การเปลี่ยนแปลงฟลักซ์ของซิลิเกตจากแผ่นดินลงสู่ทะเลที่ผ่านทางแม่น้ำเจ้าพระยา

นางสาววทานีย์ ฮึงรักษา

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THE CHANGE IN LAND-SEA SILICATE FLUXES THROUGH THE CHAO PHRAYA RIVER

Ms. Watanee Heungraksa

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วทานีย์ ฮึงรักษา : การเปลี่ยนแปลงฟลักซ์ของซิลิเกตจากแผ่นดินลงสู่ทะเลที่ผ่านทางแม่น้ำเจ้าพระยา (THE CHANGE IN LAND-SEA SILICATE FLUXES THROUGH THE CHAO PHRAYA RIVER) อ. ที่ปรึกษา : ศ.ดร. มนุวดี หังสพฤกษ์, อ. ที่ปรึกษาร่วม : ผศ.ดร. วิไลวรรณ อุทุมพฤกษ์พร 70 หน้า. ISBN 974-13-1165-6.

การศึกษาการเปลี่ยนแปลงฟลักซ์ของซิลิเกตจากแผ่นดินลงสู่ทะเลที่ผ่านทางแม่น้ำเจ้าพระยาเน้นการศึกษาหลักสองระการคือการเปลี่ยนแปลงตามฤดูกาลของซิลิเกตและสารอาหารอื่นๆ ในแม่น้ำเจ้าพระยาในปีพ.ศ. 2542 และการเปลี่ยนแปลงของปริมาณซิลิเกตในตะกอนของอ่าวไทยตอนบน ตอนกลางและตอนล่างรวมทั้งสิ้น 8 สถานีและตัวอย่างปะการังอายุ 40 ปีจากอ่าวไทยตอนบนโดยมีวัตถุประสงค์หลักเพื่อหาความสัมพันธ์ระหว่างฟลักซ์ของซิลิเกตกับประวัติการใช้ที่ดินบริเวณที่ราบลุ่มภาคกลางของประเทศไทยในอดีต

ผลการศึกษาพบว่าความเข้มข้นเฉลี่ยของซิลิเกตที่ละลายน้ำในแม่น้ำเจ้าพระยาปี พ.ศ. 2542 มีค่าเฉลี่ย 181.58 μM ความเข้มข้นในช่วงฤดูน้ำมากมีค่าสูงกว่าในฤดูน้ำน้อยเพราะในฤดูน้ำมากหน้าดินถูกชะล้างลงสู่แม่น้ำในปริมาณที่สูงกว่าในฤดูน้ำน้อยมีผลทำให้ปริมาณความเข้มข้นของซิลิเกตที่ละลายจากดินสูงตามไปด้วย นอกจากนั้นความเข้มข้นของซิลิเกตที่ละลายน้ำมีแนวโน้มลดลงเมื่อเข้าใกล้ปากแม่น้ำเนื่องจากการผสมผสานกันระหว่างน้ำในแม่น้ำกับน้ำทะเลที่มีปริมาณความเข้มข้นของซิลิเกตที่ละลายต่ำกว่า สำหรับปริมาณ biogenic silica ในตะกอนซึ่งก่อนการทดลองคาดว่าน่าจะมีการสะสมของปริมาณซิลิเกตในตะกอนชั้นบนต่ำกว่าในชั้นที่ลึกลงไปเนื่องจากการกักตะกอนของเขื่อนในตอนต้นของลำน้ำ จากการศึกษาพบว่าแนวโน้มการสะสมของซิลิเกตกลับเป็นไปในลักษณะตรงกันข้าม กล่าวคือความเข้มข้นมีแนวโน้มเพิ่มขึ้นในดินตะกอนชั้นบนของเกือบทุกสถานีแม้ว่าจะไม่ชัดเจนมากนัก ซึ่งสันนิษฐานว่ามีสาเหตุจากการผุพังของหน้าดินบริเวณตอนล่างของแม่น้ำที่มีมากขึ้นเนื่องจากการพัฒนาพื้นที่เพื่อทำการเกษตรและกิจกรรมอื่นๆ ทำให้ปริมาณซิลิเกตที่ถูกชะล้างลงสู่แม่น้ำมีค่าสูงกว่าปริมาณที่ถูกกักเก็บไว้เหนือเขื่อนนอกจากนั้นเปลือกของไดอะตอมอาจสามารถละลายน้ำได้ดีในทะเลเขตร้อนทำให้ปริมาณซากซิลิเกตจากไดอะตอมเพียงเล็กน้อยเท่านั้นที่ยังเหลืออยู่ในดินตะกอน

การศึกษาปริมาณ biogenic silica ในตัวอย่างปะการัง *Porites lutea* ไม่พบการเปลี่ยนแปลงที่ชัดเจนของปริมาณ biogenic silica ทั้งก่อนและหลังการสร้างเขื่อน อย่างไรก็ดีเราพบว่าความเข้มข้นของซิลิเกตมีค่าสูงผิดปกติในช่วงปีพ.ศ. 2493-2503 ซึ่งตรงกับช่วงที่มีการขุดพื้นที่บริเวณตอนบนของแม่น้ำเพื่อการสร้างเขื่อน

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สาขาวิชา วิทยาศาสตร์สภาวะแวดล้อม	ลายมือชื่ออาจารย์ที่ปรึกษา
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KEY WORD: DISSOLVED SILICATE / BIOGENIC SILICA / FLUX / CHAO PHRAYA RIVER / GULF OF THAILAND

WATANEE HEUNGRAKSA : THE CHANGE IN LAND-SEA SILICATE FLUXES THROUGH THE CHAO PHRAYA RIVER. THESIS ADVISOR : PROF. MANUWADI HUNGSPREUGS, Ph.D. THESIS CO-ADVISOR : ASSIST. PROF. WILAIWAN UTOOMPRURKPORN, Ph.D. 70 pp. ISBN 974-13-1165-6.

The study of the change in land-sea silicate fluxes through the Chao Phraya River focuses on two areas of interest: the seasonal change in silicate and other nutrients in the Chao Phraya River in 1999 and possible historical change in biogenic silica in eight sediment box cores and one 40-year old coral core taken from the Gulf of Thailand. The main objective is to try to evaluate the relationship between silicate fluxes and the historical land use changes in the Central Plain of Thailand.

The year-round average of dissolved silicate concentration in the Chao Phraya River in 1999 was 181.58 μM. The silicate concentration in the wet season was higher than silicate concentration in the dry season. In the wet season, larger amount of freshwater transported more dissolved and particulate materials into the river. This amount of materials released more silicate into the river water. Dissolved silicate concentration in the river water decreased toward the river mouth by dilution through the mixing process with low-silicate seawater. In the sediment box cores, we had expected that the biogenic silica concentration accumulated in the upper part of the cores would be lower than in the deeper part because a certain amount of sediment was trapped in major dams upstream. However, the opposite trend was found. The result showed a trend of slight increase in biogenic silica concentration in the upper part of the cores from most stations although the increase was not very distinct. This could be because of the increase in soil erosion downstream in recent years due to land clearance for agricultural practices and other uses was higher than the amount of suspended matter trapped in the dam reservoirs. It is also expected that the fragile siliceous diatom shells would dissolve faster in the tropical seas .

The analysis of biogenic silica concentration in coral bands of *Porites lutea*, showed no clear change in biogenic silica concentration either just before or after the dam construction. However, a very distinct peak was observed during late 1950s to the early 1960s which was the time of the major dam construction.

Program Environmental Science Student's signature

Field of study Environmental Science Advisor's signature

Academic year 2000 Co-advisor's signature

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CONTENTS

PAGE

ABSTRACT (THAI) iv
ABSTRACT (ENGLISH) v
ACKNOWLEDGEMENT vi
CONTENTS vii
LIST OF TABLES ix
LIST OF FIGURES x
CHAPTER
1. INTRODUCTION 1
1.1 Background 1
1.2 Objectives 7
1.3 Scope of the research 7
1.4 Research Terminology 7
1.5 Expected Output 9
2. LITERATURE REVIEW 10
2.1 Literature Review 13
3. METHODOLOGY 17
3.1 Study Area 17
3.2 Sampling 19
3.3 Sample Analysis 22
3.3.1 Water Sample Analysis 22
3.3.2 Sediment Sample Analysis 23
3.3.3 Coral Sample Analysis 24
3.4 Flux Estimation Method 25
4. RESULTS AND DISCUSSIONS 27
4.1 Weather Characteristics During the Sampling Period 27
4.2 Seasonal Variation of River Discharge 29

PAGE

4.3 Spatial Distribution of Physical Water Quality in the
Chao Phraya River 35
4.4 Spatial Distribution of Nutrients in the Chao Phraya River 41
4.5 Spatial Distribution of dissolved trace metals in river water 46
4.6 Spatial Distribution of biogenic silica in river sediment 48
4.7 Vertical Distribution of Biogenic Silica in Sediment Box Cores
from the Gulf of Thailand 49
4.8 Distribution of Biogenic Silica in Coral Bands 54
4.9 Material Fluxes 55
5. CONCLUSIONS AND RECOMMENDATIONS 57
REFERENCES 60
APPENDIX 64
BIOGRAPHY 70

LIST OF TABLES

TABLE PAGE

Table 2-1 Water Quality of the Chao Phraya River 16
Table 3-1 Sampling Stations in the Chao Phraya River 17
Table 3-2 Sampling Stations of Sediment Box Cores in the Gulf of Thailand 20
Table 4-1 Data of Discharge at the Ban Re Rai, Sanphaya, Chainat (C.13) in the dry and wet season 1999 30
Table 4-2 The Spatial Variation of Physical Parameters in the Chao Phraya River in the Dry Season 1999 37
Table 4-3 The Spatial Variation of Physical Parameters in the Chao Phraya River in the wet season 1999 39
Table 4-4 The Spatial Distribution of Nutrient Concentration in the Chao Phraya River in the Dry Season 1999 42
Table 4-5 The Spatial Distribution of Nutrient Concentration in the Chao Phraya River in the Wet Season 1999 44
Table 4-6 The Spatial Distribution of Dissolved Trace Metal Concentration in the Chao Phraya River in the Dry Season 1999 46
Table 4-7 The Spatial Distribution of Biogenic Silica in the River Sediment 48
Table 4-8 The Vertical Distribution of Biogenic Silica in Sediment Box Core from the Gulf of Thailand 50
Table 4-9 Comparison of daily net fluxes in <u>*metric tons*</u> per day of suspended particulate matter, total phosphorus, total nitrogen, dissolved silicate flowing through the lower basin of the Chao Phraya River in the dry and wet season 1999 55

LIST OF FIGURES

FIGURE PAGE

Figure 1-1 Biogeochemical cycle of Si in the world ocean at steady state 2
Figure 1-2 Carbon pumps in the ocean 3
Figure 1-3 The major players in the functioning of the marine biological pump 4
Figure 1-4 The major dams in the Chao Phraya River Basin 6
Figure 2-1 Silicate concentration in the Black Sea 12
Figure 3-1 Location of sampling stations in the Chao Phraya River 18
Figure 3-2 Sampling locations of sediment box core in the Gulf of Thailand 21
Figure 3-3 X-radiographed coral sample 24
Figure 3-4 The upper part of coral block, *Porites lutea*, collected from the Upper Gulf of Thailand in 1985 25
Figure 4-1 Comparison of daily discharge (m^3/s) at below theChao Phraya Dam between April 1999 and October 1999 29
Figure 4-2. Discharge condition of the Chao Phraya Watershed in the dry season (8 April 1999) 32
Figure 4-3 Discharge condition of the Chao Phraya Watershed in the dry season (25 April 1999) 33
Figure 4-4 Discharge condition of the Chao Phraya Watershed in the wet season (31 October 1999) 34
Figure 4-5 Spatial Distribution of Physical Parameters of Surface Water Quality in the Chao Phraya River in the Dry Season 1999 38
Figure 4-6 Spatial Distribution of Physical Parameters of Bottom Water Quality in the Chao Phraya River in the Dry Season 1999 38
Figure 4-7 Spatial Distribution of Physical Parameters of Surface Water Quality in the Chao Phraya River in the Wet Season 1999 40
Figure 4-8 Spatial Distribution of Physical Parameters of Bottom Water Quality in the Chao Phraya River in the Wet Season 1999 40

FIGURE PAGE

Figure 4-9 Spatial Distribution of Nutrients of Surface Water in the Chao Phraya River in the Dry Season 1999 43

Figure 4-10 Spatial Distribution of Nutrients of Bottom Water in the Chao Phraya River in the Dry Season 1999 43

Figure 4-11 Spatial Distribution of Nutrients of Surface Water in the Chao Phraya River in the Wet Season 1999 45

Figure 4-12 Spatial Distribution of Nutrients of Bottom Water in the Chao Phraya River in the Wet Season 1999 45

Figure 4-13 Spatial Distribution of Trace Metals of Surface Water in the Chao Phraya River of the Dry Season 1999 47

Figure 4-14 Spatial Distribution of Trace Metals of Bottom Water in the Chao Phraya River of the Dry Season 1999 47

Figure 4-15 Spatial Distribution of Biogenic Silica in river sediments of the Chao Phraya River in the Dry Season 1999 49

Figure 4-16 Vertical Distribution of Biogenic Silica in Sediment (Box) Core from the Upper Gulf of Thailand 52

Figure 4-17 Vertical Distribution of Biogenic Silica in Sediment (Box) Core from the Middle and Lower Gulf of Thailand 53

Figure 4-18 Temporal Accumulation of Biogenic Silica in Coral Bands 54

CHAPTER 1
INTRODUCTION

1.1 Background

Silicon, representing 27% of the lithosphere, is a major source of silicic acid, $Si(OH)_4$. This form of silicon represents more than 95% of all silicon compounds found in the world ocean. Silicic acid enters the world ocean via three different pathways. The first way is from chemical weathering of continental rocks and minerals through surface runoff and groundwater flow. The second important pathway, especially for long distance transport of siliceous materials, is the eolian erosion of the land surface or the advection of small lithogenic particles into the atmosphere, which is often found in desert areas. Some of these airborne materials enter the ocean surface and parts of them dissolve in seawater. Additionally, the weathering of submarine basalt resulting from hydrothermal high temperature reactions at mid-oceanic ridges and low temperatures alteration of the basalts of the oceanic crust is the third major geological pathway of the net transfer of dissolved silicate in the ocean (Figure 1-1) (Tréguer et al 1995).

In addition to being the major element composition of the earth crust, silicon is also one of major nutrient compositions in natural water. Diatoms need silicon as well as nitrogen and phosphorus for their growth. In pristine rivers, there used to be an excessive amount of silicon over nitrogen and phosphorus for diatom. However, this situation is being changed because of human activities. In many river systems, silicon is no longer present in an excessive amount. The worldwide proliferation of freshwater reservoirs has driven the decrease of Si/N rations since dissolved silicates is trapped and, unlike nitrogen and phosphorus, it can not be compensated by anthropogenic inputs from the drainage basin downstream the reservoirs. Modeling approach applied to a hypothetical river coastal zone system for a chronological succession of land use and management scenarios showed that if the Si/N ratio changes to smaller than 1, then the dominant species of phytoplankton will change from diatoms to non-diatoms instead. (LOICZ 1999).

The decrease in dissolve silicate flux to the sea and/or the change in nutrient composition (DSi:N:P ratio) is suggested to be responsible for a dramatic shift in species composition of phytoplankton. A good example is a case in Black Sea where a regulation of river by damming in river basins has substantially reduced dissolved silicate loads transported to the Black Sea and the Baltic Sea. This causes the decrease of diatom blooms in spring while flagellates bloom increases significantly. In addition to this effect, there are also several long-term impact to the food web since diatom is a primary producer in the food web. This includes the introduction of more algal blooms, less fish in the impact area, and change in carbon cycle (Ittekkot, Humborg, and Schäfer, 2000)

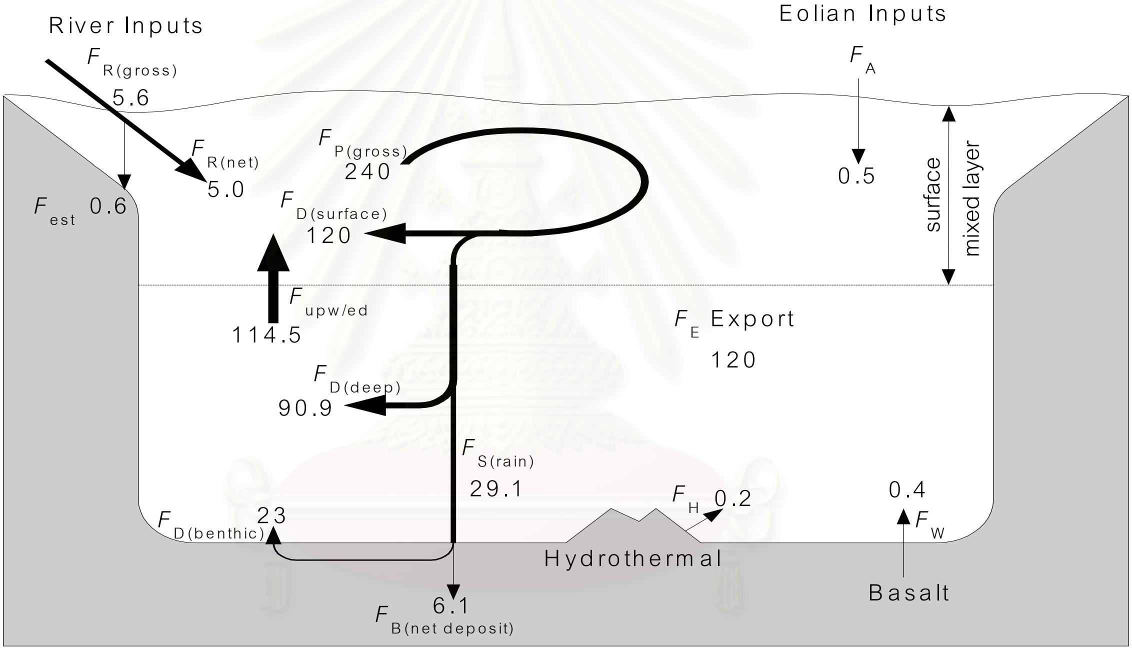


Figure 1-1 Biogeochemical cycle of Si in the world ocean at steady state. All fluxes are in teramoles of Si per year. $F_{R(gross)}$: River fluxes gross inputs, $F_{R(net)}$: River fluxes net inputs, F_A : Eolian inputs, F_W : Seafloor weathering inputs, F_H : Hydrothermal inputs, F_{est} : Net deposit of biogenic silica in estuaries, F_B : net deposit of biogenic silica in coastal and abyssal sediments, $F_{P(gross)}$: Biogenic silica gross production, $F_{D(surface)}$: Flux of silicic acid recycled in the surface reservoir, F_E : Flux of biogenic silica exported toward the deep reservoir, $F_{D(deep)}$: Flux of silicic acid recycled in the deep reservoir, $F_{D(benthic)}$: Flux of silicic acid recycled at the sediment-water interface, $F_{S(rain)}$: Flux of biogenic silica that reaches the sediment-water interface, $F_{upw/ed}$: Flux of silicic acid transferred from the deep reservoir to the surface mixed layer (Source : Tréguer et al. 1995)

