF for 30 minutes. Pour the clear supernatant transfer into 10 ml volumetric flask and make up the solution to a volume of 10 ml with Milli-Q water.

2. 0.05 M EDTA extraction

I. Reagents

0.05 M EDTA is prepared from EDTA (AR grade) diluted with Milli-Q water.

II. Analytical procedure

Weigh 1.5 g of dried sediments and transfer it into a propylene centrifuge tube. Add 10 ml of 0.05 M EDTA. Shake slowly in a mechanical shaker for 12 hours, prior to separate the solution and sediment by centrifuging at 3,500 RCF for 30 minutes. Pour the clear supernatant transfer into 10 ml volumetric flask and make up the solution to a volume of 10 ml with Milli-Q water.

3. 25% (v/v) HOAc extraction

I. Reagents

25% (v/v) HOAc is prepared from HOAc (AR grade) diluted with Milli-Q water.

II. Analytical procedure

Weigh 0.8 g of dried sediments and transfer it into a propylene centrifuge tube. Add 10 ml of 25% (v/v) HOAc. Shake slowly in a mechanical shaker for 6 hours, prior to separate the solution and sediment by centrifuging at 3,500 RCF for 30 minutes. Pour the clear supernatant transfer into 10 ml volumetric flask and make up the solution to a volume of 10 ml with Milli-Q water.

4. 1 M HCl extraction

I. Reagents

1 M HCl is prepared from HCl suprapur® diluted with Milli-Q water.

II. Analytical procedure

Weigh 0.5 g of dried sediments and transfer it into a propylene centrifuge tube. Add 10 ml of 1 M HCl. Shake slowly in a mechanical shaker for 4 hours, prior to separate the solution and sediment by centrifuging at 3,500 RCF for 30 minutes. Pour the clear supernatant transfer into 10 ml volumetric flask and make up the solution to a volume of 10 ml with Milli-Q water.

B-2 Acid Volatile Sulfide (AVS) and Simultaneously Extracted Metals (SEM)

I. Reagents

(i) Sulfide standard solution

Weight approximately 12 g of sodium sulfide ($N_{a2}S \cdot 9H_2O$) dissolved in 1 L of Milli-Q water.

(ii) 6 M Hydrochloric acid (HCl)

Volume 500 ml of 37 % (v/v) HCl diluted in 1 L of Milli-Q water.

(iii) 0.5 M Sodium Hydroxide (NaOH)

Weight approximately 20 g of NaOH diluted in 1 L Milli-Q water.

(iv) Starch indicator

Weight approximately 1 g of starch power in 100 ml DI-water and boiled to dissolve.

(v) Mixed Diamine Reagent (MDR)

The solution A is 2.25 g of 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 of $FeCl_3 \cdot 6H_2O$ in 100 ml conc. HCl and then dilute to 200 ml with DI water, and mixing solution A with solution B.

II. Analytical procedure

The system to generate hydrogen sulfide (H_2S) gas (so-called AVS) from sediments is set up as seen in Fig. B-1. Flask "A" is reactive flask (purge flask), added with 100 mL DI-water. Flasks "B" and "C" are Erlenmeyer flasks (trap flask) with ground glass joints, each flask added with 80 mL of 0.5 M NaOH.

Purge the system with nitrogen gas (N_2) at the flow rate of 100 cm^3 min^{-1} for 10 minute. Approximately 10 g of wet sediment was accurately weighed into Flask "A", and then purge with N_2 gas at the flow rate of 40 cm^3 min^{-1} for 10 minute and inject 20 ml of 6 M HCl into the Flask "A". The N_2 gas purged through the sample for 1 hr at the flow rate of 20 cm^3 min^{-1}.

After stop flow of N_2 gas, 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 spectrophotometer at 670 nm. The quantity of AVS was compare with standard calibration curve. The AVS concentration in micromoles per gram dry weight of sediment is calculated using Eq. B-1.

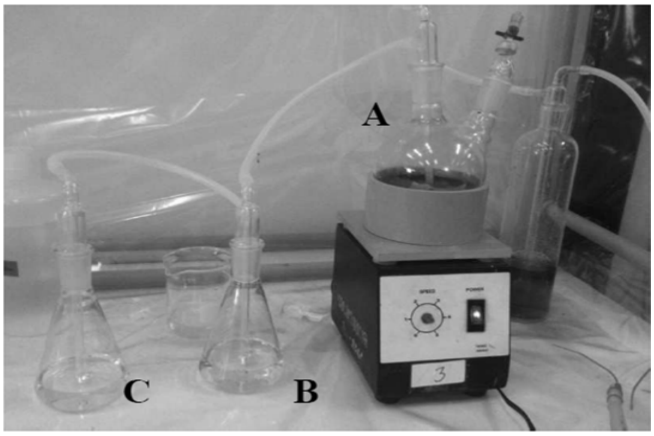


Figure B-1 The system for acid volatile sulfide analysis (Sirirat, 2011)

The remaining solution in Flask "A" (so call SEM) was through a GF/C glass filters which resistant to acid. The filter apparatus should be soaked in 1 M HNO_3 and rinsed with DI-water prior to use. Transfer the acid solution into volumetric flask and make volume to 250 ml. SEM is determining with graphite furnace-AAS for Cd, Cu, and Pb and flame-AAS for Zn.

$$\text{AVS } (\mu \text{ moles g}^{-1}) = \frac{S}{R \times W_W} \qquad \text{(B-1)}$$

$$R = \frac{W_d}{W_w}$$

where AVS: amount of acid volatile sulfide in dry sediment (μ moles g^{-1} dry wt.)
S: amount of AVS in sediment (μ moles)
W_w: weight of sediment wet (g) taken for AVS analysis
R: ratio of dry weight to wet weight
W_d: weight of dry sediment
W_w: weight of wet sediment

B-3 Grain Size Composition Analysis

I. Reagents

(i) 10 % (v/v) Hydrogen Peroxide (H_2O_2)

Volume 10 ml of H_2O_2 diluted 100 DI-water.

(ii) 10 % (v/v) Hydrochloric acid (HCl)

Volume 10 ml of HCl diluted 100 DI-water.

(iii)10% (w/v) Sodium hexametaphosphate $(NaPO_3)_6$

Weight approximately 10 g of $(NaPO_3)_6$ diluted in 100 L DI-water.

II. Analytical procedure

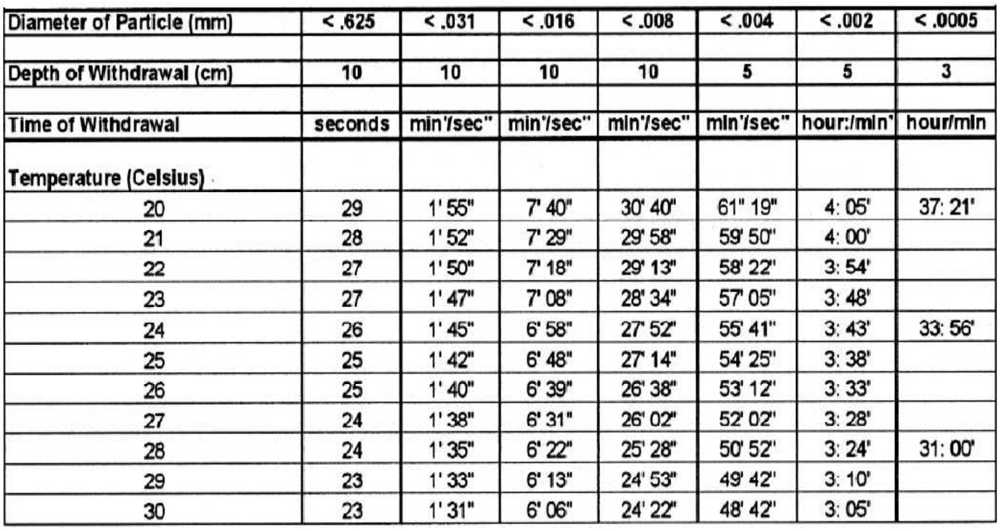
(i) Removal of organic matter and carbonate (Pre-treatment)

Approximately 20 g of homogenize dry sediment, adding 10 % H_2O_2 until the sample frothing ceased in water bath at 80 °C to increase the speed and completeness of H_2O_2 digestion for removal of organic matter. Next the 10% HCl solution for carbonate removal was added to sediment in water bath at 80 °C for 5 hours. Besides $CaCO_3$ also Fe, Mg, and Al were dissolved. When the all active reaction ended, the sample was washed with DI-water, to stand at room for several days and draw clear water until sample is neutral pH (Vaasma, 2008).

(ii) Sieve and pipette method

The sediment samples were dried by oven 105 °C over night. Approximately 10 g of dry sediment was accurately weighed. The samples were sieving by sieve mash 63 µm for sand fraction and oven 105 °C over night and other sample was pipette method by transfer to 1,000 ml cylinder. The 10 ml of 10% (w/v) Sodium hexametaphosphate $(NaPO_3)_6$ was added to avoid grain flocculation in a column of a particle sedimentation, and make volume to 1,000 ml by DI-water. A cylinder was stand to control temperature room (23 ºC) and time of withdrawal (3 hrs. and 48 min.) follow in Table A-1. Pipette was draw a clay faction for 10 ml by auto pipette in depth withdrawal 5 cm, and oven 105 °C over night. Calculation of percent sand, silt, and clay are follow in Eq. (B-2, B-3, and B-4).

Table B-1 Time table for pipette withdrawal (Indiana University-Purdue University Indianapolis: IUPUI (2010)).



Diameter of Particle (mm)	< .625	< .031	< .016	< .008	< .004	< .002	< .0005
Depth of Withdrawal (cm)	10	10	10	10	5	5	3
Time of Withdrawal	seconds	min'/sec"	min'/sec"	min'/sec"	min'/sec"	hour:/min'	hour/min
Temperature (Celsius)							
20	29	1' 55"	7' 40"	30' 40"	61" 19"	4: 05'	37: 21'
21	28	1' 52"	7' 29"	29' 58"	59' 50"	4: 00'	
22	27	1' 50"	7' 18"	29' 13"	58' 22'	3: 54'	
23	27	1' 47"	7' 08"	28' 34"	57' 05"	3: 48'	
24	26	1' 45"	6' 58"	27' 52"	55' 41"	3: 43'	33: 56'
25	25	1' 42"	6' 48"	27' 14"	54' 25"	3: 38'	
26	25	1' 40"	6' 39"	26' 38"	53' 12'	3: 33'	
27	24	1' 38"	6' 31"	26' 02"	52' 02'	3: 28'	
28	24	1' 35"	6' 22"	25' 28"	50' 52'	3: 24'	31: 00'
29	23	1' 33"	6' 13"	24' 53"	49' 42'	3: 10'	
30	23	1' 31"	6' 06"	24' 22"	48' 42'	3: 05'	

$$\% S = \frac{S \times 100}{TS} \qquad \text{(B-2)}$$

$$\% Si = \frac{\left(ST - (S + 200C)\right) \times 100}{TS} \qquad \text{(B-3)}$$

$$\% C = \frac{(200C) \times 100}{TS} \qquad \text{(B-4)}$$

where S: weight of sand fraction (g)
Si: weight of silt fraction (g)
C: weight of clay fraction (g)
TS: weight of total sediment (g)

B-4 Determination of Organic Matter

I. Reagents

(i) 1 N Potassium dichromate, $K_2Cr_2O_7$

Approximately weight 49.04 g of $K_2Cr_2O_7$ diluted in 1 L DI-water.

(ii) Sulfuric acid (H_2SO_4) with silver sulfate (Ag_2SO_4)

Dissolving 2.5 g of Ag_2SO_4 in conc. H_2SO_4

(iii) 0.5 N Ferrous ammonium sulfate solution, $Fe(NH_2)(SO_4)_2{\cdot}6H_2O$

Approximately weight 196.1 g of $Fe(NH_2)(SO_4)_2{\cdot}6H_2O$ dissolved 800 m L of DI-water containing 20 ml of conc. H_2SO_4 .

