THESIS APPROVAL

GRADUATE SCHOOL, KASETSART UNIVERSITY

Master of Engineering (Environmental Engineering)

DEGREE

Environmental Engineering — **FIELD**

Environmental Engineering — **DEPARTMENT**

TITLE: Seasonal Variation of Heavy Metals in Riverbank Sediments from Lower Chao Phraya River, Thailand

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THESIS

SEASONAL VARIATION OF HEAVY METALS IN RIVERBANK SEDIMENT FROM LOWER CHAO PHRAYA RIVER, THAILAND

AJITH U K ETHUGALA

A Thesis Submitted in Partial Fulfillment of
the Requirement for the Degree of
Master of Engineering (Environmental Engineering)
Graduate School, Kasetsart University
2013

Ajith U K Ethugala 2013: Seasonal Variability of Heavy Metal in Riverbank Sediments from Lower Chao Phraya River, Thailand. Master of Engineering (Environmental Engineering), Major Field: Environmental Engineering, Department of Environmental Engineering. Thesis Advisor: Mr. Suchat Leungprasert, Ph.D. 78 pages.

This study presents the results of seasonal (summer, rainy and winter) variations of heavy metals and their speciation in riverbank sediment from the lower Chao Phraya River, Thailand. Surface sediment (between 0-5cm) samples were collected from both left and right bank of the river. The total concentration of ten element (Zn, Ni, Cd, Cr, Pb, Cu, Mn, Fe, As and Hg) and the chemical speciation of eight elements (except As and Hg) were analyzed by following the USEPA standard method and by following the slightly modified sequential extraction technique suggested by Tessier et al. (1979), respectively. For the Chemical speciation four fractions were analyzed including; exchangeable, carbonate bound, oxide bound and organic bound. The results showed that the physicochemical parameters, such as Electrric Conductivity (EC) and total organic carbon (TOC) of the sediments were negatively correlated with distance from the river mouth. The representation of Cd dominated all three seasons in exchangeable fraction while Cr dominated in the same in summer only. The high environmental risk of Cd, Cr, Mn, Zn, and Ni is observed due to their higher availability in bioavailable fractions. These toxic chemicals, the availability of Ni, Pb, Mn, Zn, Cu and Cd in carbonate bound fraction also showed the variations in three seasons probably due to their special affinity towards carbonate and their co-precipitations with its minerals. Dominating representation of Fe and Mn may provide colloids of Fe-Mn oxides which can be act as the scavengers of other heavy metals such as Pb, Zn, Cr, Ni and Cu in oxide bound fraction. Thus, the proportions of the concentration of heavy metal in each fraction differ with metal type and have seasonal variations in their dominating order. Toxic chemicals such as Cr, Cd, Pb, Cu and Ni have been concerned due to the threshold levels of sediment Quality Guidelines(SQG) and severity levels differ with each season.

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Student's Signature   Thesis Advisor's Signature

ACKNOWLEDGEMENTS

This research would have never been a reality at the end of twenty two months successful period without the guidance and strong support I received from my academic advisor, Dr Suchat Leungprasert throughout my candidature and his constructive suggestions for the development of my research papers and thesis manuscripts. First and foremost I would like to express my sincere thanks to him and secondly my co-supervisor Associate Professor Dr. Sanya Sirivithyapakorn for his continues guidance and courage provided me not only for the induction to research, but morally when I was in difficult situations. Thirdly I express my sincere gratitude to all members of academic and non-academic staff of Department of Environmental Engineering specially, Associate Professor Mrs. Patcharaporn Suwanvitaya (Chairperson of the program) and Associate Professor Dr. Wilai Chiemchaisri (Laboratory in-charge), Ms Viriya Paksasuk, Ms. Supa Vihok (Secretaries), Ms. Piyakan Boonsuwan, Ms. Kanchana Tuyweang (Laboratary Assistants) Ms. Saowalak Naowasarn, Mr. Ratchakorn Pitakkomtorn and Mr. Thammasak Rojviroon for their valuable guidance and continues support not only for the academic tasks but also for the comfort stay at Thailand within the period of study

Thailand International Development Cooperation Agency (TICA) is gratefully acknowledged for giving me the continuous financial assistance. Also the valuable supports I received from International Studies Centre and Graduate School of Kasetsart University, Government of Sri Lanka (GOSL) Central Environmental Authority (CEA) of Sri Lanka are greatly appreciated.

Last but not least, my sincere thanks to all my family members, in particularly the enthusiastic courage, support, constant love, patient and understanding of my wife Chandika. I owe an apology to my little kids Dulana and Bimsara for their great tolerance on my absence with them for two years period.

Ajith U K Ethugala

April 2013

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LIST OF ABBREVIATIONS

CB TEC	=	Consensus based Threshold Effective Concentration
EC	=	Electro conductivity
ERL	=	Effects Range Law
LEL	=	Lowest Effect Level
MET	=	Minimal Effect Threshold
PEL	=	Probable Effective Level
PTM	=	Potentially Toxic Metal
SEL	=	Severe Effect Level
SET	=	Sequential Extraction Technology
SQG	=	Sediment Quality Guideline
TEL	=	Threshold Effective Level
TET	=	Toxic Effect Threshold
TOC	=	Total Organic Carbon
USEPA	=	United State Environmental Protection Authority

SEASONAL VARIATION OF HEAVY METALS IN RIVERBANK SEDIMENT FROM LOWER CHAO PHRAYA RIVER, THAILAND

INTRODUCTION

Sediment is an integral and dynamic part of the river basins, including estuaries and coastal zones. Sediment originates from the weathering of minerals and soils upstream and is susceptible to transport downstream by the river water. Sediments are usually considered as a sink or reservoir for many harmful elemental and biological compounds including heavy metals and trace metals (Chapman et al., 1998; Segura et al., 2006; Zimmerman and Weindorf, 2010; Qiu et al., 2011; Zhang et al., 2012). Sediments receive and absorb above pollutants resulting from industrial and agricultural sources, domestic sewage, runoff and atmospheric depositions (Liu et al., 2007) and have been recognized as an important indicator of water pollution (Bermejo et al., 2003). Thus, the heavy metals accumulated in sediments are of great interest and concerns all around the world due to their toxicity, persistence and bio-accumulation characteristics (Zhang et al., 2009). Introduction of metallic pollutants into the river, whether it is natural or above mentioned anthropogenic sources, can occur in dissolved or particulate form and the dissolved pollutant can be precipitated later with the favorable physicochemical conditions (Jain and Sharma, 2001). As a result, the heavy metals inert in the sediments often considered as conservative pollutants (Olivares-Rieumont et al., 2005; Periáñez, 2012), while they can be released back to river water in response to certain impacts and pose potential threats to aquatic biota and human health (Liu et al., 2007; Yi et al., 2011). Arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) are some of the most common heavy metal pollutants (Hakanson, 1980; Zhang et al., 2012). Sediments bound heavy metals have a tendency to adsorb and accumulate on the fine grained particles that eventually move to the depositional areas (Zhang et al., 2001; Zhang et al., 2012). According to Quevauviller et al. (1992) and Qiao et al. (2003), the determination of specific chemical forms, or the nature of binding, is much more valuable than determination of total metal content since the toxic effects and geochemical pathways of heavy metals are mainly determined by their mobile species. The knowledge of such chemical forms enables prediction and prevention of the adverse effects of heavy metals to communities as well as aquatic ecosystems by enforcing sediment and water quality standards (Zimmerman and Weindorf, 2010).

The Chao Phraya Basin, the largest and most important river basin in Thailand, covers an area of approximately 177,000 km^2 representing 30 % of the country's total land area and is home to 40% of the country's population (UNESCO, 2003b). The Chao Phraya Basin is divided into 2 parts (Figure 1). The upper part is mountainous alternating with lowland areas along the river, while the Lower Chao Phraya Basin is an enormous floodplain area and covers 55,290 km^2, i.e. 35% the total basin area. The Chao Phraya River begins at the junction of four major rivers (Nan, Ping, Wong and Yom) in the Upper basin, at Nakhon Sawan Province. The total length of river is about 380 km and drains through ten provinces into the Gulf of Thailand. It supplies water and supports many activities such as municipal uses, agriculture, fisheries, light and heavy industries, recreation and transportation. Thus the River, receives the discharge of wastewater from many sources, especially those from household, industrial and agricultural activities, and makes the water polluted. The major sources of pollutants in the upper portion were from agricultural waste and in the lower part of the river course form communities and industries (UNESCO, 2003a). The typical average discharge of Chao Phraya is718 m^3s^{-1} and maximum discharge level recorded is 5960 m3s-1. These discharge levels shows seasonal variations in dry and wet season as 1657 m^3s^{-1} and 74.8 m^3s^{-1} respectively. All the above discharge levels affected with both industrial and domestic waste water discharges with high organic matter content and degraded the quality of sediment in the river system. Since the end of 1980s, there have been some studies on heavy metals in various environmental medium of Chao Phraya River, while most of them have focused on heavy metals concentration, distribution pattern, sources, chemical fractions, potential toxic risk, enrichment and contamination in surface water or suspended sediments and it was reviled the readily available updated information on levels of heavy metal distribution in the bottom sediments or its seasonal variations along the lower Chao Phraya River itself is very few (Menasveta, 1978; Menasveta and Cheevaparanapiwat, 1981; Polprasert, 1982; Hungspreugs and Yuangthong, 1983; Onodera and Tabucanon, 1986; Cheevaporn and Menasveta, 2003). As mentioned earlier large quantities of domestic sewage and industrial waste directly discharged into Chao Phraya with and without adequate treatment. As a consequence, the river is polluted by many kinds of chemicals, including organo-chlorine pesticides, polychlorinated biphenyls (PCB) and heavy metals (Menasveta, 1978; Onodera and Tabucanon, 1986). The Chao Phraya River, together with several other major rivers, flows into the Upper Gulf of Thailand, carrying a high suspended load (Menasveta, 1978). Analysis of sediment cores at the mouth of the Chao Phraya River has revealed that high contamination of heavy metals, including cadmium, lead, nickel and chromium (Menasveta and Cheevaparanapiwat, 1981; Hungspreugs and Yuangthong, 1983). Since the readily available updated information are rare and the study of the distribution of metals in sediments is very important from the point of view of environmental pollution because sediment concentrates metals from aquatic systems, and represents an appropriate medium to monitor contamination, the determination of the distribution pattern and the environmental risk of the pollutants in the sediments should be considered in this study.

OBJECTIVES

The main objectives of this study are as follows;

1. To determine the distribution pattern of selected heavy metal concentration and speciation with seasonal variations in riverbank sediment along lower Chao Phraya River.

2. To determine the environmental risk of the actual heavy metal loads in the study area with comparison of sediment quality guidelines (SQG)

Scope of the Study

The Chao Phraya River itself exhibited massive variations of turbidity and sedimentation along the river bank with seasonal changes. Heavy metals can be accumulated in sediment and leached into bioavailable forms which can be harmful for the biota of river ecosystem. Hence this study expected to have variations of heavy metal contaminations in sediment in four major categories;

1. Total metal concentration and chemical speciation for eight elements
2. Along the river 8 sample sites with different distances from the river mouth
3. Both left and right bank of the river at each site
4. Three major climatic seasons' summer in April, rainy in September and winter in November.

To obtain the objectives, the study was derived in to two phases; preliminary assessment on distribution patterns and speciation of 10 elements including Cd, Cr, Ni, Mn, Zn, Pb, Fe, Cu, Hg, and As in the surficial riverbank sediments of the lower Chao Phraya River in summer season. For this preliminary study, riverbank sediment samples were collected from 16 sites form both riverbank sides along the lower Chao Phraya River begunning from Chai Nat province and river mouth at Samutprakarn Province (Figure 2). (ii) On the basis of results obtained from preliminary assessment, the main three sites that exhibit significantly high concentrations for all 10 elements were selected for further study and focused mainly the heavy metal contamination of riverbank sediments in these three major contaminated sites (Ayuththaya, Nonthaburi and Samutprakarn) along Chao Phraya River in rainy (September 2012) and winter (November 2012) seasons.

LITERATURE REVIEW

1. The river system

The aggregate of stream or channels draining a river basin or a system of watercourses or drains for carrying off excess water can be defined as river system. A river system is at least consists with four subsystems (1) the drainage basin; (2) the alluvial valley; (3) the receiving basin; and (4) the delta plain. Within each of these subsystems, climatic, geologic, geomorphic, hydrologic, and biologic events mutually interact (Figure 1). The drainage basin supplies water and sediment to the rest of the river system and is characterized by net erosion; the alluvial valley is a graded conduit which, over the long term, experiences neither significant erosion nor deposition and through which water and sediment are transported end route from the drainage basin to the sea. The receiving basin serves as a sink for the water and sediment discharged by the river and supplies energy which opposes the seaward-directed riverine energy. The delta is characterized by sediment dispersal and accumulation and results from the interactions between riverine and marine forces.

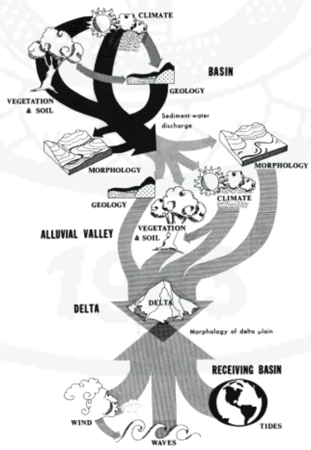


Figure 1 Processes responsible for causing river system variability

Source: World Water Assessment Program (WWAP) (UNESCO, 2003a)

Rivers are the circulatory systems of the landmasses and they are the conduits for water, solute and sediment movements of the land to sea and shape much of the landscape. Throughout history, rivers have sustained the community by providing drinking water, transportation mode, waterpower, hydroelectric power, fisheries and wildlife habitats. Today utilization of the river expanded to multibillion dollar industries such as boating, swimming, fishing and tourism. The study of processes affecting river systems can be referred as river science. It is integrated with multiple disciplines such as how geological, hydrological, chemical and ecological processes interact to influence the form and dynamics of riverine ecosystems and seeks to understand the linkages among them at multiple levels

- From small streams to large rivers
- From pristine to heavily urbanized watersheds
- From daily to century scale dynamics

Thus river science includes the study of relationships between watersheds, riparian zones, floodplains, sediment load, ground water, headwater and downstream rivers. In general, river basins occupy about 69% of the land area and transporting an estimated 19 billion tons of material annually, about 20% of which is in solution and large rivers are significant because they are important links of the sediment transfer system from the continents to the ocean basing and play a major role in sculpturing the topography of the earth (Survey, 2007)

2. Rivers in Southeast Asia

Southeast Asia in general, is a subcontinent with surplus water as evidences by the formerly widespread tropical rainforests. Most of the region receives at least 2000mm rainfall annually, and positive water balance prevails for the majority of months. Mekong, Irrawaddy, Salween and Red, the four large rivers originate close to each other on the eastern Tibetan Plateau north of the region, and flow through large structure-guided valleys towards the southeast like outstretched fingers. Other major rivers of the region (Chao Phraya, Pahang, Brantas, Mahakam, etc.) start and end within Southeast Asia. The upland slopes are drained by a large numbers of tributaries and short, wide estuaries wind through coastal plains. The selective physical dimensions of the large rivers of Southeast Asia are listed in table 1 (Gupta, 2005b).

Table 1 Characteristics of major rivers in Southeast Asia

Measures	Irrawaddy	Salween	Chao Phraya	Mekong	Song Hong
Basin area (km^2)	413700	271900	117500	795000	155000
Channel length (km)	2010	2820	1110	4880	4880
Mean annual discharge at mouth (m^3 x10^9)	430	300	16.7	470	120
Average annual suspended sediment discharge (t x 10^6)	260	100 est	97 est	160	160

est - estimated

Source: (Gupta, 2005b)

3. Chao Phraya River

The Chao Phraya Basin, the largest and most important river basin in Thailand, covers an area of approximately 177,000 km^2 representing 30 % of the country's total land area and is home to 40% of the country's population (UNESCO, 2003a). The Chao Phraya Basin is divided into 2 parts (Figure 2). The upper part is mountainous alternating with lowland areas along the river, while the Lower Chao Phraya Basin is an enormous floodplain area and covers 55,290 km2, i.e. 35% the total basin area. The whole river basing can be classified as a tropical rain forest with high biodiversity. The lower part of the basin has extensive irrigation networks and hence intensive rice paddy cultivation and recently exhibits problematic encroachment's in to forest areas due to expansion of agricultural lands. These anthropogenic activities automatically increase the suspended and bottom sediment loads which flows through the river to upper gulf of Thailand.

The Chao Phraya River originates as four rivers that drain the hills of northern Thailand belongs to physiographic provinces of hills of northern Thailand and Lao PDR and Central plain of Thailand according to the Southeast Asia landforms(Gupta, 2005a). The four headwaters (Ping, Wong, Yom and Nam) rise at an elevation of about 1000m and flow north-south. The 400 km Wang is the shortest stream, the rest are 700 km long or more. The rivers flow through steep gorges and sharp, near right angled bends, over rapids and along stretches of flatter gradient. Such characteristics plus the localized straight reaches indicate geological control. A number of dams and reservoirs interrupt the flow of these rivers including the Bhumipol Dam on the ping and the Sirikit dam on the Nan. The two western streams, the Ping and the Wong join below the Bhumipol Dam; the eastern two streams, the Yom and Nan, about 30 km north of Nakhon Sawan Province. The augmented Ping and Nang come together at Nakhon Sawan to form the Chao Phraya. At Nakhon Sawan, 370km from its mouth, the Chao Phraya only 23.5 m above sea level. From there the Chao Phraya travels through alluvial plains and the depth of the river ranges from 5 to 20 m and the width ranges from 200 to 1,200 m. At Ayuththaya, the Chao Phraya is joined by a major tributary, the 570km long Pa Sak. Here at Auththaya the river is 3.5m above the -

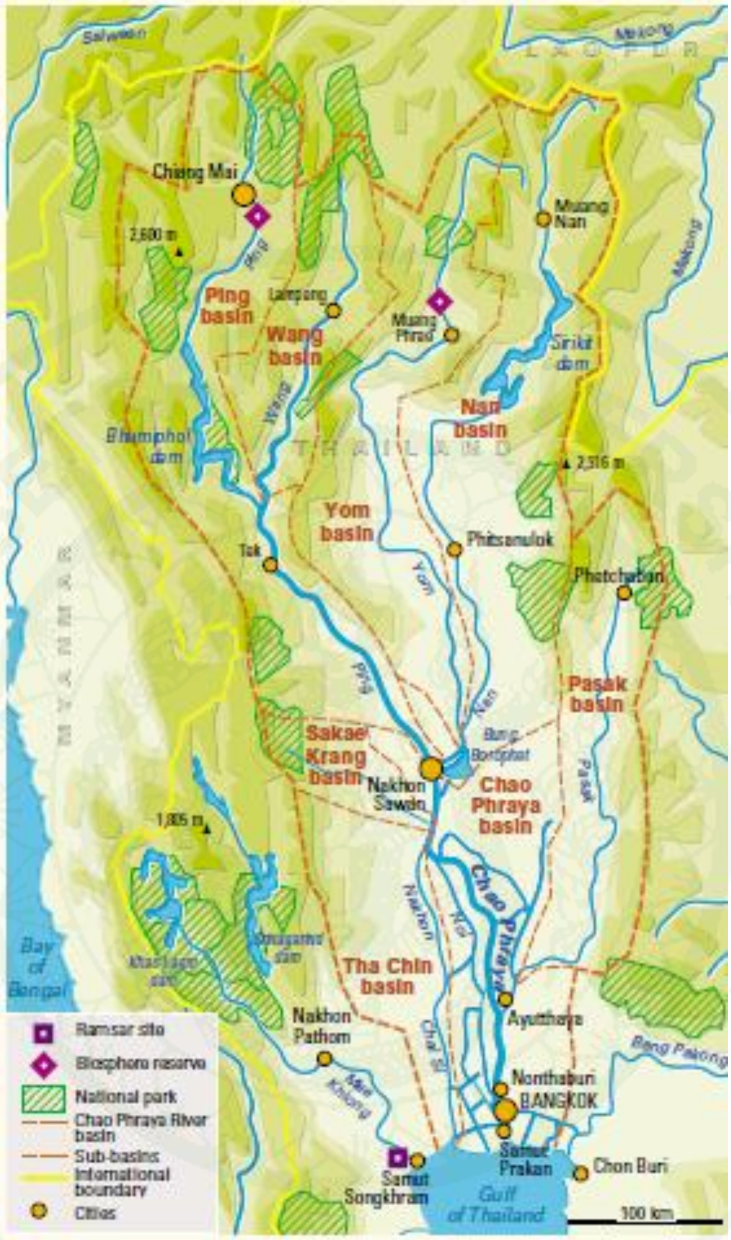


Figure 2 Map of Chao Phraya River basin

Source: World Water Assessment Program (WWAP) (UNESCO, 2003a)

-mean sea level and at Bangkok it is only one meter. Several rivers leave the Chao Phraya at certain locations on the flat plain. The first, Thai Chin, leaves the mainstream near Chai Nat and flow south nearly parallel to it and after running 35- 40 km west of Chao Phraya it reaches the sea at Samut Sakhon. The Lopburi River an old channel of Chao Phraya separated at Sin Buri and flows east to the Pa Sak. The Chao Phraya is a seasonal river carrying the rain of the southeast monsoon. As seen in the available satellite images, the river has a single distributary and the river mouth is quite embayed. Tidal range is quite high, about 2.38 m in range. Offshore slope is extremely low, averaging only 0.0041 degrees along the delta front. As a result, wave energy is quite low. The delta is about 11,329 km^2 in area and the sub-aerial delta is approximately seven times larger than the subaqueous delta. The front of the delta is rather smooth with the ratio of the shoreline length to the width being 1.15. This smoothness is not the result of extensive wave action, but occurs of the extremely large fine-grained sediment load that is delivered to the coast each year. Extremely muddy plume of the river can be seen during flood periods

The Chao Phraya supplies water and supports many activities such as municipal uses, agriculture, fisheries, light and heavy industries, recreation and transportation. Thus the River, receives the discharge of wastewater from many sources, especially those from household, industrial and agricultural activities, and makes the water polluted. The major sources of pollutants in the upper portion were from agricultural waste and in the lower part of the river course form communities and industries (Simachaya et al., 2000). The typical average discharge of Chao Phraya is $718m^3s^{-1}$ and maximum discharge level recorded is 5960 m^3s^{-1}. These discharge levels shows seasonal variations in dry and wet season as 1657 m^3s^{-1} and $74.8m^3s^{-1}$ respectively. All the above discharge levels affected with both industrial and domestic waste water discharges with high organic matter content and degraded the quality of sediment in the river system.