Moreover, dissolved silicate is related to the carbon cycle (Figure 1-2). It plays an important role in the biological uptake of carbon dioxide (CO_2) by the ocean by the so called biological pump. Diatoms and coccolithophores (Figure 1-3), two major players in the process, uptake dissolved silicate and carbon dioxide in seawater for producing their skeletons. The efficiency of the biological pump in the short term is determined by the relative abundance of the two species which diatoms appear to be more efficient in carbon sequestration than coccolithophores. In the open ocean dissolved silicate demand of diatoms is met by silicate-rich water reaching the sea surface by upwelling. In the coastal waters diatoms populations are additionally sustained by silicate inputs by rivers. So any change in the river nutrient mix resulting from silicate reduction can have significant impact on carbon cycling in the coastal marine region

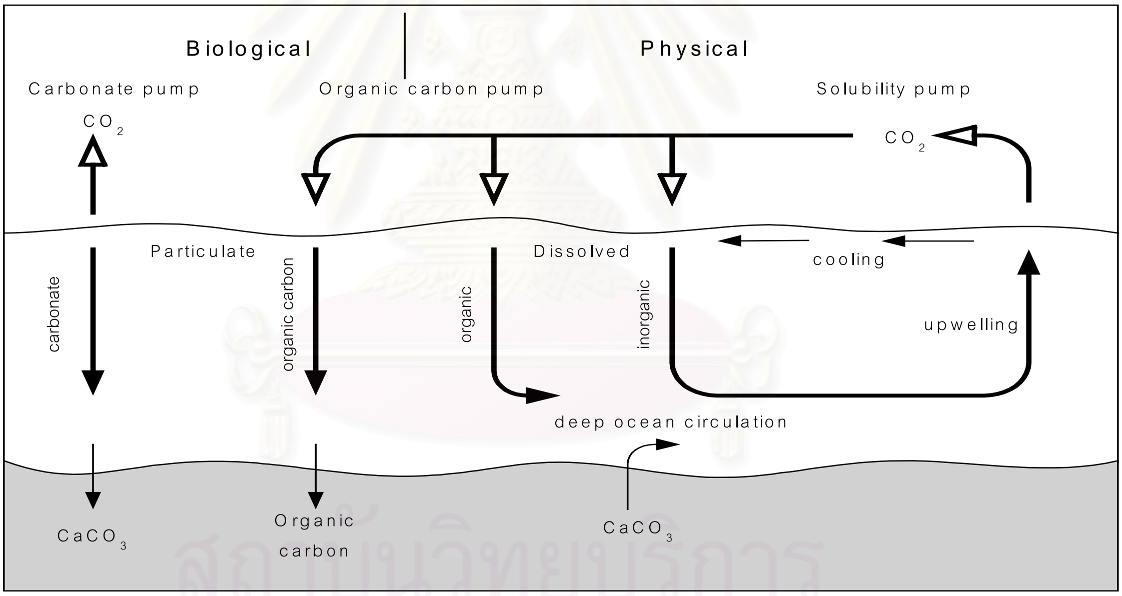
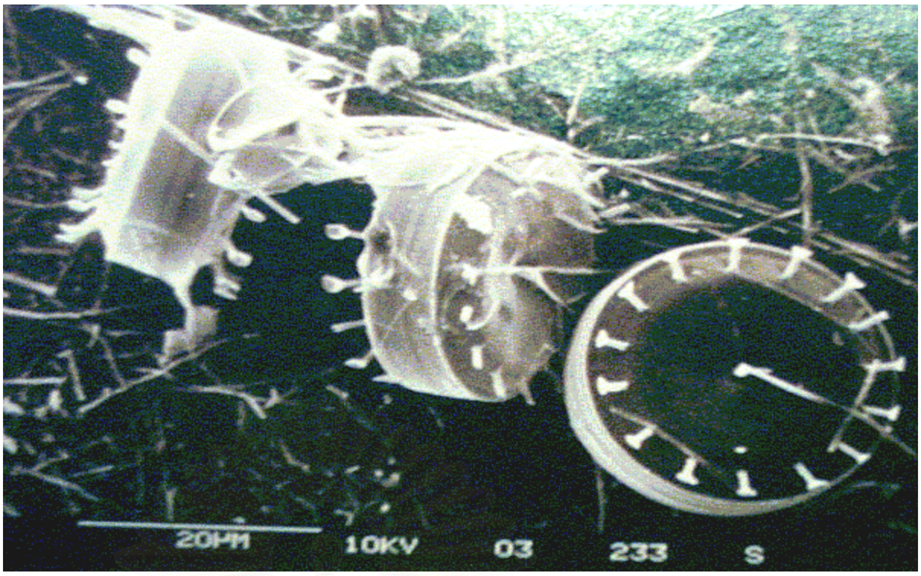


Figure 1-2 Carbon pumps in the ocean. Both physical and biological processes affect the exchange of CO_2 between the atmosphere and the ocean. The biological processes that are highlighted on the left are the formation of carbonate (the carbonate pump) and the formation of particulate matter during photosynthesis (the organic carbon pump). The right side of the diagram highlights the physical exchange processes, namely the dissolution of CO_2 in surface waters and its transfer to the deep sea in sinking water masses known as the solubility pump. CO_2 is brought back to the atmosphere via upwelling of water masses. (Source : Ittekkot, Humborg and Schäfer 2000)



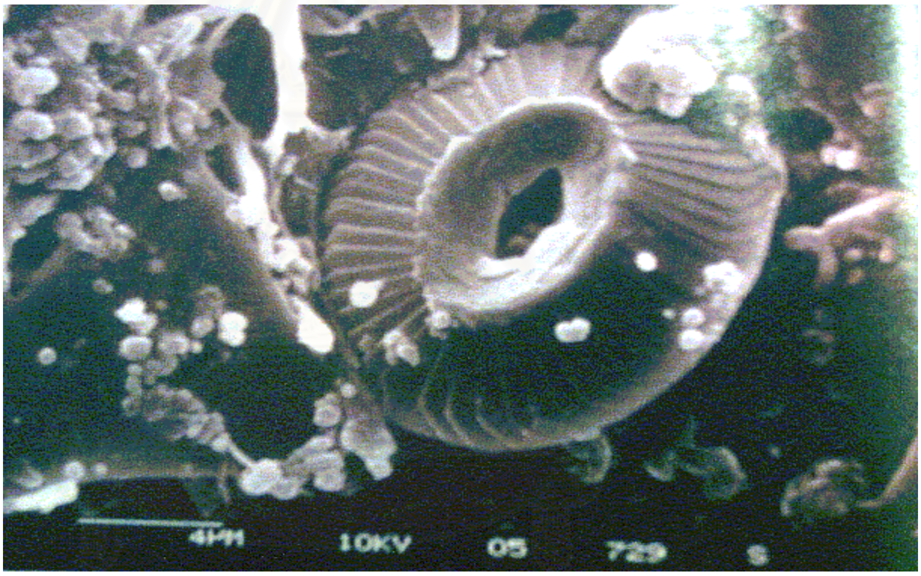


Figure 1-3 The major players in the functioning of the marine biological pump trapped on their way to the deep sea. Silica-shelled diatoms (upper). Carbonate-shelled-coccolithophorids (lower). Photos: Courtesy of Gerhard Fischer, University of Bremen (Source : Ittekkot, Humborg and Schäfer 2000)

The Chao Phraya River is the largest river located in the northern and central part of Thailand. It has a large influence on the population in the Central Plain for agriculture, industries and livelihood. As it flows through the agricultural and industrial zones and many populated towns and carries suspended sediments and a lot of domestic and industrial wastes to the Gulf of Thailand. Land use development from the past 40 years in the Chao Phraya River Basin for various irrigation projects such as the Chao Phraya Barrage Project (Chainat Dam) to divert water to irrigation canals and natural channels both on the left and right banks of the Chao Phraya River, Bhumibhol and Sirikit Reservoirs in the upper part of the basin and Chao Phraya Dam in the lower Basin (Figure 1-4) for regulating water flow for irrigation, salinity control, navigation, industry and domestic consumption including electricity generation of Bhumibhol Dam. Dam construction is an example of human activities which cause river diversion and river damming impacting on land-sea silicate fluxes through the river. Moreover, the situation of water quality caused by amount of phosphorus and nitrogen in the river especially the lower part from the Km 0 to 62 from the mouth of the river up to Nonthaburi Province which are lower than standard of Thai River (Department of Pollution Control 1997) would worsen nutrient composition to the sea. Those can be implied that the nutrient composition (DSi:N:P ratio) to the Gulf of Thailand might be changing as mentioned that silicon was trapped while nitrogen and phosphorus were increased. Any changes in nutrient compositions to the sea could have the continuous impacts on phytoplankton species composition to food web structures and to carbon cycle.

From those considerations, the research addressed the issue of the historical change in land-sea silicate fluxes through the Chao Phraya River of Thailand in order to determine whether historical land use changes in the Chao Phraya Watershed such as dam construction and/or river diversion for agriculture lead to reduced land-sea silicate fluxes.

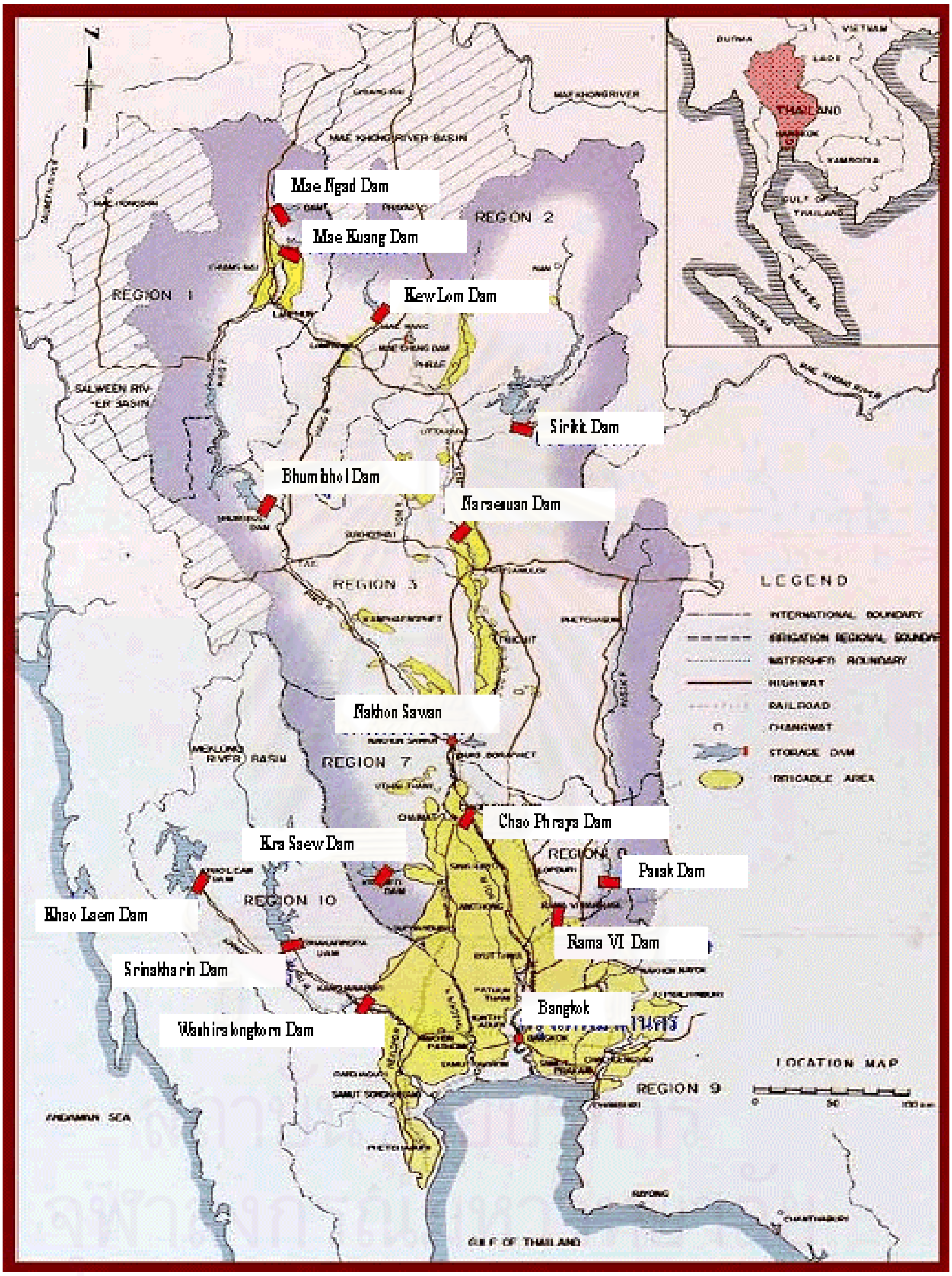


Figure 1-4 The major dams in the Chao Phraya River Basin
(Source : Royal Irrigation Department 2001)

1.2 Objectives

1. To study silicate fluxes through the Chao Phraya River to the Gulf of Thailand in the dry and the wet season 1999

2. To study the historical change in land-sea silicate fluxes through the Chao Phraya River

1.3 Scope of the research

1. The study area covered the Chao Phraya River from Kilometer 0, the mouth of the river (Samutprakarn Province), to Kilometer 94, Amphur Muang, Pathumthani Province

2. The study emphasized mainly on the amount of dissolved silicate in water and sediment samples taken from the Chao Phraya River in 1999. The samples of sediment box cores were taken from the Gulf of Thailand at Station 8a, 12a, 17a, 23a, 2, 20, 30 and 54 (Figure 3-2) by Office of Atomic Energy for Peace (OAEP) in 1992 and 1994 were studied for vertical biogenic silica profiles

1.4 Research Terminology

Silicon Compounds

Compounds of silicon are important in geochemistry and in biochemistry. The basic unit is the SiO_4 tetrahedra, the building block of many minerals and of amorphous precipitates in the cell walls of diatoms, the skeletons of radiolarians and silicoflagellates and the phytoliths in the stems of grasses. Each subdiscipline has developed its own terminology. The following terminology of silicon compounds can be distinguished for marine science discipline:

- Silicon, the element, used in connection with other nutrient elements, like phosphorus and nitrogen. In the earth crust silicon is not present in elemental form.

- Silicic acid, $Si(OH)_4$ or H_4SiO_4, produced when silica or silicates dissolve in water. It is a very weak acid. At the pH of seawater about 5% is dissociated into a monovalent anion $H_3SiO_4^-$

- Silicates, only present in the solid state, can be considered as salts of silicic acid.

- Silica, SiO_2, the oxide of Si. The mineralogical stable form is quartz, but it also occurs in less ordered, amorphous compounds which often contain impurities.

- Biogenic silica, amorphous silica produced by living organisms. It always contains some water, in the living organisms it is bound to an organic matrix.

Some other frequently used names

- Dissolved forms : "Dissolved silica" or "dissolved silicate" (both abbreviated as DSi) or "Reactive silicate", an operational definition, formally those dissolved Si-compounds measured with molybdenum blue colorimetry, widely used for its determination. Dissolved siliceous compounds, unreactive in the "molybdenum blue procedure" did not exist in natural waters (Burton et al 1970). DSi, silicic acid, reactive silicate all refer to the same compound, H_4SiO_4. It would be less confusing if this compound would always have the same chemically correct name, silicic acid. DSi is widely used. There is no confusion when molar units are used for its concentration. The use of mg/l should be discouraged. It is often difficult to decide if mg/l SiO_2-Si (molecular weight 28) or mg/l SiO_2 (molecular weight 60) is used.

- Particulate forms : Biogenic silica (the same as biogenic opal) is often abbreviated as BSi, both in suspension and in sediments. Non-biogenic silica in suspension is abbreviated as LSi (Lithogenic)

Silicate Fluxes

The terms “gross” and “net” silicate fluxes are used to define the amount of silicate transported to the marine environment and the amount transported through the estuarine-nearshore region to the open ocean, respectively. The concept of gross and net land-sea silicate flux implies a boundary zone through which silicate passes. For the research this zone is assumed to be the estuary of the Chao Phraya River.

The gross flux of silicate is dominantly influenced by biogeochemical characteristics of the Chao Phraya Watershed and its hydrology. There are natural contributions to its gross fluxes depending on watershed geology, land use, climatology and weathering regime.

The processes that control net fluxes are primarily those that affect distribution of silicates between phases during transport through the estuarine-nearshore (or continental shelf) environment. These regions are sedimentary traps thus contaminants associated with particles accumulate nearshore. Important processes include adsorption-desorption and precipitation-dissolution reactions, biological uptake and microbial degradation of organic matter that results in remobilization of some siliceous materials.

1.5 Expected Output

1. Comparison of current land-sea silicate fluxes through the Chao Phraya River with the earlier time
2. Assessment of the impact of change in land-sea silicate fluxes on living resources in the Gulf of Thailand and carbon cycle
3. Impact assessment of hydrological cycle changes on land-sea silicate fluxes

CHAPTER 2
LITERATURE REVIEW

Little is known about the change in land-sea silicate fluxes although it is well-known that any change in land-sea silicate fluxes resulting from either land use change by human activities or the decrease of diatom production in natural inland waters would have an impact on nutrient composition (DSi:N:P ratio) of river water and seawater. The assumption that nitrogen and phosphorus fluxes have increased as a result of human activities and they are likely to remain high is begun with the decrease of silicate fluxes by the retention of dams upstream. This will result in the decrease in Si/N, P fluxes to the sea. The ratios of Si/N or Si/P have probably declined from > 4:1 to 1:1 or less (LOICZ 1999) which will cause the changes in the species composition of phyto- and zooplankton in the coastal zone. The changes in flux ratio have evolved with the responses of the ecosystem which can be summarized as follows :

1. The decrease in diatom population because it requires silicon.

2. The increase in nitrogen and phosphorus fluxes will encourage primary production of other phytoplankton groups that do not require high amount of silicon. It results in eutrophication of flagellates, for instance.

3. Silicon limitation may terminate diatom blooms and leave excess nitrogen and phosphorus in the water column. This residual nitrogen and phosphorus may then lead to subsequent blooms of non siliceous organisms as seen in the cases in the Southern North Sea, Black Sea, Japanese Coastal Waters, the Great Lakes and some Danish Estuaries (LOICZ 1999).

However, the evidence of changes in planktonic ecosystems in response to changing Si/N, P inputs are not widespread. These may be the result of several factors as follows :

1. The scale of perturbation of nutrient ratios may not yet reach the changing point of producing effects in those environments except in the areas of particularly intense environmental pressures.

2. The samplings have not been done in the areas most seriously affected.

3. Some coastal areas are strongly influenced by offshore exchange, the process that is subject to climatic control, but insensitive to changes in riverine nutrient inputs.

Although the evidence for widespread perturbations of coastal ecosystems by changes in Si/N, P inputs is limited, some impacts in some areas that justify serious concerns can be identified as follows :

1. Loss of diatoms may lead to perturbations of food webs based on those diatoms, as grazers adapt to the new dominant phytoplankton

2. Anoxia condition may occur in deep waters. The severity of this condition depends on the vertical mixing and the fluxes of carbon in deep water which is controlled by the size of phytoplankton and grazing regime.