(iv) Phosphoric acid (H_3PO_4)

(v) Sodium fluoride (NaF)

(vi) Diphenylamine indicator

Approximately weight 0.5 g of diphenylamine dissolved with 20 ml of DI-water and 100 ml of conc.H_2SO_4.

II. Analytical procedure

The following procedure, accurately weight 0.5 g of dry sediment in a 500 ml Erlenmeyer flask, add 10 ml of 1 N $K_2Cr_2O_7$ solution by volumetric pipette and 20 ml of conc. H_2SO_4 with Ag_2SO_4 and shake for 1 min, allow the mixture to stand for 30 min, add 170 ml DI-water and 10 ml of 85% H_3PO_4 and 0.2 g of NaF, add 15 drop of diphenylamine indicator. Follow the back titrate the solution with the 0.5 N of $Fe(NH_2)(SO_4)_2{\cdot}6H_2O$ to end point (brilliant green). Calculation of readily oxidization organic matter contents is follow in Eq. B-5.

$$\%\ \mathrm{OM} = 10 \times \left(1 - \frac{V_T}{V_S}\right) \times F \times 1.72 \qquad \text{(B-5)}$$

$$F = 1\ \mathrm{N} \times \frac{12}{4000} \times \frac{100}{S}$$

where V_T: volume of ferrous solution used titration sample (ml)
V_S: volume of ferrous solution used titration blank (ml)
F: factor derived as above
S: weight of sediment (g)

A-5 Determination of Calcium Carbonate

I. Reagents

(i) 0.5 N HCl

Volume 5 ml of 37 % (v/v) HCl diluted in 1 L of DI-water.

(ii) 0.25 M Sodium Hydroxide (NaOH)

Weight approximately 10 g of NaOH diluted in 1 L DI-water.

(iii) Phenolphthaline

Weight approximately 100 mg of phenolphthaline dissolved 100 ml of 80% ethyl alcohol.

II. Analytical procedure

The following procedure, accurately 1.0 g of dry sediment in a 250 ml Erlenmeyer flask, add 10 ml of 0.5 N HCl, heat at about 90 °C for 20 min, dilute by DI-water to about half of flask, following back titrate with 0.25 N of NaOH using phenolphthaline as an indicator. The end point is color change from colorless to purple. HCl and NaOH should be standardizing before use. Calculation 1 M HCl 1 M HCl of calcium carbonate contents is follow in Eq. B-6.

$$\mathrm{CaCO_3}\ (\mathrm{g/g_s}) = \left[\left\{\frac{\left(\frac{\mathrm{N_{HCl}} \times \mathrm{V_{HCl}}}{1000}\right) - \left(\frac{\mathrm{N_{NaOH}} \times \mathrm{V_{NaOH}}}{1000}\right)}{2}\right\} \times 40\right] \div S \qquad \text{(B-6)}$$

where N_{HCl}: concentration of HCl (N)
V_{HCl}: volume of HCl (ml)
N_{NaOH}: concentration of NaOH (N)
V_{NaOH}: volume of NaOH (ml)
S: weight of sediment (g)
40: atom weight of calcium carbonate

APPENDIX C

Graphite Furnace Atomic Absorption Spectroscopy and Flame Atomic Absorption Spectroscopy

Graphite furnace atomic absorption spectroscopy (GFAAS) optimal condition of PERKIN ELMER Zeeman Atomic Absorption Spectrometer 4100 ZL for the determinate of Cd, Cu, Pb and Zn for overlying water and interstitial water samples; and sediment reported in Table C-1 to C-6. Flame atomic absorption spectroscopy (FAAS) optimal condition of Flame VARIAN SpectA 220 FS Atomic Absorption Spectrometer for the determination of Zn reported in Table C-7.

Table C-1 GFAAS conditions for the determination of metals in HNO_3 solution of overlying water and interstitial water samples

Metals	Operation conditions	Graphite furnace temperature program				
		Step	Temperature (°C)	Ramp (s)	Hold (s)	Ar flow rate (ml min^{-1})
Cd	Wavelength 228.8 nm	Drying 1	120	20	30	250
	Slit width 0.7 nm	Drying 2	130	30	30	250
	Injection volume 20 µl	Pyrolysis	300	10	25	250
		Atomization	1200	0	5	0
		Cleaning	2500	1	2	250
Cu	Wavelength 228.8 nm	Drying 1	110	20	40	250
	Slit width 0.7 nm	Drying 2	130	20	40	250
	Injection volume 20 µl	Pyrolysis	700	20	20	250
		Atomization	1900	0	5	0
		Cleaning	2500	1	5	250
Pb	Wavelength 228.8 nm	Drying 1	110	30	40	250
	Slit width 0.7 nm	Drying 2	130	25	40	250
	Injection volume 20 µl	Pyrolysis	700	20	25	250
		Atomization	1400	0	5	0
		Cleaning	2400	1	3	250
Zn	Wavelength 228.8 nm	Drying 1	110	10	30	250
	Slit width 0.7 nm	Drying 2	120	15	30	250
	Injection volume 10 µl	Pyrolysis	600	20	20	250
		Atomization	1500	0	5	0
		Cleaning	2500	3	5	250

Table C-2 GFAAS conditions for the determination of metals in 0.01 M $CaCl_2$ solution of sediment samples

Metals	Operation conditions	Graphite furnace temperature program				
		Step	Temperature (°C)	Ramp (s)	Hold (s)	Ar flow rate (ml min^{-1})
Cd	Wavelength 228.8 nm	Drying 1	110	1	20	250
	Slit width 0.7 nm	Drying 2	130	5	30	250
	Injection volume 20 µl	Pyrolysis	400	10	20	250
	Matrix modifier 5 µl	Atomization	1400	0	5	0
	(0.2 % $PdCl_2$)	Cleaning	2400	1	2	250
Cu	Wavelength 228.8 nm	Drying 1	110	1	20	250
	Slit width 0.7nm	Drying 2	130	5	30	250
	Injection volume 20 µl	Pyrolysis	400	10	20	250
		Atomization	1900	0	5	0
		Cleaning	2400	1	2	250
Pb	Wavelength 228.8 nm	Drying 1	110	1	20	250
	Slit width 0.7nm	Drying 2	130	5	30	250
	Injection volume 20 µl	Pyrolysis	700	10	20	250
		Atomization	1500	0	5	0
		Cleaning	2400	1	3	250

Table C-3 GFAAS conditions for the determination of metals in 0.05 M EDTA solution of sediment samples

Metals	Operation conditions	Graphite furnace temperature program				
		Step	Temperature (°C)	Ramp (s)	Hold (s)	Ar flow rate (ml min^{-1})
Cd	Wavelength 228.8 nm	Drying 1	110	1	20	250
	Slit width 0.7 nm	Drying 2	130	5	30	250
	Injection volume 20 µl	Pyrolysis	400	10	20	250
		Atomization	1400	0	5	0
		Cleaning	2400	1	2	250
Cu	Wavelength 228.8 nm	Drying 1	110	1	20	250
	Slit width 0.7nm	Drying 2	130	5	30	250
	Injection volume 20 µl	Pyrolysis	700	10	20	250
		Atomization	1300	0	5	0
		Cleaning	2500	1	3	250
Pb	Wavelength 228.8 nm	Drying 1	110	1	20	250
	Slit width 0.7nm	Drying 2	130	5	30	250
	Injection volume 20 µl	Pyrolysis	400	10	20	250
		Atomization	1500	0	5	0
		Cleaning	2400	1	3	250

Table C-4 GFAAS conditions for the determination of metals in 25% (v/v) HOAc solution of sediment samples

Metals	Operation conditions	Graphite furnace temperature program				
		Step	Temperature (°C)	Ramp (s)	Hold (s)	Ar flow rate (ml min^{-1})
Cd	Wavelength 228.8 nm	Drying 1	120	20	30	250
	Slit width 0.7 nm	Drying 2	130	30	30	250
	Injection volume 20 µl	Pyrolysis	400	10	25	250
		Atomization	1400	0	5	0
		Cleaning	2400	1	2	250
Cu	Wavelength 228.8 nm	Drying 1	110	1	20	250
	Slit width 0.7nm	Drying 2	120	5	20	250
	Injection volume 20 µl	Pyrolysis	700	10	20	250
		Atomization	1900	0	5	0
		Cleaning	2500	1	5	250
Pb	Wavelength 228.8 nm	Drying 1	110	1	20	250
	Slit width 0.7nm	Drying 2	130	5	30	250
	Injection volume 20 µl	Pyrolysis	700	10	20	250
		Atomization	1500	0	5	0
		Cleaning	2400	1	3	250

Table C-5 GFAAS conditions for the determination of metals in 1 M HCl solution of sediment samples

Metals	Operation conditions	Graphite furnace temperature program				
		Step	Temperature (°C)	Ramp (s)	Hold (s)	Ar flow rate (ml min^{-1})
Cd	Wavelength 228.8 nm	Drying 1	110	1	20	250
	Slit width 0.7 nm	Drying 2	120	5	30	250
	Injection volume 20 µl	Pyrolysis	400	10	20	250
		Atomization	1400	0	5	0
		Cleaning	2400	1	2	250
Cu	Wavelength 228.8 nm	Drying 1	110	1	20	250
	Slit width 0.7nm	Drying 2	120	5	30	250
	Injection volume 20 µl	Pyrolysis	700	10	20	250
		Atomization	2100	0	5	0
		Cleaning	2500	1	3	250
Pb	Wavelength 228.8 nm	Drying 1	110	1	20	250
	Slit width 0.7nm	Drying 2	120	5	30	250
	Injection volume 20 µl	Pyrolysis	700	10	20	250
		Atomization	1500	0	5	0
		Cleaning	2400	1	3	250

Table C-6 GFAAS conditions for the determination of metals in SEMs solution samples

Metals	Operation conditions	Graphite furnace temperature program				
		Step	Temperature (°C)	Ramp (s)	Hold (s)	Ar flow rate (ml min^{-1})
Cd	Wavelength 228.8 nm	Drying 1	120	20	30	250
	Slit width 0.7 nm	Drying 2	130	30	30	250
	Injection volume 20 µl	Pyrolysis	400	10	25	250
		Atomization	1400	0	5	0
		Cleaning	2400	1	2	250
Cu	Wavelength 228.8 nm	Drying 1	110	1	20	250
	Slit width 0.7nm	Drying 2	120	5	20	250
	Injection volume 20 µl	Pyrolysis	700	10	20	250
		Atomization	1900	0	5	0
		Cleaning	2500	1	5	250
Pb	Wavelength 228.8 nm	Drying 1	110	1	20	250
	Slit width 0.7nm	Drying 2	130	5	30	250
	Injection volume 20 µl	Pyrolysis	700	10	20	250
		Atomization	1500	0	5	0
		Cleaning	2400	1	3	250

Table C-7 FAAS conditions for the determination of metals in solution samples

	working condition
Lamp current	5 mA
Fuel	Acetylene
Support	Air
Wavelength	213.9
Silt width	1 nm

APPENDIX D

Standard Calibration Curves

The calibration curve and standard addition method were used for quantification of the analysis. The matrix would interfere with the measurement of dissolved Cd, Cu, Pb, and Zn by GFAAS and FAAS for Zn.

The below Figures are show interference from the sample matrix, since difference between the slope of standard calibration curve (STD curve) and standard calibration addition curve (STD addition), as shown in Fig. D-1 to Fig. D-28.

