ธรณีเคมีของปรอทในเอสทูรีของแม่น้ำเจ้าพระยา

นาย สิทธิพันธ์ ศิริรัตนชัย

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต
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GEOCHEMISTRY OF MERCURY IN THE CHAO PHRAYA RIVER ESTUARY

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สิทธิพันธ์ ศิริรัตนชัย : ธรณีเคมีของปรอทในเอสทูรีของแม่น้ำเจ้าพระยา (GEOCHEMISTRY OF MERCURY IN THE CHAO PHRAYA RIVER ESTUARY)
อ. ที่ปรึกษา : ผศ.ดร. วิไลวรรณ อุทุมพฤกษ์พร, อ. ที่ปรึกษาร่วม : ศ.ดร. มนุวดี หังสพฤกษ์, 106 หน้า. ISBN 904-03-0574-1.

ความเข้มข้นของปรอทรีแอคทีฟที่ละลายน้ำ $(Hg-R)_D$ ปรอทรวมละลายน้ำ $(Hg-T)_D$ และปรอทแขวนลอย (Hg-P) ในเอสทูรีของแม่น้ำเจ้าพระยา มีค่าความเข้มข้นอยู่ในช่วง <0.15-5.23 ng/L, 2.16-18.1 ng/L และ 0.09-3.49 μg/g dry weight (10.2-112 ng/L) ตามลำดับ ค่าความเข้มข้นของปรอทดังกล่าวมีค่าเช่นเดียวกับที่พบในเอสทูรีอื่นๆ

การกระจายของปรอทในชั้นน้ำระหว่างฤดูแล้งและฤดูน้ำหลาก พบว่ามีความแตกต่างกันระหว่างฤดูกาล โดยปรอทรวมละลายน้ำในฤดูน้ำหลากมีค่าประมาณ 30% ของปริมาณปรอทรวมทั้งหมด (ปรอทที่ละลายน้ำ+ปรอทแขวนลอย) ขณะที่ในฤดูแล้งมีค่าเพียง 15% ของปรอทรวมทั้งหมด ปรอทที่ละลายน้ำส่วนใหญ่อยู่ในรูปปรอทที่ไม่รีแอคทีฟ $(Hg-NR)_D$ ซึ่งมีจำนวนมากกว่า 85% ของปรอทรวมละลายน้ำ

ชนิดของปรอทส่วนใหญ่ในเอสทูรี จะอยู่ในรูปของปรอทแขวนลอย (Hg-P) ซึ่งจะจับกับอนุภาคที่แขวนลอยถาวร โดยพบค่าสัมประสิทธิ์การแยกชั้น (K_D) ระหว่างปรอทแขวนลอยและปรอทที่ละลายน้ำมีค่าสูงในเขตที่น้ำมีความขุ่นสูงทั้งสองฤดู และพบค่า K_D ของฤดูแล้งสูงกว่าในฤดูน้ำหลาก ค่า K_D ของปรอทละลายน้ำที่ไม่รีแอคทีฟมีค่าสูงในฤดูแล้ง แสดงว่าปรอทละลายน้ำที่ไม่รีแอคทีฟระหว่างฤดูแล้งกับฤดูน้ำหลากมีพฤติกรรมแตกต่างกัน ในเอสทูรีของแม่น้ำเจ้าพระยาพบว่า K_D มีค่าเพิ่มขึ้นตามความเค็มที่เพิ่มขึ้นด้วยเช่นกัน การทดลองในห้องปฏิบัติการแสดงให้เห็นว่า การดูดซับบนสารแขวนลอยและการคายออกของปรอทเกิดขึ้นได้ในระหว่างการผสมของน้ำแม่น้ำและน้ำทะเล การทดลองในห้องปฏิบัติการเพื่อศึกษาการละลายกลับของปรอทในตะกอนแสดงให้เห็นว่า ปรอทสามารถละลายออกมาจากตะกอนได้อย่างรวดเร็ว จากนั้นจะถูกดูดซับกลับไปยังตะกอนภายใน 6 ชั่วโมง

ความเข้มข้นของปรอทที่ชั้นผิวของตะกอนมีความเข้มข้นในช่วง 0.2-0.77 μg/g (dry weight) ค่าความเข้มข้นของปรอทตามแนวดิ่งในท่อตะกอนแสดงให้เห็นว่า ความเข้มข้นของปรอทที่ชั้นผิวหน้า (ประมาณ 10 ซม แรก) มีค่าต่ำกว่าความเข้มข้นความเข้มข้นของปรอทเมื่อ 20 ปีก่อน ถึง 3-5 เท่า ทั้งนี้เป็นผลเนื่องมาจากการใช้ปรอทในกระบวนการผลิตของอุตสาหกรรมบางประเภทในขณะนั้น

ภาควิชาวิทยาศาสตร์ทางทะเล ลายมือชื่อนิสิต ....
สาขาวิชาวิทยาศาสตร์ทางทะเล ลายมือชื่ออาจารย์ที่ปรึกษา ....
ปีการศึกษา 2544 ลายมือชื่ออาจารย์ที่ปรึกษาร่วม ....

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KEY WORD : GEOCHEMISTRY, REACTIVE MERCURY, TOTAL DISSOLVED MERCURY, NON-REACTIVE MERCURY, SUSPENDED PARTICULATE MERCURY, CHAO PHRAYA RIVER ESTUARY

SITTIPUN SIRIRATTANACHAI: GEOCHEMISTRY OF MERCURY IN THE CHAO PHRAYA RIVER ESTUARY. THESIS ADVISOR : ASSIST. PROF. WILAIWAN UTOOMPRURKPORN, Ph.D., THESIS COADVISOR: PROF. MANUWADI HUNGSPREUGS, Ph.D., 106 pp. ISBN 974-03-0574-1.

Concentrations of dissolved reactive mercury, $(Hg\text{-}R)_D$, total dissolved mercury, $(Hg\text{-}T)_D$, and suspended particulate mercury, Hg-P, in the Chao Phraya River estuary were <0.15-5.29 ng/L, 2.16-18.1 ng/L, and 0.09-3.49 μg/g (dry weight) (10.2-112 ng/L) respectively. These are in a similar concentration range to those found in major estuaries elsewhere.

The seasonal variation of mercury distribution in the water column was observed between the dry and the wet season. Total dissolved Hg in the wet season was about 30% of the combined dissolved and particulate concentrations, while in the dry season it was only 15% of the combined Hg. Most of the dissolved Hg was in the non-reactive Hg [$(Hg\text{-}NR)_D$] form, which accounted for more than 85% of the total dissolved Hg.