3. The phytoplankton that develop to utilise residual N and P after Si exhaustion may produce nuisance algal species.

4. Changes in phytoplankton species can modify emissions of trace gases such as dimethylsulphide (DMS), organohalogens, CO_2, CO and N_2O (via denitrification) and hence may have climatic effects and impacts on atmospheric acidity, raising the possibility of a feedback on weathering rates.

Hydrological alterations such as river damming and river diversion for regulating river flow has substantially reduced dissolved silicate loads to the sea and changed in the chemistry of river inputs with long-term consequences for coastal ecosystems. The Danube River impacting on the Black Sea is an example of river damming by a placed call "Iron Gate" where located approximately 1,000 Km upstream, on the Yugoslavian Rumanian border by the year 1970-1972 (Figure 2-1). The available data of pre- and post-dam periods showed significant changes in silicate inputs as a result of water and sediment trapped in the reservoirs with consequent changes in the biogeochemistry of the river, the adjacent coastal waters, and the entire Black Sea Basin. Retention of silicate in the upstream reservoir has decreased in silicate concentration from pre-dam levels of 140 μmol/L to post-dam levels of 58 μmol/L with a drop in the annual silicate load from 800 $\times 10^3$ tons to 230-320 $\times 10^3$ tons (Humborg et al 1997).

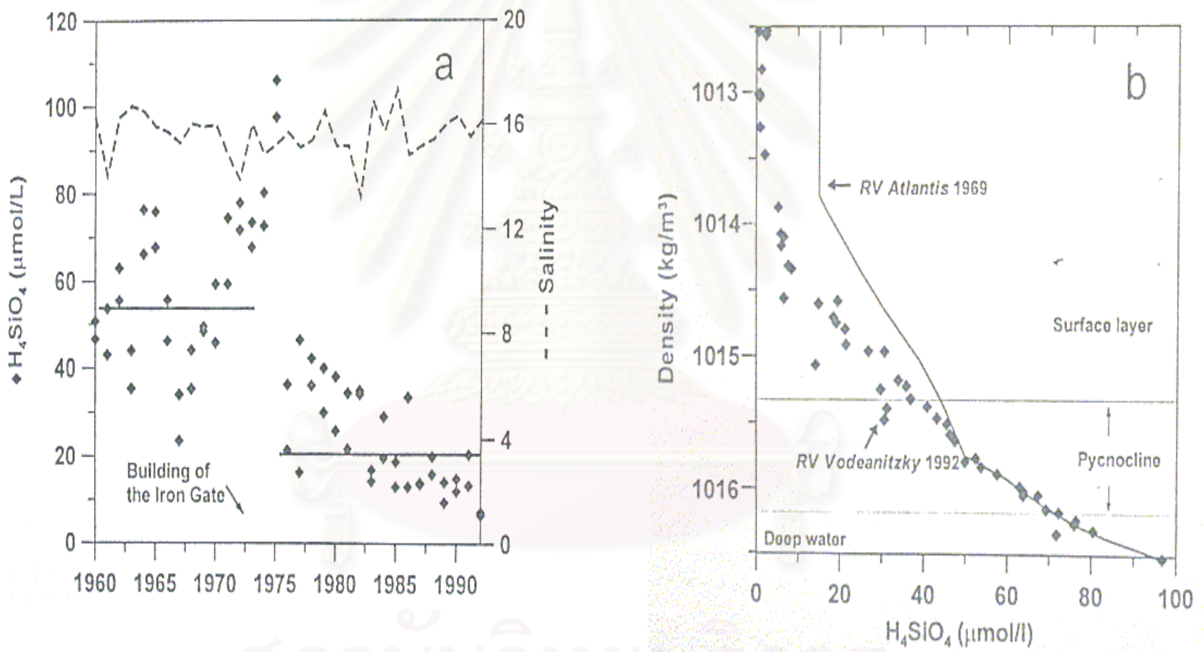


Figure 2-1 Silicate concentration in the Black Sea. (a) Mean winter silicate concentration at a coastal station (Constanta, Romania) approximately 60 nautical miles south of the Danube River Mouth. The bold lines show overall medians from 1960-1972 and 1973-1992. The salinity at this station has remained at approximately S = 15 (dashed line), indicating that the effect of the Danube on salinity has not changed over time. (b) Composite profiles of silicate plotted against density; observations for 1969 from RV Atlantis and observations for 1992 from RV Vodeanitzky. (Source : Humborg et al. 1997)

2.1 Literature Review

Most studies of the impact of changing Si/N, P inputs have been done in temperate latitudes. The general principles arising from those studies are likely to apply in other areas. At low latitude, for example, high temperature produce faster degradation and dissolution of silicon hence it may affect to changes in Si/N, P fluxes. Climate change effects are likely to be more important than the effects of increasing anthropogenic inputs at high latitude by which rises in temperature may increase weathering rates and mobilization of glacial flour via glacier retreat causing the increase of Si fluxes.

The net inputs of silicic acid (dissolved silica) to the world ocean was 6.1±2.0 teramoles of silicon per year (1 teramole = 10^{12} moles) and the major contribution about 80% comes from rivers, whose world average silicic acid concentration is 150 micromolar. These inputs are reasonably balanced by the net outputs of biogenic silica of 7.1±1.8 teramoles of silicon per year in modern marine sediments. The gross production of biogenic silica (the transformation of dissolved silicate to particulate skeletal material) in surface waters was estimated to be 240±40 teramoles of silicon per year, and the preservation ratio (opal accumulation in sediment/gross production in surface waters) averages 3%. In the world ocean the residence time of silicon relative to total biological uptake in surface waters is about 400 years (Tréguer, et al 1995)

The resulting changes in the ratios of nutrient elements (Si:N:P) have caused shifts in phytoplankton populations in water bodies. The evidence of coastal eutrophication near the Mississippi River Delta indicated that riverine nitrogen loading increased substantially by 1980 while the silica loading had declined by 50 % (Turner and Rabalais 1994). Additionally, early eutrophication evidence in the lower Great Lakes studied from biogenic silica in down-core sediments showed that eutrophication in the lower Great Lakes resulted from nutrient enrichment associated with early settlement and forest clearance (Schelske, Stoermer, Conley, Robbins, and Glover 1983)

Silicate inputs fertilize the seas by stimulating the production of diatoms. It links to the food webs and play a crucial role in the biological uptake of CO_2 by the ocean through the operation of the so-called "biological pump" (Smetacek 1998). The exchange of CO_2 between the atmosphere and the ocean is affected by both physical and biological processes (Heinze, Maier-Reimer, Winn 1995). The equatorial Pacific upwelling area provides another example of the linkage between $Si(OH)_4$ and carbon. The net flux of CO_2 is from the ocean to the atmosphere. The dominant phytoplankton in terms of numbers are the picoplankton. However, diatoms are present in smaller numbers and also in biomass (12% of the total chlorophyll), but appear to take up most of the NO_3. Apparently, most of the flux processes are related to diatoms and most of the regenerated production is related to the picoplankton. Upwelled equatorial water is low in $Si(OH)_4$ compared to NO_3 and so is expected to be limiting to diatom growth. Since some critical measurements have not been made in this upwelling system, modelling has been the major source of information on the $Si(OH)_4$ related processes in the euphotic zone. These results suggest that there is a threshold $Si(OH)_4$ source water concentration below which the picoplankton dominate the CO_2 processes and above that diatoms control CO_2 export and evasion to the atmosphere. Such model results compare well with observed vertical distribution of NO_3, $Si(OH)_4$ and CO_2 (Dugdale 1999)

The hydrological alterations on land such as river damming and river diversion caused silicate reductions to the coastal sea (Humborg et al 1997). It is a retention of water and sediment discharge and a possibility of impact on the change in chemistry of river inputs with consequences for coastal ecosystems. Long-term data sets of water and nutrient discharge from the Danube River to the Black Sea revealed a reduction in the dissolved silicate loading by about two-thirds since dam construction in the early 1970s. The decrease in wintertime of dissolved silicate concentrations by more than 60% was observed in central Black Sea surface waters. The consequent changes in silicon to nitrogen ratio of the Black Sea nutrient load appear to be larger than those caused by eutrophication alone, and seem to be responsible for dramatic shifts in phytoplankton species composition from diatom to coccolithophores and flagellates (non-siliceous). The large number of dams in operation around the world could similarly affect the change as mentioned above.

Historical data sets on silicate input to the Gulf of Thailand through the Chao Phraya River showed no trend of decreasing silicate concentration while concentrations of nitrogen and phosphorus nutrient showed some increase during the past 20 years (Table2-1) (Utoomprurkporn, 1999). The higher concentration and more discharge in the wet season caused the fluxes of these nutrients to the Gulf of Thailand were much higher (Pitiwatanakul 1990). In the low flow season a silicate removal was observed along the estuary while in the high flow season it behaved conservatively (Umnuay 1984) which it showed the seasonal variation to the behavior of silicate controlling by flow rate between two seasons. From the study of abundance, species composition and distribution of phytoplankton in relation to the water conditions in the Chao Phraya Estuary and its adjacent waters (Boonyapiwat 1983), dissolved silicate concentration decreased rapidly in December during the bloom of *Chaetoceros pseudocurvisetum*. However the study showed no change in phytoplankton species composition in the Upper Gulf of Thailand

For the Gulf of Thailand silicate data sets were available only during 1973-1983 (Department of Fisheries, unpublished data) which was part of the monitoring programme of the Sub-Committee on Water Quality and the Quality of Living Resources in Thai Waters. High concentration were observed at stations near the river mouths and there was no clear seasonal variation of silicate concentration.

The impact of dam reservoirs on material fluxes to the coastal sea was also observed by investigating biogenic silica profiles from down-core sediments and 40-year bands of coral, *Porites lutea*, taken from the Upper Gulf of Thailand. The study in sediment cores showed no clear decreases in biogenic silica in the upper part of sediment cores corresponding the post-dam period. However, the record in the coral bands seems to be more promising in reflecting the material flux change due to dam construction. (Hungspreugs et al 2000)

Table 2-1 Water Quality of the Chao Phraya River[1]

Date	Salinity	Silicate (μM)	Phosphate (μM)	Nitrate (μM)	Reference
High Flow					
August 92	0-0.3	-	1.6-7.7	11-82	PCD., 1994
October 89	0.18-22.5	118-301	3.6-17.7	84-251	Utoomprurkporn et al., 1990
August 89	0-20.0	110-292	4.1-10.7	0-28	Piyakarnchana et al., 1991
October 83	0-20.3	40.2-120.2	0.3-2.8	-	Umnuay, 1984
June 83	0-17.7	13.3-141.3	1.1-3.5	-	Umnuay, 1984
1980-1981	0.08-21.48	0-158	0.1-3.7	1-23	Boonyapiwat, 1983
Low Flow					
April 98	0.2-14.2	46.5-188.4	3.9-9.2	15-48	Unpublished data
March 93	0-23.1	-	1.9-12.3	6-41	PCD., 1994
March 90	0.5-25.76	84-180	4.3-8.3	11-119	Utoomprurkporn et al., 1990
December 89	0-16.5	199-253	0.8-3.0	1.5-4.4	Piyakarnchana et al., 1991
April 83	0-15.8	13.5-124.2	3.3-6.7	-	Umnuay, 1984
1980-1981	9.62-21.81	31-190	1.2-9.7	0-29	Boonyapiwat, 1983

[1] Utoomprurkporn, W. and Hungspreugs, M. 1999. A review of historical data set of silicate input into the Gulf of Thailand. Paper presented at LOICZ/SCOPE Workshop on Land-Ocean Nutrient Fluxes: The Changing Silica Cycle, Linköping, Sweden. 3-5 October 1999.

CHAPTER 3
METHODOLOGY

3.1 Study Area

The study area was focused on the Lower Chao Phraya River from Km 94, north of Bangkok, till it enters the sea in the Upper Gulf of Thailand. The River at Km 94 was not affected by seawater intrusion in both studied seasons. The 16 sampling stations (Figure 3-1) were selected accordingly to the river flow system and environmental characteristics on the banks which can be described in Table 3-1

Table 3-1 Sampling Stations in the Chao Phraya River

Station	Distance in kilometer from the River Mouth	Environmental Characteristics on the Nearest River Bank
1	94	Low density residential zone and some agricultural area
2	88	Low density residential zone
3	78	Low-medium density residential zone
4	72	Medium density residential zone
5	64	Medium density residential zone
6	60	Medium density residential zone and Power house
7	52	High density residential and commercial zone
8	37	High density residential zone
9	27	Bangkok Port
10	17	High density industrial zone
11	12	High density industrial zone
12	7	High density industrial zone
13	0	The Chao Phraya River Mouth
14	-5	The Chao Phraya Estuary
15	-5(R)	The Chao Phraya Estuary (right hand)
16	-5(L)	The Chao Phraya Estuary (left hand)

Figure 3-1 Location of sampling stations in the Chao Phraya River
(Source : National Research Council of Thailand 1995)

3.2 Sampling

Samplings were carried out in the dry season (9 and 24 April 1999) and in wet season (12 and 13 October 1999). Hydrological parameters recorded in field measurements in each sampling station were depth, pH, temperature, dissolved oxygen and salinity at surface and bottom water levels by probe meters and STD Instrument.

Surface and bottom water samples were collected by using 2.5 L GO-Flo teflon bottle which had been thoroughly cleaned. Water samples for nutrient determination were transferred to 500-ml high density polyethylene bottles and for trace metal determination were transferred to 1 L low density polyethylene bottles then stored at temperature below $4^{o}C$.

Sediment samples in the river particularly the top layer from each sampling station were collected by using Van Veen Grab Sampler and transferred to clean polyethylene bags then kept frozen for determination biogenic silica.

An extensive review of the available historical data set (Table 2-1) on nutrient inputs through the rivers, especially silicate, to the Gulf of Thailand was carried out but it did not show any trend of the change. Thus, another alternative methodology used in the research for studying the historical change in land-sea silicate fluxes through the Chao Phraya River was the investigation of biogenic silica accumulated in sediment core and coral cores.

Out of 22 box cores taken up from the Upper Gulf, the Middle Gulf, and the Lower Gulf of Thailand for radionuclide study during 1992 and 1994 by Radioactive Waste Management Division, Office of Atomic Energy for Peace (Srisuksawad et al 1997), the study was made on 8 cores located at the Station 8a, 12a, 17a, and 23a from the Upper Gulf, Station 2, 20, 30 from the Middle Gulf, and Station 54 from the Lower Gulf (Figure 3-2). Approximate sedimentation rates as determined by radionuclide distribution are shown in Table 3-2.

Table 3-2 Sampling Stations of Sediment Box Cores in the Gulf of Thailand

Station	Location		Water Depth (m)	Accumulation Rates		
				$mg/cm^2/yr$	At Interface (cm/yr)	At Depth (cm/yr)
Upper Gulf						
8a	13° 20' N	100° 40' E	18	270	0.78	0.35
12a	13° 02' N	100° 31' E	20	270	0.31	0.25
17a	12° 59' N	100° 30' E	24	490	0.41	0.47
23a	12° 45' N	100° 30' E	25	310	0.21	0.18
Mid-Gulf (west side)						
2	11° 55' N	100° 20' E	30	310	0.39	0.29
20	9° 50' N	99° 35' E	23	260	0.40	0.35
Lower Gulf						
30	10° 20' N	101° 45' E	70	140	0.15	0.29
54	7° 35' N	103° 00' E	51	190	0.40	0.25

Source : Srisuksawad et al 1997

The coral sample was taken up in February 1985, was a domed-shaped *Porites lutea* coral block, of approximately 1 m in height and 1.5 m in width dislodged from the shallow water off Kangkao Island, near Si Chang Island to the east of Station 12a approximately 14 Km offshore (Figure 3-2). Biogenic silica in individual bands was analyzed to compare the concentration between the period of pre- and post-dam construction in the Central Plain of Thailand

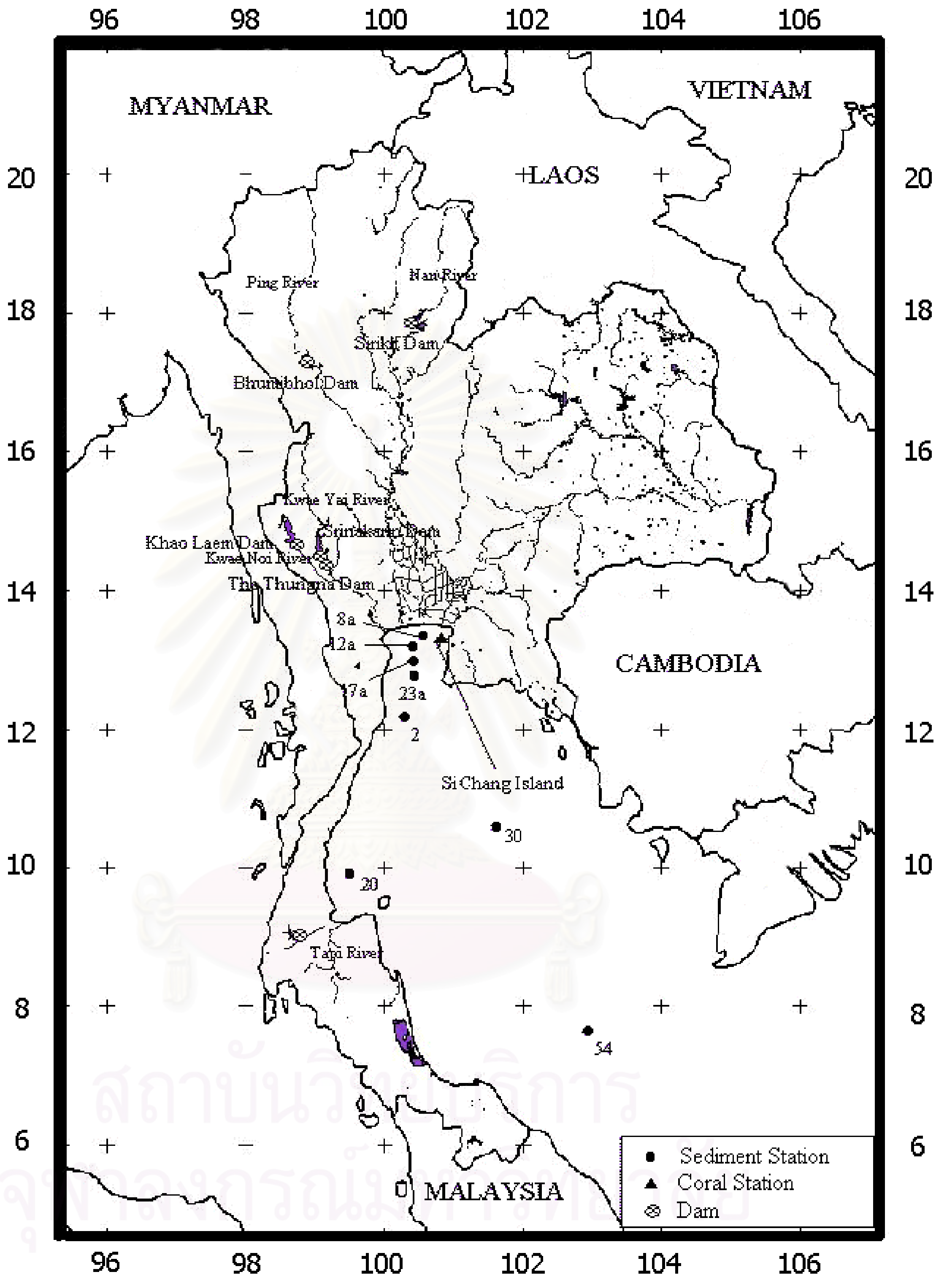


Figure 3-2 Sampling locations of sediment box core in the Gulf of Thailand collected during 1992-1994 by Radioactive Waste Management Division, Office of Atomic Energy for Peace (Srisuksawad et al 1997)