The seasonality is pronounced in the middle of the hot, dry summer in April, when the upper headwaters run very low. The Chao Phraya itself starts to rise in May and normally reach its peak in September. By November the rains have stopped for weeks and the river has started to drop the water level. The floods in the delta are augmented by the arrival of high tides in the middle of the wet season, when river is with high water level. The average temperature is range from 20 ^{0}C to 40 ^{0}C in April except in high altitude locations.

Socio economically the Chao Phraya basin provide home to 40% of the country's population and generates 70% of Gross Domestic Product (GDP). Specially the lower Chao Phraya River basing provide residence for nearly 14 million people and highly populated including Bangkok Metropolitan Area (MBA) and its environs of Samut Prakarn, Nonthabury and Pathumthani (UNESCO, 2003a). The basin also accommodated number of industries and industrial estates which release there treated and non-treated effluents to the tributaries or main stream of Chao Phraya River. Thus the entire basing is entering a critical period where population and pollution levels are very high and small changes in the hydraulic conditions can create drastic socio economic destructions.

3. Metals in the environment and its contamination in sediment

There have been several schemes for designating heavy metals based upon atomic number, toxicity or other factors. In general the heavy metals exhibit good electrical and thermal conductivity when in their pure form and most often enter reactions as positive ions or cations. True heavy metals, however, are those with an atomic weight between 200 and 210 and have a density relative to greater than 5. The elements fulfill these requirements include lead, mercury, thallium and bismuth. Most of the other metals that act as pollutants are actually transition metals which that occur in transitional groups 3 through 12 on the periodic table with sequential filling of the d orbitals (incomplete d shell). These elements have valances of 2 or 3 and take part in electron transfer reactions (VanLoon and Duffy, 2005; Walker, 2006; Lewinsky, 2007). However the usage of this item has centered on the treatment of certain metallic elements which have an impact upon plants or animals when discharged in to the natural environmental in relatively high concentrations (Lewinsky, 2007). Often the term heavy metal is used to refer to the majority of metals that are considered as anthropogenic pollutants. The toxic elements including antimony, arsenic, beryllium, cadmium, copper, lead, mercury, nickel, silver, thallium and zinc are important because they are non-biodegradable, toxic in solution and subject to bioaccumulation or bio magnification. The chemistry of many of these compounds is complex in sediments. In general, a portion is chemically fixed and largely unavailable to fish and higher organisms without chemical changes in the sediments. Often another portion is ion exchangeable that can become available simply with the addition of a more strongly held contaminant and another portion soluble, mobile and directly available for uptake by organisms (Chien et al., 2004).

The equilibrium state for metal and other elemental species depends on the chemical state of the water and sediment, particularly the pH and oxidation-reduction conditions. The ratio of sediment loading to equilibrium water concentration is often very large for metals, but only a small fraction of the metals are typically available. As a result of this variability, a site-specific measurement of the sediment-water partition coefficient is preferred over any predictive approach.

4. Sequential Extraction Technique (SET):

Environmental pollution from potentially toxic metals (PTM) is of concern because they exhibit behavior consistence with those persistence toxic chemicals. Unlike many organic contaminants that lose toxicity with biodegradation, metals cannot be degraded and their toxic effect can therefore be long lasting. Although their concentration in biota can increase through bioaccumulation, some heavy metals are known to have toxic effects even at very low levels. The total concentration of potentially toxic elements in the environment does not provide information about the distribution, mobility and potential bioavailability of elements. Consequently, the knowledge of the strength of bonds between the metals and the sediments is necessary to evaluate the availability and the capacity of mobilization of the PTM in the sediments. To acquire this information, operationally define speciation is necessary. This can be carried out by Sequential Extraction Technique (SET), which consist of a several extraction steps based on the use of different chemical reagents and conditions (Badri and Aston, 1983; Mester et al., 1998; Filgueiras et al., 2002; Bradl, 2005; Naji et al., 2010). During reason decades various SET methods have been proposed. One of the most widely applied procedure was proposed by Tessier et al. (1979) and its modified or complemented versions has been applied not only to soil and sediment but also to atmospheric particulate matter (Tessier et al., 1979; Badri and Aston, 1983;

Calmano and Forstner, 1983; Qiao et al., 2003; Segura et al., 2006). All these SET's facilitate fractionation. Tessier et al. (1979) named these fractions; exchangeable, carbonate bound, Fe and Mn oxide bound, organic matter bound, and residual. These are also often referred to in the literature as exchangeable, weakly absorbed, hydrous-oxide bound organic bound and lattice material components respectively (Maiz et al., 2000). Typically metals of anthropogenic inputs tend to reside in the first four fractions and metals found in the residual fraction are natural occurrence in the parent rock (Ratuzny et al., 2009).

Most of the SET's follow similar fractional degradation with little variations. Ure et al. (1993) extracted the exchangeable and carbonate-bond fraction together in single step versus the two steps used in the Tessier's procedure. The SET used by the Geological Survey of Canada (GSC) divided the Fe and Mn oxide fractions into the amophorous oxyhydroxides and crystalline oxides, thereby increasing sequential fractionation from five to six steps. Other SET's with greater fractions include the procedure developed by Zeien and Brummer which included EDTA extractable, moderately reducible, and strongly reducible fractions for a total of seven. Miller et al. (1986) considered nine fractions designed to test waste amended and agriculturally polluted sediments (Zimmerman and Weindorf, 2010). Oyeyiola et al. (2011) reviled that the different fractions SET protocols depend strongly on the extractant as well as the sequence in which the reactants are applied. They further concluded that on the contrary, the five steps protocol gives more information about the fractions of metal bound to different phases of the sample. Anyhow the user or researcher who applies different type of SET's should consider many factors including type of sediment/soil, contamination level and result comparison method as well as the potential problems or limitations associated with specific SET.

4. Sediment Quality Guideline

Sediment quality has become a serious ecological and possibly costly economical issue in various aspects such as water quality management, navigation dredging, water way restoration, commercial and recreational fisheries and natural resources management. Thus during last four decades, environmentalists, engineers and regulatory authorities all over the world have devoted considerable resources to assessment, management and necessary remediation of chemical contaminant in sediments. Numerous scientific and engineering studies have shown that addressing contaminated sediment is a complex undertaking which engage diverse elements of society. Complexities arise from the great variability in the physical and biogeochemical characteristics; human and ecological receptors; and the cultural, social, and economic values associated with different freshwater, estuarine, and marine environments. Because of these complexities the assessment and management of contaminated sediments in ports and harbors, rivers, lakes, and at hazardous waste sites does not easily lend it to simple "one-size-fits-all" investigation methods and presumptive management decisions. To response the increasing demands for greater environmental protection of aquatic resources and restorations of degraded rivers and estuaries, scientists in several countries have developed a variety of methods for evaluating the degree to which sediment-associated chemicals might adversely affect aquatic organisms. These methods have resulted in chemically based numerical or narrative SQGs designed to protect benthic organisms; support and maintain designated uses of freshwater, estuarine, and marine environments. SQG can be defining as numerical chemical concentrations intended to be either protective of biological resources, or predictive of adverse effects to those resources or both. Currently available SQGs derived using both mechanistic and empirical approaches are listed in table 2. Most of the listed SQGs derived for USA and European region and still these SQGs are continuously improving for their quality and accuracy and applicably to the other geographic areas all around the world. The unique strengths and limitations of each of the various assessment methods dictate that a weight of evidence approach should define the significance of sediment-associated contaminants and then effects on the aquatic environment and also through food web

Table 2 Currently available Sediment Quality Guidelines

	Approach	Authors	Year
1	Equilibrium Phase (EQP)	Di Toro, Mahony et el,	1991
		Di Toro. Zarba et al.	1991
		Ankley et al	1996
		NYSDEC	1998
		Di Toro and McGrath	2000
2.	Screening –level concentration	Persaud et al.	1993
		Von Stackelberg & Manzie	2002
3	Effects range -low (ERL)	Long et el.	1995
	Effects range-median (ERM)	USEPA	1996
4	Threshold-effects level (TEL)	McDonald et al.	1996
	Probable-effect level(PEL)	Smith et al.	1996
		USEPA	1996
5	Apparent-effects threshold (AET)	Barrick et al.	1997
		Ginn and Pastorok	1992
		Cubbage et al.	1998
6	Consensus-based evaluation (CB)	Swartz	1999
	Minimal effect threshold (MET)	Mac Donald, DiPinto et al.	2000
	Lowest effects level (LEL)	Mac Donald, Ingersoll et al	2000
7	Logistic regression modeling (LRM)	Field et al.	1999
			2002

Source: Burton (2002)

transfer to terrestrial species. This integrated approach ideally should identify and rank stressors using habitat, physical and chemical measures, biological community structure, toxicity, and bioaccumulation descriptors. Use of these tools can provide essential characterizations of key watershed sources, sensitive receptors, natural variation, and both natural and anthropogenic stressors. Comparison of several empirical approaches specially for heavy metals are summarized in Table 3 to 6. These are based on the co-occurrence of benthic macro invertebrate effects and total sediment concentrations. Rather than being theoretically based, like the EpQ approach, these are based on actual field and laboratory data that show adverse effects to benthic organisms when exposed to field-contaminated sediments. They differ in the way they determine the threshold effects, but many are quite similar.

Table 3. Threshold effect sediment quality guidelines for metals (mg/kg)

SQG	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn	Reference
TEL	5.9	0.6	37.3	35.7	35	0.17	18	123	4
ERL	33	5	80	70	35	0.15	30	120	3
LEL	6	0.6	26	16	31	0.2	16	120	6
MET	7	0.9	55	28	42	0.2	35	150	6
CB TEC	9.79	0.99	43.4	31.6	35.8	0.18	22.7	121	6

Source: Burton (2002)

Table 4. Midrange effect sediment quality guidelines for metals (mg/kg)

SQG	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn	Reference (Table 2)
PEL	17	3.53	90	197	91.3	0.486	36	31.5	6
ERM	85	9	145	390	110	1.3	50	270	3

Source: Burton (2002)

Table 5. Extreme effect sediment quality guidelines for metals (mg/kg)

SQG	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn	Reference (Table 2)
TET	17	3	100	86	170	1	61	540	6
SEL	33	10	110	110	250	2	75	820	6
CB PEC	33	4.98	111	149	128	1.06	48.6	459	6

TET, toxic effect threshold; SEL, severe effect level; CB, consensus based; PEC

Source: Burton (2002)

MATERIAL AND METHOD

1. Sampling sites:

The eight sampling sites were selected along the lower Chao Phraya River, starting from Chai Nat Province and ends at the river mouth at Samutparkarn province (Fig. 3). The geographic locations of the sites were listed in Table 6.

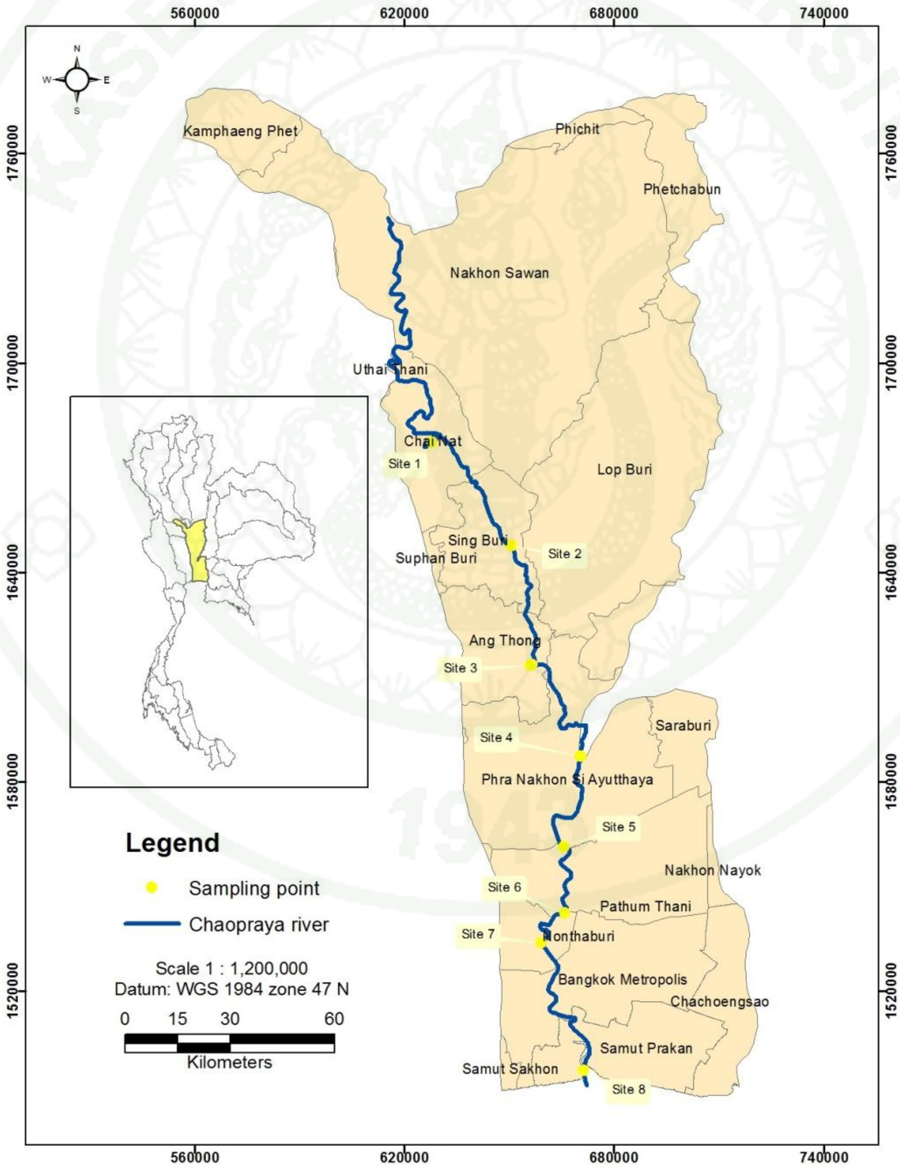


Figure 3 Location map of the sampling sites along the lower Chao Phraya River

Table 6 Locations of the study sites along the Chao Phraya River

Site name (distance from the Gulf (km))	Site Code	Left Bank		Right Bank	
		Latitude	Longitude	Latitude	Longitude
Chao Phraya Dam at Chinat (277)	Site 1	15°10'4.86"N	100°11'25.97"E	15° 9'59.00"N	100°11'29.94"E
Chao Phraya Bridge at Sinburi (227)	Site 2	14°53'58.11"N	100°24'11.20"E	14°53'56.53"N	100°24'4.99"E
Chao Phraya Bridge at Angthon (183)	Site 3	14°35'25.04"N	100°27'13.04"E	14°35'19.45"N	100°27'2.30"E
Ayutthaya (143)	Site 4	14°21'10.36"N	100°34'54.45"E	14°21'8.51"N	100°34'51.34"E
Samcoak at Pathumthani (101)	Site 5	14° 7'9.85"N	100°32'8.88"E	14° 7'1.18"N	100°32'7.07"E
Nonthaburi Bridge (58)	Site 6	13°56'49.30"N	100°32'9.00"E	13°56'49.30"N	100°32'9.00"E
Phranamgklao bridge (Bangkok) (36)	Site 7	13°52'16.65"N	100°28'38.39"E	13°52'13.69"N	100°28'28.41"E
Pear at Samut Prakarn (12)	Site 8	13°33'32.83"N	100°34'48.01"E	13°32'22.44"N	100°35'5.31"E

2. Sample Collection and Preparation

2.1 Sediment

All sediment samples of the above listed sites were collected by using sediment sampling techniques of USEPA from surface sediments consisting of the first 5cm of the streambed along the river bank. Sediment samples were taken with grab sampler. Sampler was rinse with river water very well between grab samples.

Figure 4 Grab sediment sampler

Two replicate samples were obtained from each site for both left and right bank. The river bank was minimally disturbed before and during sampling to maintain the sediment integrity. To prevent the losses of fine silts overlaying water was not decanted. The collected samples returned to the laboratory in polyethylene bags and stored at 4 ^{0}C prior to analysis. After removing visible organisms, coarse, shell fragments and pebbles the sediment samples will be dried at 60 ^{0}C for 48 hours and sieve the dried sample with 6ooμm and stored the homogeneous sample at 4 ^{0}C for further analysis. Samples were collected in summer (April 2012) rainy (September 2012) and winter (November 2012) according to the aforementioned technique.

3. Physicochemical analysis

The collected sediment samples will be analyzed in duplicates and average values recorded to determine the physicochemical parameters listed in Table 7

Table 7 Parameters for physicochemical analysis

Item	Parameter	Unit	Analytical Method
1	pH		US EPA 4500 –H^+B (water and sediment)
2	Electro Conductivity	mS	US EPA 9050 A (water and sediment)
3	Total Organic Carbon	% mg/kg	Calciometry method
4	Total Metal Concentration	mg/kg	US EPA3050 B

3.1 pH

10 g of each sample were taken in 50 ml of deionized distilled water and agitated for 10 minutes and the solution keep undisturbed 1 hour and pH values were measured by a combined glass electrode connected to the pH meter.

3.2 Electrical Conductivity (EC)

10 g of each sample were taken in 50 ml of deionized distilled water and agitated for 10 minutes and the solution keep undisturbed 1 hour and conductivity was measured by a platinum electrode connected to the conductivity meter.

3.3 Total Organic Carbon (TOC)

In this research, TOC-VCSH (SSM-5000A) has been used to measure TOC following its manual standard:

Total Carbon = Total Organic Carbon + Inorganic Carbon

TOC = TC – IC

Where SSM-5000 A analyzes TC and IC to find TOC

3.4 Total Metal Concentration

The total metals were extracted from the sediment samples by using digestion according to the USEPA standard method (Figure 5). The final filtrates of the digestate will be received in 100 ml volumetric flasks and Total metal concentrations will be determined by using a Perking –Elmer atomic adsorption spectrophotometer (AAanalyst 100) in flame mode (Fig 4).