Suspended particulate mercury was the main species of Hg in the estuary and was associated with permanently suspended particles. The partition coefficients (K_D) between particulate and dissolved forms were higher in the high turbidity zone during both seasons and the K_D value of the dry season was higher than in the wet season. The higher K_D for non-reactive dissolved Hg in the dry season suggested that the behavior of $(Hg\text{-}NR)_D$ was different between the dry and the wet season. Increase of K_D with increasing salinity was also found in the Chao Phraya estuary. Laboratory experiments showed that adsorption and desorption of mercury occurred during mixing along a salinity gradient. Resuspension experiments, in the laboratory, showed that mercury desorbed from sediments rapidly, however, the readsorption occurred within 6 hours.

The Hg concentration of surface sediments ranged from 0.2 to 0.77 μg/g (dry weight). The vertical profile of Hg in core sediment indicated that the Hg concentrations in surficial sediment (about upper 10 cm) were about three to five times lower than concentration found 20 years ago due to the use of mercury in the production process of some industries during that period.

Department of Marine Science	Student's signature…………………………………………..
Field of Study Marine Science	Advisor's signature………………………………………...
Academic year 2001	Co-advisor's signature…………………………………….

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Finally I would like to thank my family.

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Chapter 1

Introduction

1.1 Background

River is a major source of particulate and dissolved metals to the sea. Therefore, the studies of biogeochemistry of major world rivers are of common interest to the understanding of their global cycling and transport. The transport and behavior of trace metals in rivers, either in the dissolved form or as part of the suspended matter, has been studied by a large number of investigators (Groot et al., 1976). The study of the distribution and concentration of potentially toxic trace elements during estuarine transportation have received a great deal of attention. Mercury is one of the most toxic elements and the mercury pollution in the aqueous environment has been known for several decades, as the case of Minamata in Japan (Forstner and Wittmann, 1981; Sadiq, 1992).

Mercury occurs in a wide variety of environments. It is transported in air, land and water at all scales (Porcella, 1994). During the 1980s it was recognized that mercury can be transported long distances in the atmosphere and thus may be deposited great distances from the source areas. The global background of atmospheric mercury is increasing by about 1% per annum (Lindqvist, 1994).

In recent years, mercury levels in the vicinity of the gas exploration platforms in the Gulf of Thailand has been found to be above the background level. The impact of metal release on fish in the Lower Gulf of Thailand associated with gas production was investigated and evaluated based on the concentration in marine organisms and on the composition of sediment (Windom and Cranmer, 1998). However, the result showed no evidence of widespread mercury contamination in the Gulf. The ratios of inorganic mercury to total mercury in seawater samples were considerably higher than such ratio in other areas. However, this was the first report on tropical sea (Hungspreugs et al., 1998). The distribution and behavior of trace elements in the major rivers in Thailand have been studied for many years , especially in the Chao Phraya River which is the most important river and is directly affected by anthropogenic activities.(Umnuay, 1984; Hungspreugs et al.,; 1988; 1989; and 1991; Hungspreugs and Utoomprurkporn, 1998)

The Chao Phraya River is the largest river in Thailand, originating from the northern mountain area and flowing down south into the Gulf of Thailand. The river flows through agricultural areas, industrial areas and many populated towns, carrying suspended sediment, domestic and industrial wastes to the gulf. The geochemical interactions of trace element between sediment and water in the Chao Phraya River estuary is not well understood, least of all mercury. The study of geochemistry of mercury in the Chao Phraya River estuary is proposed to obtain further understanding of the behavior and cycling of mercury in aquatic environment.

1.2 Literature review

1.2.1 Physical and chemical properties of mercury

Mercury is the only common metal liquid at ordinary temperature and pressure, which atomic weight 200.59, atomic number 80, and belong to II B group of the periodic table. At 20 ^{O}C the specific gravity of the metal is 13.546, it has a melting point at –38.842 ^{O}C and boiling point at 356.58 ^{O}C. It is a heavy, silver – white metal, a rather poor conductor of heat, as compared with other metals, and fair conductor of electricity (Weast and Astle, 1980; WHO, 1989).

There are three states of inorganic mercury : Hg^{O} (metallic), Hg^{+} (mercurous), and Hg^{++} (mercuric) mercury. Mercury (II), or mercuric salts are very much more common than mercury (I) salts. Mercury is also form organometallic, the simple salts, such as chloride, nitrate and sulfate, mercury (II) form an important class of organometallic. Organic form are those in which mercury is attached covalently to at least one carbon atom. The organometallic compounds are stable, though some are readily broken down by living organism, while others are readily biodegraded.

Elemental mercury has a very high vapor pressure, the saturated at 20 °C has a concentration over 200 times greater than the currently accepted concentration for occupational exposure.

Mercurials differ greatly in their solubilities. The solubility in water increases in the order: elemental mercury < mercurous chloride < methylmercury < mercury chloride. Elemental mercury and the halide compounds of alkylmercurials are more soluble in non–polar solvents than in water (WHO, 1989; WHO, 1991).

In addition, mercury easily forms alloy with many metals, such as gold, silver, and which are called ***amalgams***. Its case in amalgamating with gold is made use of in the recovery of gold from its ores (Weast and Astle, 1980).

1.2.2 Sources and uses of mercury

Mercury in the environment come from natural and anthropogenic sources. The natural emissions are weathering of rocks, wind blow dust, volcanic activity, thermal fluids, degassing of earth's mantle, emanations from the oceans, transpiration and decay of vegetation and forest fires (Fergusson, 1991). The natural emissions are estimated at the order of 2,700-6,000 tons per year (WHO, 1991).

Anthropogenic sources are probably less than natural sources. The worldwide mining of mercury is estimated to yield about 10,000 tons/year (WHO, 1989). The main ore is cinnabar (HgS). The metal is obtained by heating cinnabar in a current of air and by condensing the vapor (Weast and Astle,1980). Mining activity result in losses of mercury through the dumping of mine tailing and direct discharges to the atmosphere. Other important sources are the combustion of fossil fuel, the refining of gold, the production of cement, refuse incineration, and industrial metal application, total global release of mercury to the atmosphere due to human activity has been estimated to be of the order of 2,000-3,000 tons/year (WHO, 1991).

Mercury metal and mercury compounds are widely used in a variety of industrial and agricultural applications (WHO,1986). A major use of mercury is an a cathode in the electrolysis of sodium chloride solution to produce caustic soda and chlorine gas, which has important uses in the paper – pulp industry. Mercury is widely used in the electrical industry (lamps, arc rectifiers, and mercury battery cell, in control instruments in the home and industry switches, thermostats, barometers) and in other laboratory and medical instruments. It is also widely used in the dental profession for tooth amalgam fillings, pharmaceutical and cosmetic preparations. Organic mercury compounds are used in antifouling and mildew – proofing latex paints and to control fungus infections of seeds, bulb plants and vegetation (Weast and Astle, 1980; Forstner and Wittman, 1981).