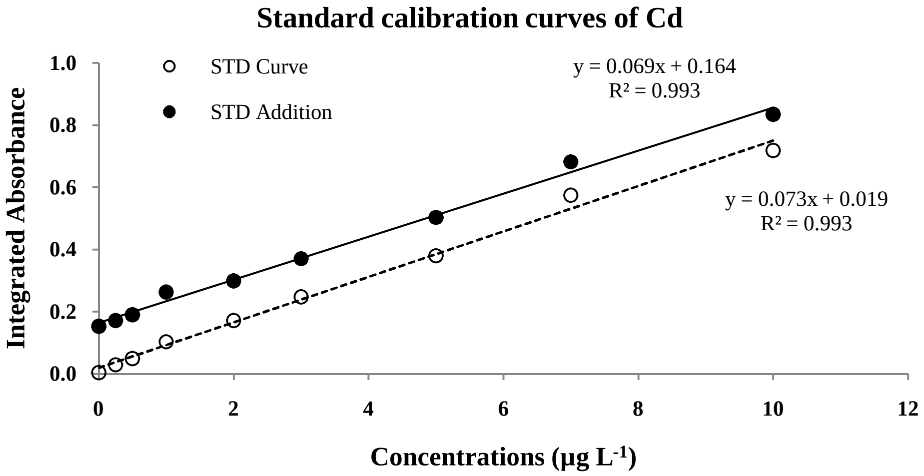


Figure D-1 Comparison of calibration curve between normal and addition curves of GFAAS for Cd in overlying water

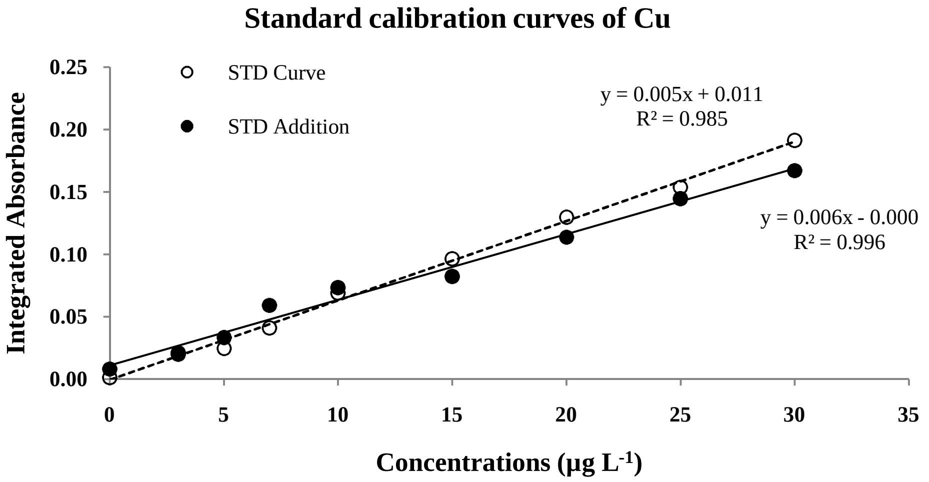


Figure D-2 Comparison of calibration curve between normal and addition curves of GFAAS for Cu in overlying water

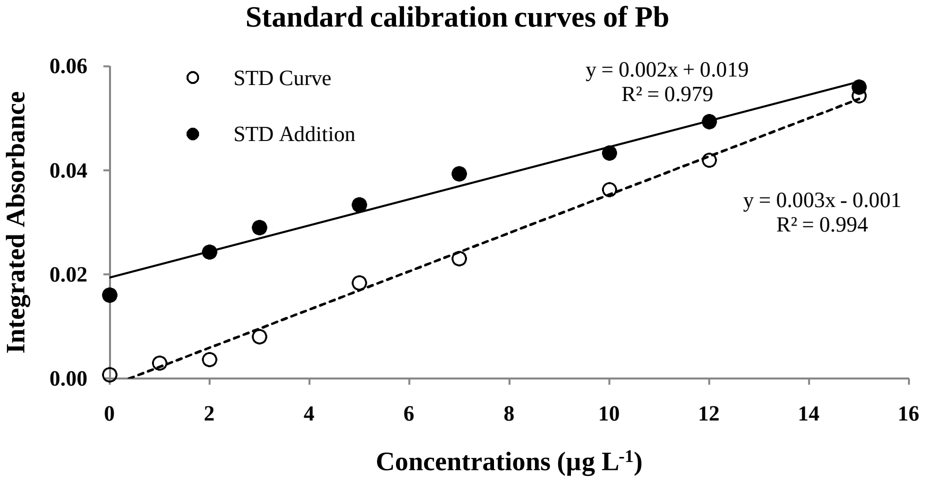


Figure D-3 Comparison of calibration curve between normal and addition curves of GFAAS for Pb in overlying water

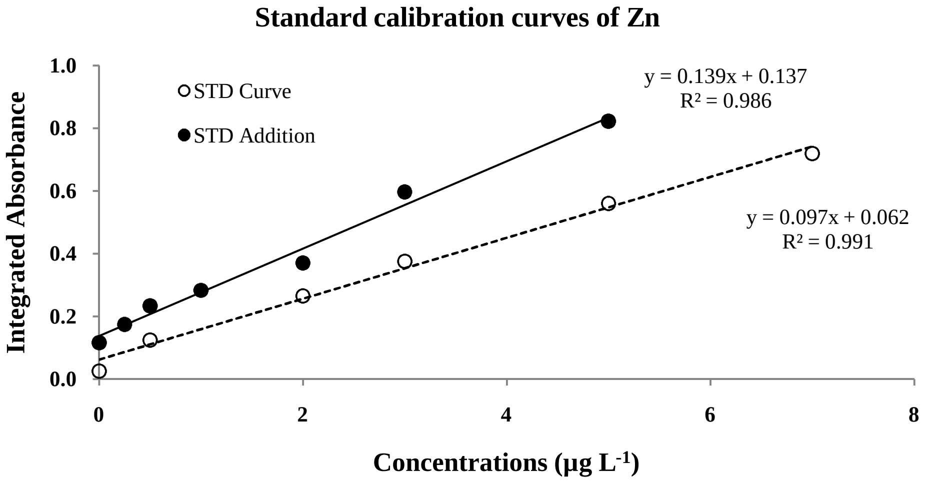


Figure D-4 Comparison of calibration curve between normal and addition curves of GFAAS for Zn in overlying water

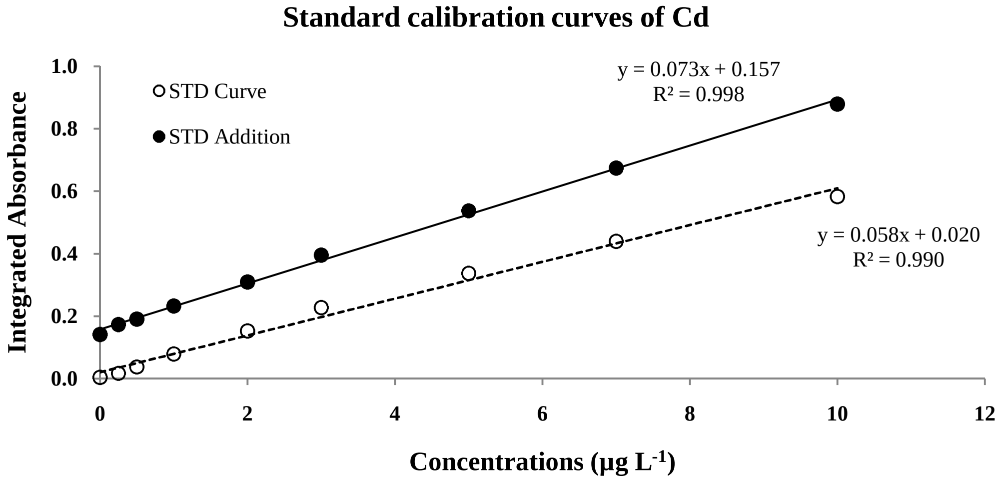


Figure D-5 Comparison of calibration curve between normal and addition curves of GFAAS for Cd in interstitial water

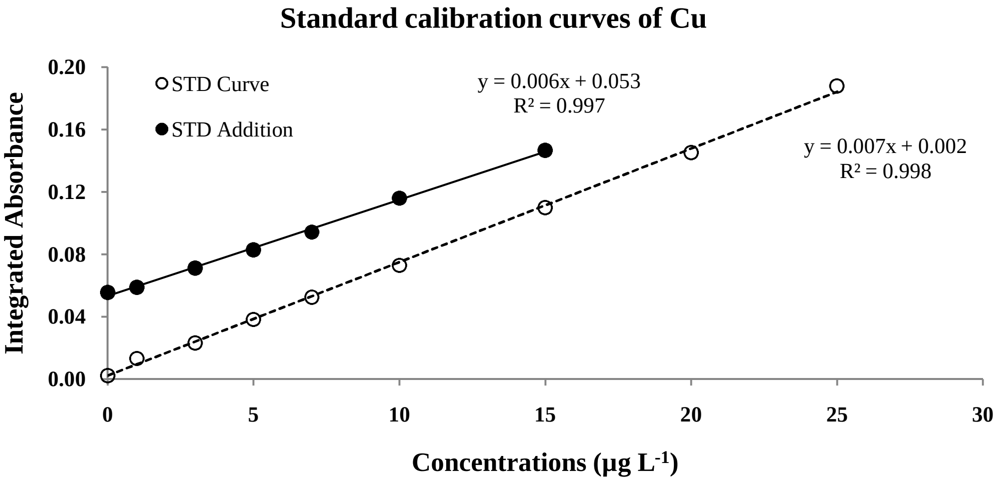


Figure D-6 Comparison of calibration curve between normal and addition curves of GFAAS for Cu in interstitial water

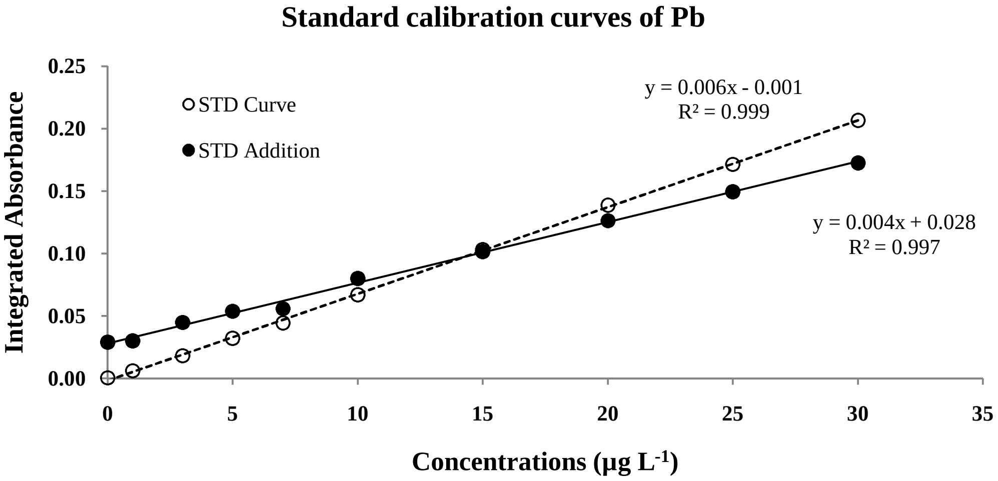


Figure D-7 Comparison of calibration curve between normal and addition curves of GFAAS for Pb in interstitial water