Figure 5 Perkin Elmer spectrophotometer AA analyst 100

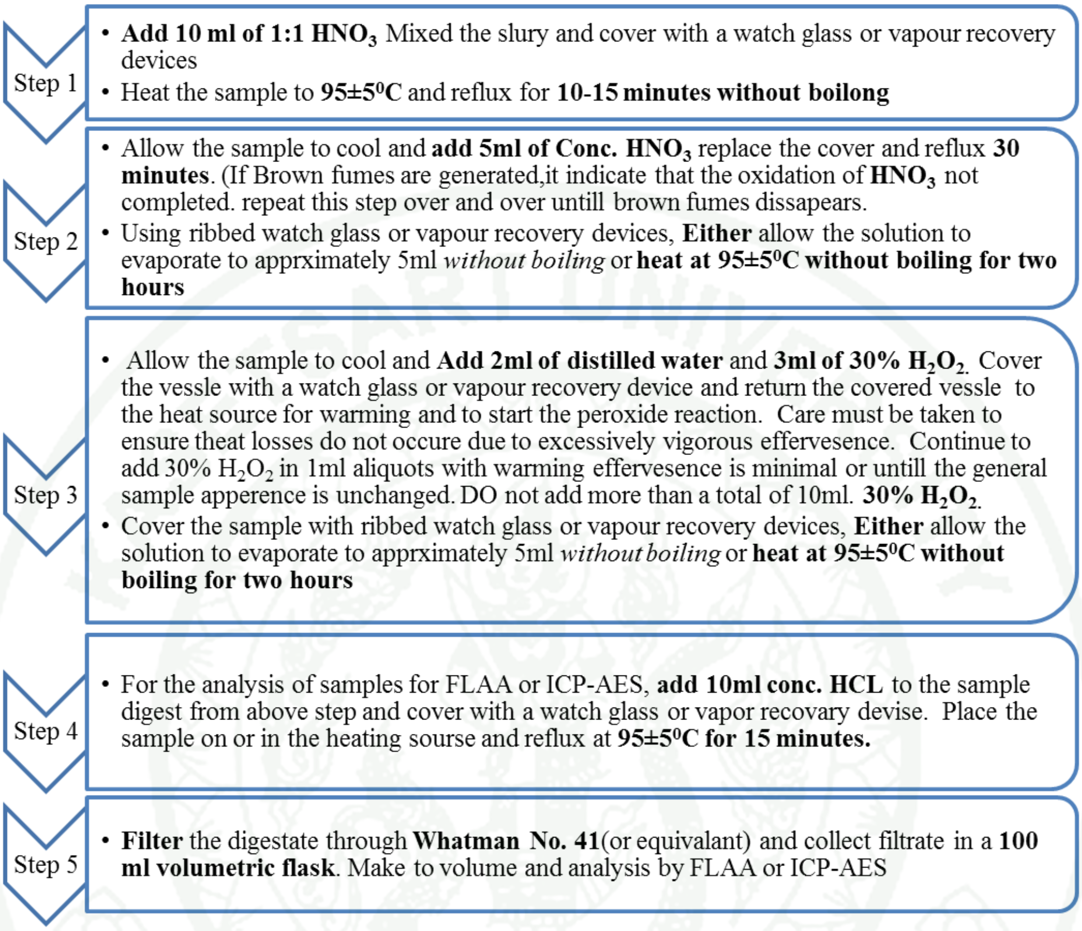


Figure 6 Steps for analysis of Total Metal Concentration according to the USEPA 3050B

4. Sequential extractions

Heavy metal concentrations in sediment samples were sequentially extracted from fractions of sediments following the slightly modified four steps method proposed by Tessier et al. (1979) in to operationally defined as exchangeable (F1), carbonate bound (F2), Fe-Mn hydroxide or oxide bound (F3) and organic bound (F3). The different fractions and reagents will be used in the sequential extractions are shown in flow diagram (Fig. 6). After each successive extraction samples were centrifuged at 1000rpm for 30 minutes to separate the extract from the sediment. The concentrations of selected heavy metals in each fraction were determined by using a Perking –Elmer atomic adsorption spectrophotometer (AAanalyst 100) in flame mode.

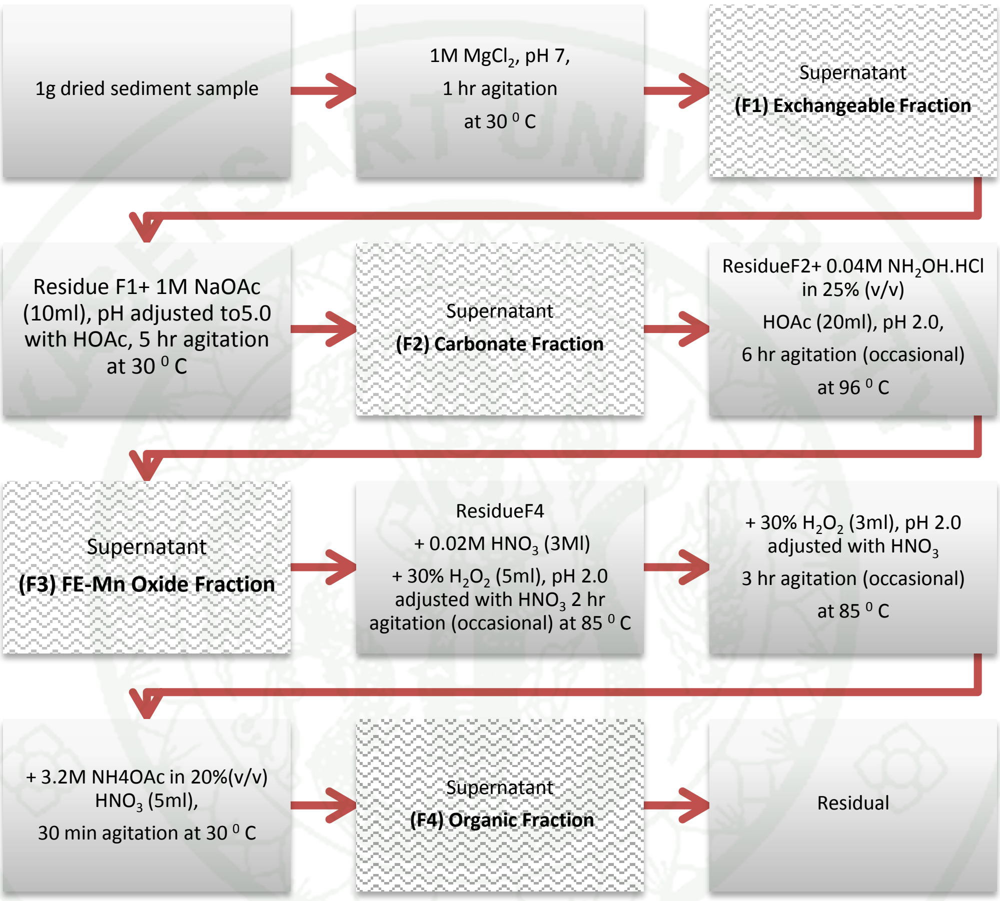


Figure 7 Steps for sequential extractions method modified by Tessier et al. (1979)

RESULT AND DISCUSSION

1. Physicochemical parameters of sediment

The samples collected from 8 locations of both sides of river bank with different distances beginning from the river mouth (DFRM) were analyzed pH, electrical conductivity, total organic carbon and total metal concentrations in three climatic seasons.

pH can be identified as one of the stable measurement which measures acidity and alkalinity of water, sediment or soil. It is a simple and important parameter which controls the chemical reactions in aquatic environment by changes of its value. Aquatic organisms are very sensitive with this pH changes and chemical formation due to this pH changes. pH can use as a primary important parameter for decisions on water and sediment contamination. If the pH value is below 5 it can be harmful for aquatic life and if pH value exceed about 10 may be reflect contamination by strong base pollutant as NaOH and $Ca(OH)_2$ (Langmuir, 1997).

Table 8 Measured physicochemical parameters for all sampling sites both right and left bank of the lower Chao Phraya River in summer (S) rainy (R) and winter (W) seasons

	DFRM (km)	TOC (mg/kg)			EC (mS/m)			pH		
		S	R	W	S	R	W	S	R	W
Right bank	12	1.69	1.10	2.64	40.05	6.18	15.26	7.53	7.51	7.20
	36	0.60	1.97	4.05	17.75	18.68	70.60	7.61	7.18	7.18
	58	1.78	0.42	0.38	11.01	6.30	4.86	7.01	7.39	7.85
	101	0.75	2.68	0.77	9.71	6.18	23.08	6.93	7.22	7.85
	143	1.74	1.58	2.10	24.47	10.31	32.16	7.30	6.98	7.54
	183	0.20	0.35	0.29	5.35	6.44	9.28	7.56	6.97	7.61
	227	0.17	1.74	0.63	4.08	4.53	5.66	7.79	6.98	7.32
	277	0.20	0.45	0.31	4.24	4.33	5.89	6.96	6.65	6.80

Table 8 (Continued)

	DFRM (km)	TOC (mg/kg) S	TOC (mg/kg) R	TOC (mg/kg) W	EC (mS/m) S	EC (mS/m) R	EC (mS/m) W	pH S	pH R	pH W
Left Bank	12	1.26	1.32	3.51	39.85	43.80	14.60	7.10	7.82	7.28
	36	1.24	2.21	1.68	9.72	97.30	41.80	7.01	7.86	7.23
	58	0.42	0.57	2.21	11.24	33.71	75.70	7.33	7.45	7.34
	101	0.40	1.68	0.28	14.73	28.05	4.93	7.25	7.54	7.93
	143	3.55	0.64	2.52	38.00	15.88	30.65	7.46	7.68	7.64
	183	1.41	0.38	0.68	5.51	9.68	17.06	7.38	7.84	7.54
	227	0.59	1.23	0.71	8.75	13.94	12.73	7.04	7.74	7.32
	277	0.19	0.45	0.56	4.14	10.68	9.18	7.09	7.44	7.38

The current study revealed that pH values ranges from 6.65, the lowest value in the rainy season at Samutprakarn site to 7.85, the highest value in winter season at Sinburi site with the distance from the river mouth (Fig.8). Thus, there is no variation of pH in the sediment with seasonal changes.

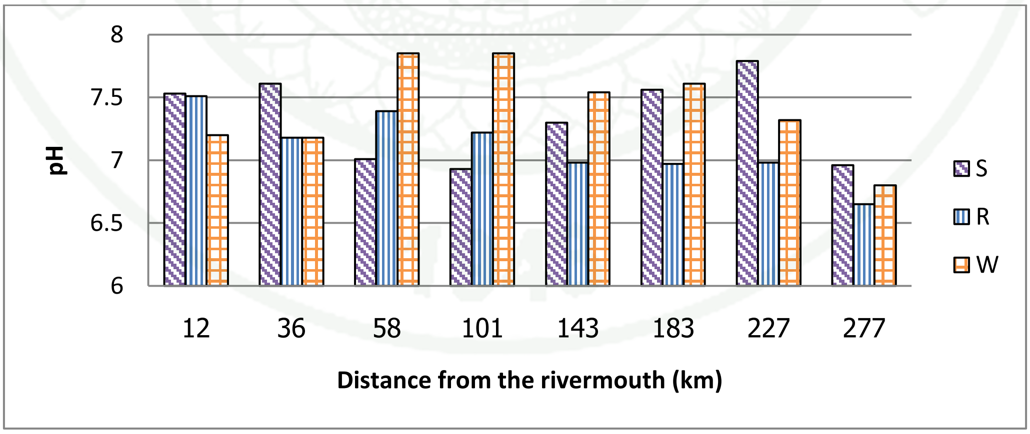


Figure 8 pH variations with the distance from the river mouth in summer (S) rainy (R) and winter (W) season and for the right bank sampling sites.

In left bank pH values were ranged in 7.01, the lowest in summer season at Sinburi site and 7.93, the highest in winter season at Pathumthani site. The pH variation trend for the left bank sampling locations almost similar for summer and winter season and slightly differs with rainy season but the overall pH values not shows significant variations as right bank (Fig.9).

Thus the pH values of right bank locations, specially nearest to the river mouth are slightly acidic in all three seasons and sites at Ayuththaya, Pathumthani, Nonthaburi and Pranamklao in rainy season as well. All the other sites both right and left banks were in optimal pH range for sustainable aquatic life (Adeyemo et al., 2008). The overall statistical analysis reviled that there is no significant correlation with pH and distance from the river mouth or seasonality (Fig.10)

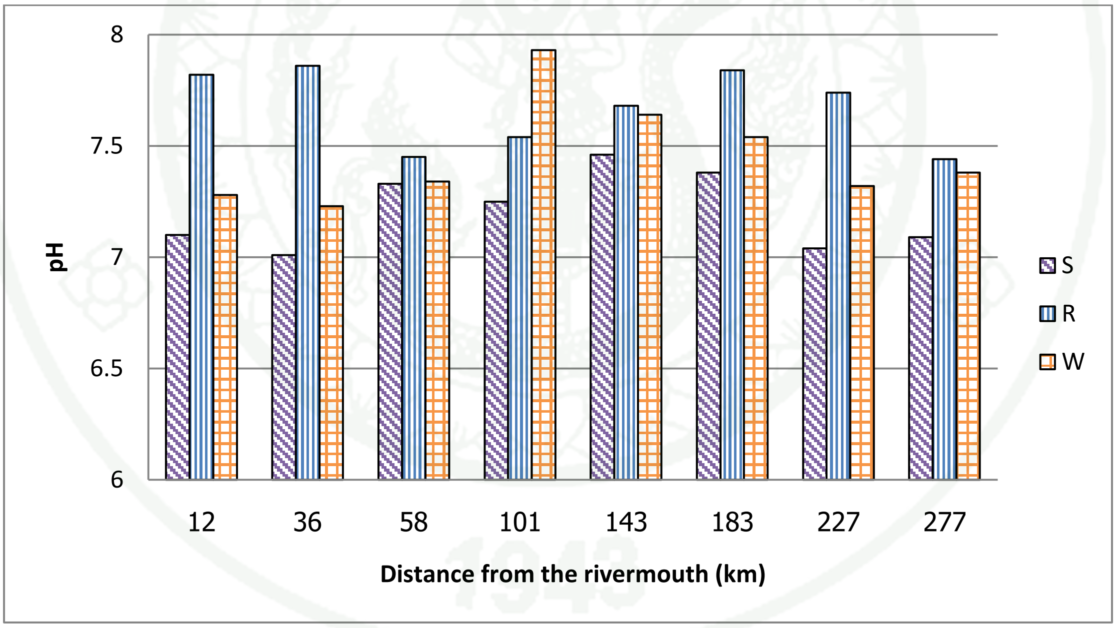


Figure 9 pH variations with the distance from the river mouth in summer (S) rainy (R) and winter (W) season for the left bank sampling sites.

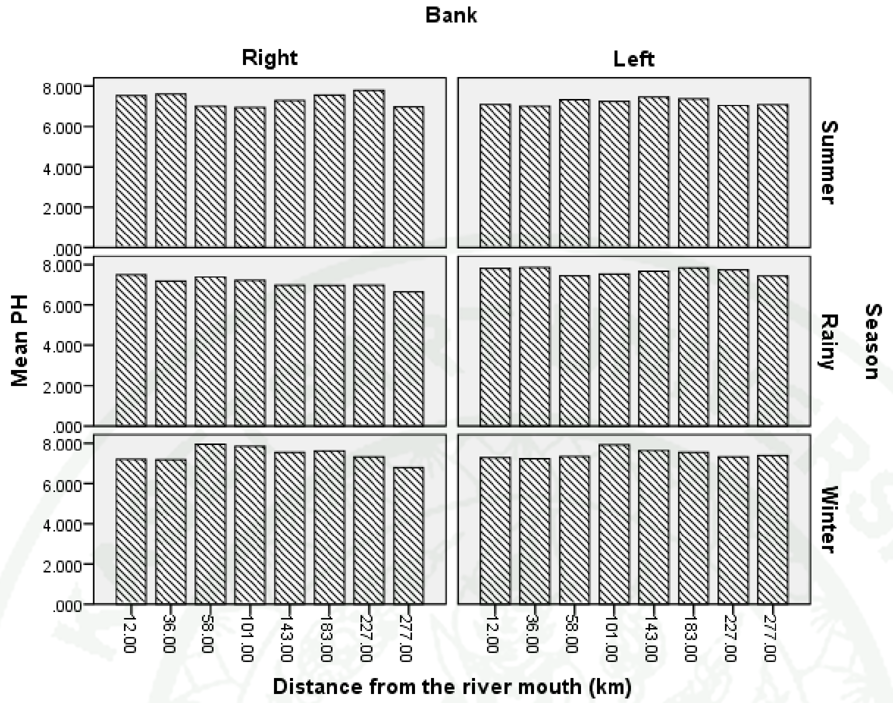


Figure 10 Statistical comparison of pH variations with the distance from the river mouth in summer (S) rainy (R) and winter (W) season for both right and left bank of the lower Chao Phraya river.

Electrical conductivity (EC) is good parameter which can be used to determine the mineralization of sediment and its ion contents. These ions can be affected with aquatic biota and its chemical speciation too. The current study revealed that the EC values of sediments ranges from 4.08 mS/m, minimum value at Pranamklao site in the summer to 97.3 mS/m, maximum at the Ang Thong site in rainy season. The obtained EC values for the right bank sample sites showed the similar trend with distance from river mouth as pH (Fig.11). Chainat, most distant sample site to the river mouth shows the lowest Ec values for all three seasons. The maximum EC value for right bank sites was exhibited by site at Pranamklao in winter (70.6 mS/m) and followed by site at Samutprakarn for summer (40.5 mS/m) and site at Ayuththaya for winter (32.6 mS/m) season (Fig.11). The pH values and EC values of sample sites in right bank were exhibited slightly similar linear trend among each other. In left bank, the EC values were showed similar pattern as the right bank (Fig 12).

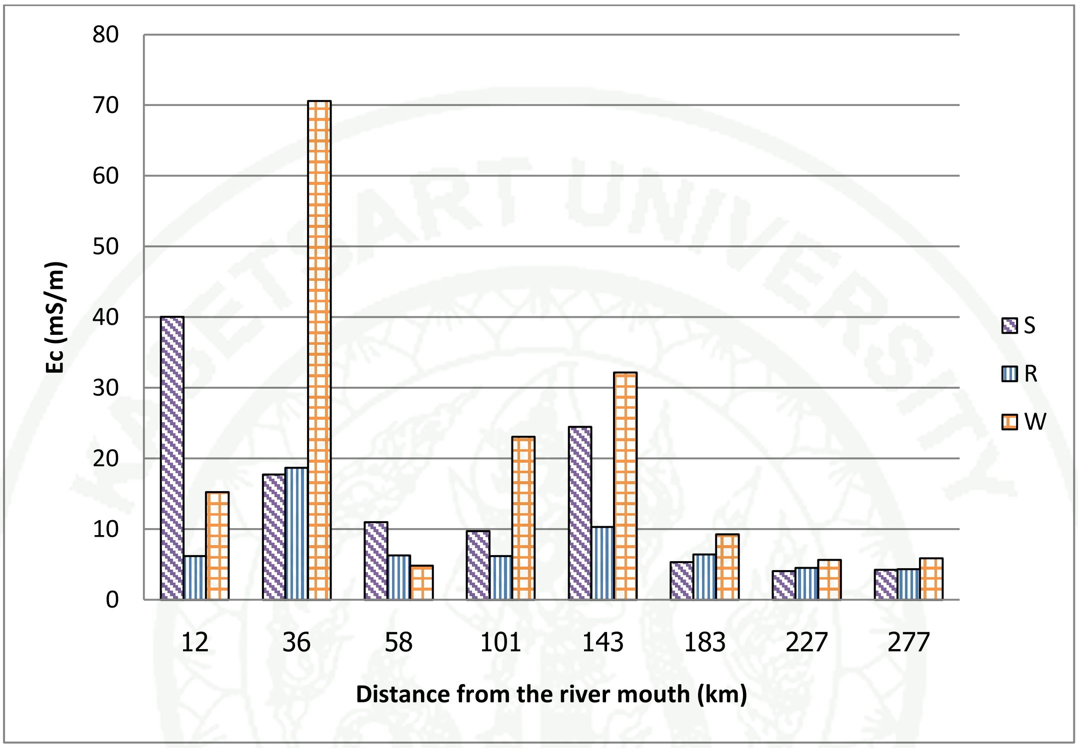


Figure 11 EC variations with the distance from the river mouth in summer (S) rainy (R) and winter (W) season for the right bank sampling sites.