Mercury as an environmental pollutant has been documented in numerous studies in recent decades and Hg pollution has been reported in a large number of waters all over the world (Johansson et al., 1991). Because of it's wide use, anthropogenic inputs to the aquatic environment are regarded as the main source of mercury contamination (Sadiq, 1992).

1.2.3 Chemical speciation of mercury in water

Mercury is very dynamic in aquatic environments, it exists in several forms due to its easily transformation to various physical and chemical forms (Sadiq, 1992).

Lindquist et al., (1984) cited in WHO (1989) proposed that the speciation of mercury compound can be divided into 3 groups, V, R and NR, where, V stands for volatile, e.g. Hg^{O} (elemental mercury), $(CH_3)_2Hg$

R for water soluble or particle – borne reactive species, e.g. Hg^{2+}, HgX_2, HgX_3^-, and HgX_4^{2-} (where X = OH^-, Cl^-, or Br^-), Hg^{O} on aerosol particles, Hg^{2+} complexes with organic acids.

NR for non – reactive species, e.g. CH_3Hg^+, CH_3HgCl, CH_3HgOH, and other organo – mercuric compounds, $Hg(CN)_2$, HgS, and Hg^{2+} bound to sulfur in fragments of humic matter.

Speciations of mercury in aquatic environment are mainly inorganic and organic species. The dominant inorganic species in fresh water is $Hg(OH)_2$, which forms at pH ~6 while the dominant species in seawater is chloro–complexes. The mercury species as a function of chloride ion concentration and pH and it is clear that in sea water $Hg(OH)_2$ has a negligible existence. Significant changes occur on mixing of fresh water with seawater as found in an estuary. Because of the stability of Hg/Cl complexes, a salinity of 3–5 psu is sufficient for the chloro–species to be dominant (Fergusson, 1991). $HgCl_2$ being the major species at low salinity and anionic form ($HgCl_3^-$, $HgCl_4^{2-}$) being predominant with increasing salinity (Coquery, 1997).

Hg species released into the aquatic environment are the Hg^{2+}, Hg^{O}, and organic Hg. All of these compounds tend to move into the sediments. Hg^{O} is not very soluble in water, while the Hg^{2+} form very strong complexes with many organic and inorganic substances and also particles in the water and will settle down with them (Jernelov, 1974). Both organic and inorganic compound undergoes methylation are interconvertible to form organic Hg compound (Sadiq, 1992). The methylation can occurs both in sediment and in the water column with surface reducing bacterial being the principal methylation organism in both freshwater and marine environments (Gilmour and Henry, 1991). A part of biological processes, the mercuric ion is methylated to monomethyl – or dimethylmercury. The monomethylmercury will leach into the water and the further accumulate in fish, algae, and other living aquatic organisms, while dimethylmercury will have more tendency to move with gas bubbles through the water up to the atmosphere, under acidic conditions or ultraviolet light, dimethylmercury will break down and form monomethylmercury that might fall with precipitation in some nearby body of water or over land. If it is converted to elementary Hg it might also fall with precipitation, or take part in the global circulation of elementary Hg vapor (Jernelov, 1974). The major pathways of the Hg cycle can be illustrated in simple diagram in Fig.1-1.

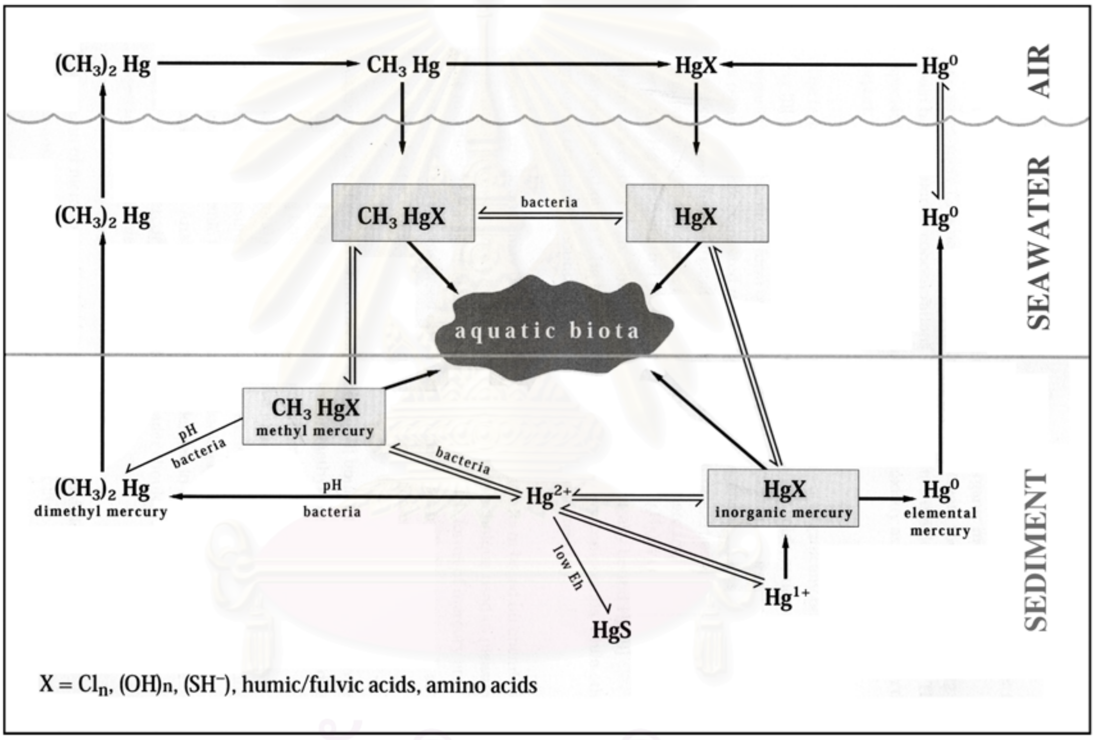


Fig.1-1 Important pathways of mercury speciation in the aquatic environment (Beckvar et al., 1996)

1.2.4 Chemistry of Mercury in Aquatic Environment

The estuarine chemistry of Hg actually refers to it chemical behavior in estuarine water and sediment. Once entered in estuaries environment as a pollutant largely from anthropogenic sources, its chemical behavior determines how much Hg will remain dissolved in estuaries and in which chemical forms. Estuarine and marine chemistry also determines the rate of Hg losses to the sediments and terrestrial environments. All these chemical interactions influence Hg bioaccumulation and toxicity to estuarine biota (Sadiq, 1992).