3.3 Sample Analysis

3.3.1 Water Sample Analysis

3.3.1.1 Determination of reactive dissolved silicate

The collected water samples were filtered through 0.45 μm GF/C filter papers in the laboratory. These filtered water samples were then diluted appropriately depending on the concentration of dissolved silicate containing to the measurable concentration at wavelength of 810 nm in the spectrophotometer. Ten milliliter of diluted water samples were added to the 4 ml molybdate solution in 50 ml plastic tubes and stood for 10 minutes. Then, add 6 ml reducing reagent consisting of metol sulphite solution, oxalic acid solution, sulphuric acid solution and distilled water in the ratio of 5:3:3:4. The solution was allowed to stand for 2 hours to complete the reduction of the silicomolybdate complex before measuring the absorbance at 825 nm with a spectrophotometer comparing with the absorbance of standard silicate solution at various concentrations between 0-50 μM. (Strickland and Parsons, 1972)

3.3.1.2 Determination of total dissolved phosphorus

After filtration of the water sample (from 3.3.1.1 above), ten milliliter of water sample was added with 1 ml mixed reagent containing molybdate solution, sulphuric acid solution, ascorbic acid solution and potassium antimonyl tartrate solution. The resulting complex heteropoly acid was reduced *in situ* to give the blue solution. The absorbance was measured in a spectrophotometer at wavelength of 885 nm within the first 2-3 hours comparing with the absorbance of standard phosphate solution at various concentrations between 0-100 μM. (Strickland and Parsons, 1972)

3.3.1.3 Determination of total phosphorus

Total phosphorus in unfiltered water samples were determined by oxidizing total phosphorus to inorganic phosphate with oxidizing agent (25 g potassium persulphate, 15 g boric acid in 175 ml 1 M sodium hydroxide solution making up the volume to 500 ml with distilled water) in autoclave at temperature 110-115 $^{\circ}$C for 30 minutes. Then analyzed total phosphosrus in the samples as described in item 3.3.1.2 (Strickland and Parsons, 1972)

3.3.1.4 Determination of total nitrogen

Total nitrogen in unfiltered water samples were determined similarly with the same oxidizing reagent in determining total phosphorus (in 3.3.1.3 above). After oxidizing organic to inorganic nitrogen, the water samples were run through a column containing cadmium filings loosely coated with metallic copper. The nitrite thus produced was determined by diazotizing with sulphanilamide and coupling with *N*-(1-napthyl)-ethylenediamine to form a highly coloured azo dye then measuring in a spectrophotometer at wavelength of 540 nm comparing with the absorbance of standard nitrate solution at various concentrations between 0-100 μM (Strickland and Parsons, 1972)

3.3.1.5 Determination of trace metals

After filtration with 0.45 μm nuclepore membrane filters, filtered water samples were acidified with concentrated HNO_3 (Suprapure) to yield a 0.1% acid solution. The concentration of dissolved trace metals were preconcentrated by using the cobalt-APDC coprecipitation technique then measuring the absorbance of the samples in a flameless graphite furnace atomic absorption spectrophotometer (AAS) comparing with the absorbance of each standard trace metal solution. (Boyle and Edmond, 1977 modified by Huizenga, 1981)

3.3.2 Sediment Sample Analysis

3.3.2.1 Determination of biogenic silica

The sediment sample was freeze-dried overnight and crushed in an agate mortar with its pestle. Biogenic silica in each sediment samples were extracted with alkaline solution (2M Na_2CO_3) after treatment with 10% H_2O_2 to remove organic matter and 1N HCl solution. Dissolved silicon concentration in the extract was determined by molybdate-blue spectrophotometry (Mortlock and Froelich, 1989)

3.3.3 Coral Sample Analysis

3.3.3.1 Determination of biogenic silica

The coral sample was left to dry in the sun for a week before coring along the line of growth at the Asian Institute of Technology Laboratory. The core was sliced vertically into slabs of about 8 mm thick. Then, the section was X-radiographed (Figure 3-3) and an exact size print was made for identification of bands. Individual bands were cut off using a stainless steel file. It was note that the top three-quarter of the coral show the band-width of the low density band of approximately 4-6 mm alternating with the high density band of 3-5 mm thickness (Figure 3-4). Nearest the bottom of the coral, the bands were more dense with narrower band width. The fragments of each band after cleaning with distilled water in an ultrasonic bath and subsequently dried were kept in a clean white plastic bottle until analysis

An approximately 500 mg coral sample of individual band was weighed into a teflon beaker and digested with 10% HNO_3 by which complete dissolution occurred. The extract was determined for dissolved silicon by molybdate-blue spectroscopy (as described by Hungspreugs et al. 2000)

Figure 3-3 X-radiographed coral sample

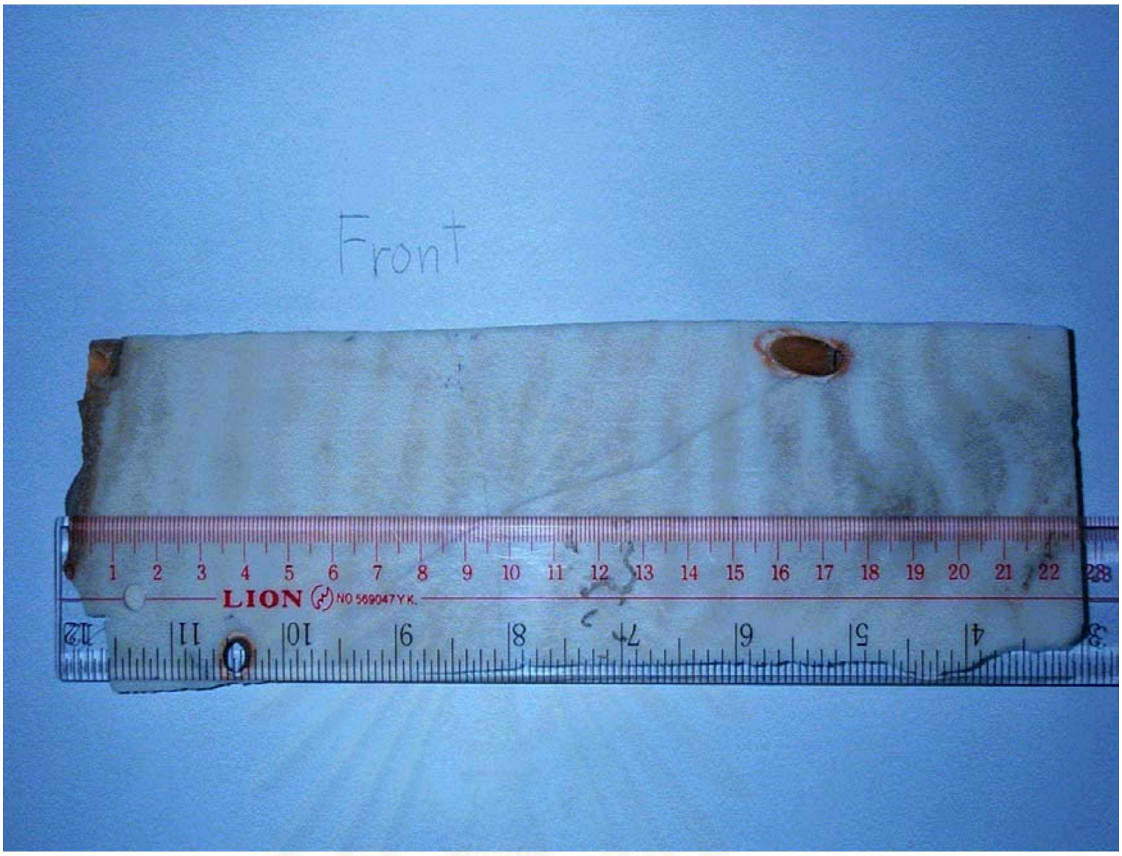


Figure 3-4 The upper part of coral block, *Porites lutea*, collected from the Upper Gulf of Thailand in 1985

3.4 Flux Estimation Method

The procedure of estimating the land-sea silicate fluxes through the Chao Phraya River was the interpolation method proposed by Joint Group of Experts on the Scientific Aspects of Marine Pollution - GESAMP (1987). It based on the instantaneous values of dissolved silicate concentration and volume of river flowing across the channel section at estimating station. The flux calculation was described as follows :

$$\text{Silicate Flux} = \Sigma C_n V_n = \int_0^t CnVndt$$

Where C_n = the instantaneous values of dissolved silicate concentration (μg/l)

V_n = the instantaneous values of volume of the Chao Phraya River flow across a channel section at estimating station (m^3/s)

t = period of flux estimation (day)

Silicate fluxes in 1999 were then estimated by comparing flux variation between the wet and the dry season

CHAPTER 4
RESULT AND DISCUSSION

4.1 Weather Characteristics During the Sampling Period

Dry Season 1999 (April)[1]

The Chao Phraya River is located in the central plain of Thailand. During May to October the climate is normally influenced by the southwest monsoon which in 1999 arrived unusually early in April. The monsoon originates from the Indian Ocean with high humidity blowing through the continent causing rainfall.

In April 1999, the numbers of rainy days were 15 with the monthly rainfall at 189.6 mm. The daily maximum rainfall was 43.6 mm on 6^{th} April 1999. The monthly evaporation was 120.4 mm with the daily mean evaporation at 4.2 mm. The monthly mean relative humidity was 77% and the monthly mean temperature was 29.7 °C

During the first 7 days (2^{nd}-8^{th} April 1999) of the first sampling (9^{th} April 1999) there were three days of rain and one of them (6^{th} April 1999) had the maximum rainfall of the month. The total rainfall for the whole 8 days was 52.1 mm, the evaporation was 36.9 mm, mean relative humidity was 76% and mean temperature was 29.8 °C.

For the daily rainfall of 9^{th} April 1999 was 1.6 mm while the daily evaporation was 4.4 mm, the daily mean relative humidity was 73% and the daily mean dry temperature was 30.5 °C

On the second sampling of the dry season (24^{th} April 1999) there was no rain. The daily evaporation was 4.4 mm with the daily relative humidity at 71% and the daily mean temperature was 29.6 °C. During the seven days before the sampling (17^{th}-23^{rd} April 1999) there was the rainfall of about 6.3 mm, the evaporation was 28.3 mm, the mean relative humidity was 75% and the mean temperature was 30.3 °C

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[1] Source : Royal Irrigation 1999. Summary Report of Monthly Discharge Condition as of April 1999

Wet Season 1999 (October)[2]

At the beginning of October 1999, a low-pressure atmospheric zone covered the lower part of the Southern region until mid-October. After that, a high-pressure atmospheric zone from South China Sea moved down and covered the lower part of Central and Southern region. On 23rd October, a low-pressure atmospheric zone developed around the Indo-China Peninsula and developed to a depression on 25th October around Amphur Pranburi, Prachuab-Khirikan Province. Then, the depression moved to Bengal Gulf and developed to a cyclone in Indian Ocean.

This depression caused a heavy rainfall covering a large area of Thailand including the Eastern region, Western region, the upper area of Southern region, and Bangkok. The other part of Thailand had only little rainfall.

In October 1999, the numbers of rainy days were 17 with the monthly rainfall at 383.8 mm. The daily maximum rainfall was 96.4 mm on 3rd October 1999. The monthly evaporation was 99.3 mm with the monthly mean evaporation at 3.5 mm. The monthly mean relative humidity was 80% and the monthly mean temperature was 28.0 °C

During the first seven days (5th-11th October 1999) of the first sampling (12th October 1999) there were three days of little rain at 1.5 mm, the evaporation was 23.5 mm, mean relative humidity was 76% and mean temperature was 29.3 °C.

The daily rainfall of 12th October 1999 was 4.4 mm while the daily evaporation was 3.2 mm, the daily mean relative humidity was 78% and the daily mean dry temperature was 29.2 °C

For the second sampling of the wet season (13th October 1999) there was rain at 32.5 mm. The daily evaporation was 6.2 mm with the daily relative humidity at 82% and the daily mean temperature was 28.1 °C.

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[2] Source : Royal Irrigation 1999. Summary Report of Monthly Discharge Condition as of October 1999

4.2 Seasonal Variation of River Discharge

Dry Season 1999 (April)

Daily discharge at below the Chao Phraya Dam, Chainat Province as of 1st April 1999 was 8.6×10^6 m^3/day (99.8 m^3/s) which had decreased to 4.8×10^6 m^3/day (56.2 m^3/s) at the end of April (Figure 4-1). The approximate discharge through the Chao Phraya River in Bangkok Area as of 9th April 1999 was 7.2×10^6 m^3/day (83.9 m^3/s) and as of 24th April 1999 was 5.6×10^6 m^3/day (65.0 m^3/s) (Table 4-1) (Royal Irrigation Department 1999)

Wet Season 1999 (October)

Daily discharge at the Chao Phraya Dam (Chainat Province) as of 1st October 1999 was 149.9×10^6 m^3/day (1,735.6 m^3/s) which increased to reach maximum at 192.6×10^6 m^3/day (2,229.8 m^3/s) on 21st October 1999 (Figure 4-1). The average discharge of sampling day in the wet season was 142.6×10^6 m^3/day (1,651.0 m^3/s) for 12th October 1999 and 145.0×10^6 m^3/day (1,679.2 m^3/s) for 13th October 1999 (Table 4-1) (Royal Irrigation Department 1999)

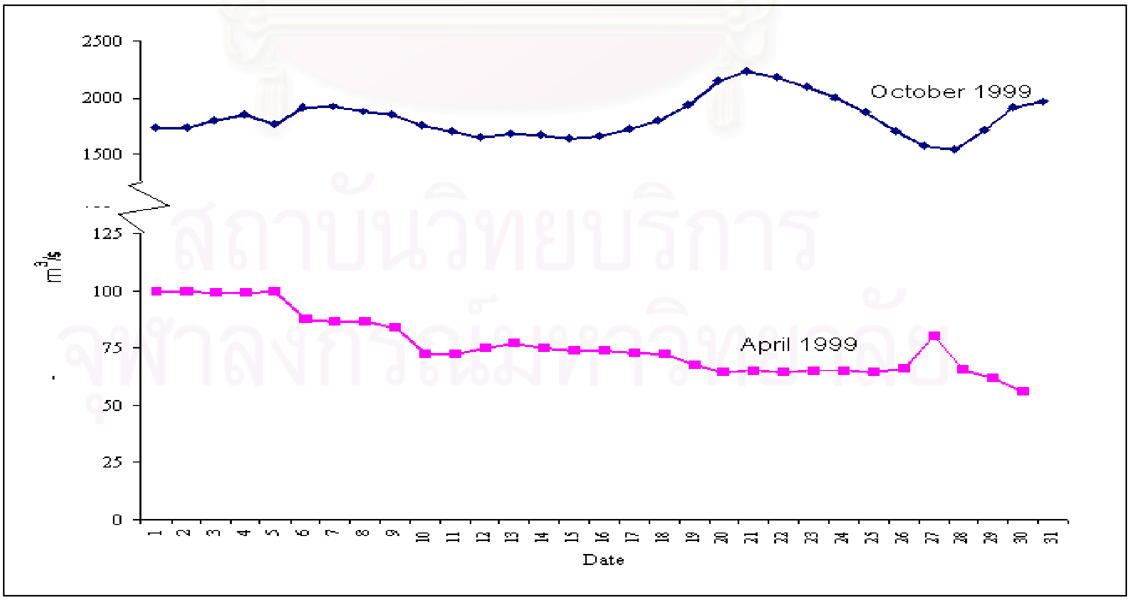

Figure 4-1 Comparison of daily discharge (m^3/s) at below the Chao Phraya Dam between April 1999 and October 1999 (Royal Irrigation Department 1999)

Table 4-1 Data of discharge at the Ban Re Rai, Sanphaya, Chainat (C.13) in the dry and wet season 1999

Date	Discharge (m^3/s)	
	April 1999	October 1999
1	99.8	1,735.6
2	99.8	1,735.6
3	99.1	1,800.0
4	99.1	1,848.3
5	99.8	1,759.7
6	87.5	1,915.0
7	86.7	1,919.3
8	86.7	1,876.8
9	83.9	1,852.4
10	72.5	1,751.7
11	72.5	1,703.3
12	75.1	1,651.0
13	77.1	1,679.2
14	75.1	1,667.1
15	73.8	1,642.9
16	73.8	1,655.0
17	73.2	1,723.5
18	72.5	1,800.0
19	68.0	1,927.8
20	64.4	2,140.5
21	65.0	2,229.8
22	64.4	2,178.8
23	65.0	2,089.4
24	65.0	2,000.1
25	64.4	1,872.5
26	66.0	1,699.3
27	80.4	1,574.4
28	65.5	1,546.3
29	61.9	1,715.4
30	56.2	1,915.0
31		1,966.1
Average	76.47	1,824.9
Min	56.2	1,546.3
Max	99.8	2,229.8

(Source : Hydrology Division, Royal Irrigation Department of Thailand, 2001)

In the Chao Phraya Watershed water from the drainage area in the Northern region of Thailand is retained at two major dams, Bhumibhol Dam on Ping River and Sirikit Dam on Nan River, for hydro-power electric generation and agricultural uses. These rivers and two other rivers, Wang and Yom River, meet at Pak Nam Pho in Muang District of Nakhon Sawan Province and start the Chao Phraya River. From Nakhon Sawan, the Chao Phraya River flows through several water gates which draw water from the river to agricultural areas in the Central Plain of Thailand. Before entering Bangkok, the river is blocked again by the Chao Phraya dam at Sanphaya district, Chainat Province. Water discharged from the dam flows through Ayuthaya, Patumthani, Nonthaburi, Bangkok and Samut Prakan then entering the Gulf of Thailand. Discharge condition of the Chao Phraya Watershed depends on its tributaries, Ping, Wang, Yom and Nan. In the dry season when low precipitation is not enough for agricultural practice in the Central Plain of Thailand, Bhumibhol and Sirikit dam reservoirs are used for supplying water to those areas (Figure 4-2 and Figure 4-3). In the wet season no discharge occurs below the dams since they have to control water quantity in the basin to prevent flooding (Figure 4-4).