The EC values of both banks of the river were exhibited a significant negative correlation with the distance from the river mouth (Pearson correlation is significant at 0.01 level = -0.476). The statistical comparison of EC values in both left and right bank of the river in three seasons with the distance from the river mouth is shown in figure 13.

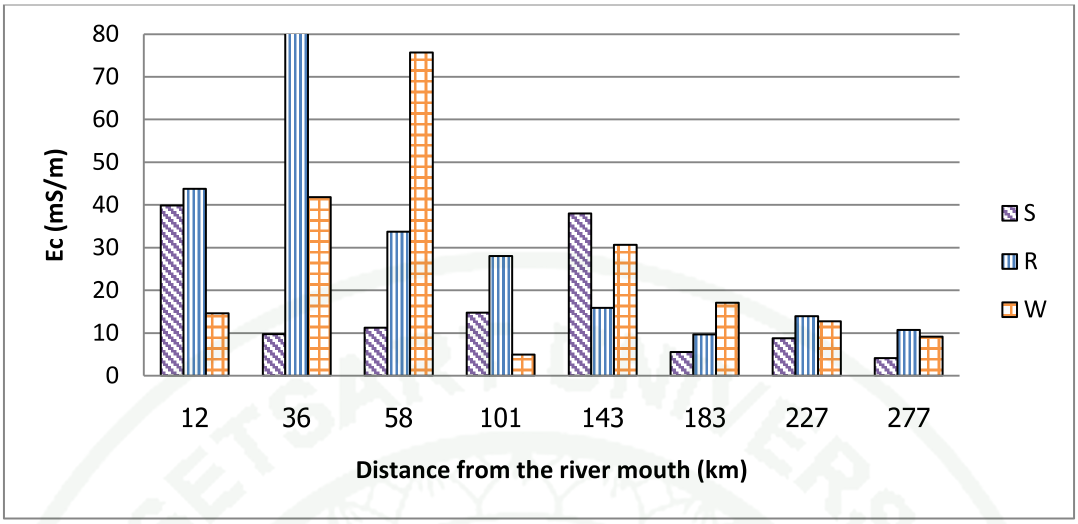


Figure 12 EC variations with the distance from the river mouth in summer (S) rainy (R) and winter (W) season for the left bank sampling sites.

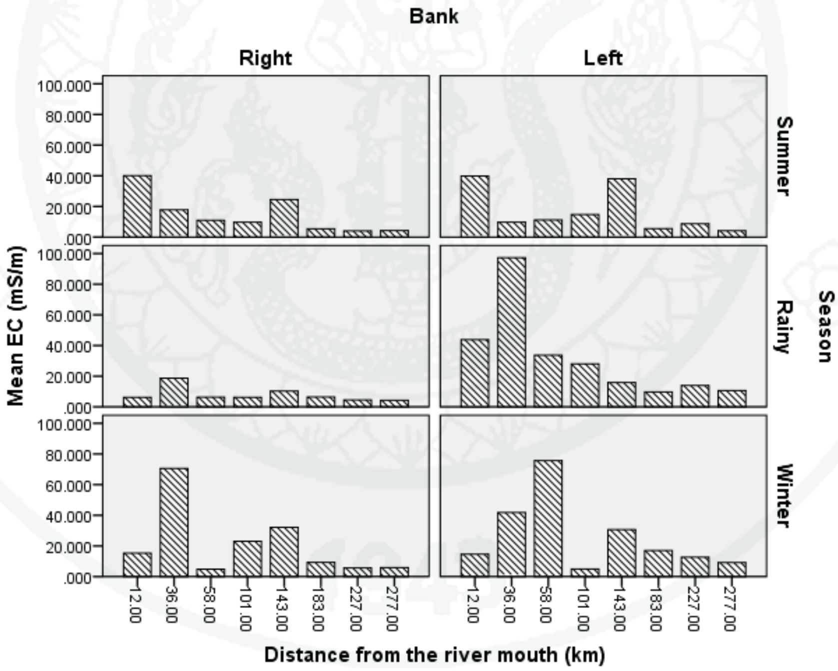


Figure 13 Statistical comparison of EC variations with the distance from the river mouth in summer (S) rainy (R) and winter (W) season for both right and left bank of the lower Chao Phraya river.

Determination of the present of TOC in sediment is an important parameter on environmental investigations and monitoring practices. Most important character of organic carbon in sediment is their ability to bind with ions of metals present in the sediment and to form complex components soluble or insoluble. These complexes interact with the minerals present in the clay to form particles that are capable to absorb other contaminants too. The highest TOC value was recorded at Pranamklao site (4.05 mg/kg) in winter season followed by sites at Pathumthani and Samutprakarn (2.638 mg/kg) in rainy and winter seasons respectively for right bank (Fig.14).

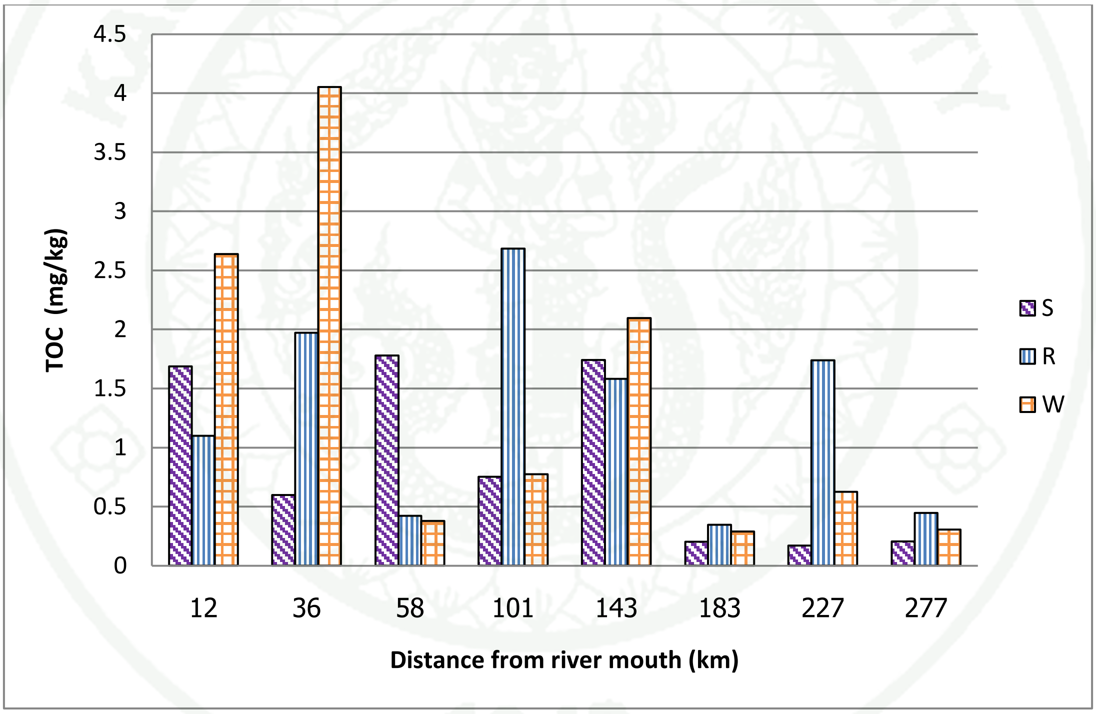


Figure 14 TOC variations with the distance from the river mouth in summer (S) rainy (R) and winter (W) season and their trend lines for the right bank sampling sites.

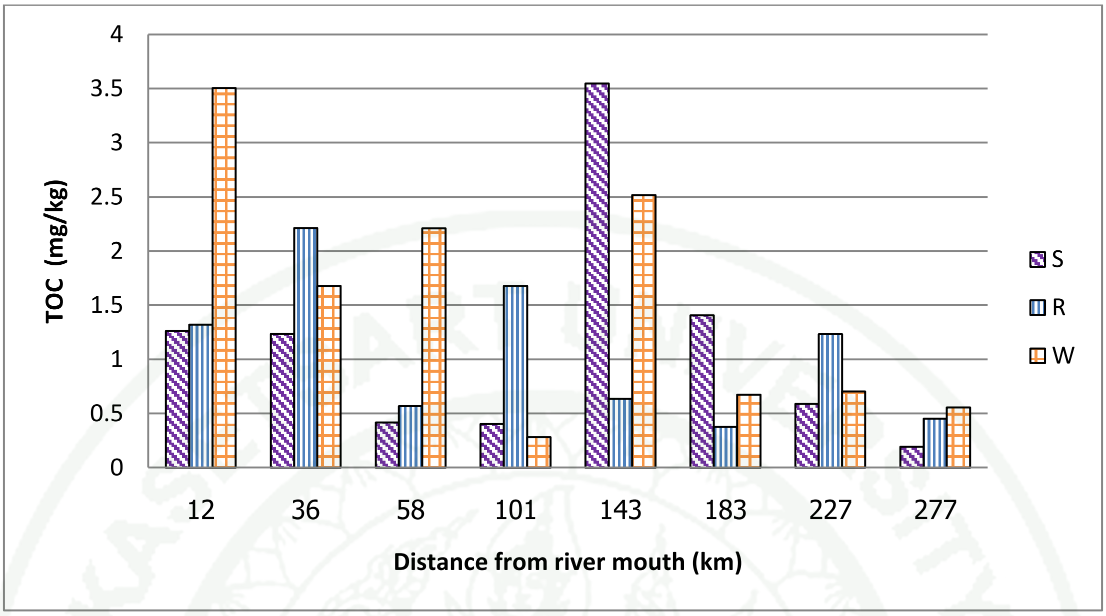


Figure 15 TOC variations with the distance from the river mouth in summer (S) rainy (R) and winter (W) season and their trend lines for the left bank sampling sites.

In left bank, site at Ayuththaya was showed highest TOC values in summer and rainy season (3.54 and 2.51 respectively) while site at Samutprakarn shows highest value in winter season (3.5). Sirivithayapakorn and Thuyviang (2010) also reviled that higher level organic matter content from Samutprakarn site. Topography and land use pattern of the Chao Phraya basing contribute this high level suspended sediment load and TOC (Fig 14). For overall statistical comparison the TOC values of both banks in three seasons have significant negative correlation with distance from the river mouth (Pearson correlation is significant at 0.01 level = -0.464) (Fig 16).

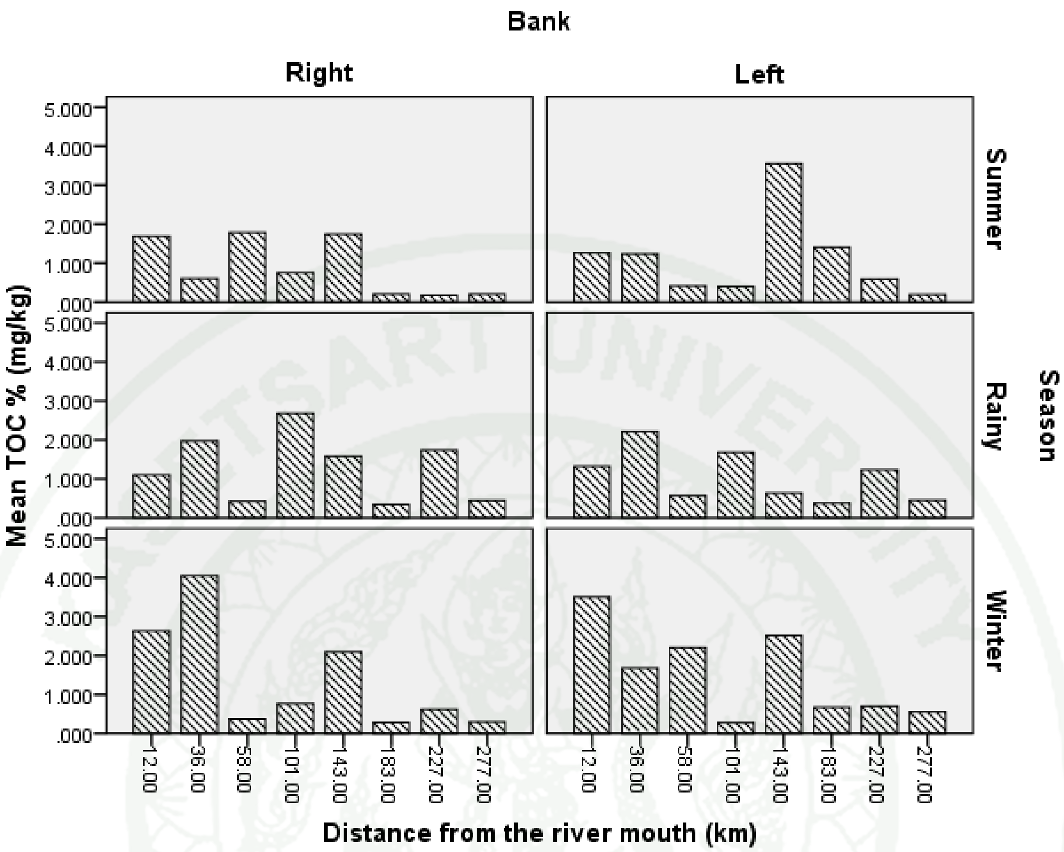


Figure 16 Statistical comparison of EC variations with the distance from the river mouth in summer (S) rainy (R) and winter (W) season for both right and left bank of the lower Chao Phraya river.

2. Total metal Concentration

The total metal concentrations were analyzed for Zn, Cr, Ni, Cu, Pb, Mn, Fe, Cd, Hg and As by using USEPA 3050B standard method and detected concentrations levels were summarized for each season (Table 9 - 11). The grain size differences detected from sediments of all 8 sites from both left and right banks reviled that the sediments in this study area were dominated by clayey silt and sand in the size range of 8.2 – 148.5 µm. In summer season all ten elements were exhibited their disperse distribution with all sampling sites in both right and left banks of the lower Chao Phraya river (Fig 17 & 18). The highest concentration of Zn (85.49 mg/kg), Cr (186.17 mg/kg), Ni (13.328 mg/kg), Cu (20.28 mg/kg), Pb (28.23 mg/kg), Cd (7.06 mg/kg), Hg (30.01 mg/kg) and As (22.20mg/kg) were recorded in sites at Ayuththaya (143 Km), Nonthaburi (58 Km) and Samutprakan (12Km) in summer season. The contents of Hg at all sites in both banks, As at Sinburi site (227 Km), Ang Thong(183Km), Ayuththaya (143Km) of right bank and Sinburi (227 km), Ayuththaya (143 Km) and , Pranamklao (36Km) of left bank, Cd at all five sites from Chi Nat to Pathumthani (277Km to 101 Km) and Samutprakarn site (12Km) of right bank and sites from Chi nat to Pranamklao of left bank, Cu at Pranamklao site of right bank and sites at Ayuththaya and Samutprakarn (12Km) of left bank, Cr at Ayuththaya, Pathumthani and Samutprakarn sites of right bank and site all sites of left bank exceeded the Threshold Effect Level of SQG values which are concentrations that roughly relate to low probability of sediment toxicity (MacDonald et al., 2000).

In rainy and winter season the overall heavy metal concentrations were exhibited variations with the level and availability among the sites than summer season. The highest concentration of Zn (69,07mg/kg) at Pranamklao site left bank, Cr (95.65mg/kg) and Ni (20.078 mg/kg) at Pranamklao site right bank, Cu (62.39mg/kg) at Nonthaburi site right bank, Pb (1488.56mg/kg) at Pranamklao site left bank, Cd (0.299mg/kg) at Sinburi site left bank, Hg (0.096 mg/kg) at Pranamklao site left bank, As (5.461mg/kg) at Sinburi site left bank were recorded among the sites in rainy season (Fig. 19, 20). Hg contaminated only sites at Pranamklao and Samutprakarn of the left bank while As contaminated only sites at Chainat, Sinburi, Ang Thong and Pathumthaniof the right bank in rainy season. Sediment quality in rainy season is differ than summer season and only Cr, Ni, and Pb exceeded the TEL for the Samutprakarn site of left bank, sites at Sinburi, Ayuththaya, Pathumthani and Pranamklao of right bank and site at Pranamklao of left bank respectively. Cu drastically exceeded the TEL and PEL at the site Pranamklao for both banks. .

Table 9 Total metal concentrations of all sites in summer season

	Distance (Km)	Elements (mg/kg)									
		Zn	Cr	Ni	Cu	Pb	Mn	Fe	Cd	Hg	As
Right bank	277	14.033	11.843	2.986	3.185	6.369	187.400	9525.179	7.066	22.295	3.987
	227	8.390	12.984	1.798	3.196	5.094	115.162	9149.920	6.592	58.164	6.897
	183	7.965	22.202	1.693	3.982	4.281	367.184	10584.329	6.571	8.100	2.374
	143	29.919	46.076	0.000	12.367	9.873	1006.084	25671.587	6.981	43.562	17.231
	101	56.902	88.977	0.000	5.462	2.781	211.519	9603.674	6.058	19.139	1.497
	58	58.167	0.000	0.000	11.554	24.104	1253.785	22540.737	0.000	3.654	1.890
	36	26.449	0.000	3.269	20.802	19.217	999.307	13938.484	0.000	29.842	10.392
	12	58.149	186.116	10.174	13.565	10.672	1534.809	37064.532	6.284	8.114	0.094
Left bank	277	13.351	178.041	2.889	4.284	3.387	182.923	8280.263	6.476	22.320	4.249
	227	18.847	174.312	0.499	7.379	6.083	467.491	12226.665	6.382	4.886	7.188
	183	37.694	175.708	7.978	13.961	12.365	1823.694	29707.718	6.681	0.000	8.441
	143	42.846	171.582	8.768	20.227	15.046	1423.675	39090.175	6.477	30.018	22.206
	101	11.577	142.216	2.096	0.000	1.597	166.467	7575.749	5.888	14.506	2.294
	58	18.057	130.886	0.599	6.484	1.097	161.313	6505.287	6.185	4.888	1.699
	36	66.242	130.097	13.328	12.632	5.172	239.606	7739.109	6.266	5.439	1.191
	12	85.488	95.493	0.000	20.208	28.232	1732.343	27925.607	0.000	0.761	0.394

Table 10 Total metal concentrations (mg/kg) of all sites in rainy season

	Distance	Elements (mg/kg)									
	(km)	Zn	Cr	Ni	Cu	Pb	Mn	Fe	Cd	Hg	As
Right bank	277	0.000	2.486	7.360	1.492	0.298	238.389	7852.909	0.298	0.000	2.794
	227	0.000	14.155	17.245	13.557	2.193	1067.285	22728.369	0.299	0.000	5.461
	183	0.000	7.393	11.089	5.794	31.668	414.286	13802.298	0.100	0.000	4.211
	143	18.890	13.323	17.300	12.030	32.014	515.709	17738.218	0.000	0.000	3.602
	101	2.279	14.667	17.540	12.288	35.576	291.051	15871.668	0.099	0.000	3.251
	58	0.000	2.292	9.567	62.388	13.853	220.949	5253.239	0.000	0.000	2.165
	36	8.291	15.283	20.078	24.773	536.410	842.773	21142.843	0.000	0.000	4.467
	12	0.000	22.892	14.134	11.546	16.423	1069.673	26073.554	0.000	0.000	5.375
Left bank	277	0.000	8.187	9.085	2.596	3.894	254.293	7948.383	0.000	0.000	2.805
	227	0.000	9.872	9.972	6.582	0.299	327.782	9369.864	0.000	0.000	3.939
	183	0.000	12.136	12.036	6.167	0.000	405.551	13514.473	0.000	0.000	4.157
	143	0.000	10.770	10.969	4.986	0.000	352.712	10541.584	0.000	0.000	2.845
	101	0.000	12.476	14.754	12.278	17.427	272.997	10556.590	0.000	0.000	3.513
	58	0.000	2.897	7.993	2.897	16.885	229.493	4921.670	0.000	0.000	2.358
	36	69.065	20.490	17.291	25.087	1488.256	964.218	23339.430	0.000	11.096	5.232
	12	46.277	93.653	9.095	19.190	20.090	514.443	12359.920	0.000	1.796	4.293