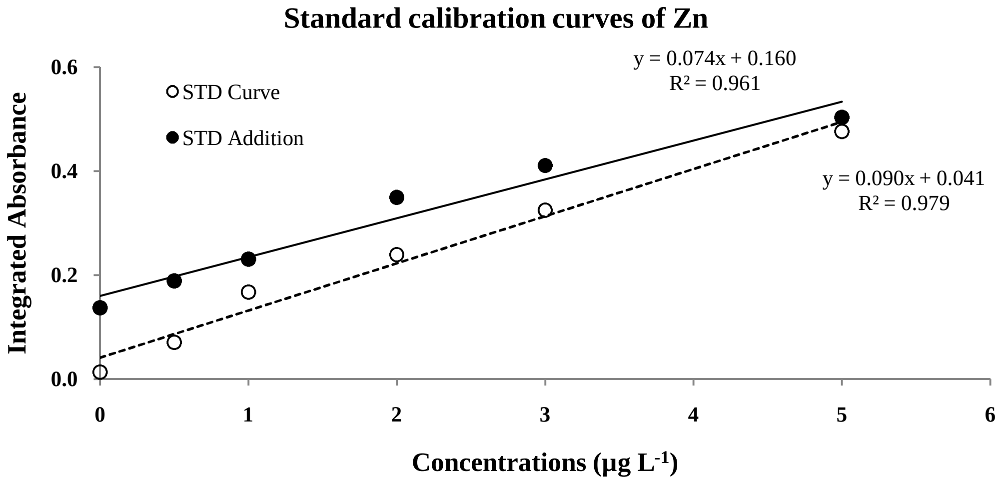


Figure D-8 Comparison of calibration curve between normal and addition curves of GFAAS for Zn in interstitial water

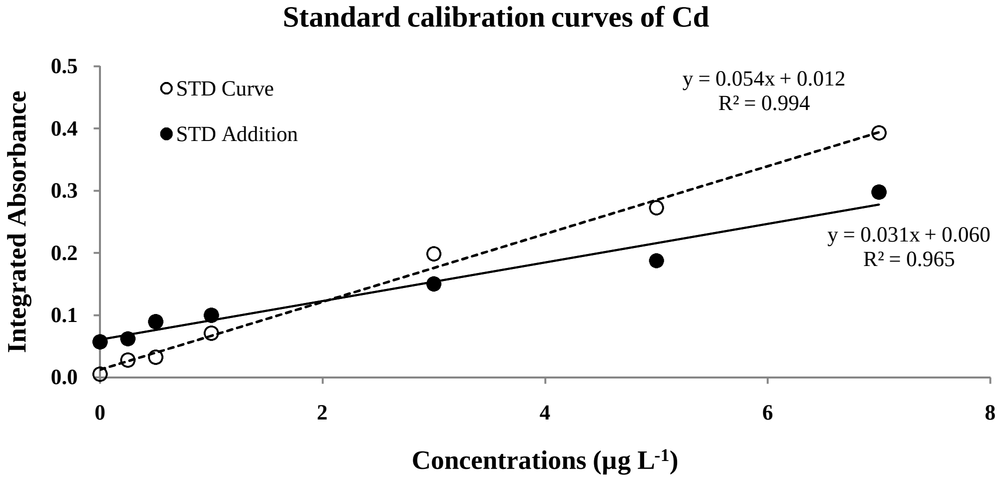


Figure D-9 Comparison of calibration curve between normal and addition curves of GFAAS for Cd in sediment extracted by 0.01 M $CaCl_2$

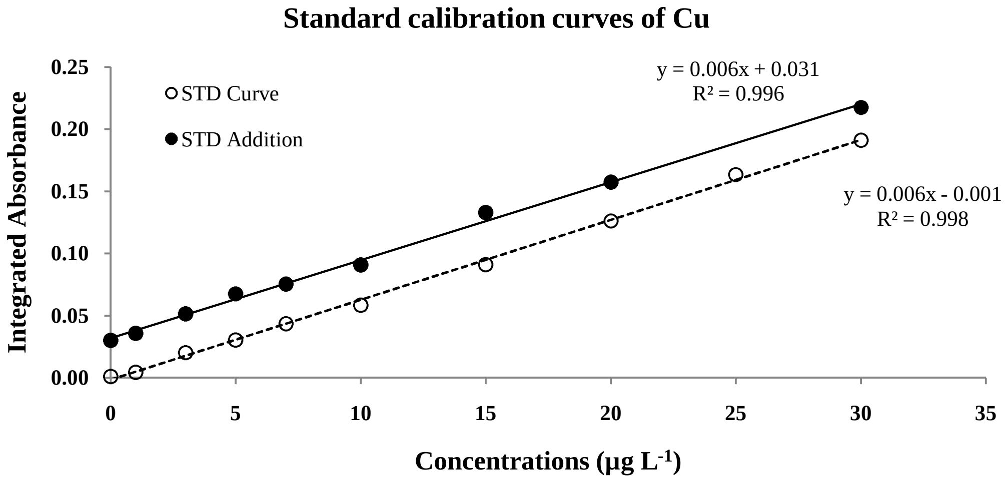


Figure D-10 Comparison between STD and STD addition curves of GFAAS for Cu in sediment extracted by 0.01 M $CaCl_2$

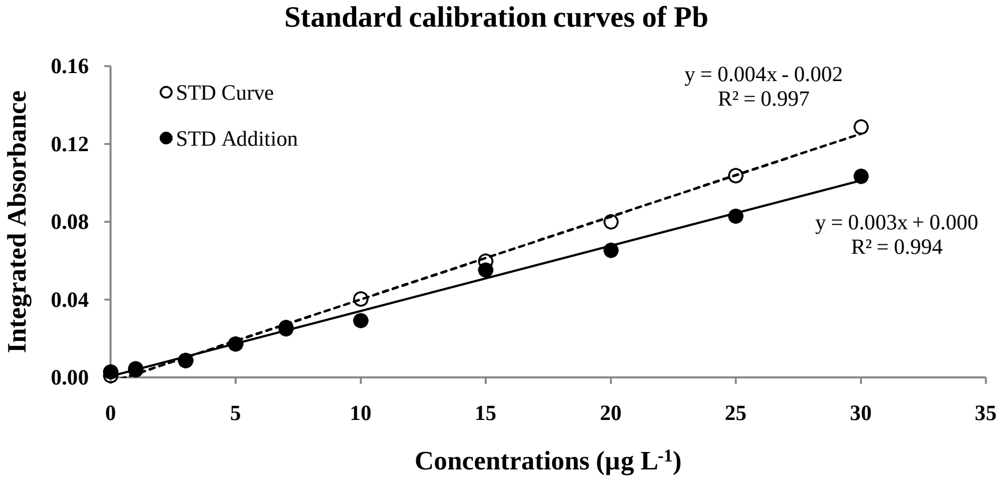


Figure D-11 Comparison of calibration curve between normal and addition curves of GFAAS for Pb in sediment extracted by 0.01 M $CaCl_2$

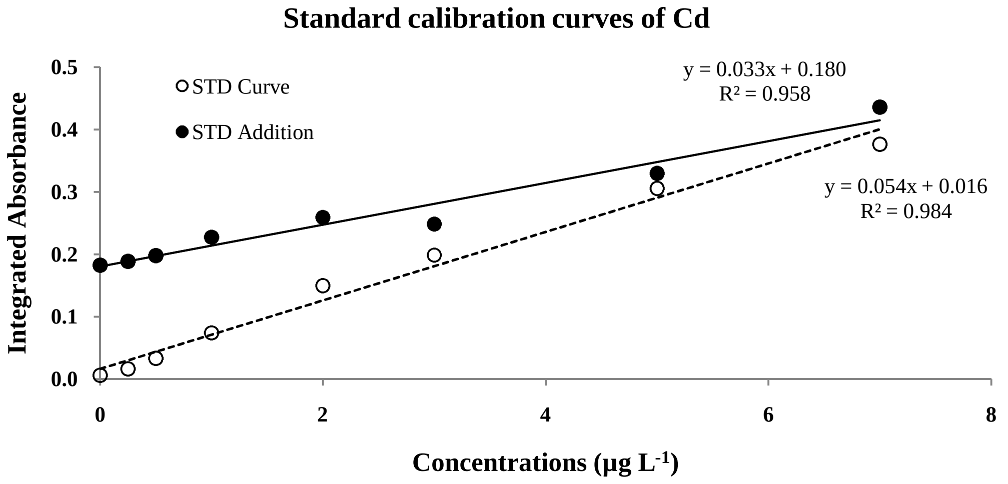


Figure D-12 Comparison of calibration curve between normal and addition curves of GFAAS for Cd in sediment extracted by 0.05 M EDTA

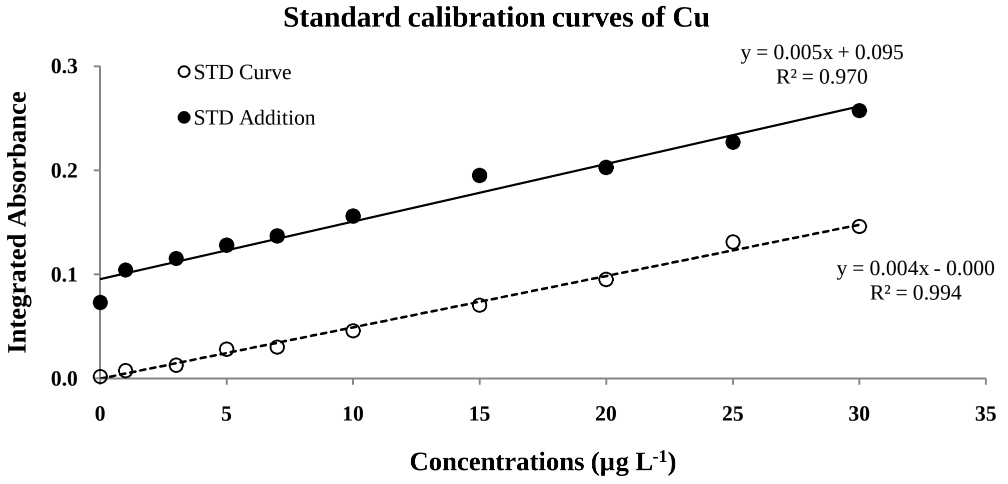


Figure D-13 Comparison of calibration curve between normal and addition curves of GFAAS for Cu in sediment extracted by 0.05 M EDTA

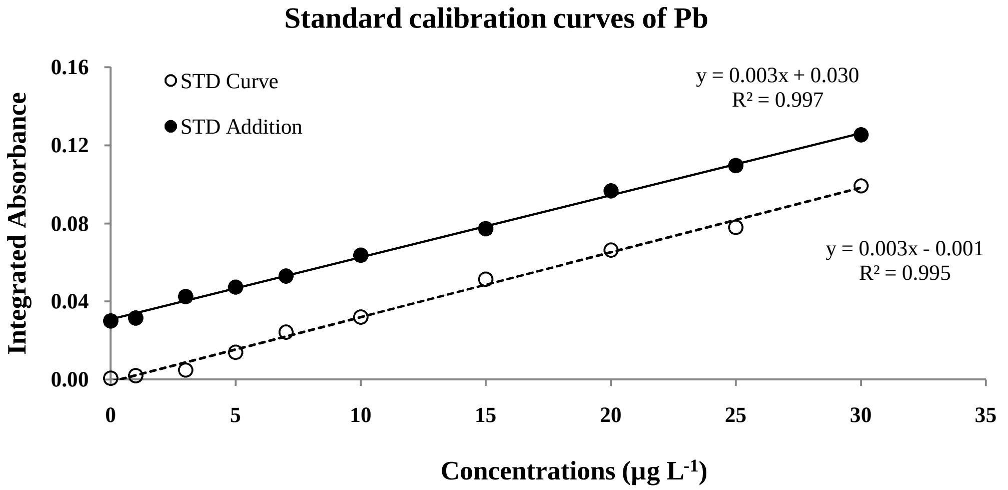


Figure D-14 Comparison of calibration curve between normal and addition curves of GFAAS for Pb in sediment extracted by 0.05 M EDTA