The variation of Hg reported from coastal water is an indication of the dynamic character of the coastal zone (Dalziel, 1992). In general, most of Hg in open ocean water (>80 %) is reactive Hg (Gill and Fitzgerald, 1987), while 25% – 50% of reactive Hg was found in the coastal water (Dalziel and Yeats, 1985). About 20% of the total dissolved mercury was found at the upper part of the Scheldt estuary and increase gradually to over 90% at the river mouth (Leermakers et al., 1995). Cossa et al. (1988) reported that the Hg concentration in the St.Lawrence estuary decreased nonconservatively as salinity increased. They concluded that 50 – 80% of Hg was strongly bond to organic matter and suggested that the removal of Hg in the estuary was attributed to the coagulation of organic colloids. A maximum in dissolved Hg at low salinity had been observed in several estuaries e.g. the Gironde, the Loire and the Rhone estuaries (Figuers et al., 1985) and Galveston Bay (Stordal et al., 1996). However, increasing of dissolved Hg with increased salinity were also found in some estuaries e.g. Scheldt estuary (Leermakers et al., 1995), the Lena, Ob and Yenisei Rivers (Coquery et al., 1995), perhaps due to the remobilization from particles under turbid conditions (Vandal and Fitzgerald, 1995)

In fresh water mercury is mostly associated with suspended particles. The average share of particulate from the whole Hg (dissolved + particulate Hg) is 87% for the Loire and 95% for the Seine River (Coquery et al., 1997).

In estuaries a variable amount of the suspended material can enter with the inshore sea water and resuspension of settled sediments within the estuary may occur (Burton, 1976). The Hg associated with particulate matters was well documented. A strong correlation has been reported between organic matter and Hg in water and sediments (Gobeil and Cossa, 1993; Leermakers et al., 1995; Driscoll et al., 1995, and

Coquery et al., 1995) and strong complexes with dissolved organic matter derived principally from fresh water input (Mason et al.,1993). Loring et al. (1983) suggested that terrigenous organic matter is the main scavenging agent for Hg in the Saquenay fjord. The association of Hg on particulate matter can be attributed to three main factors:

1) Precipitation of insoluble forms (HgS),
2) Adsorption or coprecipitation onto organic or inorganic solid phases and
3) Uptake by living organisms (Leermakers et al., 1995).

Recent observation indicate that a large fraction of the dissolved Hg may be associated with colloidal material (Mason et al., 1993; Stordal et al., 1996). In estuaries and coastal systems, most contaminants and especially trace metals show a high affinity for particulate matter and preferentially for the fine – grained fraction of suspended solid (Regnier and Wallast, 1993). Estuarine sediment serve as a repository of trace metals. They may release these metals to surrounding water in three ways :

1) by desorption from suspended particles upon contact with sea water,
2) by desorption from bottom sediments, and
3) by diffusion from interstitial water subsequent to diagenetic alteraction of sediments.

The trace metals content of estuarine sediments are function of their chemical and mineralogical composition which have been related to the grain size of the particles. Most trace metals are associated with the fine grained fraction of sediments.

Hg can form stable, soluble complex with sulphide and polysulphide species (HgS_2^{2-}, $HgHS_2^-$, $Hg(HS)_2$ etc.) which may dominate in sulphidic seawater (Paquette and Helz, 1995) and dissolved Hg can be adsorbed by several components of the solid sediment. Among these, sulphide minerals have been reported to be excellent scavengers for trace metals, including Hg (Jean and Bancroft, 1986, Hyland et al., 1990) and HgS accounts for a large fraction of total Hg in the estuarine sediments

(Leermakers et al. 1991). Hg also adsorbed to or coprecipitated with iron sulphide is a potential source of secondary contamination (Moore, et al., 1988; Morse, 1994). Hg will be release to the pore waters when iron and manganese oxides are buried and undergo reductive dissolution as a consequence of microbial degradation of organic matter (Gobeil and Cossa, 1993) and dissolved Hg concentration in the pore water were high variable, ranging from 17 to 500 ng/L in sediment of the Saquenay Fjord, Canada (Gagnon et al., 1997).

1.2.5 Partitioning of inorganic mercury in estuary.

Trace metals in estuaries occur in many different chemical and physical forms, or species. There are many researches focus on processes controlling trace metals behavior in estuaries, where river water gradually mixes with seawater leading to systematic changes in ionic strength, pH, DOC, SPM and alkalinity (Benoit et al., 1994). However, it remains an incomplete understanding of the factors controlling the speciation and particle-water reactivity of Hg in estuaries, where reaction conditions change markedly from river to sea (Le Roux, et al., 2001).

Partition coefficient (Distribution coefficient), K_D, is of fundamental significant to our understanding of geochemical and contaminant fluxes in estuaries and coastal waters. Partition coefficient, K_D is defined as the ratio of adsorbed or particulate concentration (P, w/w) to dissolved concentration (C, w/v) of a chemical constituent (Turner, 1996).

In estuaries, partitioning is important because of the human perturbation to chemical concentrations, and the strong temporal and spatial gradients of reaction controlling variables (salinity, pH, type and concentration of dissolved organic matter, etc.). For many trace metals, partitioning is reasonably well understood in terms of dissolved inorganic speciation, including the tendency of metals to form stable, soluble complexes in saline water (Turner, et al., 2001).

In general high organic matter contents and high heterotrophic activity is found in the upper estuary. Hg is preferably bound to organic matter in suspension and the degradation of this organic matter may release Hg into solution. The long residence time of suspended matter trapped in the zone of maximum turbidity may promote the more complete degradation of organic suspended matter. Dissolved mercury is predominantly complex to organic ligands, probably deriving from the degradation of particulate organic matter (POM) (Leermarkers, et al., 1995). Partitioning coefficient of Hg, K_D, generally increase with increasing salinity, despite the stability of chloro-complexes. This behavior is consistent with that of most other trace metals, including the other Group IIB metals and is attributed to the tendency of Hg(II) to form soluble and stable complexes with Cl^- (principally as $HgCl_4^{2-}$) in seawater. The effects of increasing pH on estuarine mixing have been shown to slightly reduce the sorption of Hg(II) to estuarine particles as a function of salinity, presumably because sorption of organic complexes of Hg(II) is favored at low pH. It appears, therefore, that aqueous Hg(II) species (or ligands binding Hg) are subject to some form of salting out on estuarine mixing; that is, their solubility are reduced (or sorption enhanced) with increasing salinity. Moreover, the increased Hg sorption onto the particles from a high salinity may be due to the adsorption of organic complexes onto the particles. The increased Hg(II) sorption could be explained by relatively hydrophobic and lipophilic $HgCl_2^0$ complex, which is subject to salting out, compare with the more hydrophilic $Hg(OH)_2^0$ complex. Chloro-complexes of the other Group IIB metals, Cd and Zn are ionic, more soluble (and tend to dissociated) and less lipophobic, and are, rather than salting out, subject to an increase in their solubility (or reduction in sorption) with increasing salinity.