Table 11 Total metal concentrations (mg/kg) of all sites in winter season

	Distance (km)	Elements (mg/kg)									
		Zn	Cr	Ni	Cu	Pb	Mn	Fe	Cd	Hg	As
Right bank	277	25.443	5.871	4.893	3.131	0.000	162.540	10925.727	0.000	0.233	3.378
	227	17.180	7.349	0.000	4.200	0.000	162.547	15047.246	0.286	0.083	6.291
	183	15.040	5.378	3.187	3.984	0.000	164.641	11997.012	0.299	0.051	4.014
	143	69.300	20.641	15.410	20.174	25.217	1118.894	21830.298	0.000	0.052	5.980
	101	65.219	21.611	17.444	12.017	17.153	1161.934	20674.193	0.000	0.038	4.594
	58	27.054	7.487	8.186	56.903	0.000	198.662	2734.052	0.000	0.183	1.915
	36	80.811	26.171	17.081	23.474	3.216	692.538	15378.084	1.199	0.000	5.279
	12	142.206	26.757	19.126	40.729	6.739	582.995	29184.422	0.892	0.189	5.882
Left bank	277	35.643	6.090	0.000	8.087	0.000	162.540	14596.645	0.399	0.062	4.442
	227	23.370	7.757	0.000	6.186	0.000	239.493	16712.490	0.982	0.026	3.996
	183	25.792	8.365	1.195	10.954	0.000	468.333	27778.331	0.299	0.003	4.904
	143	66.373	20.879	18.485	39.172	43.004	1221.147	21562.781	0.000	0.009	5.437
	101	15.703	5.267	5.764	0.398	7.056	253.429	1792.586	0.000	0.000	1.737
	58	48.635	25.115	16.643	18.836	17.441	937.811	23498.804	0.000	0.026	5.925
	36	80.949	19.839	10.168	32.200	23.029	695.145	27808.793	0.798	0.096	5.272
	12	137.358	253.332	15.019	46.051	0.000	2417.247	17575.094	1.392	0.137	5.858

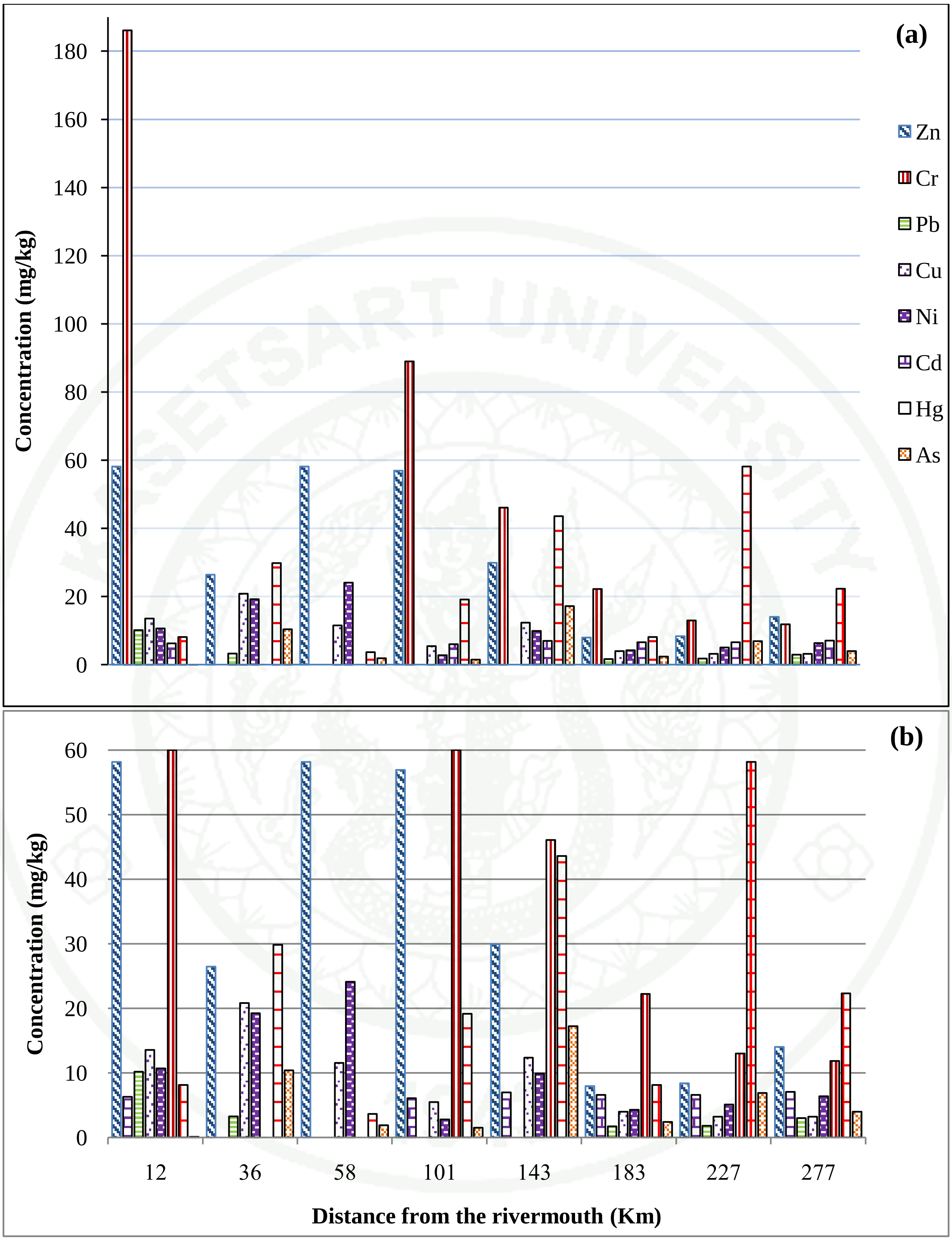


Figure 17 Total metal concentrations of sediments in summer season at the right bank (a) all the data using full Y axis (b) scaled down Y axis for small data values of lower Chao Phraya river

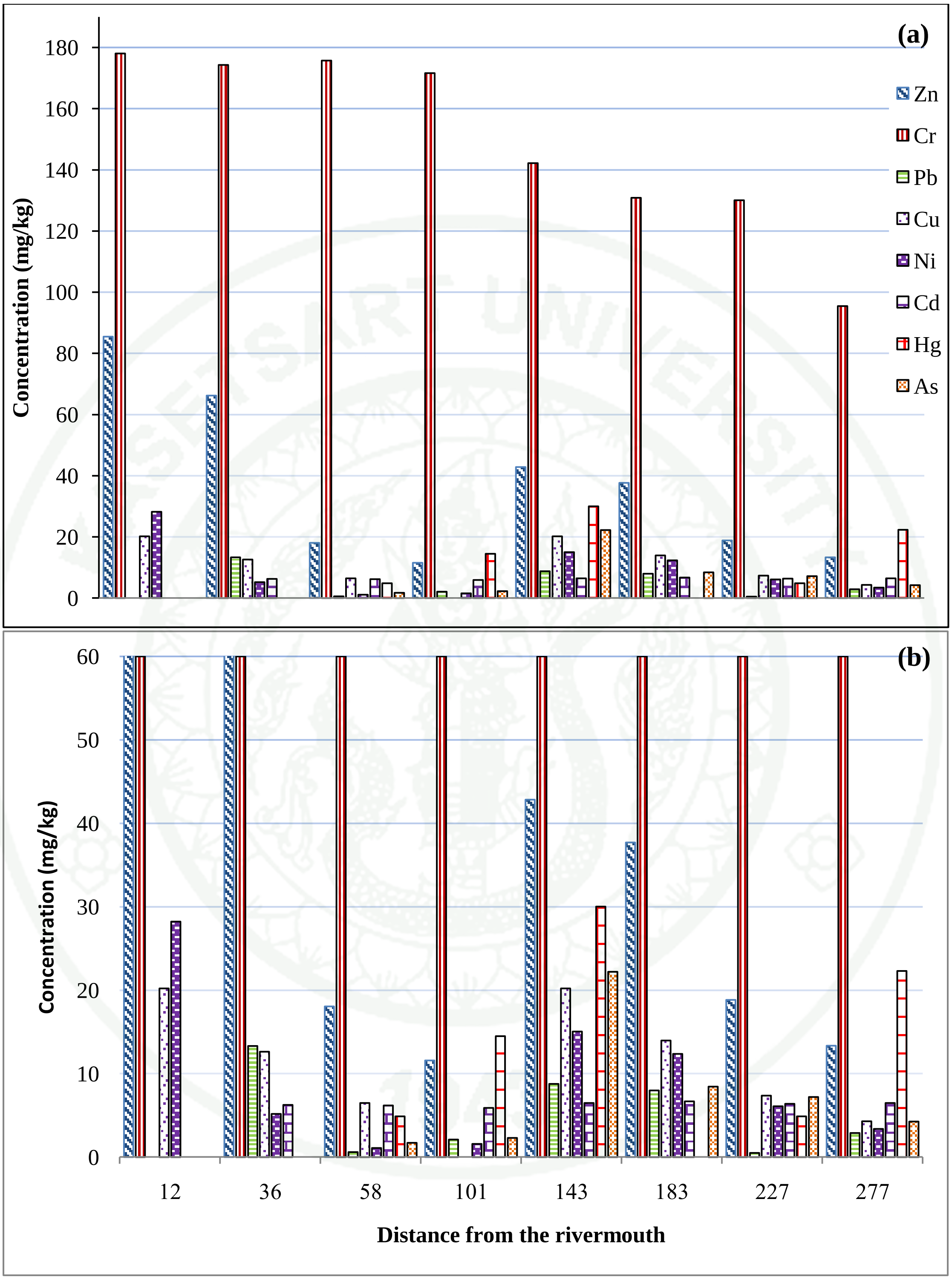


Figure 18 Total metal concentrations of sediments in summer season at the left bank (a) all the data using full Y axis (b) scaled down Y axis for small data values of lower Chao Phraya river.

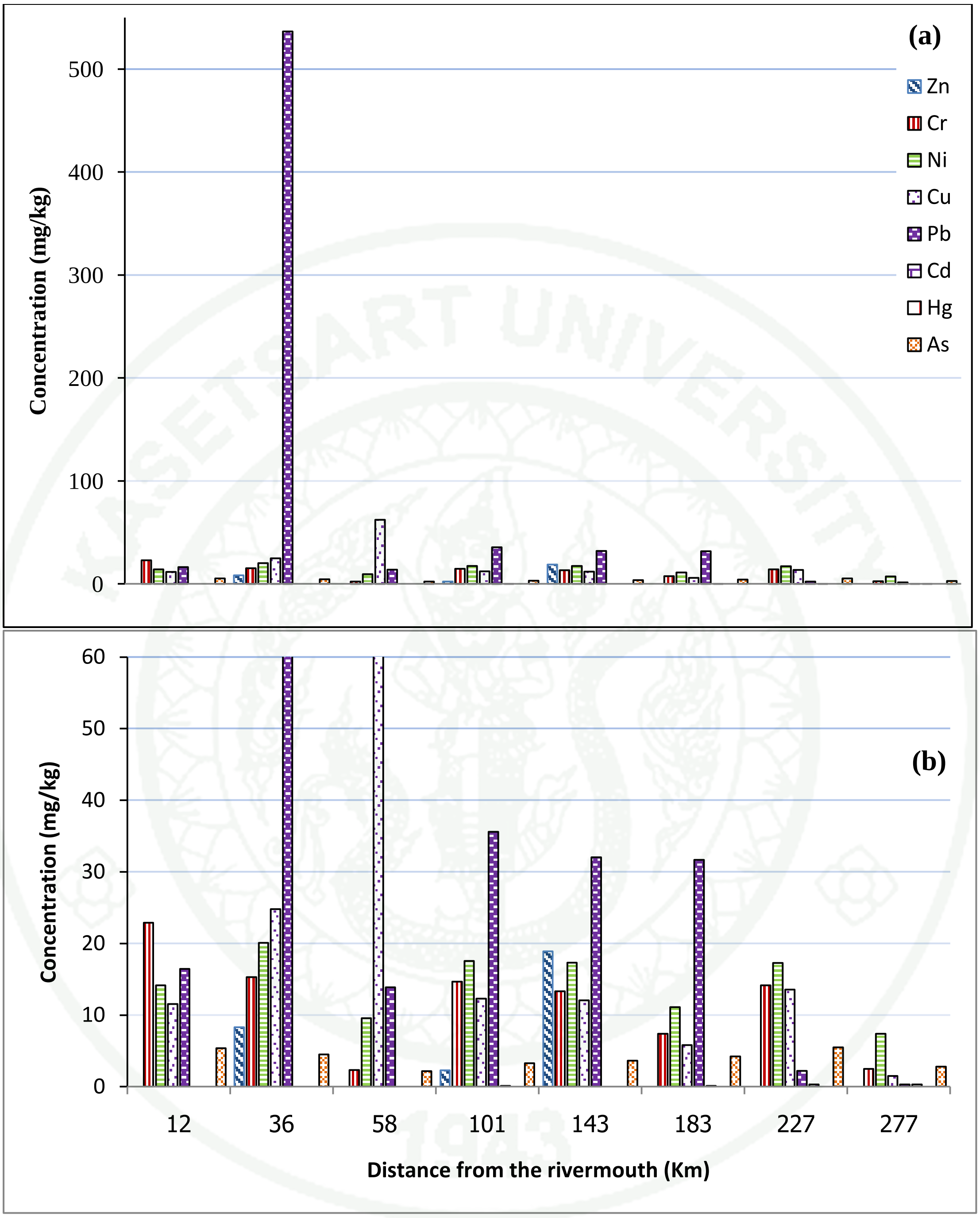


Figure 19 Total metal concentrations of sediments in rainy season at the right bank (a) all the data using full Y axis, (b) scaled down Y axis for small data values of lower Chao Phraya river.

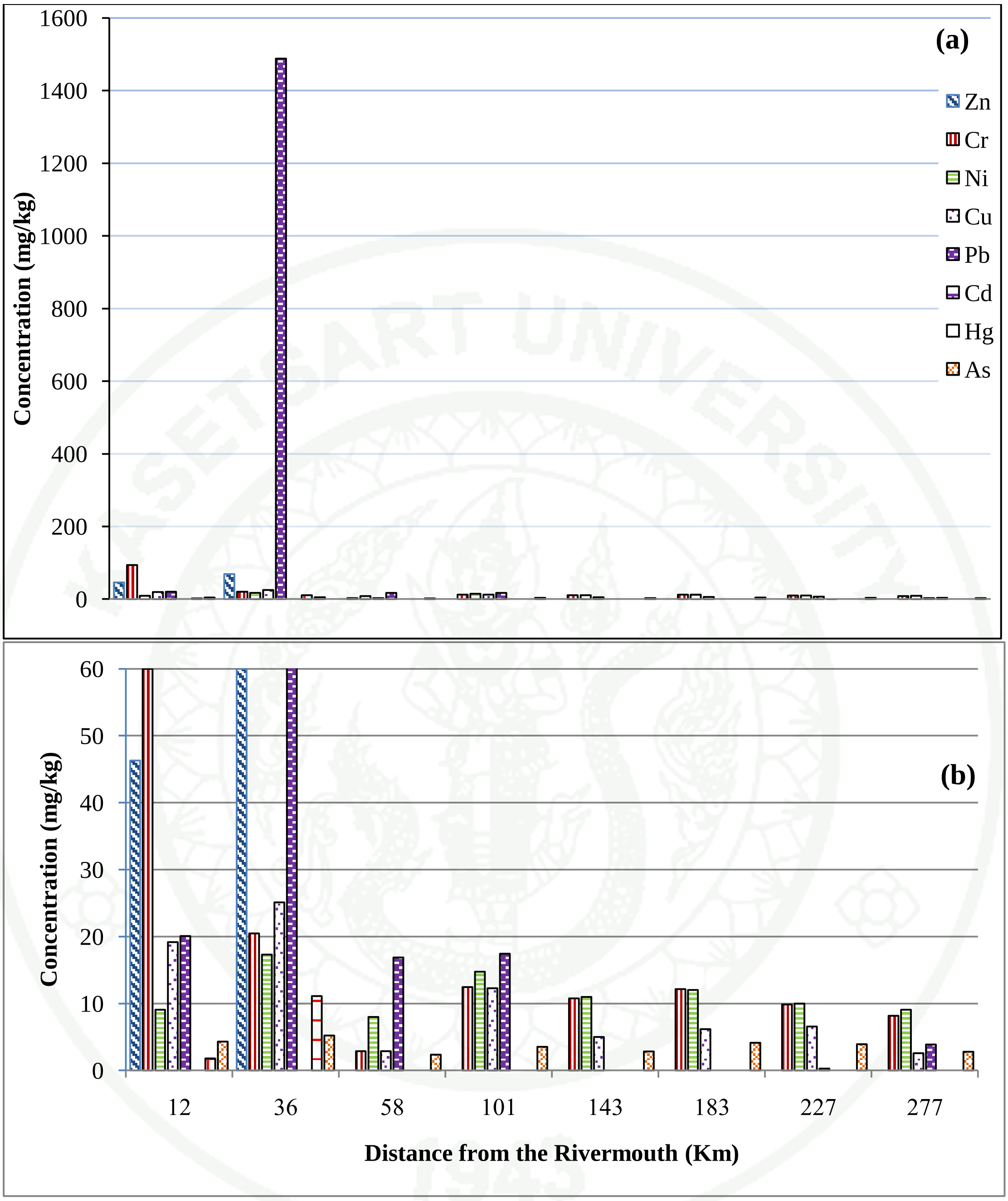


Figure 20 Total metal concentrations of sediments in rainy season at the left bank (a) all the data using full Y axis, (b) scaled down Y axis for small data values of lower Chao Phraya river .

For winter season, the highest concentration of Zn (142.20 mg/kg) at right bank of Samutprakarn site, Cr (253.332mg/kg) at left bank of Samutprakarn site, Ni (18.4 mg/kg) at left bank of Ayuththaya site, Cu (56.90mg/kg) at right bank of

Nonthaburi site, Pb (43mg/kg) at left bank of Ayuththaya site, Cd (0.892mg/kg) at right bank of Samutprakarn site, Hg (0.233 mg/kg) at right bank of Chai Nat site and As (6.29mg/kg) at right bank of Sinburi site were recorded among the sites in winter season(Fig 21 & 22). In winter season also exhibited low values for Cd and Hg but availability among the sites were quite higher than rainy season. Sediment quality in winter season also vary than rainy season and the contents of Zn at Samutprakarn Site of both banks, Cr at same but left bank, Ni at Ayuththaya, Pathumthani and Pranamklao sites right bank and Ayuththaya, Pathumthani and Samutprakarn sites left bank, Cu at right bank of Ayuththaya, Pranamklao and Samutprakarn sites, Pb at left bank of Ayuththaya site, Cd at right bank of Samutprakarn site and left bank of Sinburi, Pranamklao and Samutprakarn sites, were exceeded TEL and Cr at left bank of Samutprakarn site were exceeded the PEL of SQG derived by MacDonald et al. (2000).