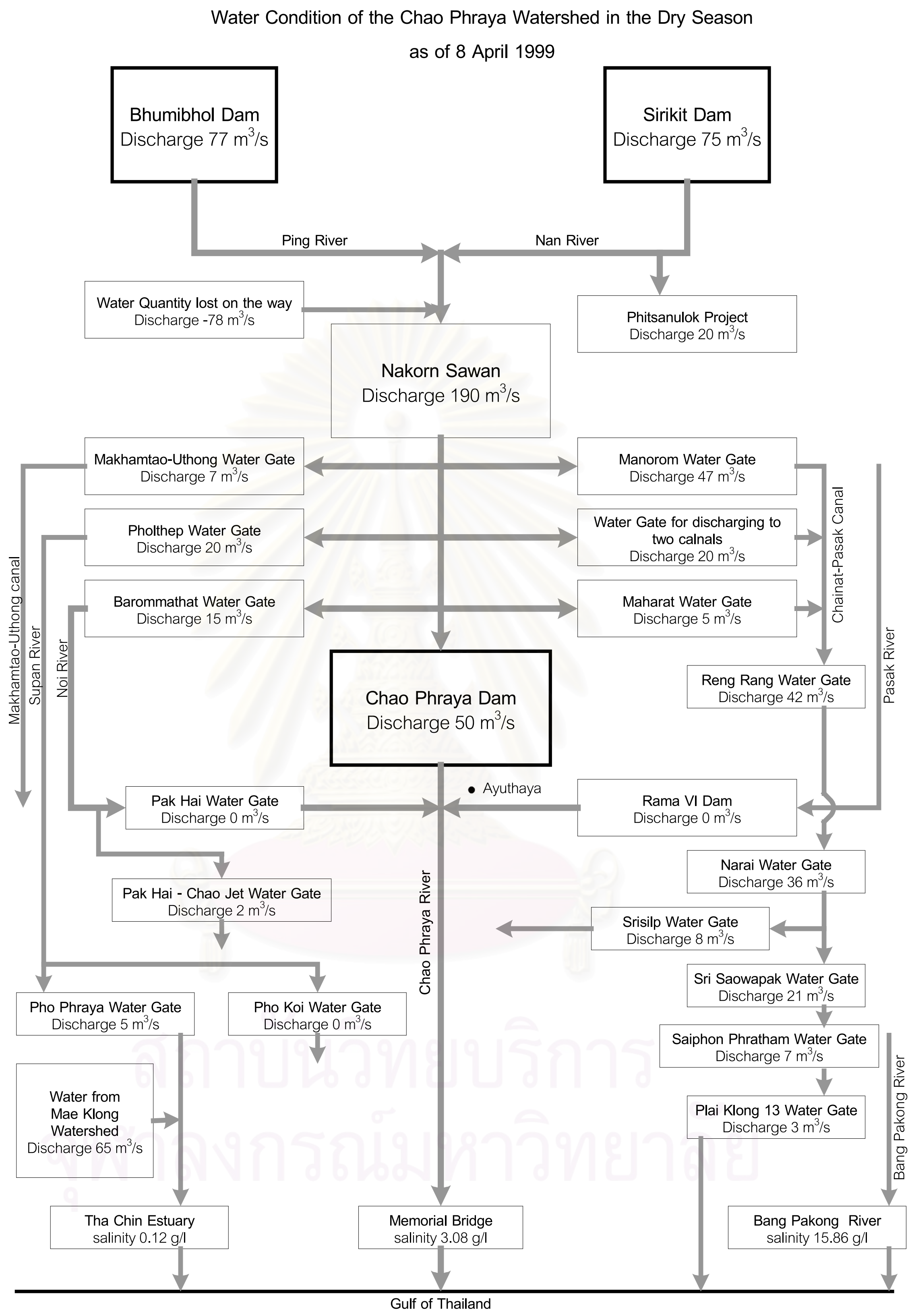

Figure 4-2 Discharge Condition of the Chao Phraya Watershed in the Dry Season (8 April 1999) (Source : Royal Irrigation Department 1999)

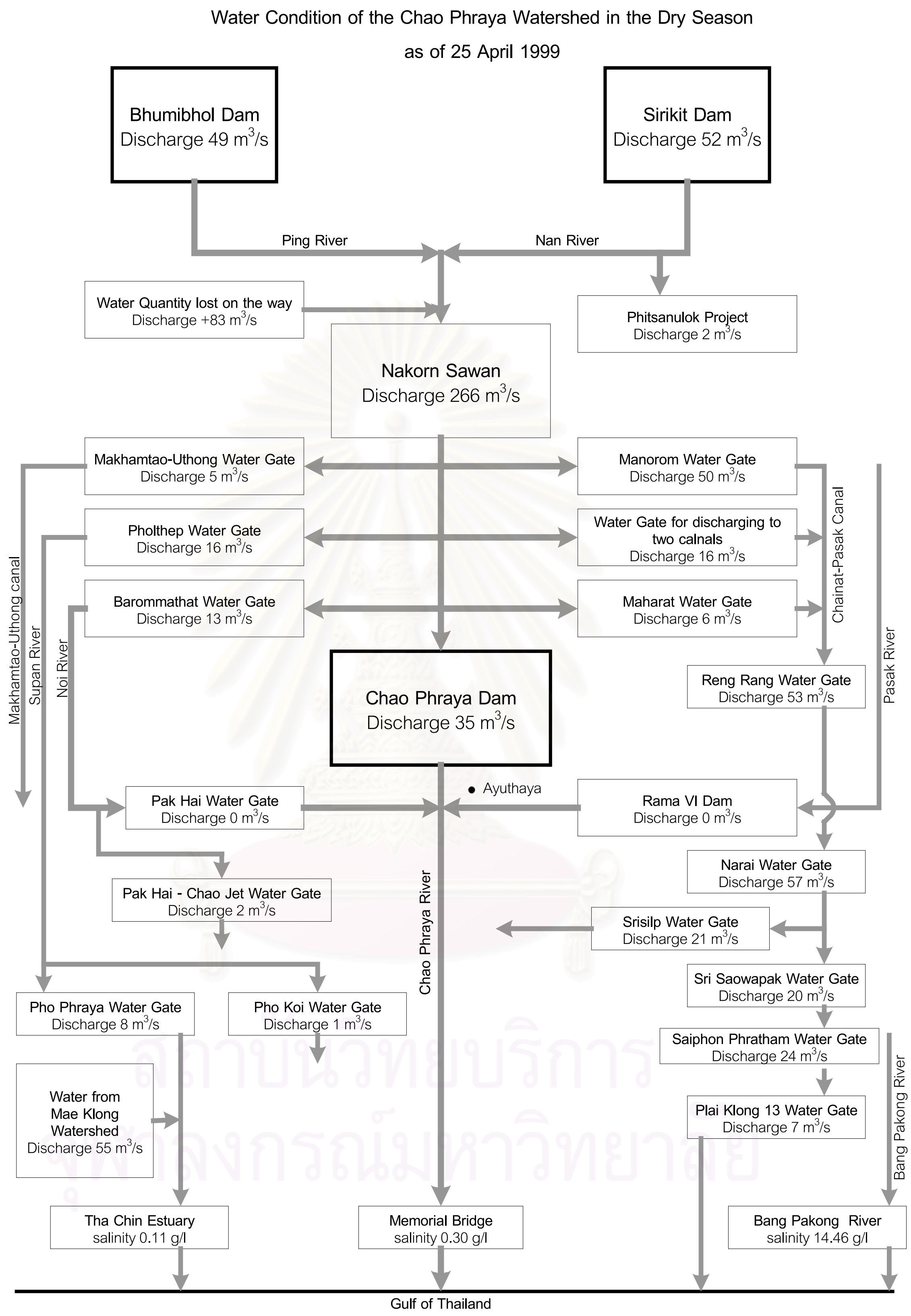

Figure 4-3 Discharge Condition of the Chao Phraya Watershed in the Dry Season (25 April 1999) (Source : Royal Irrigation Department 1999)

Water Condition of the Chao Phraya Watershed in the Wet Season
as of 31 October 1999

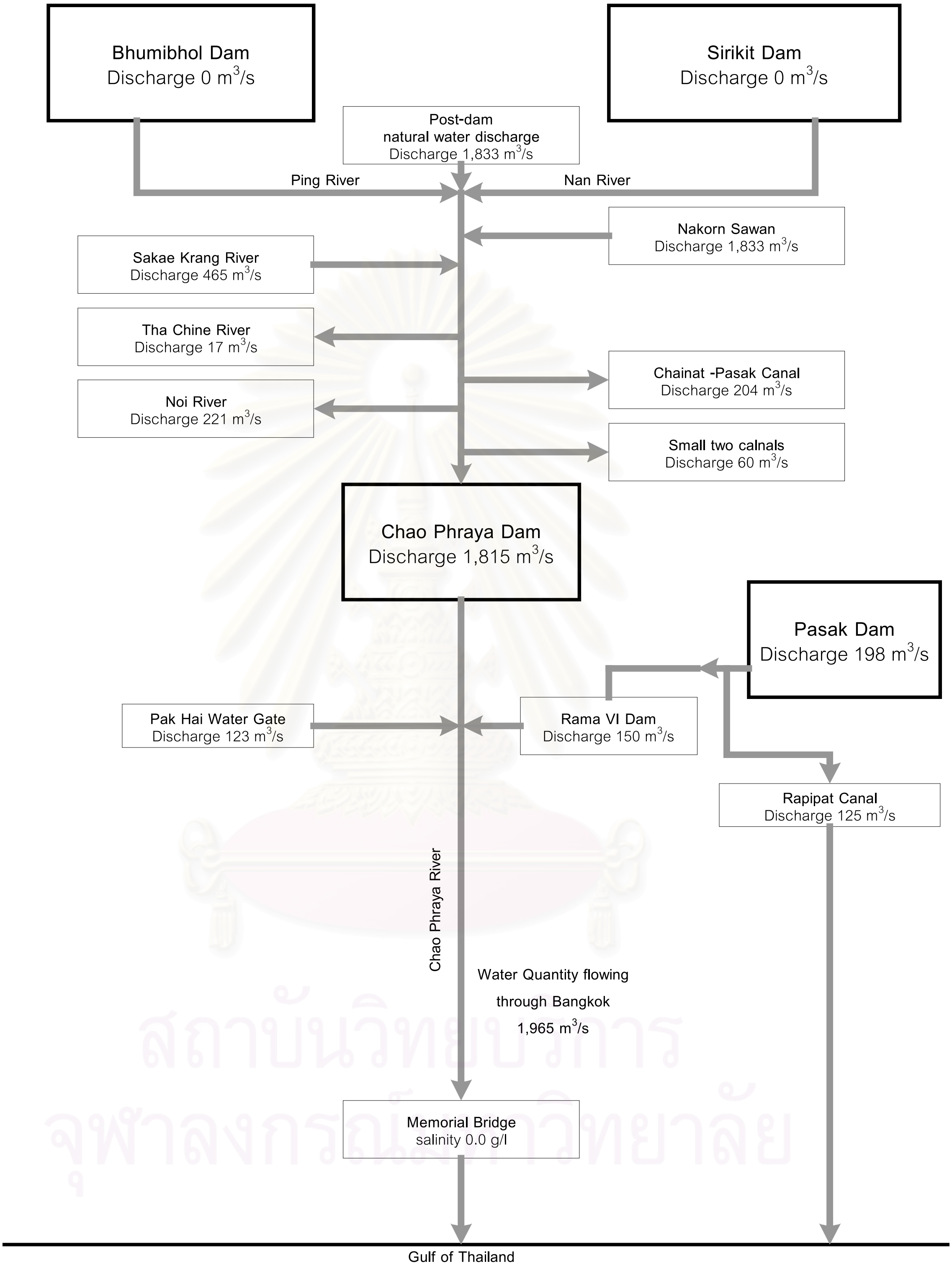

Figure 4-4 Discharge Condition of the Chao Phraya Watershed in the Wet Season (31 October 1999) (Source : Royal Irrigation Department 1999)

4.3 Spatial Distribution of Physical Water Quality in the Chao Phraya River

During April 1999, which was the dry season for Thailand, the distribution of temperature in the Chao Phraya river water showed very little variation for both surface and bottom water, ranging from 28.8-31.8 ^{o}C. This pattern also applied to the Wet Season which the water temperature distribution for both surface and bottom water showed no significant variation, ranging from 30.4-31.4 ^{o}C.

The pH value was relatively constant for both dry and wet season, ranging from 6.4-7.7 and it increased slightly when the salinity increased from Km 40 toward the river mouth in the dry season and from Km 9 toward the river mouth in the wet season.

Seasonal variation has greatly influenced the salinity distribution showing the effect of seawater in the Chao Phraya River. In the dry season, the river discharge was so low that the tidal current around the river mouth has greater effect and, thus, promoting a mixing between fresh water and seawater in the water column. During the study period, seawater penetrated up the river to Km 53 causing the water salinity to increase gradually and reached 16.8 psu at the river mouth (Figure 4-5). However, during the wet season the river runoff was so high that seawater could penetrate up only a short distance from the river mouth with almost no mixing in the water column (Figure 4-7). This behavior caused the surface water salinity to increase slightly (from 0.0 psu at Km 9 to 1.1 psu at the river mouth) while the bottom water salinity increased significantly at the river mouth (from 0.0 psu at Km 9 to 22.3 psu at the river mouth) (Figure 4-8).

In the dry season the dissolved oxygen (DO) in the river water averaged at 3.57 mg/l for surface water and 2.52 mg/l for bottom water with a significant decrease between the Km 53 to Km 60 due largely to untreated domestic waste discharged into the river via several canals flowing through Bangkok Metropolis which required a huge amount of oxygen to decompose it. However, the river downstream recovered itself by mixing with sea water and dissolved oxygen increased to a normal level after the Km 40. In the wet season, the DO of the surface water had the same characteristics as in the dry season water with the value ranging from 1.56-4.34 mg/l. However, the water flow was so high and with faster flow rate that domestic waste discharged from canals between Km 53 to 60 did not have much impact on the bottom water and, thus, there was no significant change in DO in this area.

The suspended particulate matter (SPM) for both surface and bottom water in the dry season tended to increase toward the river mouth. This behavior had a close relationship with the increase of water salinity, which started to rise since Km 40 toward the river mouth, and it also because the volume of river water was low causing the slow water flow rate that allowed enough time for long freshwater and seawater mixing to create a "turbidity maximum" condition toward the river mouth. Under this condition, the change in water salinity would caused dissolved matter to resuspend and precipitate. This relationship was also visible in the wet season when the SPM for surface water show a small variation with the average value at 51.9 mg/L while the SPM for bottom water showed a significant increase from Km 17 toward the river mouth where the salinity started to increase.

Table 4-2 The Spatial Variation of Physical Parameters in the Chao Phraya River Water in the Dry Season 1999

Station	Km.	Temp (^{o}C)		Salinity (p.s.u.)		DO (mg/L)		pH		SPM (mg/L)	
		Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom
1	94	31.7	31.3	0.0	0.0	4.36	3.76	6.4	6.6	4.0	31.0
2	88	31.6	-	0.0	0.0	3.93	-	6.7	-	14.0	29.0
3	78	31.8	31.5	0.0	0.0	3.89	3.03	7.4	7.4	11.0	14.0
4	72	31.7	31.5	0.0	0.0	3.02	2.37	7.2	7.2	34.0	52.0
5	68	31.5	31.5	0.0	0.0	2.46	2.04	7.3	7.5	14.0	75.0
6	60	31.8	31.4	0.0	0.0	0.45	0.22	7.3	7.3	51.0	8.0
7	53	31.3	31.3	0.0	0.0	0.36	0.23	7.4	7.4	6.0	11.0
8	40	29.6	-	3.4	4.5	4.50	0.50	7.7	7.5	30.0	31.0
9	30	29.6	-	4.1	7.3	6.00	4.50	7.6	7.5	34.0	173.0
10	17	29.7	-	6.5	6.6	3.40	3.10	7.5	7.5	105.0	202.0
11	13	29.5	-	12.3	12.6	4.40	2.40	7.6	7.6	61.0	80.0
12	9	28.8	-	14.5	15.3	3.50	2.70	7.6	7.6	69.0	248.0
13	0	29.0	-	16.8	16.9	3.80	3.20	7.6	7.6	43.0	144.0
14	-5	29.7	-	17.3	17.5	3.50	2.60	7.6	7.6	71.0	264.0
15	-5	30.5	-	17.5	20.4	4.90	4.60	7.6	7.7	-	90.0
16	-5	30.3	-	16.8	-	4.60	-	7.7	-	67.0	-
Average		30.5	31.4	6.8	6.7	3.57	2.52	7.4	7.4	40.9	96.8
Min		28.8	31.3	0.0	0.0	0.36	0.22	6.4	6.6	4.0	8.0
Max		31.8	31.5	17.5	20.4	6.00	4.60	7.7	7.7	105.0	264.0

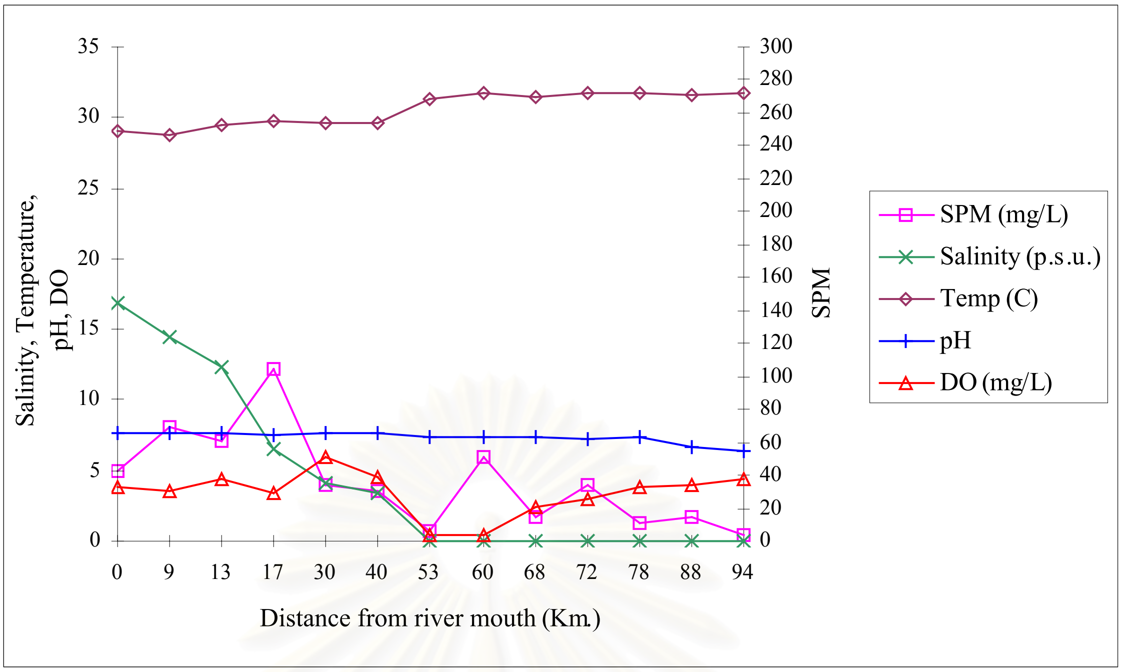

Figure 4-5 Spatial Distribution of Physical Parameters of *Surface Water Quality* in the Chao Phraya River in the Dry Season 1999