Salting out of the neutral chloro-complex is consistent with an increase in K_D with increasing salinity, and the observation that chloro-complexes of Hg(II) are reflecting the sorption of $HgCl_2^0$ into particulate organic matter. However, speciation calculation estimate that $HgCl_2^0$ comprises only about 20% of total chloro-complexes in seawater, and the greater abundance of the more soluble $HgCl_4^{2-}$ complex above salinity of about 10 is predicted to conceal or even offset any salting effects of the neutral complex (Turner, et al., 2001).

1.3 Study site

The Chao Phraya River is the largest river in Thailand, originating from four rivers in the northern mountain area, which flow to form the Chao Phraya River. The main river from the confluence to the river mouth is 396 km long. The river flows down south through Bangkok and several other large cities, the drainage area is about 177,000 km^2. The Chao Phraya River is one of the most heavily populated regions of Thailand, where agricultural and industrial activities are largely developed and as a consequence, large amounts of domestic and industrial wastes are carried by the river to the Gulf of Thailand. The river discharge is varying from less than 80 m^{3}s^{-1} during drought period in April, to more than 1,460 m^{3}s^{-1} during flood period in October. The mean river discharge is 430 m^{3}s^{-1} and the high flows can reach about 3,000 m^{3}s^{-1} during large flood conditions. The upper limit of tide influence in about 175 km upstream at the low river discharge and only 75 km at the high river discharge. The limit of salt intrusion also varies from 10 to 80 km depending on hydrodynamic conditions (Hungspreugs et al., 1989; Pollution Control Department: PCD., 1997). The mean depth of the estuary is about 15 m (8-24 m) (Port Authority of Thailand: P.A.T., 1993).

1.4 The Objective of the study

The objectives of this study are

1. To study the distribution and behavior of mercury species in the Chao Phraya River estuary.
2. To study the geochemical processes controlling the distribution of mercury in the Chao Phraya River estuary.

Chapter 2

Methodology

The field surveys and laboratory experiments were conducted to understand the geochemistry of mercury in the Chao Phraya River estuary.

2.1 Field survey

Samples were collected from the Chao Phraya River estuary in the dry and the wet season. The Chao Phraya River estuary is about 100 Km long between the river mouth at Samut Prakan province and the limit of salt intrusion located upstream at Pathum Thani province (PCD, 1997). The study area is shown in Fig.2-1.

Water and sediment samples were collected at sixteen stations in the Chao Phraya River estuary in April and October, 1999, during low tide. The locations of the sampling stations are shown in Fig.2-1. In addition, an extra survey was conducted in April, 2000. The water samples were collected from the upstream to the station 17 Km from river mouth (7 stations). Three sediment cores were collected during this survey (Fig.2-1). All manipulations was performed using rigorous trace metal clean protocols adopted from Loring and Rantala (1992); and Quemerais and Cossa (1997).

Water samples were also collected for the measurement of suspended particulate matter (SPM) and organic matter. The content of organic matter in water was determined in terms of total organic carbon (TOC) (Bishop et al., 1995). Salinity and temperature were measeured by a CTD Meter (Conductivity–Temperature –Depth). Dissolved oxygen (DO) and pH were also determined by probe meters during the field survey.

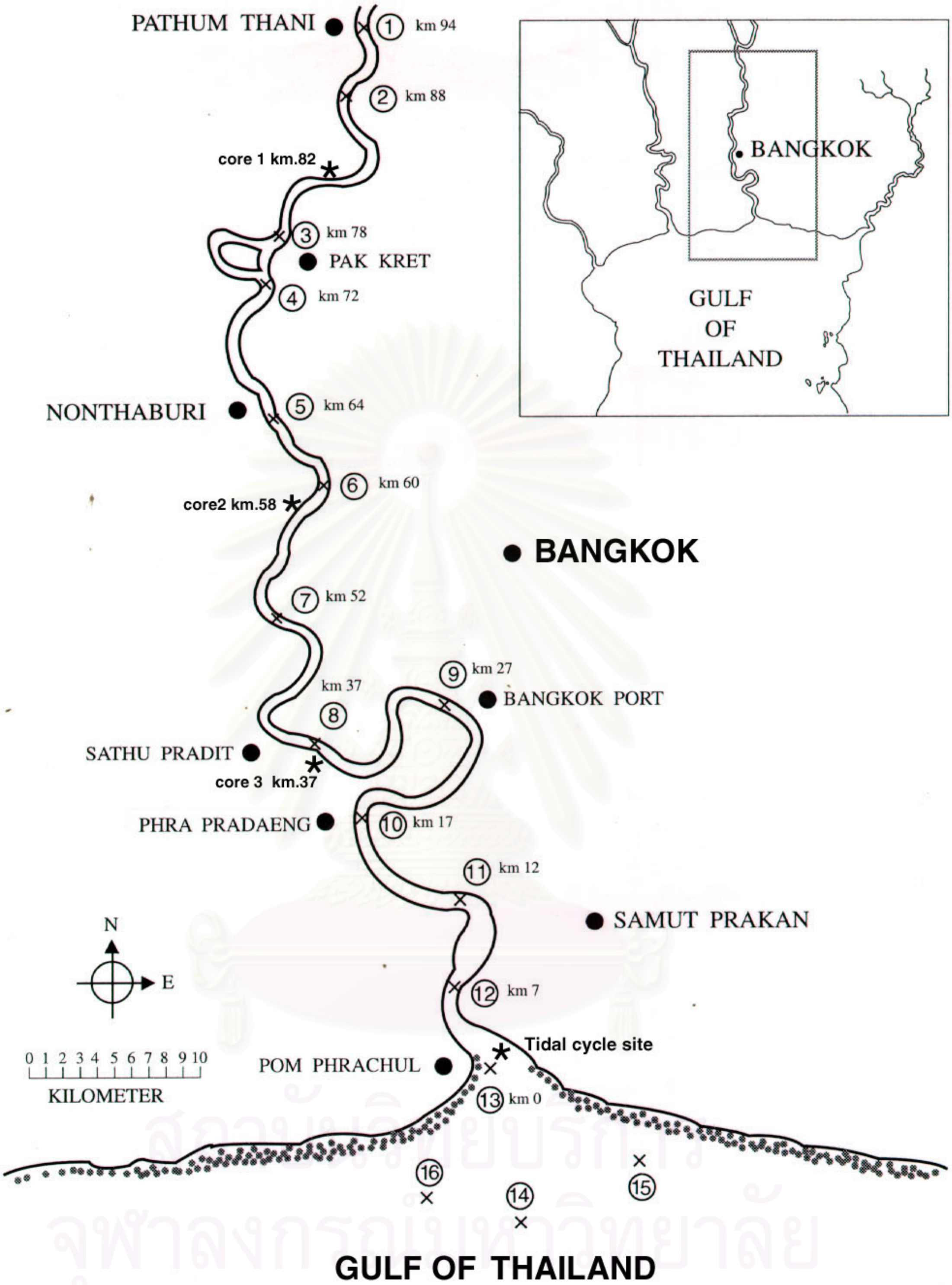


Fig.2-1 Location of sampling station in The Chao Phraya River estuary.