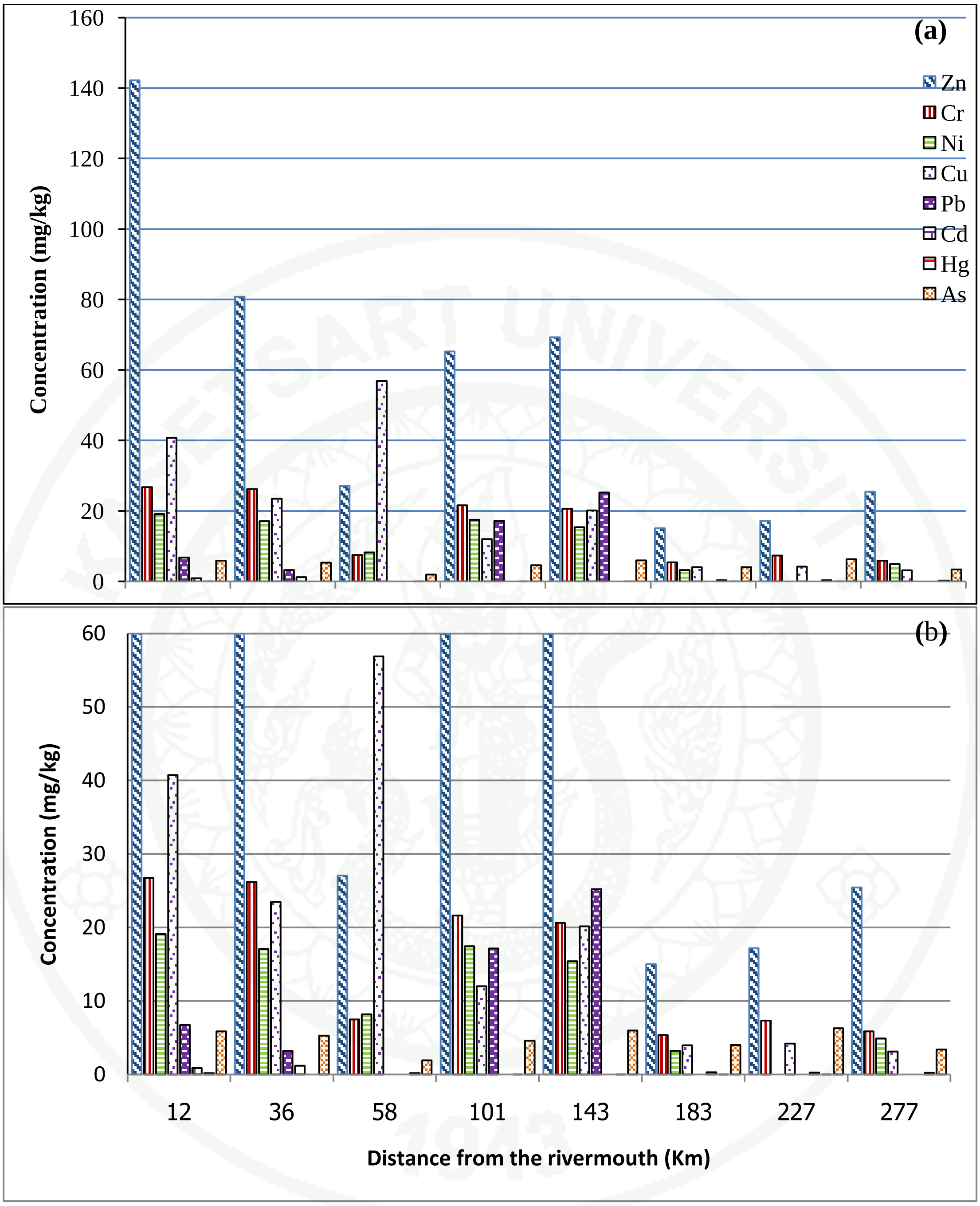


Figure 21 Total metal concentrations of sediments in winter season at the right bank (a) all the data using full Y axis, (b) scaled down Y axis for small data values of lower Chao Phraya river.

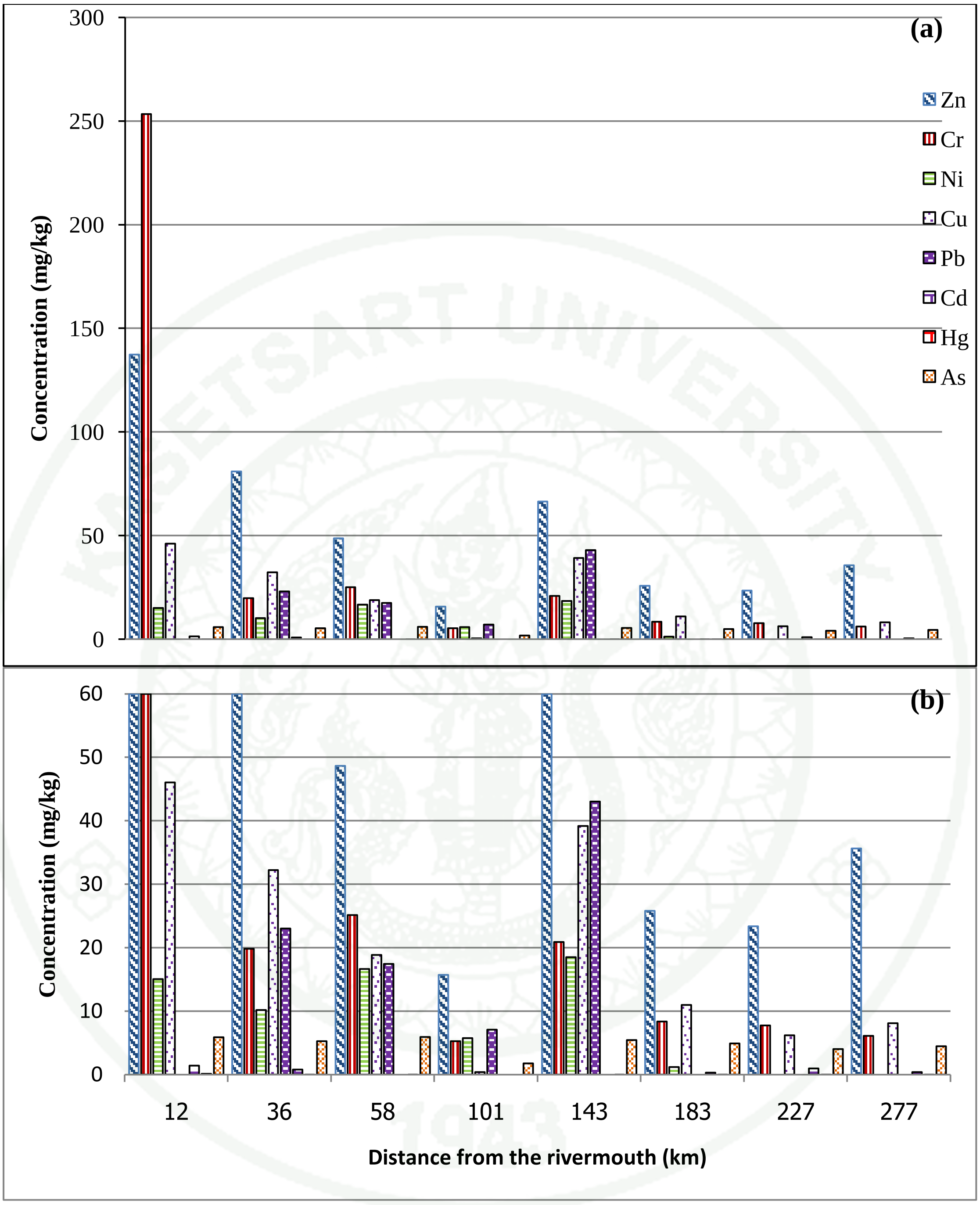


Figure 22 Total metal concentrations of sediments in winter season at the left bank of (a) all the data using full Y axis, (b) scaled down Y axis for small data values of lower Chao Phraya river.

Although the concentrations of metals were rarely exceeded the PEL values in each season the TEL values exceeded mostly in sites at Ayuththaya, Nonthaburi and Samutprakarn for all 8 elements considered. This trend lead to the conclusion that toxic metals like Cd, Cr, Ni, Pb, Hg and As are of concern in the present study area may occasionally be associated with adverse biological impacts specially in summer season.

Total metal concentration of Fe and Mn recorded for all eight sites by showing quite similar spatial distribution pattern with higher values in all three seasons. According to Yamanaka et al. (2012) for the suspended sediments in water layer also exhibit similar trend and it may due to similar transport mechanism of these two elements. In summer and winter season, Zn dominated while Ni dominated in rainy season for all sites. In all three seasons the recorded total metal concentrations of most of the elements showed higher values for sites at Ayuththay, Nonthaburi, Pranamklao and Samutprakarn. The reason for these remarkably higher values of concentration may directly relate with high suspended solid loads released in to the river due to anthropogenic activities currently practices in these areas such as industrial and municipal waste waters, irrigation discharge, mine discharge along with the erosion of rocks and soil parent materials (Tanner et al., 2000; Zhang et al., 2009; Hosono et al., 2010). The Chao Phraya River currently used as major transport mode and there are many barrage traverses through the river everyday not only using the water surface for the transport but also discharged various types of wastes. In addition, deposition of wastes emitted from vehicles, waste incinerations could also be a source of heavy metal contamination. Thus further investigations required for confirm the existence sources and mitigation strategies

3. Chemical speciation

Mostly the heavy metals chemically or physically interacted with the natural complexes or compounds and exhibit changes with their forms in the environment. These interactions and variations due to environmental properties specially climatic factors are very important because they may change the equilibrium between sediment and water resulted the leachate of toxic elements tightly bound the sediment particles. Thus this study focused with chemical speciation through sequential extraction process. Results of sequential extractions of the initial samples which were collected in summer season (April 2012) reviled that average chemical speciation of both left and right bank of the river have almost similar distribution pattern (Fig. 23 & 24). The residual fraction exhibit higher representation as usual and dominated in contents of Cr, Fe and Ni in both bank (above 50%).

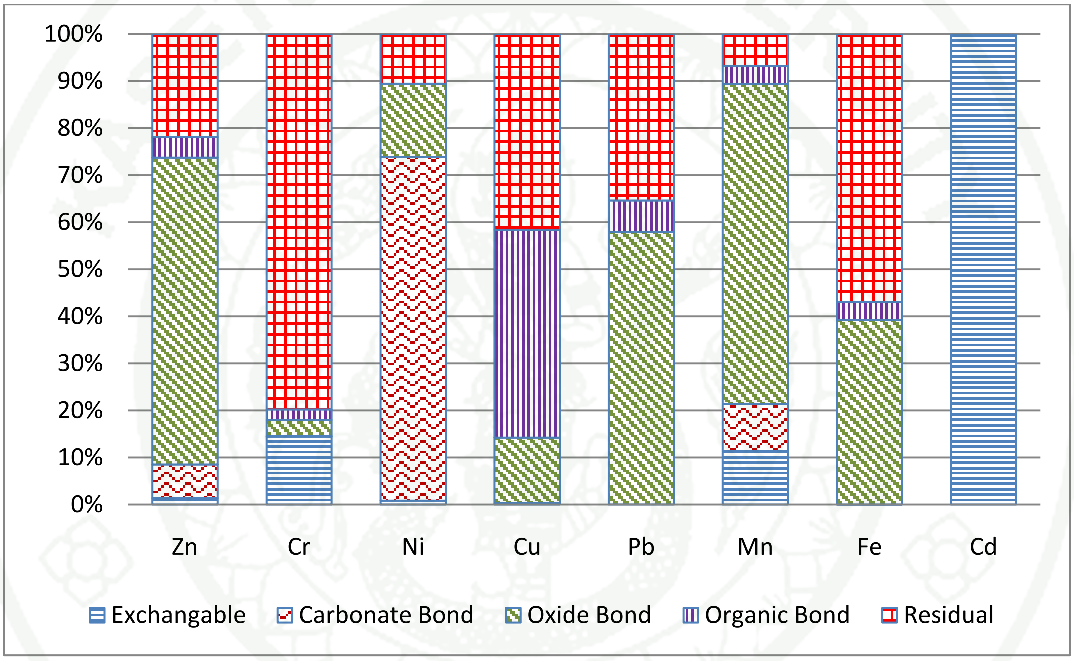


Figure 23 Comparison of distribution patterns of metals in Summer (S) season in right bank of Chao Phraya River.

Cr, Fe, Cu Pb, Zn, Ni an Mn represented residual fraction and Cd were not represented in the same. Contents of Cd totally dominated in exchangeable fraction for representing approximately 100% of the total metal concentration and Cr and Mn represent the exchangeable fraction below 20% while zn, Ni, Cu and Fe represent very low percentage (below 2). The previous studies carried out for the Cd concentration of Lower Chao Phraya River, reviled that the association level of Cd in each fraction, changes with the seasonal variations but current study reviled that summer and winter season Cd totally associated with exchangeable fraction only while shared the association with carbonate bound fraction (15%) in rainy season (McLaren et al., 2004). Fe, Pb, Cu, Ni and and Zn not represented in exchangeable fraction. Geochemical speciation data of sedimentary heavy metals suggest that high concentration of Cd, Cr, Mn, and Ni in the exchangeable fraction has an adverse effect on aquatic ecosystem.

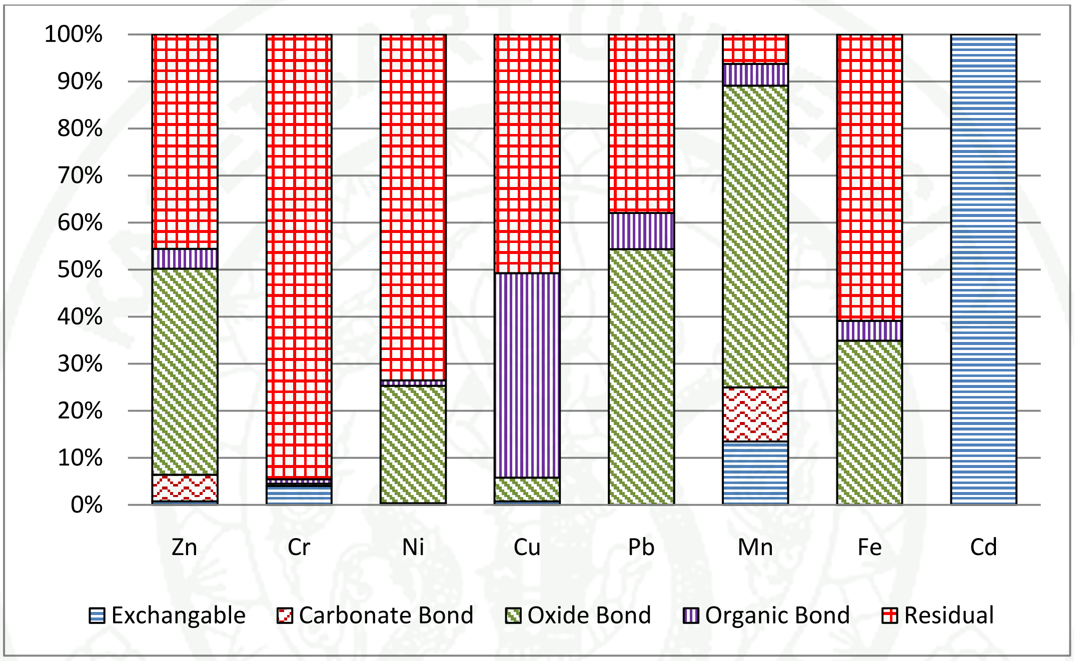


Figure 24 Comparison of distribution patterns of metals in Summer (S) season in left bank of Chao Phraya River.

The carbonate bound fraction dominated with Ni while Mn and Zn very low representation in right bank (68%, 10% and 9% respectively). For the Left bank the carbonate bond fraction represent by Zn and Mn only with very low percentages. Al the other elements not exhibit the remarkable representation for carbonate bond fraction in summer season in this study. The appropriate representations of metals like Mn, Zn, and Ni in this fraction due to their special affinity towards carbonate and may co-precipitates with its minerals. Higher representation of Mn in carbonate fraction was mostly due to its ionic similarity like that of Ca which allows them to substitute in carbonate phase (Schoer et al., 1983; Zhang et al., 1988; Rath et al., 2009).

The oxide bound fraction dominated with Zn, Mn, and Pb (representing above 60%) while Fe, Ni, Cu and Cr exhibited very low level (below 20%) for right bank. In left bank almost similar distribution pattern was recorded. Normally the oxide bound fraction act as main scavenger for all elements studied except Cd. This attributes could be due to the adsorption, flocculation and co-precipitation of heavy metals with colloids Fe and Mn oxy-hydroxides (Iwegbue et al., 2009; Passos et al., 2010).

The organic bond fraction dominated by Cu, representing 50% and Ni, Cr, Pb, exhibited moderate representation while Fe and Mn exhibited very low representation. This may resulted due to the inter fractional competition between Fe-Mn organic complex and hydrous Fe-Mn oxides forms (Ratuzny et al., 2009).

The dominating order in each fraction of summer season gave a clear picture about the variations among the fractions as follows;

Table 12 Dominating order of elements in each fraction

Fraction	Right Bank	Left Bank
Exchangeable	Cd>Cr>Mn>Zn>Ni>Cu>Fe	Cd>Mn>Cr>Zn>Ni>Cu>Fe
Carbonate Bound	Ni>Mn>Zn	Mn>Zn
Oxide Bound	Mn>Zn>Pb>Fe>Cu>Ni	Mn>Pb>Zn>Fe>Ni>Cr>Cu
Organic Bound	Cu>Pb>Fe>Mn>Zn>Cr	Cu>Pb>Mn>Fe>Zn
Residual	Cr>Fe>Cu>Pb>Zn>Ni>Mn	Cr>Ni>Fe>Cu>Zn>Pb>Mn

These variations of dominating pattern derived from the sequential extraction techniques provide basement for prediction of possible metal impact and their toxicity in riverine ecosystem of lower Chao Phraya River. The higher level representations of Cd, Cr, Ni, Zn Pb, Cu and Mn in anthropogenic fractions include exchangeable and carbonate bound which can be considered as weak bound may equilibrate with aqueous phase thus becoming more rapidly bioavailable and cause environmental toxicity (Pardo et al., 1990). In oxide bound and organic bound fractions, the bounded metals can be mobilized when environmental conditions become reducing or oxidizing (Karbassi and Shankar, 2005).

By considering results of summer season both total metals concentration and sequential extractions, further analysis were focused in three main sites namely Ayuththaya, Nonthaburi, and and Samutprakarn in rainy and winter season. Assessing the individual element profile is one of the best ways to get more clear idea about chemical speciation with the distance from river mouth

4. Individual element profiles

Individual element profiles were plotted for sample sites at Ayuththaya, Nonthaburi and Samutprakarn to determine their availability in each fraction in three different seasons. It was reviled that Cd, Cr, Zn and Ni exhibited abundant variations within sites, among fractions in three seasons.

Zn contents abundant in oxide bound fraction for both bank and it was appeared in higher levels of organic fraction in right bank. Site at Samutprakarn recorded the highest values in oxide bound fraction for all three season. Zn represented exchangeable fraction only in rainy season at Nonthabury site and the carbonate bounded fraction recorded in Samutprakarn site and Nonthaburi sites only (Fig 25).

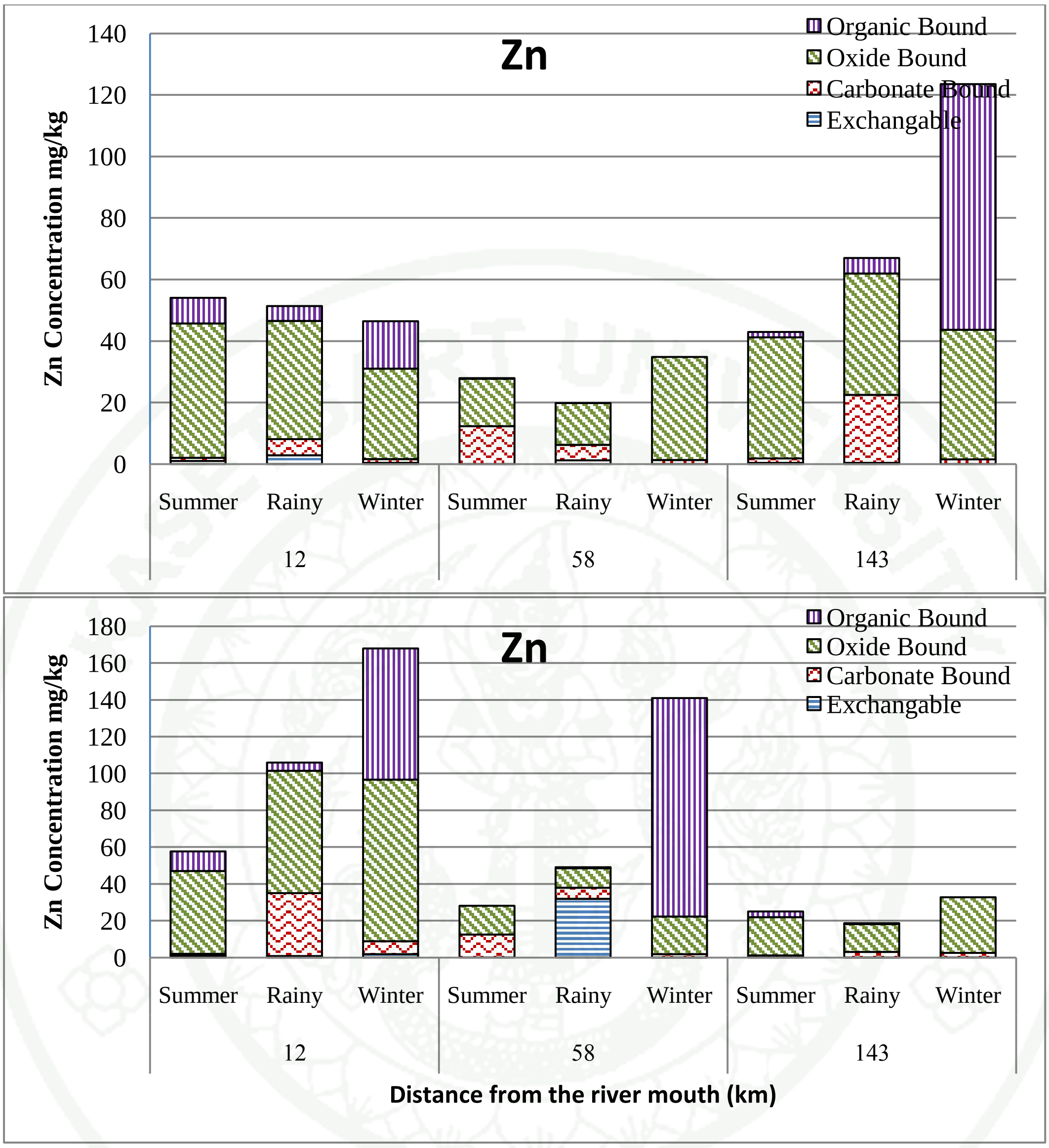


Figure 25 Comparison of distribution patterns of Zn in Summer (S) Rainy (R) and Winter (W) in (a) left and (b) right bank with distance of the river mouth.