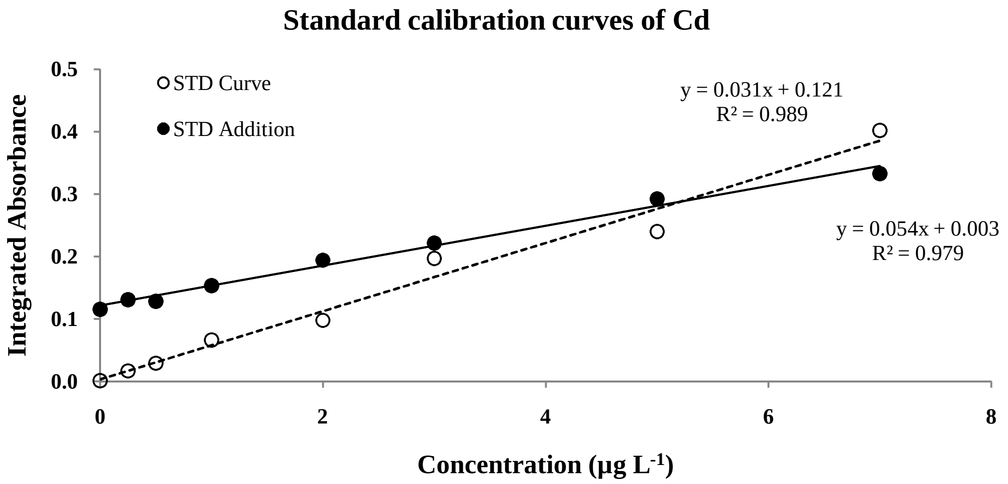


Figure D-15 Comparison of calibration curve between normal and addition curves of GFAAS for Cd in sediment extracted by 25% (v/v) HOAc

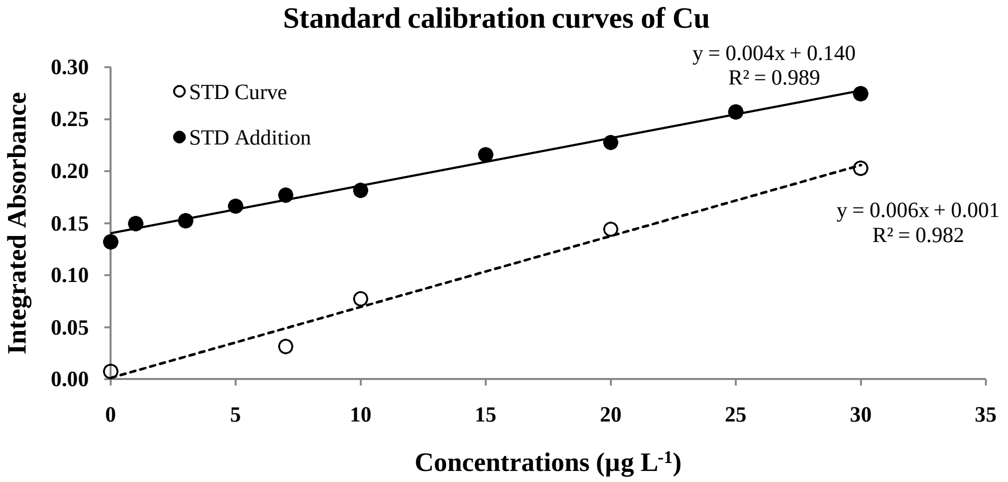


Figure D-16 Comparison of calibration curve between normal and addition curves of GFAAS for Cu in sediment extracted by 25% (v/v) HOAc

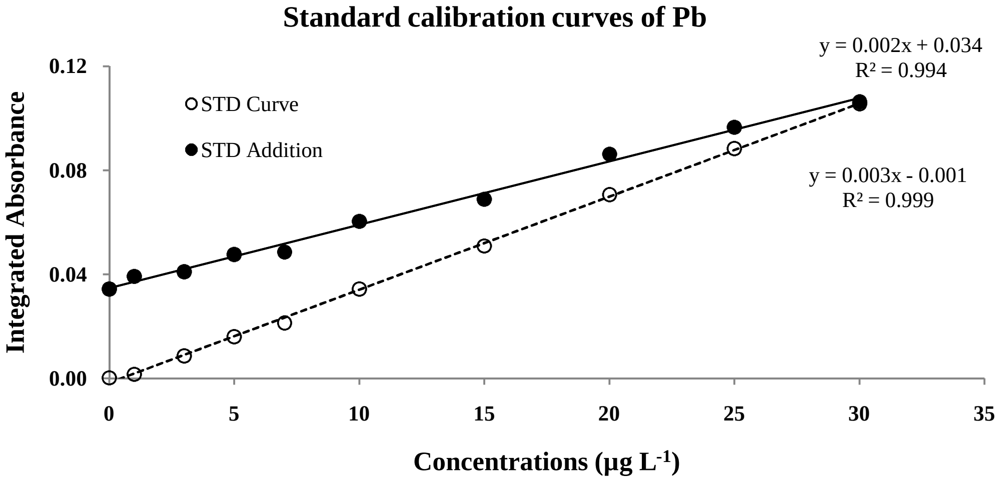


Figure D-17 Comparison of calibration curve between normal and addition curves of GFAAS for Pb in sediment extracted by 25% (v/v) HOAc

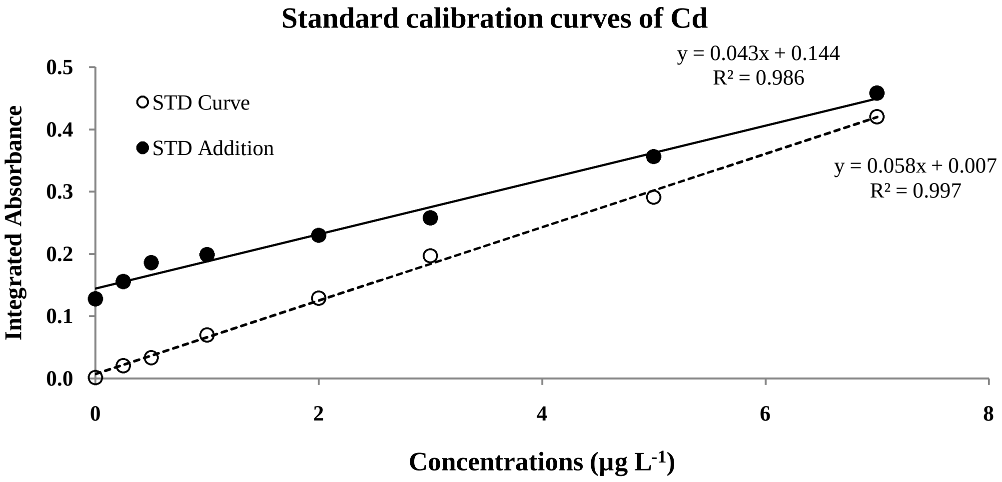


Figure D-18 Comparison of calibration curve between normal and addition curves of GFAAS for Cd in sediment extracted by 1 M HCl

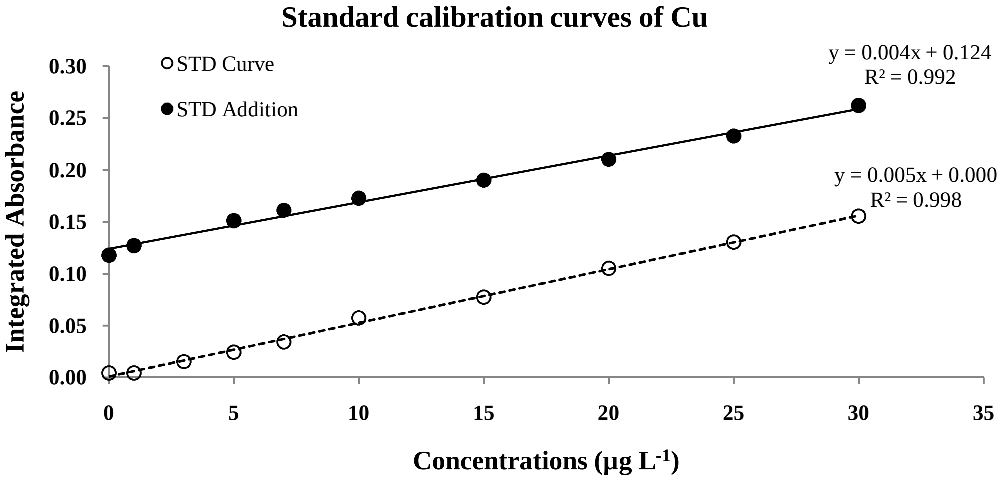


Figure D-19 Comparison of calibration curve between normal and addition curves of GFAAS for Cu in sediment extracted by 1 M HCl

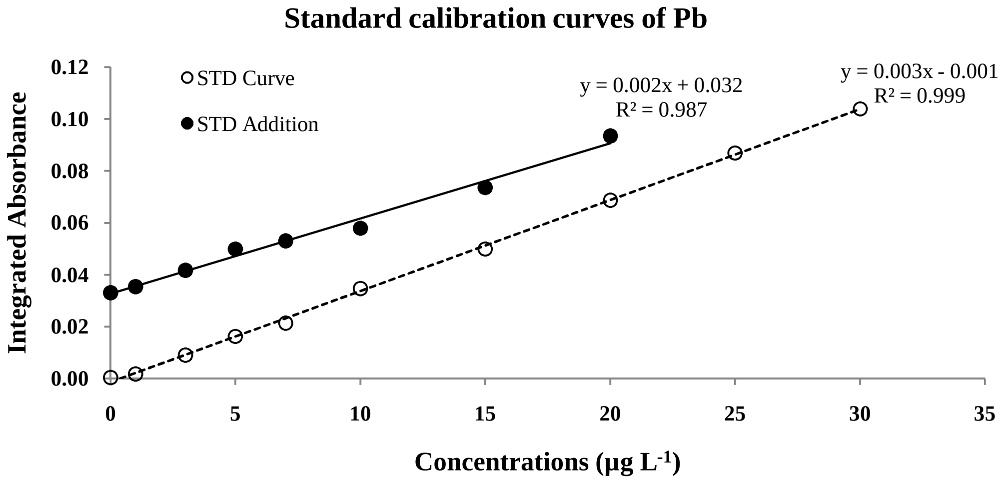


Figure D-20 Comparison of calibration curve between normal and addition curves of GFAAS for Pb in sediment extracted by 1 M HCl

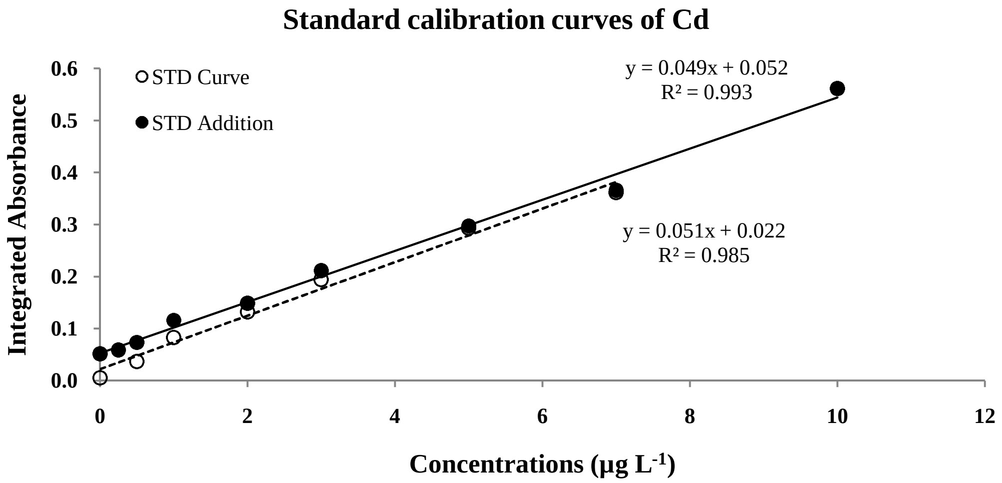


Figure D-21 Comparison of calibration curve between normal and addition curves of GFAAS for Cd in SEM fraction