2.1.1 Water samples

Surface water samples were taken directly in 500 ml Teflon (PFA) bottles by hand covering with polyethylene gloves. All sample bottles have been acid washed and rinsed thoroughly with Mili–Q water prior to use. The sampling bottles were rinsed three times with the estuarine water before being filled and were then re–bagged in double Ziplock plastic bags and transported in coolers back to the laboratory. Near bottom water samples were collected using 2.5 L Go–Flo bottle which has been thoroughly cleaned in the laboratory and drained immediately into 500 ml Teflon (PFA) bottles.

Immediately after return to laboratory, the water samples were filtered through 0.45 um pore size pre-weight Nuclepore membrane previously acid–washed and rinsed many time with Milli–Q water. The whole procedure was carried out under laminar flow hood and polyethylene gloves were used for handling operations to avoid contamination.

All Teflon and plastic – ware was washed and stored according to Quemerais and Cossa (1997). The filtered water for dissolved reactive mercury [(Hg-R)$_D$] was unacidified and stored in acid-cleaned 250 ml Teflon (PFA) bottles and kept in the dark at 4°C until analysis, which should be performed within 8–12 hours of collection. The samples for [(Hg-T)$_D$] were acidified with 0.5 % HCl (Suprapur) and stored in double bagged until analysis. The filters was individually kept in tightly sealed plastic petri-dishes and stored frozen for the determination of particulate mercury (Hg-P).

2.1.2 Sediment samples

Surface sediment samples were collected by Van Veen grab sampler. Only the uppermost layer (0–3 cm) with minimal disturbance was sampled (Regnier and Wollast, 1993). The sediments were transferred to polyethylene bags and kept frozen for determination of Hg, Al, Fe, Mn and organic carbon (OC).

2.1.3 Core sample

Sediment cores were taken using gravity core (80 cm long). Core samples were subdivided into 2-cm intervals and analyzed for total Hg distribution to see history of contamination. Daily of sediment was also performed by Pb-210 method.

2.2 Field survey during the tidal cycle

Surface and near bottom water samples were collected during tidal cycle period of spring tide (May 1999) at the river mouth (Phra Chulachomklao Fort, Samut Prakan province, Fig.2-1). In order to understand Hg behavior during mixing processes of tidal cycle. All physico–chemical parameters are follow as described in section 2.1

2.3 Laboratory experiment

In order to understand the behavior of Hg during estuarine mixing, two sets of experiments were carried out in the laboratory.

2.3.1 Sediment resuspension experiment

The experiment was carried out by adding fresh river sediment to the mixture of river water and seawater end – member at different proportions in Teflon (PFA) vessels and subsampling at 0.5, 1, 3, 6, 12 and 24 hours. Then, the water samples were filtered through pre-cleaned and pre-weighted Nuclepore membrane pore size 0.4 μm to determine the $(Hg\text{-}T)_D$ concentration.

2.3.2 Mixing experiment

Unfiltered river water and seawater were mixed in different proportion to get salinity of 0, 5, 10, 15, 20 and 30 psu in Teflon (PFA) vessels. The waters were subsample at 0, 0.5, 1, 3, 6, 12 and 12 hours, filtered and analysed for $(Hg\text{-}T)_D$ and Hg-P.

2.4 Sample analysis

Water samples were analyzed for dissolved reactive mercury $(Hg\text{-}R)_D$, total dissolved mercury $(Hg\text{-}T)_D$, and particulate mercury (Hg-P). Dissolved Hg were detected by cold vapor atomic fluorescence spectrometry (CVAFS) after transformation to Hg^0 using methods described by Quemerais and Cossa (1997) (Appendix A).

$(Hg\text{-}R)_D$ was determination in an unacidified sample (Mason et al., 1999) by gold amalgamation procedure after reduction with $SnCl_2$. The Hg volatilized from the trap was carried with Ar gas(99.999%) to detector at the flow rate of 80 ml min^{-1} and then measured using Tekran CVAFS Mercury Detector 2500. Analysis of $(Hg\text{-}T)_D$ were first wet–oxidized with BrCl for decomposition of organic complexes, followed with hydroxylamine to neutralize BrCl and then reduced to its elemental form using $SnCl_2$ and measured by CVAFS the same as in Hg-R determination.

Concentration of Hg-P were determined after HNO_3: HCl (9:1 V/V) mineralization of the particulate in Teflon (PFA) vessels, in the oven at 90°C for 90 minutes. The solutions were diluted with Milli–Q water and then measured by Flow Injection Analysis – Mercury Hydride System (FI – MH – AAS).

Sediment samples were freeze dried and separated into two fractions of grain size using 250 μm and 63 μm nylon sieves. Each fractions (<250 μm and <63 μm) of sediment were used to determine its mercury concentration by totally digested using the same method as Hg-P determination. In addition, the percentage of coarse (>63 μm) and fine (<63 μm) grain sediments were also measured by wet sieve separation.

The Al, Fe and Mn concentration in sediments were determined using microwave digestion technique described by Loring and Rantala, (1992) and measured by Graphite Furnace Atomic Absorption Spectrophotometry (GF–AAS) for Al and Mn, and Flame Atomic Absorption Spectrophotometry (F-AAS) for Fe.

Concentrations of suspended particulate matter (SPM) were determined gravimetrically after filtration on pre-weighed Nuclepore membrane filter (0.4 μm). Total organic carbon (TOC) concentration was measured according to wet oxidation with a TOC analyzer. Readily oxidizable organic carbon (%OC) of sediment was determined using the wet–oxidation described in Loring and Rantala (1992).