Thus the bioavailable fractions were exhibited lower level Zn concentrations in both right and left bank at Ayuththaya, Nonthaburi and Samutprakarn sites.

Cd was exhibited its concentration for bioavailable fractions specially significant higher levels in exchangeable fraction at all three sites in both banks, predominantly for rainy and winter season. For the summer season it was appeared only in Ayththya site right bank and Samutprakarn site left bank. The Cd appeared in low levels for carbonate fraction in winter at Samutprakarn site, rainy at Ayuththaya and Nonthabury sites in right bank and at Nonthaburi site only in left bank (Fig 26).

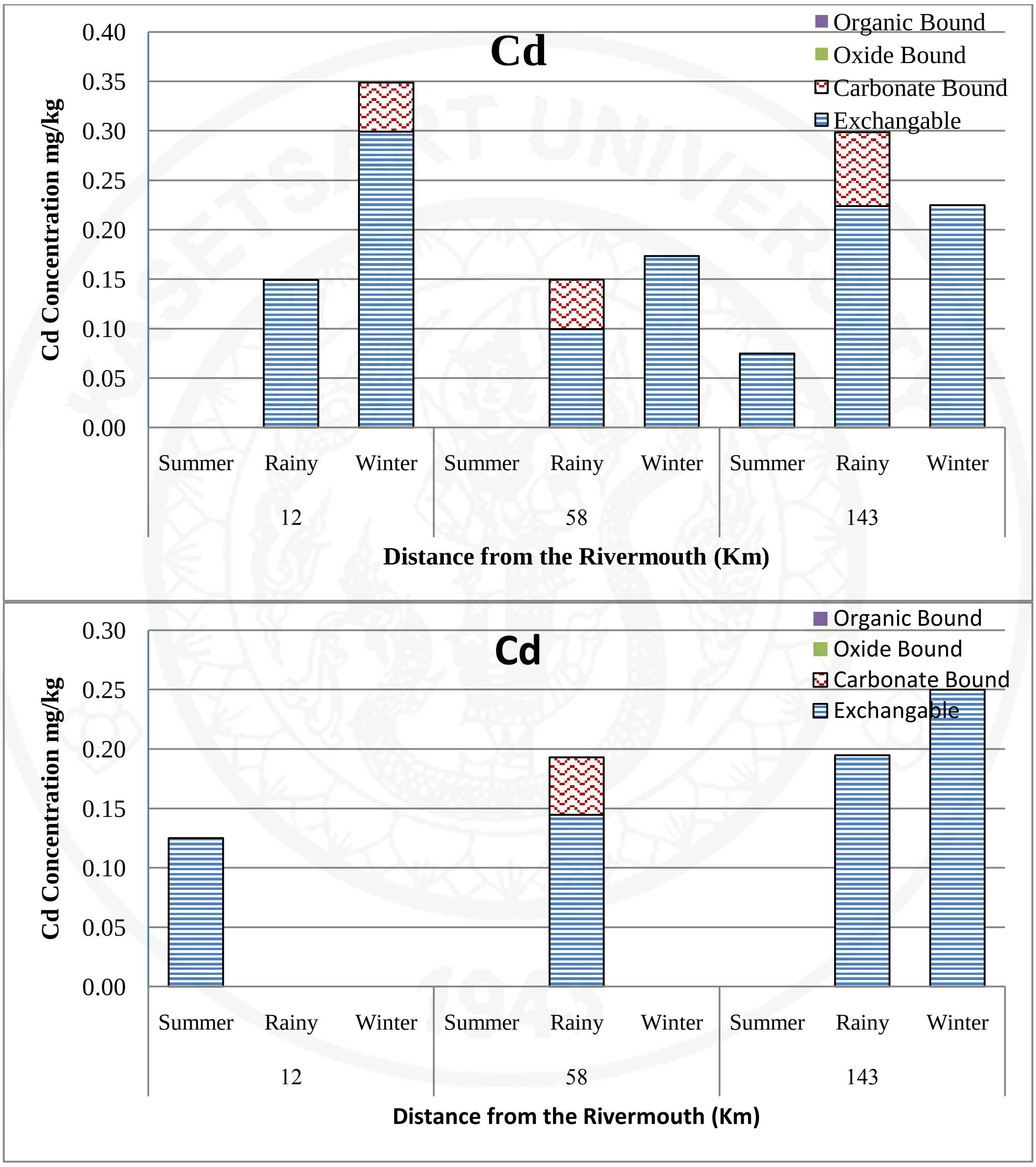


Figure 26 Comparison of distribution patterns of Cd in Summer (S) Rainy (R) and Winter (W) in (a) left and (b) right bank.

The distribution pattern varies within these three sites mostly in rainy and winter seasons with high concentration but low concentrations in summer season. For other two fractions Cd not represented any and it was This high level representation of Cd in exchangeable fraction is lead the mobility and high level environmental risk.

Cr exhibited quite different distribution than Zn and Cd with the seasonal availability (Fig. 27).

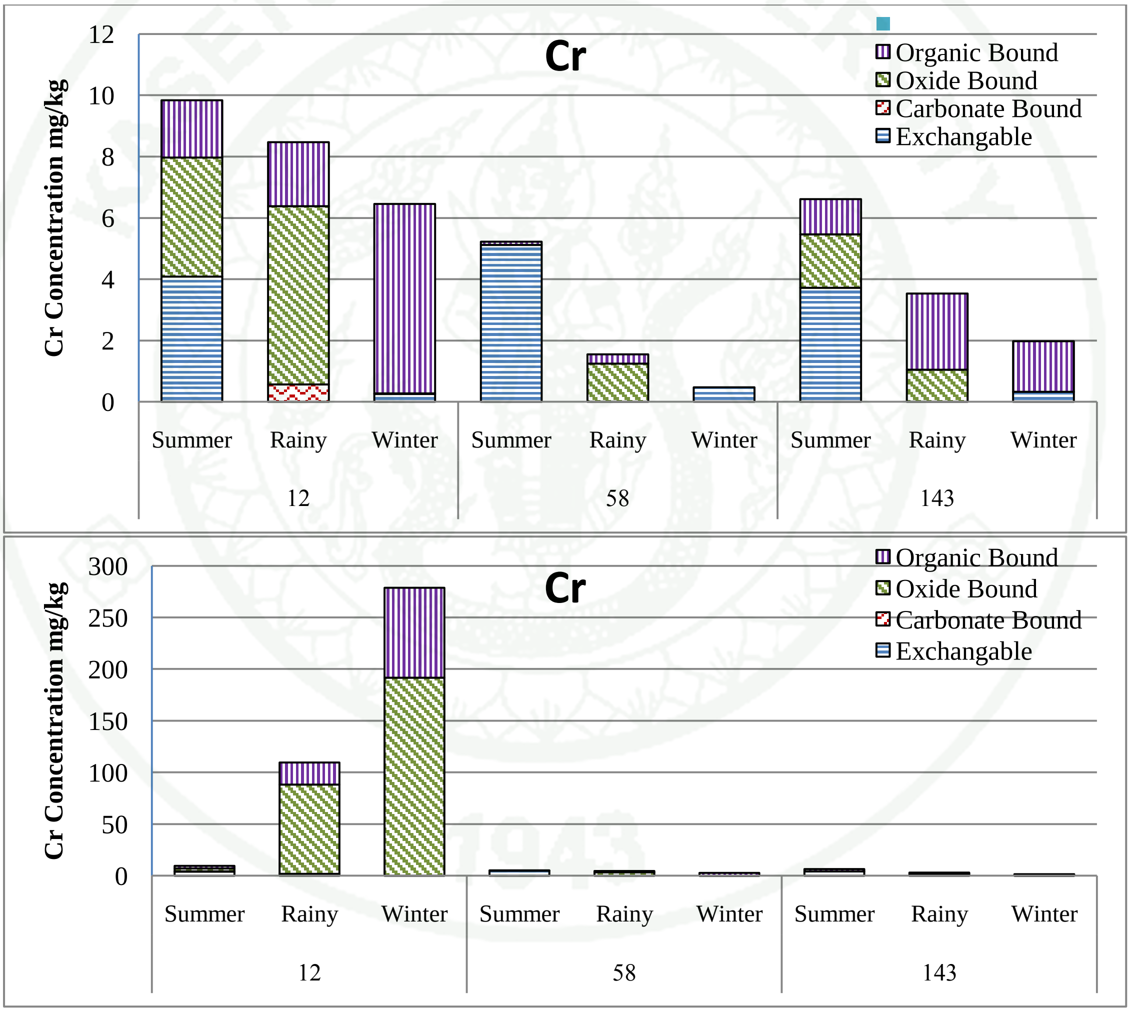


Figure 27 Comparison of distribution patterns of Cr in Summer (S) Rainy (R) and Winter (W) in (a) left and (b) right bank

It was available in exchangeable fraction in high level concentrations at summer season only. This higher level representation of Cr in exchangeable fraction may be due to Cr6+ which is liable and highly toxic. In carbonate fraction Cr was exhibited very low level representation which may arise due to the inability of Cr^{3+} to form a precipitate or complex with carbonate. It was absent in exchangeable fraction at most of the sites and distrusted its representation mostly oxide and carbonate fractions in rainy and winter seasons. On the other hand Cr exhibited low concentrations in left bank at sit 1 to 6 (below 20mg/kg) but very high at site 7 and 8 (above 80 mg/kg).

When it comes to the Ni, it was displayed a disperse variations among each fractions, site and the season (Fig. 28). Ni exhibited the higher level concentrations in exchangeable at Chainat site and Samutprakarn site in rainy season for right bank while carbonate fraction exhibited higher concentrations at site 2 in summer and rainy, at site 3 and 4 in summer and winter seasons. It was same at site 1 and at site 2-8of the of left bank very low level concentrations in exchangeable and higher level concentration in carbonate fraction. In oxide fraction and organic fraction Ni exhibited quiet high level concentrations and disperse representation for all sites in both bank but specially in winter season.

Table 13 summarized the potential level of the bioavailability based on the sum of the exchangeable and carbonate bond fractions and non- bioavailability fractions of heavy metals in each sediment samples. In bioavailable fraction the metal will be soluble and can be taken up by aquatic biota casing environmental toxicity if the pH and redox conditions are favorable. Fe and Mn were exhibited extraordinary values in both bioavailable and non-bioavailable fractions. In general Fe and Mn categorized as the most abundant metals in sediment. Present study also got higher values may be due to this reason. In Cd and Cr contribution is very low on bioavailable fraction but they exhibited a greater proportion in bioavailable form with seasonal variations. This may be impacted adversely by giving high environmental risk to the aquatic biota of the lower Chao Phraya River.

Table 13 Concentration of heavy metals in bioavailable and non-bioavailable fractions (mg/kg) in each sampling site of both banks

		Zn						Cr					
		Bio Available			Non-bioavailable			Bio Available			Non-bioavailable		
		Summer	Rainy	Winter	Summer	Rainy	Winter	Summer	Rainy	Winter	Summer	Rainy	Winter
Right bank	Site 1	0.723	10.379	2.243	10.773	36.449	287.559	3.541	0.000	0.324	0.648	2.436	0.000
	Site 2	1.844	5.329	0.575	5.879	23.508	18.785	3.587	0.000	0.425	0.000	5.080	0.000
	Site 3	1.021	8.165	0.275	4.483	27.432	137.459	3.487	0.000	0.450	0.000	2.240	0.000
	Site 4	1.795	22.449	1.574	41.189	44.550	121.977	3.715	0.000	0.325	2.892	3.534	1.649
	Site 5	4.143	13.356	1.840	43.331	46.098	96.519	4.268	0.000	0.398	0.349	4.236	0.448
	Site 6	12.309	6.224	1.363	15.629	13.593	33.456	5.118	0.000	0.471	0.100	1.544	0.000
	Site 7	4.754	20.496	15.532	60.364	45.686	94.583	3.962	0.000	0.249	2.575	2.846	8.201
	Site 8	2.042	8.099	1.646	52.046	43.277	44.788	4.083	0.571	0.274	5.756	7.900	6.185
Left bank	Site 1	2.138	12.977	1.967	7.854	19.627	53.282	4.449	0.000	0.174	0.298	2.541	0.000
	Site 2	1.244	7.911	0.449	11.444	18.947	74.065	3.931	0.000	0.175	0.697	4.067	0.000
	Site 3	1.734	5.622	0.300	24.869	12.040	30.401	4.161	0.000	0.025	0.892	2.786	0.000
	Site 4	1.193	2.968	2.547	23.755	15.616	30.170	4.324	0.000	0.150	2.187	3.211	1.299
	Site 5	1.538	9.069	2.088	8.035	29.676	5.916	4.216	0.293	0.199	0.546	5.476	0.000
	Site 6	12.506	37.861	1.837	15.627	11.286	139.049	5.067	0.000	0.099	0.050	4.823	2.631
	Site 7	4.717	14.932	8.769	56.235	45.662	127.484	3.968	0.000	0.447	2.537	7.973	2.733
	Site 8	1.995	35.058	8.866	55.596	70.815	159.039	4.317	1.873	0.000	5.336	107.671	278.950

Table 13 (Continued)

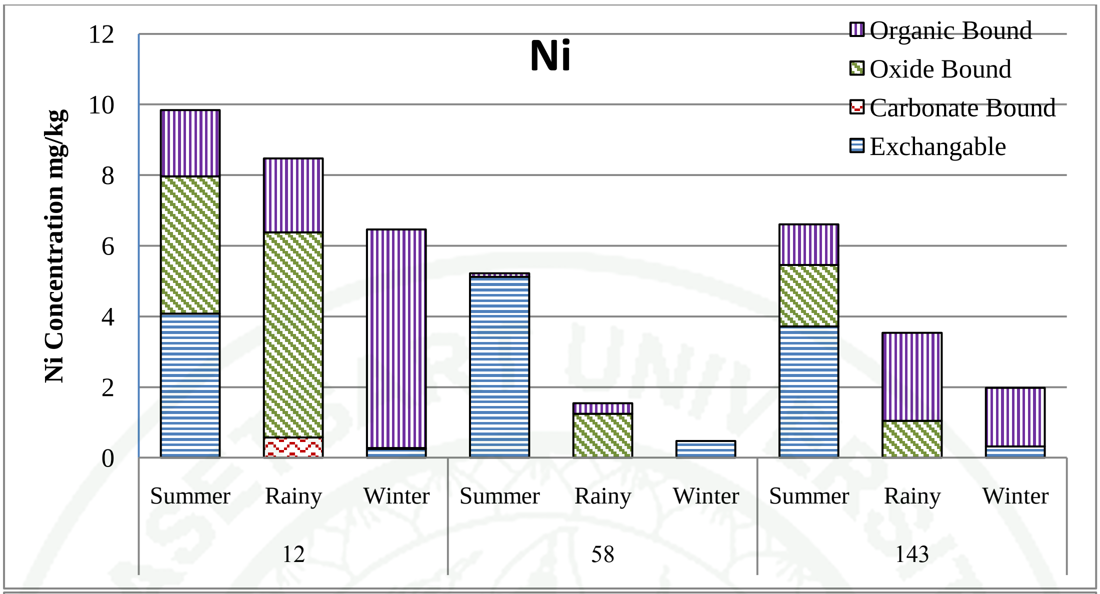
		Pb						Cd					
		Bio Available			Non-bioavailable			Bio Available			Non-bioavailable		
		Summer	Rainy	Winter	Summer	Rainy	Winter	Summer	Rainy	Winter	Summer	Rainy	Winter
Right bank	Site 1	0.000	0.000	0.000	1.297	2.826	6.679	0.274	0.195	0.249	0.000	0.000	0.000
	Site 2	0.000	0.000	0.000	0.498	7.969	9.542	0.000	0.349	0.200	0.000	0.000	0.000
	Site 3	0.000	0.000	0.000	1.544	2.290	22.093	0.050	0.224	0.175	0.000	0.000	0.000
	Site 4	0.000	0.000	0.000	7.779	1.444	15.491	0.075	0.299	0.225	0.000	0.000	0.000
	Site 5	0.000	0.000	0.000	0.000	2.641	8.702	0.100	0.299	0.249	0.000	0.000	0.000
	Site 6	0.000	0.000	0.000	1.997	0.000	11.846	0.000	0.149	0.173	0.000	0.000	0.000
	Site 7	0.000	72.923	0.000	7.081	367.985	25.596	0.000	0.175	0.373	0.000	0.000	0.000
	Site 8	12.889	0.000	0.000	3.296	0.298	19.002	0.000	0.199	0.299	0.000	0.000	0.000
Left bank	Site 1	0.000	0.000	0.000	1.243	0.847	12.897	0.000	0.149	0.224	0.000	0.000	0.000
	Site 2	0.000	0.000	0.000	3.234	0.000	12.519	0.000	0.347	0.150	0.000	0.000	0.000
	Site 3	0.198	0.000	0.125	5.895	0.348	105.881	0.000	0.199	0.200	0.000	0.000	0.000
	Site 4	0.000	0.000	0.949	1.839	0.000	22.028	0.000	0.195	0.250	0.000	0.000	0.000
	Site 5	0.000	0.000	1.143	0.000	0.000	5.568	0.000	0.196	0.075	0.000	0.000	0.000
	Site 6	0.000	0.916	1.415	1.897	0.000	34.799	0.000	0.193	0.000	0.000	0.000	0.000
	Site 7	0.000	294.671	1.813	7.632	303.982	29.412	0.025	0.198	0.000	0.000	0.000	0.000
	Site 8	15.035	0.599	1.189	3.139	0.000	28.331	0.000	0.125	0.000	0.000	0.000	0.000

Table 13 (Continued)