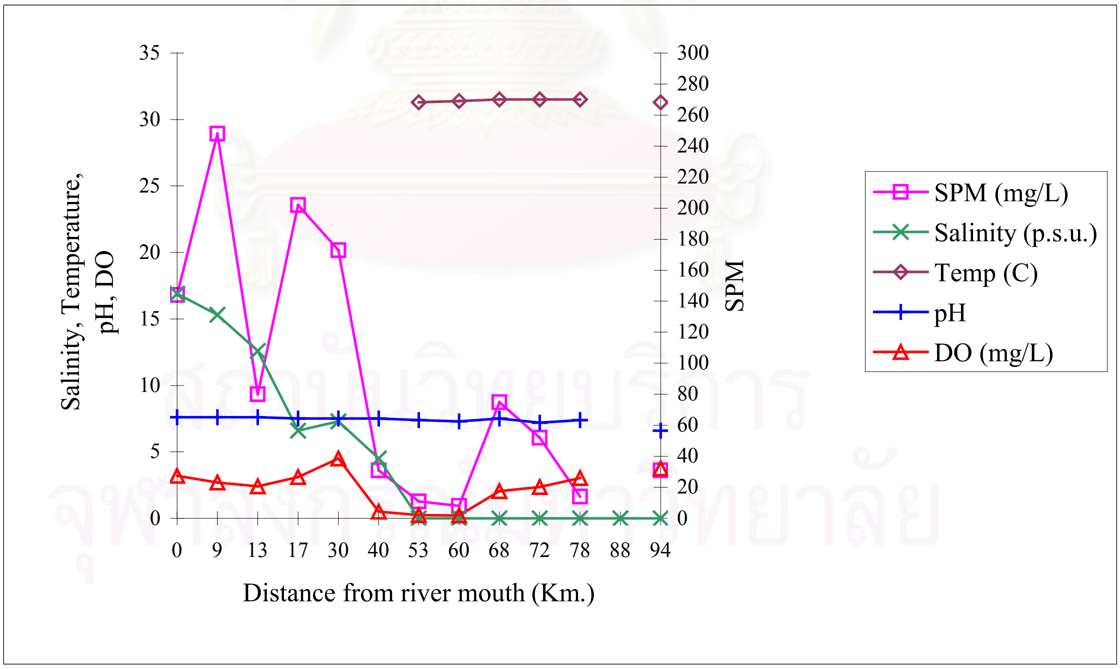

Figure 4-6 Spatial Distribution of Physical Parameters of *Bottom Water Quality* in the Chao Phraya River in the Dry Season 1999

Table 4-3 The Spatial Variation of Physical Parameters in the Chao Phraya River Water in the wet season 1999

Station	Km.	Temp (^{o}C)		Salinity (p.s.u.)		DO (mg/L)		pH		SPM (mg/L)	
		Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom
1	94	31.0	30.6	0.0	0.0	4.25	4.13	6.9	6.9	33.0	50.0
2	88	30.6	30.6	0.0	0.0	4.34	4.12	6.9	6.9	32.0	52.0
3	78	30.7	30.6	0.0	0.0	4.10	3.97	6.9	6.7	44.0	53.0
4	72	30.7	30.7	0.0	0.0	4.04	4.07	7.0	7.1	54.0	59.0
5	68	30.8	30.7	0.0	0.0	4.11	4.12	6.9	7.0	60.0	76.0
6	60	31.4	30.7	0.0	0.0	3.91	3.82	6.7	6.5	65.0	94.0
7	53	30.7	30.7	0.0	0.0	3.90	3.68	6.7	6.9	109.0	112.0
8	40	30.4	30.5	0.0	0.0	3.20	3.10	6.9	6.9	38.0	35.0
9	30	30.6	30.5	0.0	0.0	3.26	3.18	6.9	7.0	54.0	46.0
10	17	30.5	30.5	0.0	0.0	2.86	2.79	6.9	7.0	63.0	64.0
11	13	30.5	30.5	0.0	0.0	2.63	2.50	7.0	7.1	68.0	194.0
12	9	30.9	30.7	0.0	1.2	2.50	2.22	7.0	7.1	32.0	171.0
13	0	30.5	30.5	1.1	22.3	2.23	0.70	7.1	7.2	53.0	49.0
14	-5	30.8	30.7	4.3	24.6	2.29	1.30	7.1	7.3	42.0	53.0
15	-5	30.5	-	5.5	-	1.56	-	7.2	-	32.0	-
16	-5	30.5	30.5	7.1	14.3	1.97	1.42	7.2	7.3	51.0	51.0
Average		30.7	30.6	1.1	4.2	3.20	3.01	7.0	7.0	51.9	77.3
Min		30.4	30.5	0.0	0.0	1.56	0.70	6.7	6.5	32.0	35.0
Max		31.4	30.7	7.1	24.6	4.34	4.13	7.2	7.3	109.0	194.0

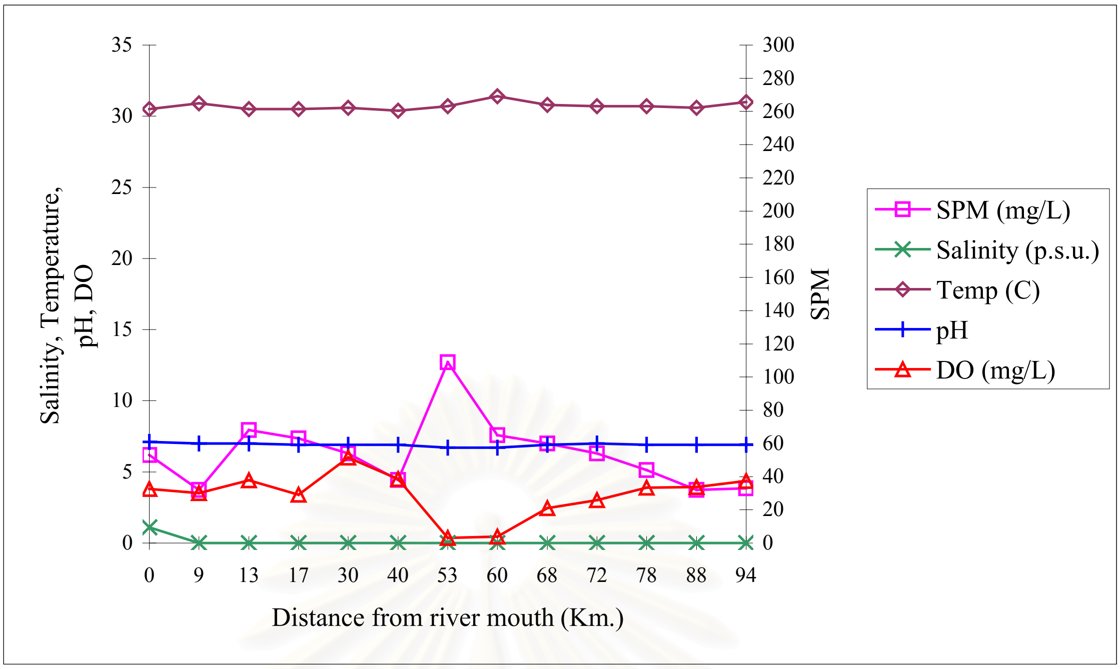

Figure 4-7 Spatial Distribution of Physical Parameters of *Surface Water Quality* in the Chao Phraya River in the Wet Season 1999

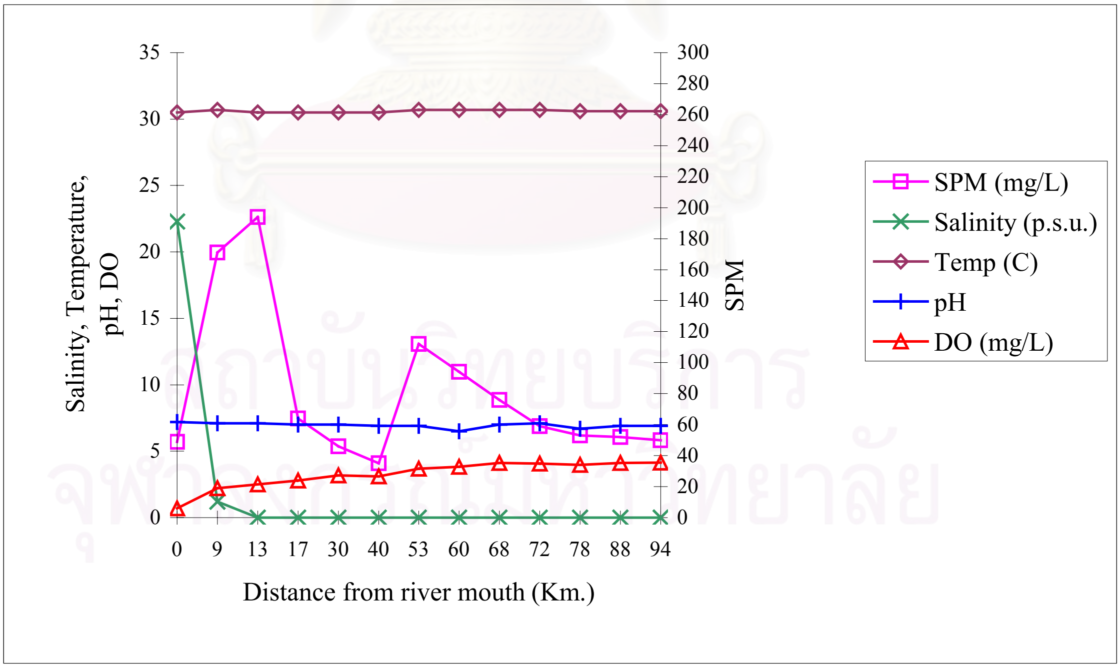

Figure 4-8 Spatial Distribution of Physical Parameters of *Bottom Water Quality* in the Chao Phraya River in the Wet Season 1999

4.4 Spatial Distribution of Nutrients in the Chao Phraya River

The spatial distribution of an individual nutrient in the Chao Phraya River was considerably different between the dry and wet season. During the dry season the concentration of total phosphorus ranging from 2.12-27.33 μM and total nitrogen ranging from 77.14-237.57 μM were relatively high comparing to the standard water quality in Thailand and appeared to be higher in the area where there are a lot of human activities and a large amount of waste, enriched with nitrogen and phosphorus, was discharged into the waterway (since km 53). On the contrary, silicate ranged from 97.48-197.39 μM between km 94 to km 53 and tended to decrease toward the river mouth (4.61-71.25 μM) This behavior may caused by a mixing with low-silicate seawater and/or the water samples were kept too long which a certain amount of silicate might had been altered to another non-reactive forms. Further test should be conducted on long-kept water samples to investigate the possible change. The nutrient distribution is shown in Figure 4-9 and Figure 4-10 showing that silicate concentration cannot be compensated from the domestic influent or human activities in the river downstream like total phosphorus and total nitrogen.

Table 4-4 The Spatial Distribution of Nutrient Concentration in the Chao Phraya River Water in the Dry Season 1999

Station	Km.	Total P (uM)		Total N (uM)		Silicate-Si (uM)	
		Surface	Bottom	Surface	Bottom	Surface	Bottom
1	94	2.44	2.55	88.64	109.86	185.00	190.13
2	88	2.12	-	124.14	-	195.71	-
3	78	2.76	3.04	93.00	77.14	192.97	190.58
4	72	3.11	3.40	92.57	205.71	193.50	190.22
5	68	3.36	3.72	158.21	163.79	190.66	197.39
6	60	4.61	4.54	176.43	176.14	184.20	185.62
7	53	5.67	15.48	211.57	151.71	191.64	97.48
8	40	15.04	12.44	151.21	185.86	4.61	8.06
9	30	27.33	14.07	236.00	233.43	71.25	12.66
10	17	17.79	17.44	208.93	215.00	28.95	18.06
11	13	14.19	10.81	237.57	225.36	29.21	25.85
12	9	8.26	13.26	199.86	232.21	24.35	40.81
13	0	11.16	12.79	223.93	203.86	57.00	46.74
14	-5	11.51	13.26	217.29	170.50	60.98	7.80
15	-5	9.65	8.14	213.57	203.21	60.54	39.39
16	-5	9.54	-	218.07	-	50.10	-
Average		9.28	9.64	178.19	182.41	107.54	89.34
Min		2.12	2.55	88.64	77.14	4.61	7.80
Max		27.33	17.44	237.57	233.43	195.71	197.39

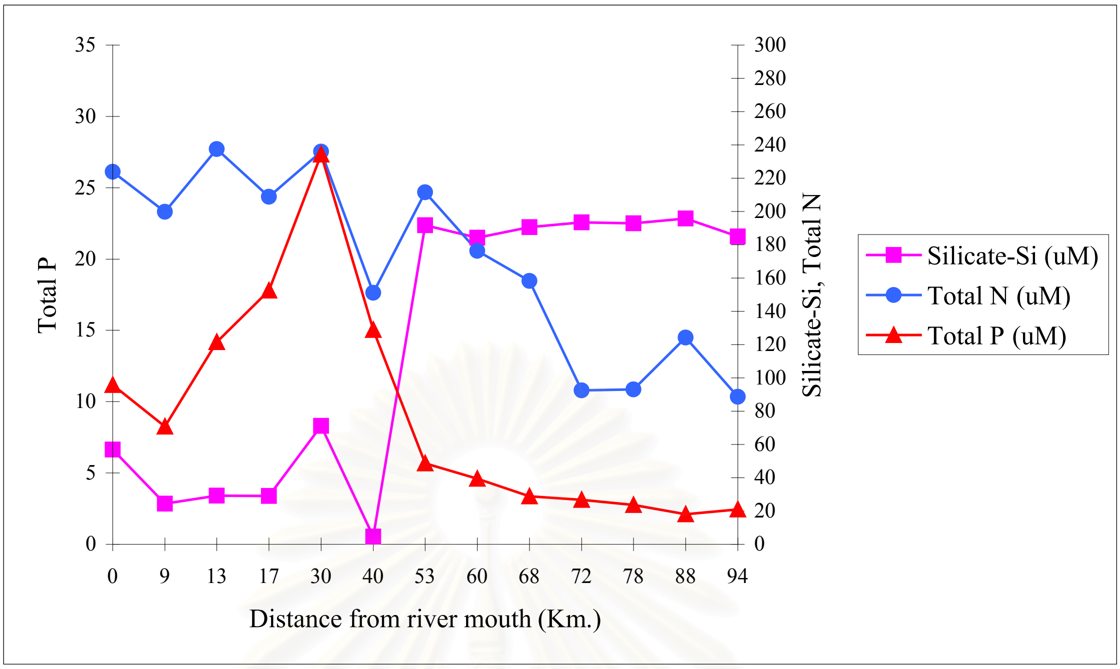

Figure 4-9 Spatial Distribution of Nutrients of _Surface Water_ in the Chao Phraya River in the Dry Season 1999

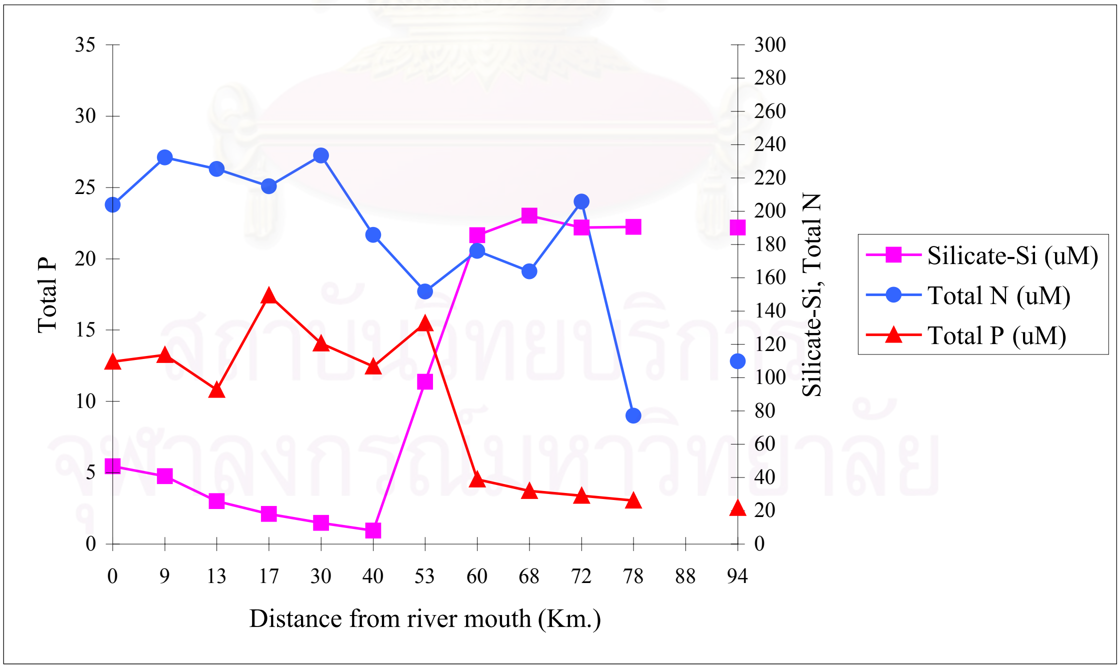

Figure 4-10 Spatial Distribution of Nutrients of _Bottom Water_ in the Chao Phraya River in the Dry Season 1999

In the wet season, a high discharge condition, silicate concentrations ranged from 185.29-276.09 μM and were higher than the concentrations in the dry season. These values were almost constant throughout the river except near the river mouth where the salinity increased slightly and a slight decrease in the silicate concentration was observed. This was caused by the mixing with low-silicate seawater, which dropped the silicate concentration in this area. The distribution of total phosphorus concentration ranging from 2.04-6.84 μM and total nitrogen concentration ranging from 34.87-137.17 μM were slightly increased toward the river mouth for both surface and bottom water (Figure 4-11 and Figure 4-12). However, the concentrations were less than the concentrations in the dry season because of the high volume of water diluting these pollutants.