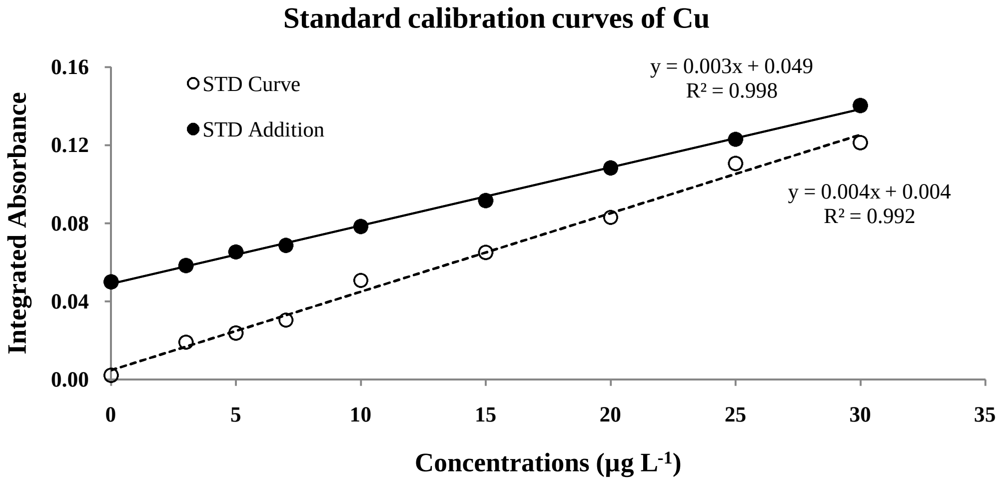


Figure D-22 Comparison of calibration curve between normal and addition curves of GFAAS for Cu in SEM fraction

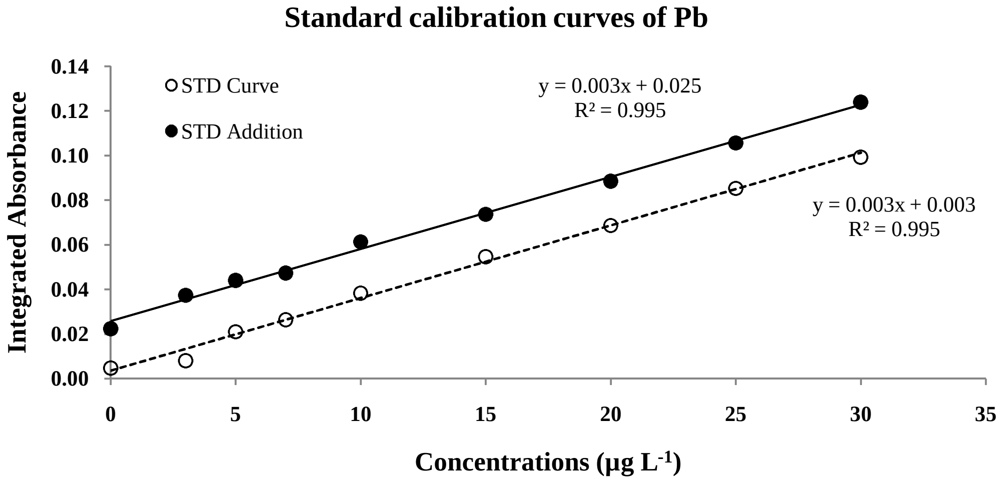


Figure D-23 Comparison of calibration curve between normal and addition curves of GFAAS for in SEM fraction

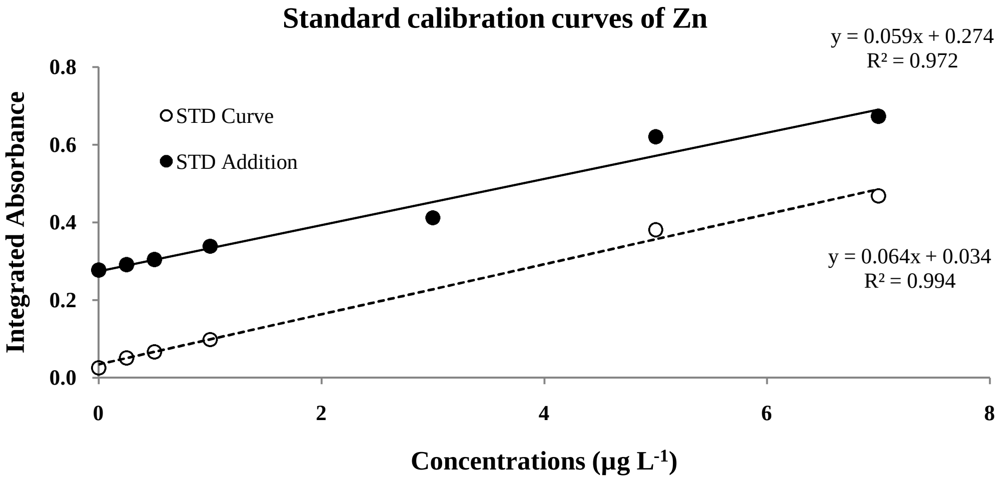


Figure D-24 Comparison of calibration curve between normal and addition curves of FAAS for Zn in sediment extracted by 0.01 M $CaCl_2$

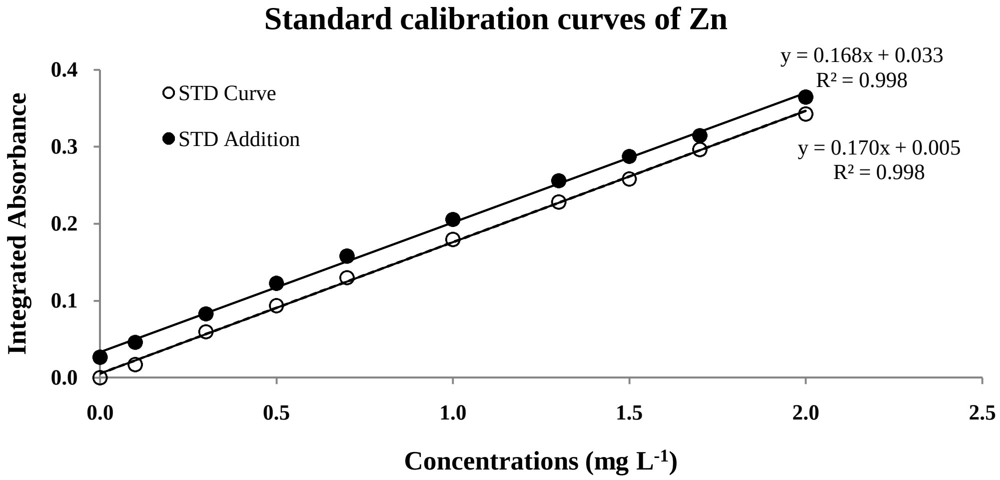


Figure D-25 Comparison of calibration curve between normal and addition curves of FAAS for Zn in sediment extracted by 0.05 M EDTA

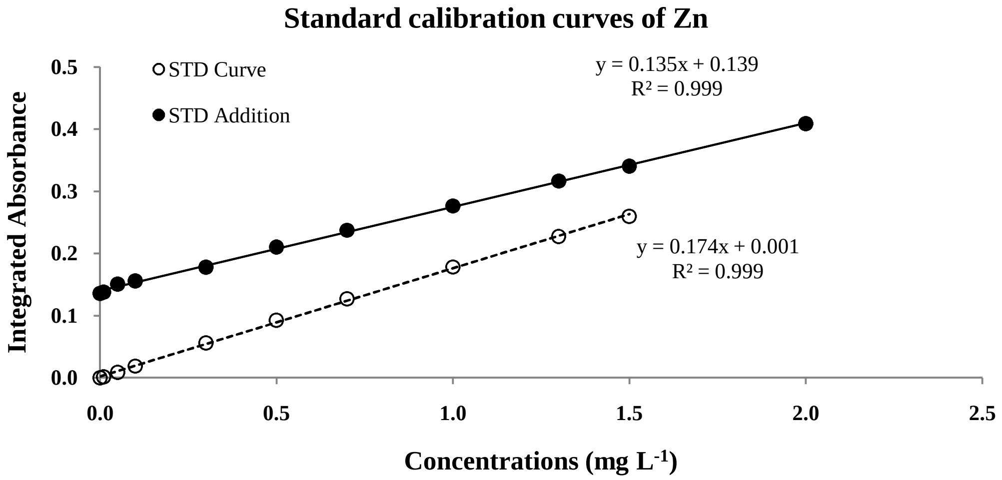


Figure D-26 Comparison of calibration curve between normal and addition curves of FAAS for Zn in sediment extracted by 25% (v/v) HOAc

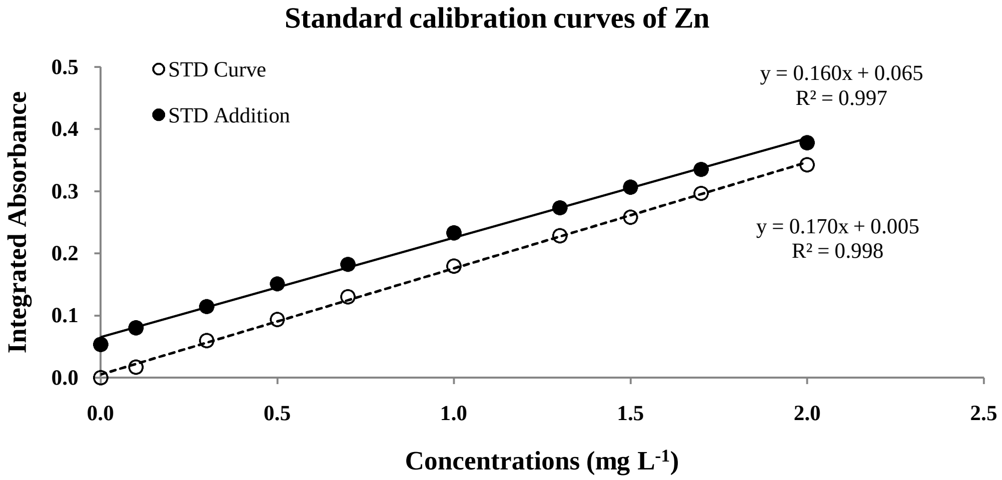


Figure D-27 Comparison of calibration curve between normal and addition curves of FAAS for Zn in sediment extracted by 1 M HCl

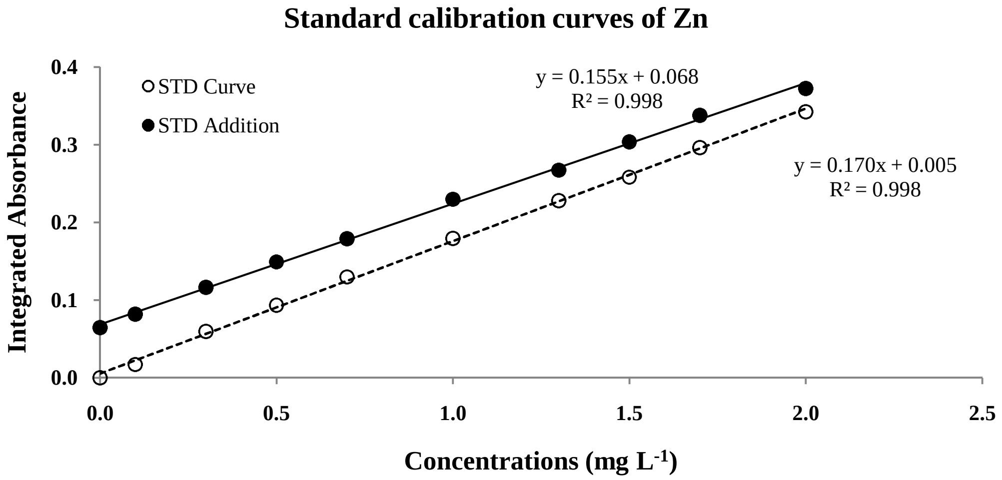


Figure D-28 Comparison of calibration curve between normal and addition curves of FAAS for Zn in SEM fraction