		Ni						Cu					
		Bio Available			Non-bioavailable			Bio Available			Non-bioavailable		
		Summer	Rainy	Winter	Summer	Rainy	Winter	Summer	Rainy	Winter	Summer	Rainy	Winter
Right bank	Site 1	0.289	0.414	0.000	1.496	0.000	2.193	0.000	0.000	0.000	0.000	1.949	0.548
	Site 2	14.888	0.647	0.000	0.100	0.000	3.497	0.000	0.000	0.000	0.000	5.827	1.099
	Site 3	20.350	0.000	1.525	0.000	0.000	2.999	0.000	0.000	0.050	0.000	1.245	0.400
	Site 4	19.487	0.000	1.324	5.286	0.000	8.945	0.025	0.373	0.025	6.283	5.376	7.795
	Site 5	0.000	0.000	1.815	0.000	0.000	3.829	0.000	0.274	0.050	1.048	4.934	5.172
	Site 6	0.000	0.000	1.933	0.499	0.299	4.956	0.000	4.655	0.273	2.195	15.784	2.181
	Site 7	0.000	0.000	2.162	1.288	5.642	12.773	0.074	1.173	2.187	6.586	16.727	25.795
	Site 8	0.187	0.522	2.020	2.952	0.745	12.768	0.000	1.863	0.000	6.051	6.906	10.673
Left bank	Site 1	0.000	0.274	0.722	0.497	0.000	3.486	0.000	0.000	0.000	0.348	2.889	0.598
	Site 2	0.000	0.000	0.549	0.149	0.000	3.392	0.000	0.000	0.000	0.846	3.025	0.848
	Site 3	0.000	0.000	0.075	2.725	0.000	4.343	0.272	0.100	0.000	2.130	2.687	1.647
	Site 4	0.000	0.000	0.924	3.876	1.605	9.291	0.000	0.219	0.000	5.516	4.378	17.532
	Site 5	0.000	0.196	0.149	1.934	2.200	1.641	0.000	1.076	0.000	1.339	6.698	0.050
	Site 6	0.000	0.000	1.589	0.399	0.965	11.418	0.000	0.892	0.000	1.997	2.556	13.255
	Site 7	0.000	0.000	1.888	1.348	5.299	13.116	0.100	0.842	0.025	6.353	15.303	20.072
	Site 8	0.187	0.000	1.065	3.995	1.848	16.741	0.000	2.322	0.000	6.273	18.228	29.866

Table 13 (Continued)

		Mn						Fe					
		Bio Available			Non-bioavailable			Bio Available			Non-bioavailable		
		Summer	Rainy	Winter	Summer	Rainy	Winter	Summer	Rainy	Winter	Summer	Rainy	Winter
Right bank	Site 1	22.0	18.6	18.2	234.0	141.8	121.6	6.9	1.2	1.8	4596.8	3629.5	3661.1
	Site 2	34.9	421.4	165.1	60.8	605.8	117.4	6.3	1.2	0.2	4514.1	7583.6	5263.7
	Site 3	25.3	35.0	22.9	402.0	127.6	311.0	5.3	59.3	1.5	4157.7	2888.9	4129.8
	Site 4	250.3	111.9	236.0	541.7	378.4	719.1	6.1	69.1	0.0	6893.8	4953.4	9452.4
	Site 5	42.4	58.0	257.4	253.2	127.3	236.4	10.2	32.6	0.0	4672.7	5592.2	8207.9
	Site 6	52.2	37.8	11.4	95.5	109.8	630.4	7.8	52.2	0.1	2356.0	11368.0	5216.0
	Site 7	71.1	298.6	384.6	211.4	433.5	349.7	5.1	139.3	1.6	4118.5	12043.8	12165.1
	Site 8	306.0	414.0	936.0	903.3	459.4	2216.4	34.6	180.9	0.5	13294.4	11006.4	10107.8
Left bank	Site 1	49.2	17.9	24.6	125.2	294.8	263.0	4.8	1.9	0.0	2963.7	3877.9	5006.6
	Site 2	53.8	17.0	23.0	446.3	200.1	213.0	19.9	0.4	0.1	7235.3	5041.7	7359.1
	Site 3	404.7	22.5	46.8	946.8	282.9	615.0	5.0	2.3	0.1	5734.1	4429.8	5522.7
	Site 4	219.6	29.2	287.8	740.7	286.4	1057.5	6.8	33.3	0.0	8426.1	4896.2	9099.0
	Site 5	182.5	59.5	9.9	249.4	124.3	128.1	8.1	30.4	0.0	4721.7	5620.6	1295.1
	Site 6	62.2	36.0	457.1	96.9	111.5	504.4	7.8	44.8	0.5	2157.9	3222.9	12175.4
	Site 7	71.5	194.5	370.5	223.7	525.5	494.4	5.3	103.2	1.8	3953.3	12758.2	11524.3
	Site 8	318.1	93.6	1333.7	916.7	240.1	1463.5	34.9	85.1	0.7	13937.1	5706.4	12202.1



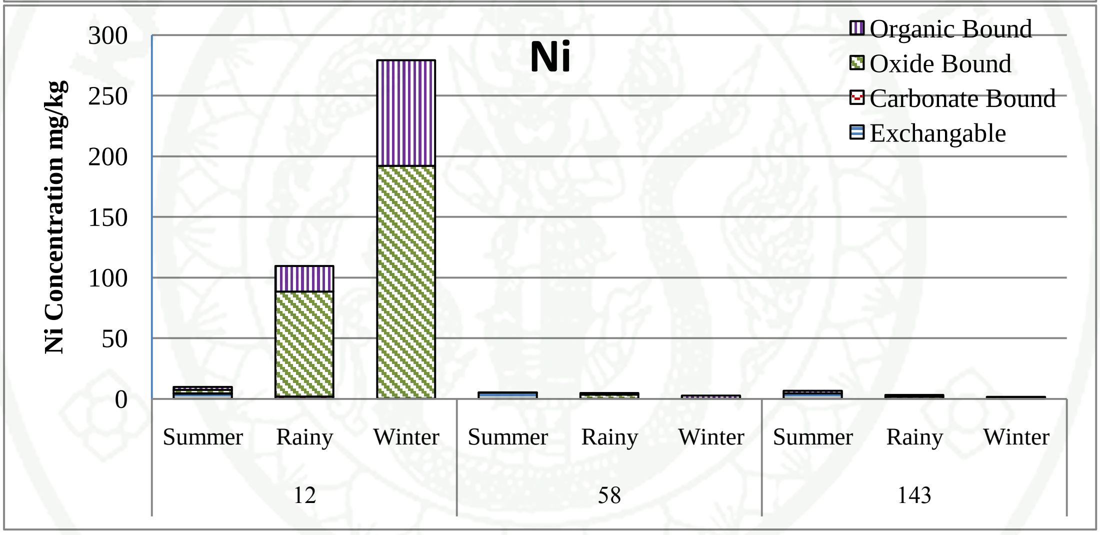


Figure 28 Comparison of distribution patterns of Ni in Summer (S) Rainy (R) and Winter (W) in (a) left and (b) right bank

The exchangeable and carbonate fractions can also be name as bioavailable fractions that when the favorable pH and redox conditions occur the metal will be soluble and can be taken up by flora or ingested by fauna of aquatic and riverine ecosystem initiating environmental toxicity. The oxide and organic bound fractions are then non-lithogenic or non-bioavailable fractions. Overall availability of metal in sediment reviled that the Fe and Mn were most abundant metals for this study too and their availability in bioavailable fractions also relatively high and contributed to environmental risk. The resulted concentrations of bioavailable fractions revealed that the Chao Phrya River has serious environmental concern on Cd, Cr, Mn, Zn and Ni contamination with seasonal and site variations. These variations may be due to weathering and transport properties of minerals, anthropogenic discharges, climate change and other components of the sediments but the contribution from the anthropogenic inputs are most significant. Thus continuous monitoring and regulating the inputs specially from the industrial and municipal effluents should be implemented as remediation measures on heavy metal contamination and environmental risk of the Lower Chao Phraya river.

CONCLUSION AND RECOMMENDATION

Conclusion

The results of the study reviled that the EC and TOC were significantly correlated with the distance from the river mouth. This variation may be due to the accumulation and deposition of the suspended particles along the river bank when it reaches the low elevations towards the river mouth. Specifically in sites at Ayuthaya ,Nonthaburi and Samutprakarn the average concentrations determined was higher than the corresponding other five sites for both bank. According to the SQGs comparison the values obtained for total metal concentration and sequential extractions reviled that toxic metals like Cd, Cr, Ni, Pb, Hg and As are of concern in the present study area may occasionally be associated with adverse biological impacts. Secondly the high level availability of toxic metals such as Cd, Cr, Ni, Pb, Mn and Cu at these three sites posing high environmental risk with the seasonal variability.

Finally can concludes that there is a considerable seasonal variation in the concentration of heavy metals and their speciation's in riverbank sediments with distance from the river mouth of lower Chao Phraya River

Recommendation

To overcome this environmental risk due to the current load of heavy metal discharges further investigations required for confirm the existence of sources and mitigation strategies. Thus integrated assessment including detailed source confirmation physicochemical analysis of water quality, vertical and surface sediment; toxicity bioassay and bio monitoring study with aquatic species is recommended for finalize the comprehensive mitigation strategy to ensure the environmental quality of the lower Chao Phraya River.

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APPENDICES

Appendix A

Appendix Table A1 Concentration of heavy metals in bioavailable and non-bioavailable fractions (mg/kg) in each sampling site

		Zn						Cr					
		Bio Available			Non-bioavailable			Bio Available			Non-bioavailable		
		Summer	Rainy	Winter	Summer	Rainy	Winter	Summer	Rainy	Winter	Summer	Rainy	Winter
Right bank	Site 1	0.723	10.379	2.243	10.773	36.449	287.559	3.541	0.000	0.324	0.648	2.436	0.000
	Site 2	1.844	5.329	0.575	5.879	23.508	18.785	3.587	0.000	0.425	0.000	5.080	0.000
	Site 3	1.021	8.165	0.275	4.483	27.432	137.459	3.487	0.000	0.450	0.000	2.240	0.000
	Site 4	1.795	22.449	1.574	41.189	44.550	121.977	3.715	0.000	0.325	2.892	3.534	1.649
	Site 5	4.143	13.356	1.840	43.331	46.098	96.519	4.268	0.000	0.398	0.349	4.236	0.448
	Site 6	12.309	6.224	1.363	15.629	13.593	33.456	5.118	0.000	0.471	0.100	1.544	0.000
	Site 7	4.754	20.496	15.532	60.364	45.686	94.583	3.962	0.000	0.249	2.575	2.846	8.201
	Site 8	2.042	8.099	1.646	52.046	43.277	44.788	4.083	0.571	0.274	5.756	7.900	6.185
Left bank	Site 1	2.138	12.977	1.967	7.854	19.627	53.282	4.449	0.000	0.174	0.298	2.541	0.000
	Site 2	1.244	7.911	0.449	11.444	18.947	74.065	3.931	0.000	0.175	0.697	4.067	0.000
	Site 3	1.734	5.622	0.300	24.869	12.040	30.401	4.161	0.000	0.025	0.892	2.786	0.000
	Site 4	1.193	2.968	2.547	23.755	15.616	30.170	4.324	0.000	0.150	2.187	3.211	1.299
	Site 5	1.538	9.069	2.088	8.035	29.676	5.916	4.216	0.293	0.199	0.546	5.476	0.000
	Site 6	12.506	37.861	1.837	15.627	11.286	139.049	5.067	0.000	0.099	0.050	4.823	2.631
	Site 7	4.717	14.932	8.769	56.235	45.662	127.484	3.968	0.000	0.447	2.537	7.973	2.733
	Site 8	1.995	35.058	8.866	55.596	70.815	159.039	4.317	1.873	0.000	5.336	107.671	278.950

Table A1 (Continued)

		Ni						Cu					
		Bio Available			Non-bioavailable			Bio Available			Non-bioavailable		
		Summer	Rainy	Winter	Summer	Rainy	Winter	Summer	Rainy	Winter	Summer	Rainy	Winter
Right bank	Site 1	0.289	0.414	0.000	1.496	0.000	2.193	0.000	0.000	0.000	0.000	1.949	0.548
	Site 2	14.888	0.647	0.000	0.100	0.000	3.497	0.000	0.000	0.000	0.000	5.827	1.099
	Site 3	20.350	0.000	1.525	0.000	0.000	2.999	0.000	0.000	0.050	0.000	1.245	0.400
	Site 4	19.487	0.000	1.324	5.286	0.000	8.945	0.025	0.373	0.025	6.283	5.376	7.795
	Site 5	0.000	0.000	1.815	0.000	0.000	3.829	0.000	0.274	0.050	1.048	4.934	5.172
	Site 6	0.000	0.000	1.933	0.499	0.299	4.956	0.000	4.655	0.273	2.195	15.784	2.181
	Site 7	0.000	0.000	2.162	1.288	5.642	12.773	0.074	1.173	2.187	6.586	16.727	25.795
	Site 8	0.187	0.522	2.020	2.952	0.745	12.768	0.000	1.863	0.000	6.051	6.906	10.673
Left bank	Site 1	0.000	0.274	0.722	0.497	0.000	3.486	0.000	0.000	0.000	0.348	2.889	0.598
	Site 2	0.000	0.000	0.549	0.149	0.000	3.392	0.000	0.000	0.000	0.846	3.025	0.848
	Site 3	0.000	0.000	0.075	2.725	0.000	4.343	0.272	0.100	0.000	2.130	2.687	1.647
	Site 4	0.000	0.000	0.924	3.876	1.605	9.291	0.000	0.219	0.000	5.516	4.378	17.532
	Site 5	0.000	0.196	0.149	1.934	2.200	1.641	0.000	1.076	0.000	1.339	6.698	0.050
	Site 6	0.000	0.000	1.589	0.399	0.965	11.418	0.000	0.892	0.000	1.997	2.556	13.255
	Site 7	0.000	0.000	1.888	1.348	5.299	13.116	0.100	0.842	0.025	6.353	15.303	20.072
	Site 8	0.187	0.000	1.065	3.995	1.848	16.741	0.000	2.322	0.000	6.273	18.228	29.866

Table A1 (Continued)

		Mn						Fe					
		Bio Available			Non-bioavailable			Bio Available			Non-bioavailable		
		Summer	Rainy	Winter	Summer	Rainy	Winter	Summer	Rainy	Winter	Summer	Rainy	Winter
Right bank	Site 1	22.0	18.6	18.2	234.0	141.8	121.6	6.9	1.2	1.8	4596.8	3629.5	3661.1
	Site 2	34.9	421.4	165.1	60.8	605.8	117.4	6.3	1.2	0.2	4514.1	7583.6	5263.7
	Site 3	25.3	35.0	22.9	402.0	127.6	311.0	5.3	59.3	1.5	4157.7	2888.9	4129.8
	Site 4	250.3	111.9	236.0	541.7	378.4	719.1	6.1	69.1	0.0	6893.8	4953.4	9452.4
	Site 5	42.4	58.0	257.4	253.2	127.3	236.4	10.2	32.6	0.0	4672.7	5592.2	8207.9
	Site 6	52.2	37.8	11.4	95.5	109.8	630.4	7.8	52.2	0.1	2356.0	11368.0	5216.0
	Site 7	71.1	298.6	384.6	211.4	433.5	349.7	5.1	139.3	1.6	4118.5	12043.8	12165.1
	Site 8	306.0	414.0	936.0	903.3	459.4	2216.4	34.6	180.9	0.5	13294.4	11006.4	10107.8
Left bank	Site 1	49.2	17.9	24.6	125.2	294.8	263.0	4.8	1.9	0.0	2963.7	3877.9	5006.6
	Site 2	53.8	17.0	23.0	446.3	200.1	213.0	19.9	0.4	0.1	7235.3	5041.7	7359.1
	Site 3	404.7	22.5	46.8	946.8	282.9	615.0	5.0	2.3	0.1	5734.1	4429.8	5522.7
	Site 4	219.6	29.2	287.8	740.7	286.4	1057.5	6.8	33.3	0.0	8426.1	4896.2	9099.0
	Site 5	182.5	59.5	9.9	249.4	124.3	128.1	8.1	30.4	0.0	4721.7	5620.6	1295.1
	Site 6	62.2	36.0	457.1	96.9	111.5	504.4	7.8	44.8	0.5	2157.9	3222.9	12175.4
	Site 7	71.5	194.5	370.5	223.7	525.5	494.4	5.3	103.2	1.8	3953.3	12758.2	11524.3
	Site 8	318.1	93.6	1333.7	916.7	240.1	1463.5	34.9	85.1	0.7	13937.1	5706.4	12202.1

Appendix B

1. The 5th ASEAN Civil Engineering Conference (ACEC), the 5th ASEAN Environmental Engineering Conference (AEEC) and the 3rd Seminar on Asian Water Environment (Asian Core Program of JSPS, NRCT and ERDT), 25-26 October, 2012. The Windsor Plaza, Ho Chi Minh City, Vietnam
2. Proceedings of the 2^{nd} International Conference on Environmental Engineering, Science and Management, March 27-29. 2013 at Pullman Khon Kaen Raja Orchid Hotel, Thailand
3. Certificate of Attendance 2^{nd} International Conference on Environmental Engineering, Science and Management, March 27-29. 2013 at Pullman Khon Kaen Raja Orchid Hotel, Thailand

Appendix B1

The 5th ASEAN Civil Engineering Conference (ACEC), the 5th ASEAN Environmental Engineering Conference (AEEC) and the 3rd Seminar on Asian Water Environment (Asian Core Program of JSPS, NRCT and ERDT) – Ho Chi Minh City, Vietnam

THE CONTAMINATION OF HEAVY METALS IN RIVERBANK SEDIMENTS FROM LOWER CHAO-PHARYA RIVER, THAILAND

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ABSTRACT

The total concentration and speciation of heavy metals (Cd, Cr, Ni, Mn, Zn, Pb, Fe, Cu, Hg, and As) were investigated in riverbank sediments (8 locations of left and right) of the lower Chao Phraya River to determine the contamination levels and bounding formations of these heavy metals. Slightly modified Tessier's analytical sequential extraction technique was applied to assess the four steps (exchangeable, carbonate bound, oxide bound and organic bound) fractions in surface sediment. Most of the elements studied were present at all locations and follows the trend as Fe> Mn> Cr> Zn> Hg> Cu> Ni> As> Cd> Pb. Three sample sites (Ayuththaya, Nonthaburi and Samutprakarn) were observed significantly high concentration levels for all elements. Substantial amount of Fe, Pb, Zn, Mn and Ni, was observed as oxide bond while Cd and Cr was totally observed in exchangeable fraction. In carbonate bound fraction the observed dominating trend was Ni> Mn> Zn. Toxic metals like Hg, As, Ni, Pb and Cd are of concern, which occasionally may be associated with adverse effects on aquatic biota based on the sediment quality guidelines (SQG). Continuous monitoring of the river sediment and deep studies on sediment size distribution, associate heavy metals, chemical speciation and risk assessment would be essential prerequisite to control the levels in threshold limits.

Key words: heavy metals, sequential extractions, speciation, sediment, risk assessment

Appendix B2

Seasonal Variations of Heavy Metals Speciation in Riverbank Sediment from the Lower Chao Phraya River, Thailand.

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ABSTRACT
This study presents the results of seasonal (summer, rainy and winter)variationof heavy metal contamination and speciation in riverbank sediments from the lower Chao Phraya River, Thailand. Surface sediment samples were collected from both left and right bank of the river (n=16) and analyzed, ten elements (Zn, Ni, Cd, Cr, Pb, Cu, Mn, Fe, As and Hg) for total metal concentration and eight elements (except As and Hg) for chemical speciation by USEPA standard method and slightly modifiedsequential extraction technique suggested byTessier, *et. al* (1979) [1](four fractions – exchangeable, carbonate bound, oxide bound and organic bound) respectively. The results reviledthatthe representation of Cd dominated all three seasons in exchangeablefractionwhile Cr dominated in the same in summer only. The high environmental risk of Cd, Cr, Mn, Zn, and Ni is observed due to their higher availability in exchangeable fraction. The availability of Ni, Pb, Mn, Zn, Cu and Cd in carbonate bound fraction also exhibits variationsin three seasons which may due to their special affinity towards carbonate and their co-precipitations with its minerals. Dominating representation of Fe and Mn may provide colloids of Fe-Mn oxides which can be act as the scavengers of other heavy metals such as Pb, Zn, Cr, Ni and Cuin oxide bound fraction.Thus, the proportions of the concentration of heavy metal in each fraction differ with metal type and have seasonal variations in their dominating order.Toxic chemicals such as Cr, Cd, Pb, Cu and Ni exceed the threshold levels of sediment Quality Guidelines(SQG) and severity levels differ with each season.

Keywords:chemical speciation; sediment, heavy metal, sequential extraction, sediment quality guideline.

Appendix B3

28R6-11

CERTIFICATE

This is to certify that

Ajith U K Ethugala

Presented the paper entitled

Seasonal Variations of Heavy Metals Speciation in Riverbank Sediment from the Lower Chao Phraya River, Thailand

at

The 2nd International Conference on Environmental Engineering, Science and Management
March 27-29, 2013 at Pullman Khon Kaen Raja Orchid Hotel, Thailand

March 28, 2013

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