Table 4-5 The Spatial Distribution of Nutrient Concentration in the Chao Phraya River in the Wet Season 1999

Station	Km.	Total P (uM)		Total N (uM)		Silicate-Si (uM)	
		Surface	Bottom	Surface	Bottom	Surface	Bottom
1	94	2.13	2.04	70.64	63.90	243.22	250.46
2	88	2.50	2.32	137.17	59.29	255.40	246.09
3	78	2.27	2.59	59.29	54.87	254.83	254.48
4	72	2.50	3.41	74.87	81.21	249.08	255.29
5	68	3.00	2.77	52.17	34.87	252.30	264.83
6	60	3.05	3.87	48.14	66.21	263.10	258.97
7	53	3.69	4.01	89.87	41.98	265.98	255.75
8	40	3.41	3.82	48.33	49.29	263.10	266.09
9	30	3.64	3.78	67.75	73.90	265.17	268.28
10	17	4.46	4.32	56.79	65.06	263.91	269.43
11	13	4.64	6.84	80.44	67.94	272.18	276.09
12	9	5.37	5.79	55.06	68.90	266.78	260.92
13	0	4.23	4.83	82.94	114.29	263.45	207.47
14	-5	4.19	4.64	60.25	97.17	261.03	185.29
15	-5	4.92	-	108.33	-	241.61	-
16	-5	4.55	5.33	74.29	86.40	254.25	231.15
Average		3.66	4.02	72.90	68.35	258.46	250.04
Min		2.13	2.04	48.14	34.87	241.61	185.29
Max		5.37	6.84	137.17	114.29	272.18	276.09

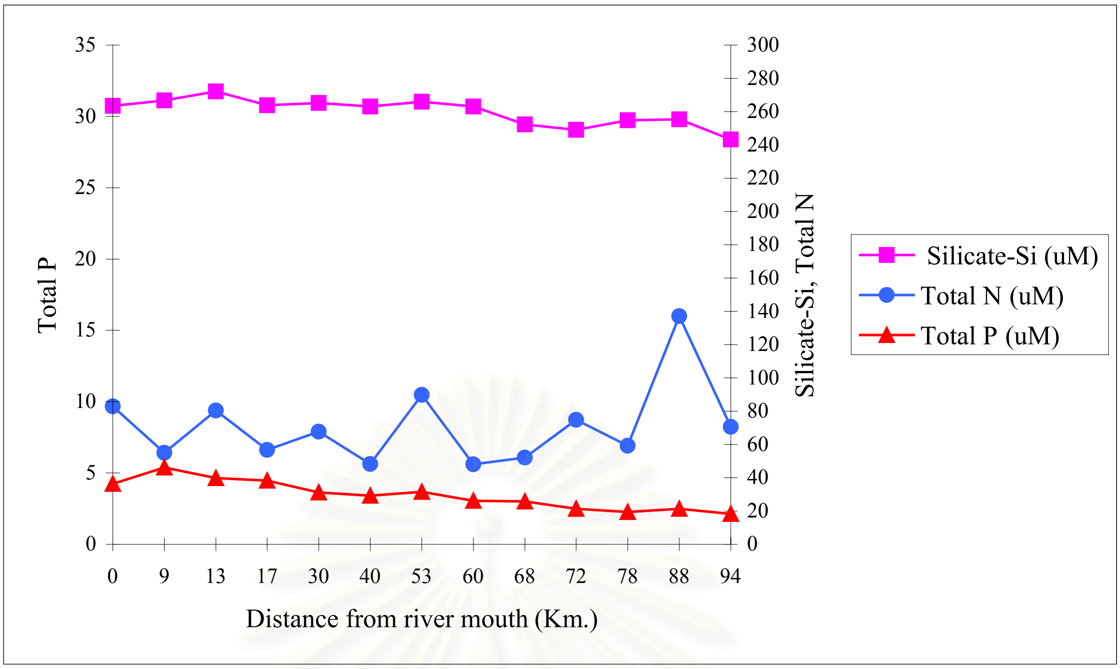

Figure 4-11 Spatial Distribution of Nutrients of *Surface Water* in the Chao Phraya River in the Wet Season 1999

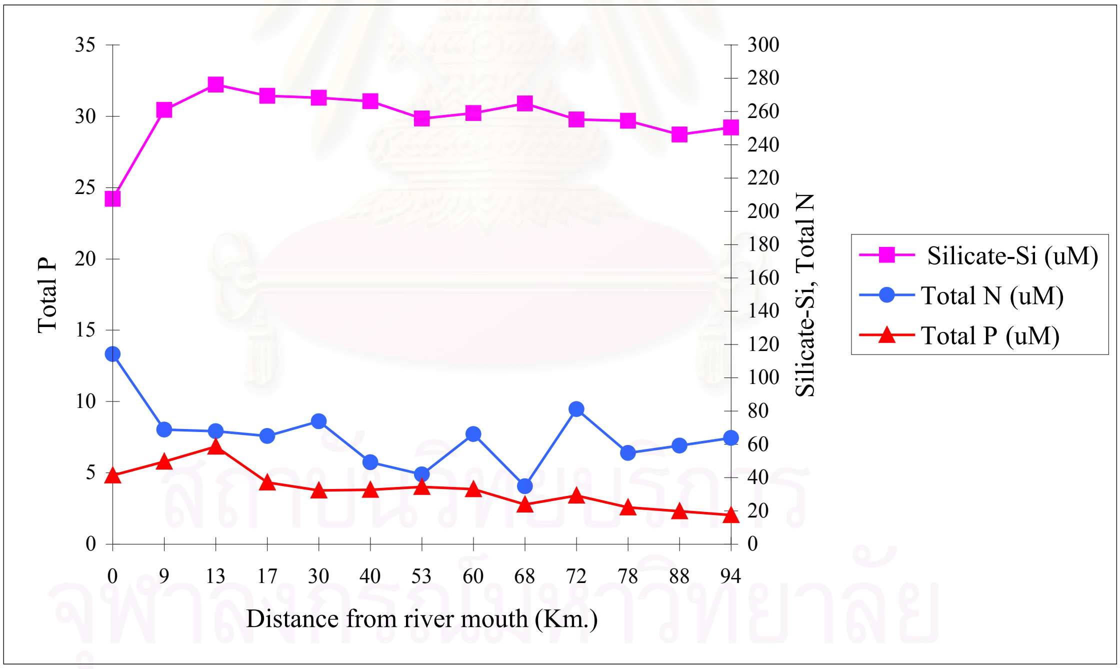

Figure 4-12 Spatial Distribution of Nutrients of *Bottom Water* in the Chao Phraya River in the Wet Season 1999

4.5 Spatial distribution of dissolved trace metals in river water

Although trace metal is not a bio-essential for diatom, there are evidences that it has some importances. An example is Aluminium which is found incorporated in diatom 's skeleton. This presence of Aluminium has been demonstrated that it helps retard the dissolution process of diatom skeleton (LOICZ 1999). The concentrations of dissolved trace metals (aluminium, cadmium and iron) in the dry season are shown in Table 4-6 which showed similar distribution patterns for aluminium and iron, two major compositions of the earth crust. Their concentration tended to decrease toward the river mouth (Figure 4-13 and Figure 4-14) which can be explained by the fact that these elements were bounded with the particulates when the salinity increased. Dissolved cadmium ,which is an element not originating from natural source, in both surface and bottom water showed no significant spatial distribution change in the Chao Phraya River.

Table 4-6 The Spatial Distribution of Dissolved Trace Metal Concentration in the Chao Phraya River Water in the Dry Season 1999

Station	Km.	Dissolved Al (ug/l)		Dissolved Cd (ug/l)		Dissolved Fe (ug/l)	
		Surface	Bottom	Surface	Bottom	Surface	Bottom
1	94	3.31	8.98	0.015	0.033	138.54	107.74
2	88	5.83	6.00	0.009	0.019	78.57	164.85
3	78	5.81	6.28	0.015	0.021	88.28	68.34
4	72	0.72	0.90	0.011	0.015	8.65	15.88
5	68	4.00	1.30	0.017	0.014	13.94	75.02
6	60	0.61	2.10	0.024	0.017	11.17	50.29
7	53	1.40	2.41	0.017	0.021	13.74	4.00
8	40	0.71	0.36	0.018	0.043	5.51	5.21
9	30	5.12	0.37	0.024	0.059	5.52	3.18
10	17	1.03	1.09	0.062	0.055	7.83	1.86
11	13	0.54	1.00	0.015	0.067	20.98	3.24
12	9	1.55	0.56	0.046	0.051	2.96	8.21
13	0	0.86	0.42	0.049	0.068	7.96	3.18
14	-5	1.36	0.54	0.068	0.052	4.03	2.66
15	-5	-	0.49	-	0.190	-	2.63
16	-5	3.21	-	0.031	-	2.21	-
Average		2.40	2.19	0.028	0.048	27.33	34.42
Min		0.54	0.36	0.009	0.014	2.21	1.86
Max		5.83	8.98	0.068	0.190	138.54	164.85

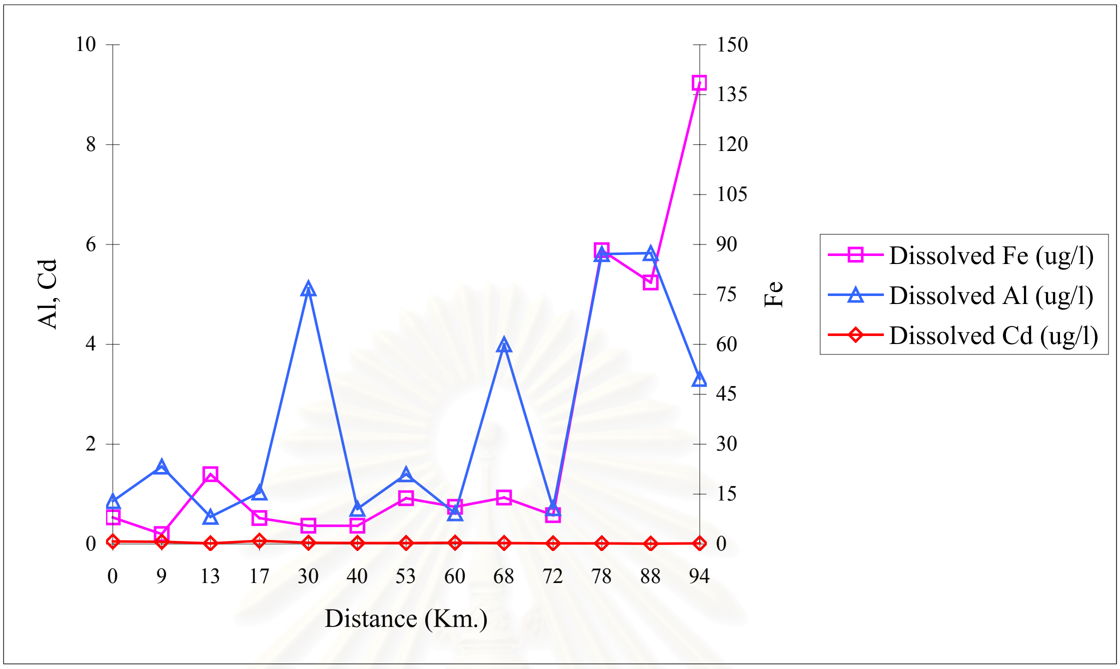

Figure 4-13 Spatial Distribution of Trace Metals of *Surface Water* in the Chao Phraya River of the Dry Season 1999

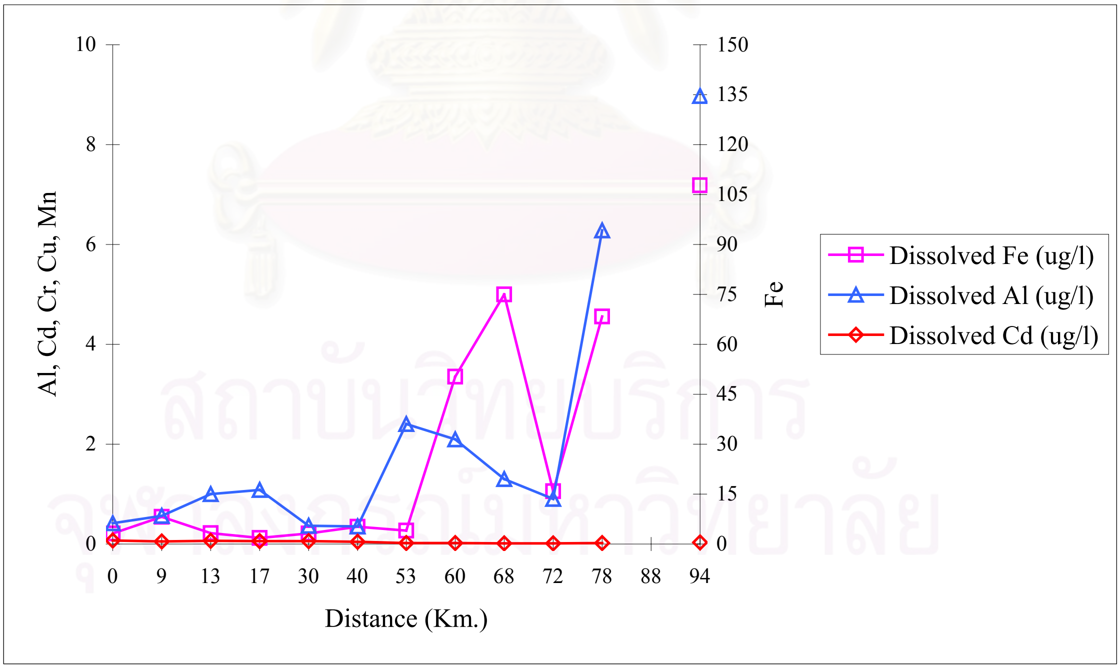

Figure 4-14 Spatial Distribution of Trace Metals of *Bottom Water* in the Chao Phraya River of the Dry Season 1999

4.6 Spatial distribution of biogenic silica in the river sediment

The accumulation of biogenic silica in the Chao Phraya River sediment were reported in the form of $\%SiO_2$ ranging from 1.43-3.69%. Their concentration tended to increase along the river toward the river mouth while the salinity increased gradually and, possibly, leading to a higher precipitation rate of diatom shells from the water columns (Figure 4-15).

Special attention should be paid at the area of Km 53 from the river mouth where the silicate concentration was significantly higher than the other area. There are evidences showing that the "turbidity maximum" often occurs in this area in the dry season of each year causing the highest sedimentation rate and highest biogenic silica in the sediment.

Table 4-7 The Spatial Distribution of Biogenic Silica in the Chao Phraya River Sediment in 1999

Station	Km.	% Si_{OPAL} [1]	% SiO_2 [2]	% OPAL [3]
1	94	0.67	1.43	1.61
2	88	-	-	-
3	78	0.75	1.60	1.80
4	72	-	-	-
5	68	1.00	2.13	2.39
6	60	-	-	-
7	53	1.73	3.69	4.14
8	40	-	-	-
9	30	1.29	2.77	3.10
10	17	-	-	-
11	13	1.07	2.28	2.56
12	9	-	-	-
13	0	1.57	3.36	3.77
14	-5	1.42	3.03	3.40
15	-5	-	-	-
16	-5	-	-	-
Average		1.19	2.54	2.85
Min		0.67	1.43	1.61
Max		1.73	3.69	4.14

[1] $\%Si_{OPAL}$ = 112.4 × (Silica Concentration, mM/Sample Mass, mg)

[2] $\%SiO_2$ = 2.139 × $\%Si_{OPAL}$

[3] %OPAL = 2.4 × $\%Si_{OPAL}$

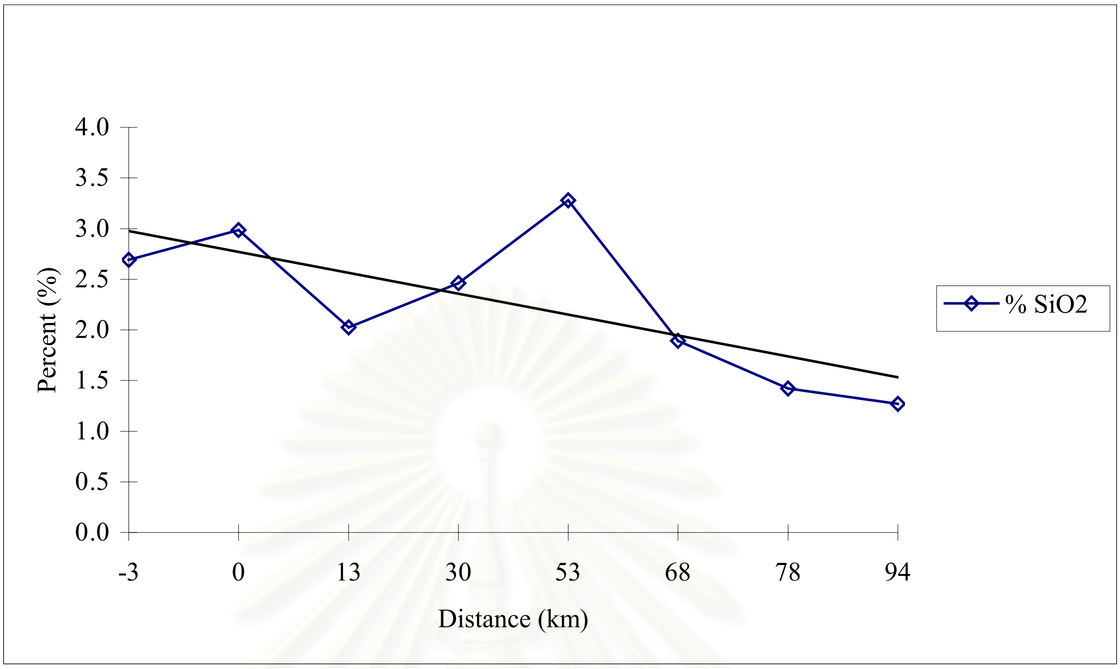

Figure 4-15 Spatial Distribution of Biogenic Silica in river sediments of the Chao Phraya River in the Dry Season 1999

4.7 Vertical distribution of biogenic silica in sediment box cores from the Gulf of Thailand

Down-core concentration profiles of biogenic silica in the form of SiO_2 are shown in figure 4-16 and Figure 4-17. The profiles did not appear that the concentrations decreased after the dam-building periods. In contrast, slight increase in biogenic silica concentration in the upper part of the cores from most stations was found. This could be because of the increase in soil erosion downstream in recent years due to land clearance for agricultural practices and other uses. Moreover it is probably due to the fact that delicate siliceous shells dissolved faster in the tropical sea comparing to the dissolution in the temperate waters and/or a bioturbation of benthic organisms and extensive use of bottom trawls disturbing the orderly stratification of the sediments. It is quite difficult to study geochronology relating to human activities via rivers by using impermanent record accumulated in sediments. However, this methodology can be used effectively in some other river systems apart from the tropical seas where human perturbation is not so high.

Even though the study could not found a clear changes in silicate fluxes from down-core biogenic silica profiles, it showed that the concentrations of silica in the station 8a ,the nearest the Chao Phraya River mouth, was higher than other stations further from the river mouth which conformed with the accumulation rate data of Srisuksawad et al, 1997 in the Gulf of Thailand that the precipitation rate increased toward the river mouth.