APPENDIX E

Quality Control

Table E-1 Quality control results in metals analysis of overlying water and interstitial water

Samples	Concentration				SE	RSD %	Recovery %
	Replications			Average			
	1	2	3				
Cd (µg L^{-1})							
DL				0.01			
LRB				0.02			
OW	0.06	0.05		0.05	0.00	21	
OW + 2 µg L^{-1}	2.20	2.15	2.17	2.17	0.01	1	106
IW 2/II	0.13	0.13		0.13	0.00	3	
IW 5/II	0.09	0.19		0.14	0.03	69	
IW	0.37	0.42	0.35	0.38	0.02	7	
IW + 5 µg L^{-1}	4.94	5.13	5.08	5.05	0.05	2	93
IW + 20 µg L^{-1}	21.42	16.54	18.56	18.84	1.16	11	92
Cu (µg L^{-1})							
DL				0.08			
LRB				0.08			
OW	1.36	1.34	1.24	1.31	0.03	4	
OW + 2 µg L^{-1}	3.29	3.49	5.35	3.39	0.07	3	104
IW 2/II	0.87	1.03		0.95	0.06	17	
IW 5/II	1.11	1.16		1.14	0.02	5	
IW	1.76	1.78	1.71	1.75	0.02	2	
IW +5 µg L^{-1}	7.03	7.18	7.39	7.20	0.09	2	109
IW + 20 µg L^{-1}	18.49	17.04	22.45	19.33	1.32	12	88

SE: standard error
RSD: percentage of relative standard deviation
DL: detection limit
LRB: laboratory reagent blank
OW: overlying water
IW: interstitial water

Table E-1 (continued) Quality control results in metals analysis of overlying water and interstitial water

Samples	Concentration				SE	RSD %	Recovery %
	Replications			Average			
	1	2	3				
Pb (μg L^{-1})							
DL				0.09			
LRB				0.27			
OW	0.22	0.37	0.15	0.25	0.05	38	
OW + 2 μg L^{-1}	1.34	1.44	1.40	1.39	0.02	3	57
IW 1/I	0.57	0.81	0.57	0.65	0.07	18	
IW 3/IV	0.93	1.13	0.93	0.99	0.06	10	
IW 5/II	0.67	0.49		0.58	0.06	30	
IW	1.05	1.23	0.60	0.96	0.15	28	
IW +5 μg L^{-1}	5.37	7.35	8.19	6.36	0.70	31	108
IW + 20 μg L^{-1}	17.93	22.05	26.04	19.99	1.46	21	95
Zn (μg L^{-1})							
DL				0.07			
LRB				1.15			
OW	5.66	3.14	2.72	3.84	0.75	34	
OW + 2 μg L^{-1}	6.43	6.86	6.79	6.69	0.13	3	143
LRB	0.97	0.85	0.99	0.94	0.03	6	
IW 2/IV	87.75	86.89		87.32	0.30	1	
IW 2/II	31.34	30.01		30.68	0.47	4	
IW	60.94	66.71	63.37	63.67	1.36	4	
IW +5 μg L^{-1}	67.47	70.24	69.33	69.01	0.81	2	107
IW + 20 μg L^{-1}	91.94	86.98	78.44	85.79	3.22	6	111

SE: standard error
RSD: percentage of relative standard deviation
DL: detection limit
LRB: laboratory reagent blank
OW: overlying water
IW: interstitial water

Table E-2 Quality control results in acid volatile sulfide analysis of the

Samples	Concentration (μmols-S^{2-} g^{-1} dry wt.)			SE	RSD %
	Replications		Average		
	1	2			
ST 1/I	0.59	0.75	0.67	0.06	24
ST 4/IV	0.90	0.99	0.95	0.03	10

SE: standard error
RSD: percentage of relative standard deviation

Table E-3 Quality control results in simultaneously extracted metals analysis

Samples	Concentration			SE	RSD %
	Replications		Average		
	1	2			
Cd (µg kg^{-1} dry wt)					
ST 1/I	49.3	66.1	57.7	5.9	29
ST 4/IV	71.3	66.0	68.7	1.9	8
Cu (mg kg^{-1} dry wt)					
ST 1/I	25.0	21.9	23.5	1.1	7
ST 4/IV	13.2	11.8	11.5	0.4	6
Pb (mg kg^{-1} dry wt)					
ST 1/I	17.2	18.3	17.7	0.27	3
ST 4/IV	17.7	13.6	15.7	1.45	13
Zn (mg kg^{-1} dry wt)					
ST 1/I	180.5	178.0	179.3	0.9	1
ST 4/IV	88.1	61.9	75.0	9.3	35

SE: standard error

RSD: percentage of relative standard deviation

Table E-4 Quality control results in grain size analysis

Samples	Grain size			SE	RSD %
	Replications		Average		
	1	2			
Sand (%)					
ST 2/I	27	27	27	0	1
ST 3/I	26	26	26	0	1
ST 4/I	66	68	67	1	3
Silt (%)					
ST 2/I	54	54	54	0	0
ST 3/I	49	55	52	3	11
ST 4/I	11	12	12	1	11
Clay (%)					
ST 2/I	20	19	20	0	1
ST 3/I	25	19	22	3	26
ST 4/I	23	20	21	2	15

SE: standard error

RSD: percentage of relative standard deviation

Table E-5 Quality control results in organic carbon analysis

Samples	Organic carbon content (%)			SE	RSD %
	Replications		Average		
	1	2			
ST 1/I	0.69	0.71	0.70	0.01	3
ST 1/II	0.41	0.40	0.40	0.00	1
ST 1/III	0.55	0.52	0.53	0.01	5
ST 1/IV	0.73	0.80	0.76	0.04	10
ST 2/I	0.40	0.46	0.43	0.02	13
ST 2/II	0.82	0.82	0.82	0.00	0
ST 2/III	0.82	0.87	0.83	0.04	7
ST 2/IV	0.79	1.02	1.01	0.01	23
ST 3/I	1.00	0.99	0.95	0.05	1
ST 3/II	0.90	1.04	1.05	0.03	13
ST 3/III	1.08	1.02	0.89	0.01	7
ST 3/IV	0.90	0.88	1.03	0.00	2
ST 4/I	1.43	1.46	0.36	0.03	8
ST 4/II	0.33	0.38	0.58	0.01	9
ST 4/III	0.57	0.59	0.78	0.01	2
ST 4/IV	0.76	0.79	0.97	0.01	2
ST 5/I	1.03	1.02	1.66	0.06	0
ST 5/II	1.60	1.71	1.27	0.04	9
ST 5/III	1.31	1.23	1.23	0.04	6
ST 5/IV	1.27	1.19	1.44	0.01	6

SE: standard error

RSD: percentage of relative standard deviation

Table E-6 Quality control results in calcium carbonate analysis

Samples	Calcium carbonate content (%)			SE	RSD %
	Replications		Average		
	1	2			
ST 1/I	1.01	1.24	1.12	0.11	20
ST 1/II	1.25	1.32	1.29	0.03	5
ST 1/III	1.43	1.76	1.60	0.17	21
ST 1/IV	2.07	2.05	2.06	0.01	1
ST 2/I	1.86	1.96	1.91	0.05	5
ST 2/II	1.59	1.55	1.57	0.02	2
ST 2/III	1.31	1.34	1.32	0.02	2
ST 2/IV	1.31	1.38	1.34	0.04	6
ST 3/I	1.85	1.60	1.73	0.13	15
ST 3/II	2.24	2.15	2.20	0.05	4
ST 3/III	8.00	9.22	8.61	0.61	14
ST 3/IV	3.46	3.48	3.47	0.01	1
ST 4/I	2.94	3.52	3.23	0.29	18
ST 4/II	5.45	5.05	5.25	0.20	8
ST 4/III	3.64	5.01	4.33	0.69	32
ST 4/IV	4.07	4.70	4.39	0.32	14
ST 5/I	3.71	3.68	3.70	0.02	1
ST 5/II	7.08	8.45	7.76	0.68	18
ST 5/III	3.78	3.47	3.62	0.16	9
ST 5/IV	2.77	3.79	3.28	0.51	31

SE: standard error

RSD: percentage of relative standard deviation

Table E-7 Quality control results in metals analysis of the sediment extracted by 0.01 M $CaCl_2$

Samples	Concentration				SE	RSD %
	Replications			Average		
	1	2	3			
Cd (µg kg^{-1} dry wt)						
ST 2/I	9.1	13.0	17.5	13.2	2.0	26
ST 3/III	7.0	8.4		7.7	0.5	18
ST 7/II	5.8	7.9	5.7	6.5	0.6	15
Cu (µg kg^{-1} dry wt)						
ST 2/I	46.7	58.6	45.8	50.4	3.4	12
ST 3/III	65.5	57.0		61.3	3.0	14
ST 7/II	36.7	37.0	31.7	35.1	1.4	7
Pb (µg kg^{-1} dry wt)						
ST 2/I	11.6	12.7	17.9	14.0	1.6	20
ST 3/III	22.7	23.2		23.0	0.2	2
ST 7/II	14.3	14.0		14.1	0.1	2
Zn (µg kg^{-1} dry wt)						
ST 2/I	236.6	250.2		243.4	4.8	6
ST 3/III	137.8	289.5		213.7	53.6	51
ST 7/II	112.5	96.3		104.4	5.7	16

SE: standard error

RSD: percentage of relative standard deviation

Table E-8 Quality control results in metals analysis of the sediment extracted by 0.05 M EDTA

Samples	Concentration				SE	RSD %
	Replications			Average		
	1	2	3			
Cd (µg kg^{-1} dry wt)						
ST 2/I	26.8	27.9	27.1	27.2	0.3	2
ST 3/IV	42.6	48.6	0.0	45.6	2.1	13
ST 4/II	29.2	27.8	25.6	27.6	0.9	5
Cu (mg kg^{-1} dry wt)						
ST 2/I	4.3	4.3	4.3	4.3	0.0	0
ST 3/IV	7.1	5.7		6.4	0.5	22
ST 4/II	3.1	3.4	3.2	3.2	0.1	4
Pb (mg kg^{-1} dry wt)						
ST 2/I	7.2	7.2	6.4	6.9	0.2	5
ST 3/IV	12.2	12.2		12.2	0.0	0
ST 4/II	9.8	10.3	13.8	11.3	1.0	16
Zn (mg kg^{-1} dry wt)						
ST 2/I	20.5	20.3	20.5	20.4	0.1	1
ST 3/IV	10.0	10.5		10.3	0.2	5
ST 4/II	8.7	8.5	8.5	8.6	0.0	1

SE: standard error

RSD: percentage of relative standard deviation

Table E-9 Quality control results in metals analysis of the sediment extracted by 25 % (v/v) HOAc

Samples	Concentration				SE	RSD %
	Replications			Average		
	1	2	3			
Cd (µg kg^{-1} dry wt)						
ST 2/I	33.3	33.4	28.7	31.8	1.3	7
ST 3/I	41.3	47.5		44.4	2.2	14
Cu (mg kg^{-1} dry wt)						
ST 2/I	3.4	3.1	3.0	3.2	0.1	5
ST 3/I	2.3	2.5		2.4	0.1	8
Pb (mg kg^{-1} dry wt)						
ST 2/I	2.4	2.3	2.3	2.3	0.0	2
ST 3/I	2.8	3.0		2.9	0.1	8
Zn (mg kg^{-1} dry wt)						
ST 2/I	35.5	35.5	33.3	34.8	0.6	3
ST 3/I	25.4	24.3		24.8	0.4	4

SE: standard error

RSD: percentage of relative standard deviation

Table E-10 Quality control results in metals analysis of the sediment extracted by 1 M HCl