2.5 Partitioning between particulate and dissolved form

The partitioning between particulate and dissolved are a fundamental significance to our understanding geochemical and contaminate fluxes in estuarine and coastal water. The partition coefficients (K_D) define as a ratio of adsorbed or particulate concentration :

$$K_D = \frac{C_P}{C_D} \qquad (1)$$

or

$$K_D = \frac{C_P,(w/v)}{SPM * C_D,(w/v)} \qquad (2)$$

Where C_P,(w/w or w/v) is particulate concentration, C_D (w/v) is dissolved concentration and SPM is the concentration of suspended particulate (w/v).

To describe the particulate capacity for Hg in the Chao Phraya River estuary, the concentrate of Hg-P as a function of suspended particulate matter (SPM) concentration were plotted with isopleths of K_D (Millward and Glegg, 1997). Having a knowledge of the partition coefficient for Hg in the estuary, the percentage of particulate Hg as be estimated as the following equation:

$$\%\text{Particulate-Hg} = 100 - \%\text{Dissolved} \qquad (3)$$

$$\%Dissolved - Hg = \frac{C_D}{C_P + C_D} \times 100 \tag{4}$$

$$\%Particulate - Hg = 100 - \frac{C_D}{C_P + C_D} \times 100 \tag{5}$$

From Eq. (5) using value of K_D from Eq. (2) therefore,

$$\%Particulate - Hg = 100 - \left(\frac{C_D}{K_D * C_D * SPM + C_D} \right) \times 100 \tag{6}$$

$$\%Particulate - Hg = 100 - \left(\frac{100}{1 + K_D * SPM} \right) \tag{7}$$

2.6 Sample calibration and quality control

The accuracy and precision of analytical were obtained throughout the study.

A) The concentration of Hg is calculated by comparing the peak height with the peak height of the standard. The standard is obtained by injecting 20 μL of Hg–saturated air. The air temperature must be noted in order to calculate the quantity of Hg injected. The quantity of Hg (in picogram) in the standard is calculated by multiplying the volume of air injected (20 μL) by the mercury vapor density (more detail in Appendix A).

B) Percentage recovery of Hg analyses in aqueous phases was conducted by spiking Hg stock standard solution to previously analyzed sample further addition of $SnCl_2$. The Hg concentrations were measured and comparing the peak height with the peak height of standard Hg vapor. The recovery is 86.2 ± 3.6%.

C) Detection limits, defined as three times the standard deviation of the blank expressed per unit sample analyzed, were 0.1 ng/L for Hg-R, 0.5 ng/L for Hg-T, and 0.01 μg/g for Hg-P. Certified Reference Material (CRM) Buffalo River sediment was also analyzed following the same procedure. The recovery (%) is 95.08 ± 7.3% for the Certified Reference Material and the precision is 7.5 %. Percent recovery of Certified Reference Material (NBS 164.6 Estuarine Sediment) for Al, Fe and Mn are 94.53± 8 %, 87.3± 3.7 % and 106.6 ± 13.0 %, respectively. The precision is 6.7, 9.2 % and 16.4 % for Al, Fe and Mn, respectively.

Chapter 3

Results

Field surveys of this study were carried out 4 times, to represent the dry season, the wet season and the tidal cycle of the Chao Phraya River estuary. Two dry season surveys were made in April 1999 and April 2000, the wet season surveys was carried out in October 1999. During the surveys, water, sediment and some physical parameters were made on 16 stations of the Chao Phraya River estuary from Pathum Thani Province (Km 94) to the river mouth at Samut Prakan Province. The field survey on a 24 hr-tidal cycle was carried out at the river mouth station in May 1999.

3.1 Physico-chemical characteristic of water in The Chao Phraya River estuary

The physico-chemical characteristics of water in the Chao Phraya River estuary during the two field surveys in April and October 1999 are listed in Table 3-1 and 3-2. The mercury species in water are shown in Table 3-3 and 3-4. The results of DO, pH and mercury concentration of the dry season (April 2000) are listed in Table 3-5. While, results of physical and chemical properties during the tidal cycle are list in Table 3-6 and 3-7. The results are summarized as follow.

3.1.1 Salinity distribution

Typical salinity distributions in the Chao Phraya River estuary were observed to be different between the two seasons. Salinity intrusion was found up to 50–60 Km from the river mouth during the dry season (April, 1999), while in the wet season (October, 1999) it was at the river mouth vicinity. The Chao Phraya River estuary was classified as a rather well mixed estuary.

Table 3-1 Physical and chemical parameters of the Chao Phraya River estuary in the dry season (April,1999).

Distance	Salinity(psu.)		pH		DO (mg/L)		SPM (mg/L)		TOC (mg/L)	
(km)	surface	bottom	surface	bottom	Surface	bottom	surface	bottom	surface	bottom
94	0.0	0.0	6.4	6.6	4.36	3.76	16	31	2.45	2.99
88	0.0	0.0	6.7	6.8	3.93	3.29	21	29	3.68	2.30
78	0.0	0.0	7.4	7.4	3.89	3.03	17	20	3.19	2.78
72	0.0	0.0	7.2	7.2	3.02	2.37	34	52	2.51	2.63
64	0.0	0.0	7.3	7.5	2.46	2.04	18	75	3.12	2.77
60	0.0	0.0	7.3	7.3	0.45	0.22	12	32	5.13	2.35
52	0.8	1.4	7.4	7.4	1.20	0.50	8	12	4.82	4.72
37	3.4	4.5	7.6	7.6	4.50	0.50	16	26	4.90	4.92
27	4.1	7.3	7.6	7.5	6.00	4.50	34	173	5.57	3.99
17	6.5	6.6	7.6	7.5	3.40	3.10	105	202	4.16	3.92
12	12.3	12.6	7.5	7.5	4.40	2.40	61	80	2.89	2.69
7	14.5	15.3	7.6	7.6	3.50	2.70	69	248	2.48	2.28
0	16.8	16.9	7.6	7.6	3.80	3.20	43	144	2.06	1.99
-5	17.3	17.5	7.6	7.6	3.50	2.60	71	264	1.84	1.89
-5	17.5	20.4	7.6	7.7	4.90	4.60	52	90	1.53	1.52
-5	16.8	*	7.7	*	4.60	*	67	*	1.92	1.92

* no sample

Table 3-2 Physical and chemical parameters of the Chao Phraya River estuary in the wet season (October,1999).