Table 4-8 The Vertical Distribution of Biogenic Silica in Sediment Box Core from the Gulf of Thailand

Station 8a		Station 12a		Station 17a		Station 23a	
Depth (cm.)	$\%SiO_2$	Depth (cm.)	$\%SiO_2$	Depth (cm.)	$\%SiO_2$	Depth (cm.)	$\%SiO_2$
4	2.11	0	1.54	0	1.64	2	1.40
6	3.13	2	1.43	2	1.48	4	1.02
8	2.43	4	1.88	4	2.01	6	1.23
10	2.45	6	1.60	6	1.37	8	1.38
13	2.95	8	1.57	8	1.98	10	1.39
16	2.32	10	1.45	10	2.15	12	1.00
19	3.29	13	1.78	13	1.13	16	1.49
22	2.43	16	1.51	16	1.26	18	1.47
25	2.84	19	1.84	19	1.07	20	1.27
28	2.93	21	1.54	22	1.22	23	1.30
31	2.90	24	1.59	25	1.29	26	1.29
34	1.88	27	1.52	28	1.28	29	1.49
37	2.44	30	1.17	31	1.08	32	1.35
40	2.18	33	1.65				
43	2.18						
Average	2.56		1.58		1.46		1.32
Min	1.88		1.17		1.07		1.00
Max	3.29		1.88		2.15		1.49

/continue…

Station 2		Station 20		Station 30		Station 54	
Depth (cm.)	%SiO_2	Depth (cm.)	%SiO_2	Depth (cm.)	%SiO_2	Depth (cm.)	%SiO_2
2	1.56	2	1.78	2	1.45	10	2.10
4	1.81	4	1.90	4	1.50	12	2.35
6	1.99	6	1.49	6	1.57	14	2.08
8	1.87	8	1.88	8	1.48	16	1.87
10	1.35	10	1.42	10	1.56	18	2.09
12	1.50	12	1.17	12	1.50	20	2.26
14	1.53	14	1.33	16	1.39	23	2.00
16	1.65	16	2.08	18	1.45	26	2.06
18	1.37	18	1.50	20	1.53	29	1.94
20	1.54	20	1.12	23	0.88	32	1.53
23	1.39	26	1.11	26	1.69	35	1.96
26	1.43	29	1.21	29	1.49	38	1.55
29	1.62	32	1.12	32	1.84	41	1.66
32	1.46	38	1.23	35	1.88	44	1.75
35	1.66	41	1.37	38	1.87	47	1.96
38	1.27			41	1.65	50	1.74
41	1.62			44	1.80		
44	1.52			47	2.19		
47	1.59			50	1.99		
50	1.24			53	2.09		
				56	1.90		
				59	2.00		
Average	1.55		1.45		1.67		1.93
Min	1.24		1.11		0.88		1.53
Max	1.99		2.08		2.19		2.35

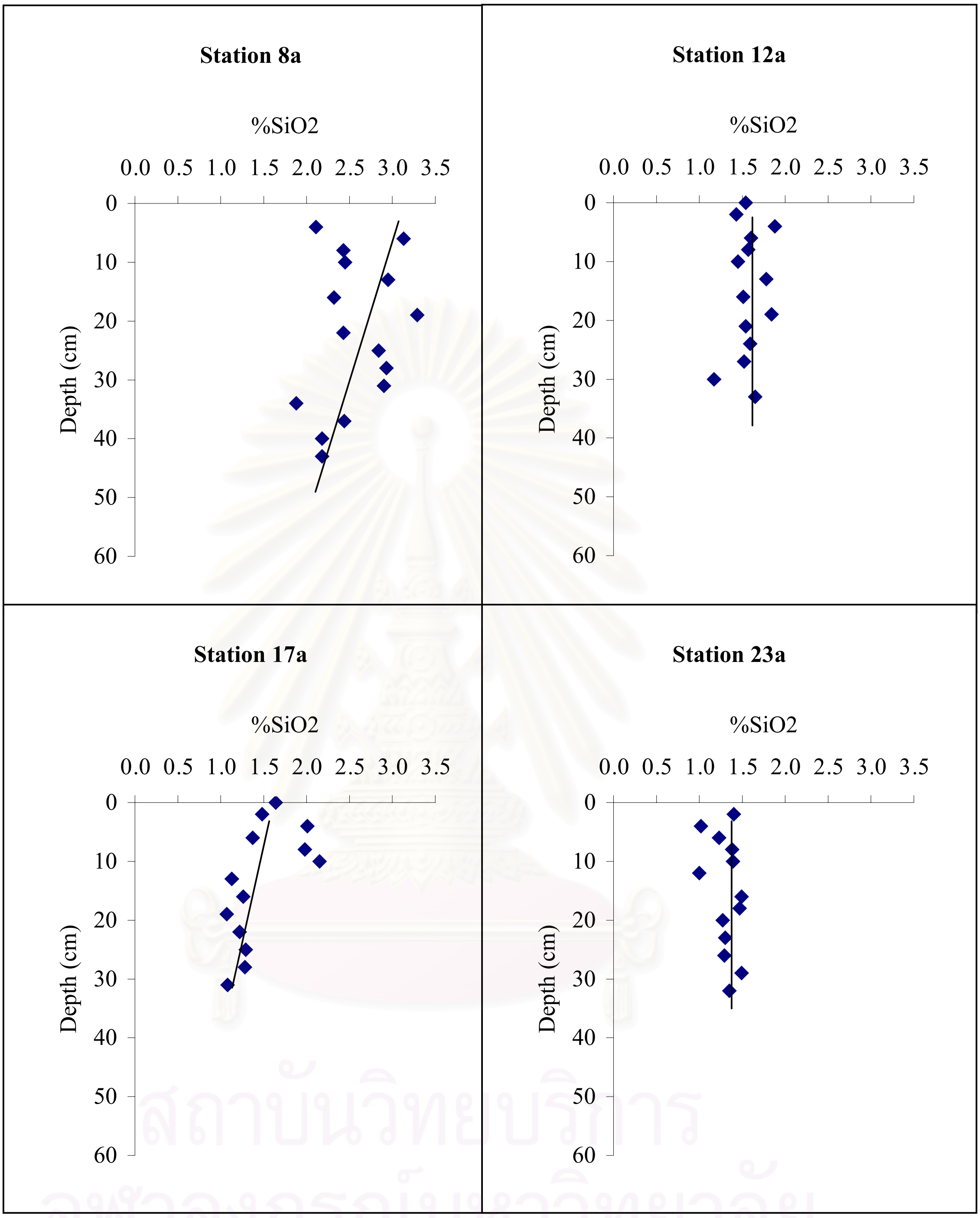

Figure 4-16 Vertical Distribution of Biogenic Silica in Sediment (Box) Core from the Upper Gulf of Thailand

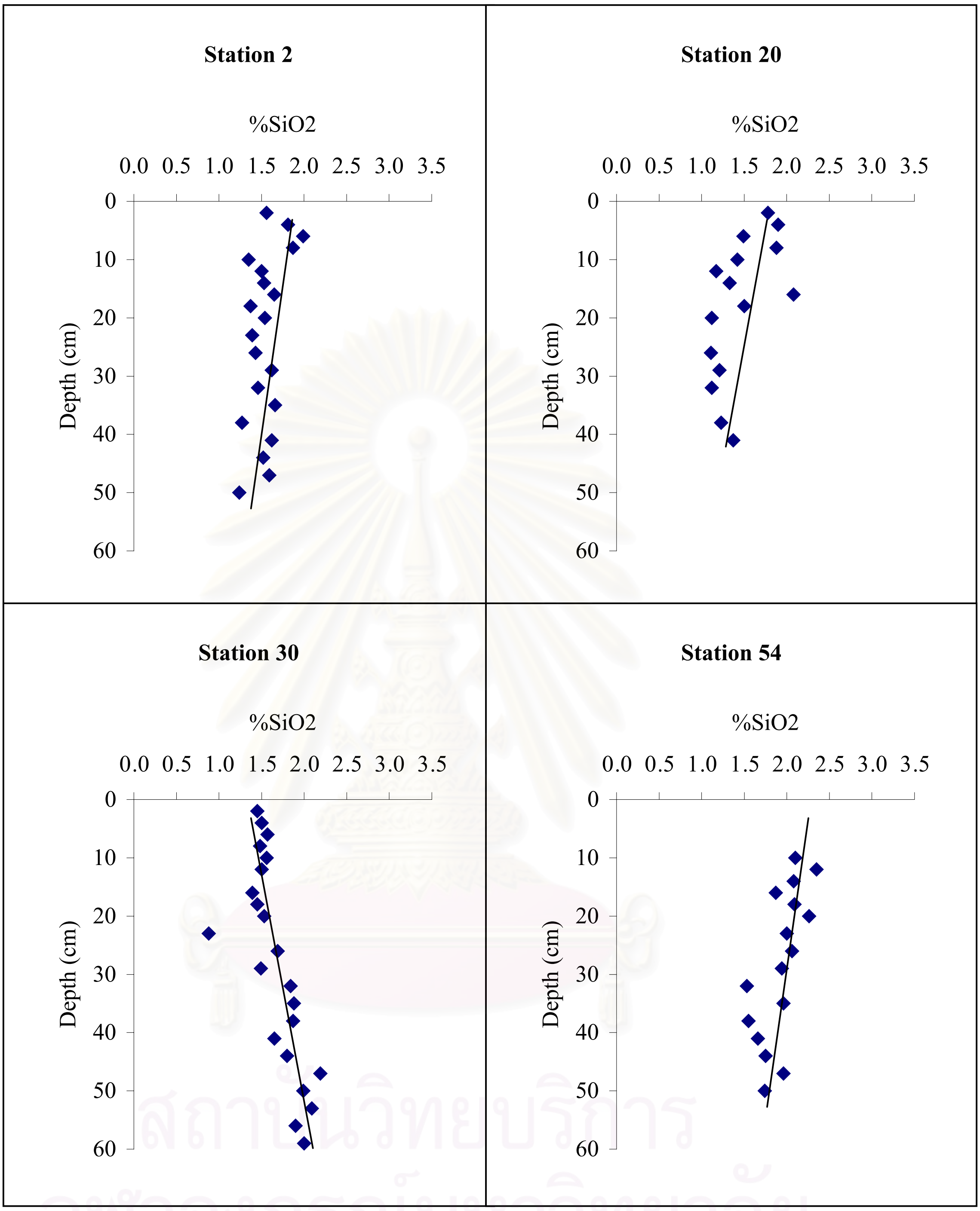

Figure 4-17 Vertical Distribution of Biogenic Silica in Sediment (Box) Core from the Middle and Lower Gulf of Thailand

4.8 Distribution of Biogenic silica in Coral Bands

A domed-shaped *Porites lutea* coral block of approximately 1 m in height and 1.5 m in width used for determining biogenic silica in individual bands corresponding the year 1945 to 1983 showed no clear change in biogenic silica concentration either before of after the dam construction. However peak values was observed during the mid-1950's to 1960, which was the soil removal period of Bhumibhol Dam construction (Figure 4-18). A better permanent record of the historical land use change in Central Plains of Thailand should be made on a large coral blocks with continuous growth dated some years before the dam building period

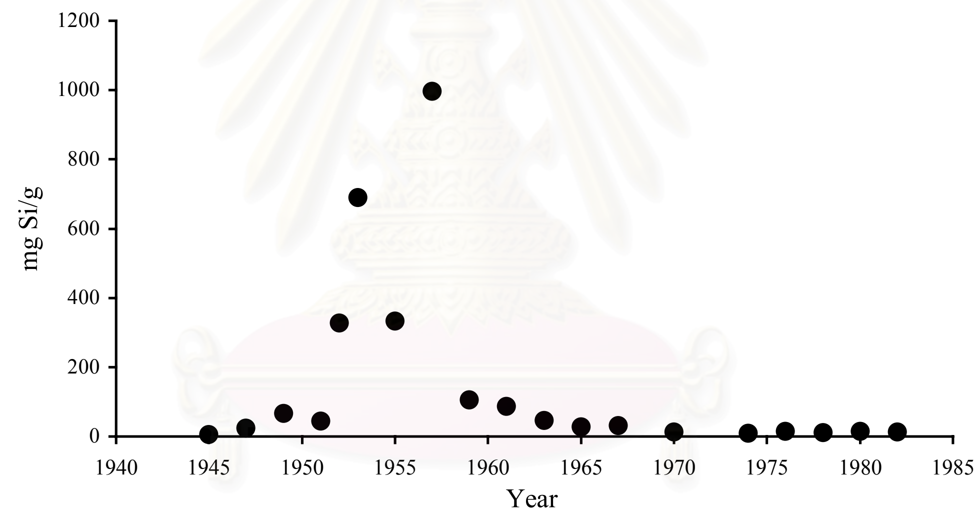

Figure 4-18 Temporal Accumulation of Biogenic Silica in Coral Bands, Porites lutea (Source: Hungspreugs et al 1985)

4.9 Material Fluxes

The material fluxes emphasizing on silicate fluxes through the lower basin of the Chao Phraya River were estimated for both daily and seasonal variations by calculating from material concentration and discharge to the lower river at a last station not influenced by influx of seawater. The daily net fluxes of suspended particulate matter, total phosphorus, total nitrogen, and dissolved silicate at the last station that was not influenced by seawater intrusion are shown in Table 4-1

Table 4-9 Comparison of daily net fluxes in *metric tons* per day of suspended particulate matter, total phosphorus, total nitrogen, dissolved silicate flowing through the lower basin of the Chao Phraya River in the dry and wet season 1999

Date	Station	Km	Discharge (m^3/s)	SPM		Total P		Total N		Silicate-Si	
				Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom
24-Apr-99	7	53	65.00	33.70	61.78	0.98	2.69	16.63	11.93	30.13	15.33
13-Oct-99	11	13	1,679.20	9,865.64	28,146.08	20.82	30.65	163.39	138.00	1,105.70	1,121.57

In the dry season on April 24, 1999 the water salinity from Km 94 to Km 53 were 0.0 psu, indicating that this area was not affected by seawater. This implied that the total material flux from the drainage area upstream of the river was transported down to Km 53 before entering the mixing process with seawater intrusion from the river mouth. On that date, the daily water runoff was 65 m^3/s (Royal Irrigation Department, 1999). This value, together with dissolved silicate, total nitrogen, and total phosphorus, were used to calculate the material flux which was at 14.28 tons/day, 1.84 tons/day, and 22.73 tons/day for total nitrogen, total phosphorus, and dissolved silicate respectively. The total nitrogen and phosphorus fluxes tended to increase toward the river mouth due to anthropogenic input while dissolved silicate flux was relatively constant throughout all seven stations. These results can clearly prove that both nitrogen and phosphorus were added to the river in the form of domestic waste and discharge from agricultural use or agroindustry. However, there was no such input for dissolved silicate since the major source of silicate is from soil erosion and weathering, but not from domestic waste.

In the wet season on October 13, 1999 the total material fluxes were calculated from Km 13 which the water salinity was 0.0. On those dates, the daily water runoff were 1,679 m^3/s (Royal Irrigation Department, 1999). From these value, the material fluxes for total nitrogen, total phosphorus, and dissolved silicate were calculated and the results were 150.70 ton/day, 25.74 ton/day, and 1,113.64 ton/day respectively. All material fluxes showed the same pattern as the one in the dry season but with much higher volume, which, confirmed that there was a seasonal variation of nitrogen, phosphorus, and dissolved silicate fluxes in the Chao Phraya River.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

A study on the change in land-sea silicate fluxes through the Chao Phraya River was conducted in 1999. Dissolved silicate, total phosphorus and total nitrogen in water samples from the Chao Phraya River in the dry and wet season were determined for comparison with physical and chemical parameters of the river water - pH, temperature, dissolved oxygen, salinity, suspended particulate matter. The river sediments and sediment core samples from the Gulf of Thailand were determined for biogenic silica concentration. And a domed-shaped *Porites lutea* coral block, taken from the shallow water off Kangkao Island was also determined for biogenic silica in each of individual growth bands to look for possible flux change of silica into the Upper Gulf of Thailand.

The year-round average of dissolved silicate concentration in the Chao Phraya River in 1999 was 181.58 μM which was normal for natural freshwater. The study showed that silicate fluxes in the river is affected by discharge conditions. Flux of silicate transported through the river to the sea in the wet season, high discharge condition, is relatively higher than the flux of silicate during the low flow condition of the dry season which was probably due to higher soil erosion by surface runoff. It can be concluded that there was a seasonal variation and possibly dominantly controlled by natural weathering processes but not by human activities in river downstream like nitrogen and phosphorus that showed trends of increasing their concentration in recent years as shown in the results.

Dissolved silicate in the Chao Phraya River Estuary showed some decrease in the concentration toward the river mouth through a mixing process with low-silicate seawater which corresponded with the silicon behavior in the estuary at low salinity (Umnuay, 1984).

An estimate of the daily silicate fluxes and other nutrients through the lower basin of the Chao Phraya River in the dry and wet season 1999 were shown in Table 4-1. Those values will be useful in comparing with the data in the future and used in assessing trends of changing fluxes of silicate impacting on nutrient composition, phytoplankton species composition and carbon cycle.

In sediment box cores we expected that the concentration of biogenic silica accumulated in the upper part of the cores would be lower than in the deeper part. But in reality, these cores showed trend of slight increase in biogenic silica concentration in the upper part of the cores from most stations. This was probably due to the increase in soil erosion downstream in recent years. Land clearance for agricultural practices and other uses was higher than the amount of suspended matter trapped in the dam reservoirs. And it could be because the fact that fragile siliceous shells are more soluble in the tropical marine environment (LOICZ 1999), thus only a small amount of it remained in sediment. And another possible reason was the disturbance of the bottom sediment by intensive bottom trawling.

Although biogenic silica in sediment cores did not show a clear systematic change with land use trapping of the suspended matter to the sea, there are still other elements such as aluminium which flux also has a close relationship with land use and is likely to be a meaningful medium in making a permanent record of the history of land use change. Besides, the geochronological study as made in sediment, the alternative way for studying historical records of the changing fluxes of silicate to the Gulf of Thailand was made on the coral cores. A domed-shaped *Porites lutea* coral block was used for biogenic silica determination. The concentration of biogenic silica in coral bands between 1950 and 1983 showed peak values during the mid-1950's to 1960 which was the soil removal period of dam construction but no clear change in biogenic silica in coral bands during pre- and post-dam construction which corresponds with the result found in sediment box cores. Coral bands are possible indicators to provide as well as better permanent record of the history of land use changes of the Central Plain of Thailand

During the last decade, only a few research on silicate were carried out in Thailand, which, limiting our knowledge on its behavior and impact on our environment. While this research was one of several efforts to fill up this gap, other short-term and long-term research and monitoring programs should be carried out to give us a better understanding on silicate in several perspectives.

For research programs:

1. A study of silicate budget through the river path should be carried out. This river path should include a river area above a dam, a dam reservoir, a river area behind a dam, estuaries, and a coastal zone around a river mouth. The data from each area will, then, be compared to find out any change in silicate budget throughout the river.

2. In addition to a study on silicate budget, a quantitative study of diatom and their productivity should be carried out in the same area since it is the major mechanism that control silicate budget in natural water. Moreover, the study can be extended to cover any other mechanisms that might play an important role in controlling silicate in natural water around the study area as well.

3. A hydro-biogeochemical model for aquatic continuums including reservoir, rivers, estuaries, and coastal zone should be developed. With this model, we can estimate the impact of human activities on silicate budget in natural water in the future.

For monitoring programs:

1. Silicate flux measurement should be included in a standard monitoring program and be carried out on a regular basis. This is to ensure that a proper action can be made when a major change on silicate that might have a severe impact to our environment such as toxic plankton bloom occur in the future.

2. It is recommended that the Si determination process in water sample should be carried out as soon as the sample is collected to avoid any loss due to an absorption onto the bottle or precipitation process

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APPENDIX

APPENDIX

LAND USE ON THE CHAO PHRAYA RIVER BANK

Figure A-1 Low Density Residential Zone and some Agricultural Area at Km 94 from the River Mouth

Figure A-2 Low-Medium Density Residential Zone at Km 78 from the River Mouth

Figure A-3 Medium Density Residential Zone at Km 72 from the River Mouth

Figure A-4 Medium Density Residential Zone and Power House at Km 60 from the River Mouth

Figure A-5 High Density Residential and Commercial Zone at Km 52 from the River Mouth

Figure A-6 Domestic Wastes Discharged to the Chao Phraya River through several small canals at Km 52

Figure A-7 High Density Residential Zone at Km 37 from the River Mouth

Figure A-8 Bangkok Port at Km 27 from the River Mouth

Figure A-9 High Density Industrial Zone at Km 12 from the River Mouth

Figure A-10 The Chao Phraya River Mouth

BIOGRAPHY

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