Samples	**Concentration**				**SE**	**RSD %**
	Replications			**Average**		
	1	**2**	**3**			
Cd (μg kg^{-1} dry wt)						
ST 2/I	43.8	41.2	45.6	43.5	1.1	4
ST 3/III	101.3	72.7		87.0	10.1	33
ST 4/II	60.2	57.9	55.7	57.9	1.1	3
Cu (mg kg^{-1} dry wt)						
ST 2/I	11.4	9.1	10.1	10.2	0.6	9
ST 3/III	12.4	11.3		11.9	0.0	9
ST 4/II	6.5	5.9	5.8	6.1	0.2	6
Pb (mg kg^{-1} dry wt)						
ST 2/I	7.0	8.3	8.7	8.0	0.4	9
ST 3/III	16.6	15.1		15.9	0.5	9
ST 4/II	13.8	14.2	14.4	14.1	0.1	2
Zn (mg kg^{-1} dry wt)						
ST 2/I	74.4	77.2	74.2	75.2	0.8	2
ST 3/III	57.0	59.8		58.4	1.0	5
ST 4/II	62.1	58.4	62.9	61.1	1.1	3

SE: standard error

RSD: percentage of relative standard deviation

APPENDIX F

Calculation of Sediment Quality Guideline based on Equilibrium Partitioning Approach

F-1 Thai coastal water quality standards (Thai Royal Government Gazette, 2007)

Sampling and method base on Standard Method for the Examination of Water and Wastewater - (APHA, AWWA, and WEF); Method of Seawater Analysis - Grasshoff (1999); Practical Handbook of Seawater Analysis - Strickland and Parson (1972); A Manual of Chemical and Biological Methods for Seawater Analysis - Parsons et.al. (1984); Recommended guidelines for measuring organic compounds in Puget Sound water, sediment, and tissue samples - Puget Sound Estuary Program (1997); Prescribed Procedures for Measurement of Radioactivity in Drinking Water - Krieger and Whittaker (1980); Proceedings of the organotin symposium; Comprehensive method for determination of aquatic butyltin and butylmethyltin species at ultra trace levels using simultaneous hybridization/extraction with GC/FPD detection - Matthias et. al. (1986). The values of the seawater quality standards of Thai’s coastline for Cd, Cu, Pb, and Zn were reported in Table F-1.

Table F-1 Thai coastal water quality standards for the metals (Thai Royal Government Gazette, 2007)

Metals	Seawater Quality Standards (μg L^{-1})	Method for Examination
Cd	< 5	Pre-concentration and Electrothermal Atomic Absorption Spectrometric Method or Inductively Coupled Plasma Method
Cu	< 8	
Pb	< 8.5	
Zn	< 50	Pre-concentration and Flame Atomic Absorption Spectrometric Method or Electrothermal Atomic Absorption Spectrometric Method or Inductively Coupled Plasma Method

F-2 Partitioning Coefficients

The K_D calculated from Eq. 2-2; using labile metals extracted by 25% (v/v) HOAc after size normalization (<63μm fraction) and calcium carbonate free basis, and dissolved metals concentrations in interstitial water (μg L^{-1}), as reported in Table F-2.

Table F-2 The partition coefficients (K_D) for the metals at various depths of the core sediments

Stations	C_S				C_{IW}				K_D			
	Cd	**Cu**	**Pb**	**Zn**	**Cd**	**Cu**	**Pb**	**Zn**	**Cd**	**Cu**	**Pb**	**Zn**
1/I	55	11,260	4,832	98,506	0.12	2.51	0.67	42.57	451	4,487	7,202	2,314
1/II	72	21,692	9,784	156,009	0.1	2.51	0.55	87.45	464	8,637	17,698	1,784
1/III	58	17,884	8,338	116,350	0.18	1.64	0.48	76.65	327	10,916	17,365	1,518
1/IV	73	23,443	9,479	106,057	0.16	0.75	0.40	49.23	446	31,092	23,758	2,155
2/I	44	4,788	2,655	48,268	0.19	2.29	0.86	75.48	237	2,091	3,104	639
2/II	70	7,485	3,875	71,745	0.13	0.93	1.28	37.76	524	8,091	3,035	1,900
2/III	82	8,337	3,823	77,806	0.17	0.94	1.53	62.85	469	8,895	2,498	1,238
2/IV	69	6,791	3,980	65,116	0.13	1.95	0.58	87.73	518	3,489	6,900	742
3/I	61	3,606	3,265	34,245	0.18	3.17	1.30	65.15	340	1,136	2,508	526
3/II	71	3,585	4,337	30,351	0.15	0.78	0.63	68.12	468	4,611	6,831	446
3/III	69	4,035	5,573	33,291	0.23	1.38	1.29	88.93	308	2,929	4,323	374
3/IV	76	3,149	5,659	27,481	0.13	2.46	1.02	52.66	601	1,280	5,527	522
4/I	68	4,413	8,273	119,154	0.20	1.53	1.90	63.47	351	2,885	4,343	1,877
4/II	79	3,471	9,406	66,935	0.10	0.68	0.41	68.26	797	5,095	22,953	981
4/III	66	2,953	4,694	30,612	0.13	0.93	1.27	50.07	526	3,158	3,706	611
4/IV	60	3,260	5,138	27,851	0.11	3.42	2.24	51.59	529	952	2,292	540
5/I	68	2,884	3,379	14,412	0.17	3.36	0.83	33.28	404	860	4,053	433
5/II	72	1,930	4,993	14,968	0.14	1.11	0.60	30.82	511	1,747	8,378	486
5/III	96	1,751	4,993	8,871	0.34	1.20	0.69	50.51	284	1,463	7,278	176
5/IV	42	1,725	5,245	10,292	0.11	4.12	1.13	82.13	396	419	4,654	125

C_S: metals concentrations in sediments (μg kg^{-1} dry wt. in < 63μm fraction and free $CaCO_3$)
C_{IW}: dissolved metals concentrations in interstitial water (μg L^{-1})
K_D: partition coefficient of metals (L kg^{-1})

F-3 Metal bound with sulfide

The M_{AVS} calculated from Eq. 2-6, using the AVS and SEMs, presented in Table F-3.

Table F-3 The metal bound with sulfide (M_{AVS}) at various depths of the core sediments

Stations	**AVS**	**AVS/5**	**SEMs**				**M_{AVS}**			
			Cd	**Cu**	**Pb**	**Zn**	**Cd**	**Cu**	**Pb**	**Zn**
1/I	0.67	0.13	0.0007	0.51	0.12	3.82	0.08	8.5	24.9	8.7
1/II	0.66	0.13	0.0007	0.47	0.19	4.69	0.08	8.4	27.2	8.6
1/III	1.35	0.27	0.0006	0.30	0.13	2.96	0.07	17.2	27.8	17.7
1/IV	1.32	0.26	0.0005	0.35	0.14	2.72	0.06	16.7	28.2	17.2
2/I	0.87	0.17	0.0003	0.07	0.04	1.05	0.04	11.0	7.9	11.3
2/II	1.50	0.30	0.0007	0.23	0.08	2.55	0.08	19.0	16.8	19.6
2/III	1.24	0.25	0.0009	0.35	0.08	2.58	0.10	15.7	16.2	16.2
2/IV	1.42	0.28	0.0009	0.40	0.08	3.49	0.10	18.1	17.3	18.6
3/I	0.04	0.01	0.0007	0.49	0.10	1.56	0.08	0.5	1.8	0.6
3/II	1.74	0.35	0.0008	0.27	0.08	1.52	0.09	22.1	17.0	22.8
3/III	1.14	0.23	0.0008	0.21	0.11	1.88	0.09	14.6	22.3	15.0
3/IV	1.51	0.30	0.0008	0.12	0.07	1.82	0.09	19.2	15.1	19.8
4/I	0.09	0.02	0.0010	0.26	0.15	6.20	0.11	1.1	3.5	1.1
4/II	0.67	0.13	0.0009	0.45	0.11	3.73	0.10	8.5	23.3	8.8
4/III	0.69	0.14	0.0007	0.29	0.09	1.92	0.08	8.8	18.2	9.1
4/IV	0.95	0.19	0.0008	0.25	0.10	1.57	0.09	12.0	21.4	12.4
5/I	0.03	0.01	0.0011	0.33	0.10	1.43	0.12	0.4	1.1	0.4
5/II	2.21	0.44	0.0013	0.19	0.07	1.27	0.15	28.1	14.1	28.9
5/III	0.53	0.11	0.0006	0.21	0.08	1.12	0.07	6.7	15.7	6.9
5/IV	1.08	0.22	0.0006	0.41	0.08	1.21	0.07	13.7	17.2	14.1

AVS: acid volatile sulfide (mmols-S^{2-} kg^{-1} dry wt.)

SEMs: simultaneously extracted metals (mmols kg^{-1} dry wt. in < 63µm fraction and free $CaCO_3$)

M_{AVS}: metals bound with sulfide (mg kg^{-1} dry wt. in < 63µm fraction and free $CaCO_3$)

F-4 Sediment Quality Guideline for Metals

The numerical SQG was calculated follow Eq. 2-4, using the K_D in Table F-2 and the M_{AVS} in Table F-3.Numerical SQG for Cd, Cu, Pb and Zn for Chao Praya river mouth sediment was reported in Table F-4.

Table F-4 Sediment quality guideline for metals at various depths of the core sediments

Stations	$K_D \times$ WQC				M_{AVS}				SQG			
	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
1/I	2.3	36	61	116	0.08	8.5	24.9	8.7	2.3	44	86	124
1/II	2.3	69	150	89	0.08	8.4	27.2	8.6	2.4	77	178*	98
1/III	1.6	87	148	76	0.07	17.2	27.8	17.7	1.7	105	175*	94
1/IV	2.2	249	202	108	0.06	16.7	28.2	17.2	2.3	265*	230*	125
2/I	1.2	17	26	32	0.04	11.0	7.9	11.3	1.2	28	34	43
2/II	2.6	65	26	95	0.08	19.0	16.8	19.6	2.7	84	43	115
2/III	2.3	71	21	62	0.10	15.7	16.2	16.2	2.4	87	37	78
2/IV	2.6	28	59	37	0.10	18.1	17.3	18.6	2.7	46	76	56
3/I	1.7	9	21	26	0.08	0.5	1.8	0.6	1.8	10	23	27
3/II	2.3	37	58	22	0.09	22.1	17.0	22.8	2.4	59	75	45
3/III	1.5	23	37	19	0.09	14.6	22.3	15.0	1.6	38	59	34
3/IV	3.0	10	47	26	0.09	19.2	15.1	19.8	3.1	29	62	46
4/I	1.8	23	37	94	0.11	1.1	3.5	1.1	1.9	24	40	95
4/II	4.0	41	195	49	0.10	8.5	23.3	8.8	4.1*	49	218*	58
4/III	2.6	25	32	31	0.08	8.8	18.2	9.1	2.7	34	50	40
4/IV	2.6	8	19	27	0.09	12.0	21.4	12.4	2.7	20	41	39
5/I	2.0	7	34	22	0.12	0.4	1.1	0.4	2.1	7	36	22
5/II	2.6	14	71	24	0.15	28.1	14.1	28.9	2.7	42	85	53
5/III	1.4	12	62	9	0.07	6.7	15.7	6.9	1.5	18	78	16
5/IV	2.0	3	40	6	0.07	13.7	17.2	14.1	2.1	17	57	20

* exclude the outlier and far-outlier values
K_D: partition coefficient of metals (L kg^{-1})
WQC: water quality criteria
M_{AVS}: metals bound with sulfide (mg kg^{-1} dry wt. in < 63µm fraction and free $CaCO_3$)
SQG: sediment quality guaideline (mg kg^{-1} dry wt. in < 63µm fraction and free $CaCO_3$)

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