Distance	Salinity(psu.)		pH		DO (mg/L)		SPM (mg/L)		TOC (mg/L)	
(km)	surface	bottom	surface	bottom	Surface	bottom	surface	bottom	surface	bottom
94	0.0	0.0	6.9	6.9	4.25	4.13	33	50	3.98	3.99
88	0.0	0.0	6.9	6.9	4.34	4.12	32	52	4.02	3.93
78	0.0	0.0	6.9	6.7	4.10	3.97	44	53	4.03	3.98
72	0.0	0.0	7.0	7.1	4.04	4.07	54	59	3.91	3.93
64	0.0	0.0	7.0	7.0	4.11	4.12	60	76	3.87	3.86
60	0.0	0.0	6.7	6.5	3.91	3.82	65	94	4.27	4.14
52	0.0	0.0	6.7	6.9	3.90	3.68	109	112	4.05	4.15
37	0.0	0.0	6.9	6.9	3.20	3.10	38	35	4.12	4.15
27	0.0	0.0	6.9	7.0	3.26	3.18	54	46	4.08	4.16
17	0.0	0.0	6.9	7.0	2.86	2.79	63	64	4.29	4.25
12	0.0	0.0	7.0	7.1	2.63	2.50	68	194	4.50	4.19
7	0.0	1.2	7.0	7.0	2.50	2.22	32	171	4.26	3.83
0	1.1	22.3	7.1	7.2	2.23	0.70	53	49	4.08	2.21
-5	4.3	14.6	7.1	7.3	2.29	1.30	42	53	3.89	1.89
-5	5.5	*	7.2	*	1.56	*	32	*	3.27	3.42
-5	7.1	14.3	7.2	7.3	1.97	1.42	51	51	3.78	2.94

* no sample

Table 3-3 Mercury species of the Chao Phraya River estuary in the dry season (April,1999).

Distance	$(Hg\text{-}R)_D$ (ng/L)		$(Hg\text{-}T)_D$ (ng/L)		Hg-P (ug/g)		$(Hg\text{-}R)_D/(Hg\text{-}T)_D$		$(Hg\text{-}NR)_D$ (ng/L)	
(km)	surface	bottom	surface	bottom	surface	bottom	surface	bottom	surface	bottom
94	0.37	0.51	4.77	4.51	3.49	1.69	0.08	0.11	4.40	4.00
88	0.94	0.66	5.16	6.01	2.98	1.67	0.18	0.11	4.22	5.35
78	1.57	1.47	7.49	8.94	1.96	2.82	0.21	0.16	5.92	7.47
72	1.06	0.85	3.65	6.66	1.68	0.61	0.29	0.13	2.59	5.81
64	1.37	1.41	3.10	8.63	1.53	0.18	0.44	0.16	1.73	7.22
60	1.92	0.90	9.61	7.85	0.71	1.12	0.20	0.11	7.69	6.95
52	1.47	0.99	7.83	11.23	2.55	0.68	0.19	0.09	6.36	10.24
37	0.54	0.26	5.85	6.55	2.77	2.91	0.09	0.04	5.31	6.29
27	0.28	0.15	11.21	18.12	2.52	0.69	0.02	0.01	10.93	17.97
17	0.25	0.74	3.06	6.66	0.95	0.65	0.08	0.11	2.81	5.92
12	0.33	0.42	7.24	16.51	1.06	0.59	0.05	0.03	6.91	16.09
7	0.26	2.30	7.18	4.67	1.04	0.53	0.04	0.49	6.92	2.37
0	0.44	0.53	6.91	10.68	1.78	0.53	0.06	0.05	6.47	10.15
-5	0.24	0.46	4.46	14.03	1.10	0.41	0.05	0.03	4.22	13.57
-5	0.23	1.12	2.16	4.60	1.68	1.52	0.11	0.24	1.93	3.48
-5	0.62	*	2.79	*	2.16	*	0.22	*	2.17	*

* no sample

Table 3-4 Mercury species of the Chao Phraya River estuary in the wet season (October,1999).

Distance	$(\text{Hg-R})_D$ (ng/L)		$(\text{Hg-T})_D$ (ng/L)		Hg-P (ug/g)		$(\text{Hg-R})_D/(\text{Hg-T})_D$		$(\text{Hg-NR})_D$ (ng/L)	
(km)	surface	bottom	surface	bottom	Surface	bottom	surface	bottom	surface	bottom
94	0.85	1.31	9.81	7.96	0.73	0.58	0.09	0.16	8.96	6.65
88	4.09	*	17.29	*	1.67	*	0.24	*	13.20	*
78	5.23	1.89	16.16	8.86	0.88	1.70	0.32	0.21	10.93	6.97
72	0.96	1.43	12.27	9.53	0.29	0.25	0.08	0.15	11.31	8.10
64	0.50	1.83	10.63	11.89	0.53	0.64	0.05	0.15	10.13	10.06
60	3.48	1.01	14.05	11.36	0.30	0.16	0.25	0.09	10.57	10.35
52	0.85	2.17	6.93	9.35	0.18	0.36	0.12	0.23	6.08	7.18
37	1.55	1.83	12.06	9.28	0.19	0.16	0.13	0.20	10.51	7.45
27	1.64	1.82	11.15	14.03	0.42	0.17	0.15	0.13	9.51	12.21
17	1.47	1.33	15.34	6.97	0.11	0.22	0.10	0.19	13.87	5.64
12	1.25	1.15	13.29	10.99	0.21	0.09	0.09	0.10	12.04	9.84
7	1.08	<0.15	10.22	8.34	0.58	0.46	0.11	ND	9.14	8.34
0	0.21	0.22	11.83	6.90	1.39	0.95	0.02	0.03	11.62	6.68
-5	0.18	0.23	7.36	4.30	1.01	1.85	0.02	0.05	7.18	4.07
-5	<0.15	*	5.32	*	1.38	*		*		*
-5	<0.15	<0.15	4.52	3.88	1.12	1.21	<0.03	<0.04	4.52	3.88

* no sample

Table 3-5 Mercury concentration of the Chao Phraya River in the dry season (April,2000)

Distance	DO (mg/L)		pH		Hg-R(ng/L)		Hg-T(ng/L)		Hg-P(ug/g)		Hg-NR(ng/L)	
(km)	surface	bottom	surface	bottom	surface	bottom	surface	bottom	surface	bottom	surface	bottom
96	2.79	3.11	6.8	7.1	2.29	4.46	14.49	12.85	1.71	0.48	12.2	8.39
90	2.64	2.77	6.9	6.8	1.12	2.41	18.31	9.6	1.05	2.79	17.19	7.19
82	2.2	2.31	6.8	6.9	0.37	3.61	10.18	7.62	2.86	1.02	9.81	4.01
72	2.04	2.2	6.9	6.9	0.37	1.15	10.4	4.73	1.03	2.14	10.03	3.58
60	1.6	1.8	6.9	6.9	0.41	0.64	10.76	2.61	0.49	1.16	10.35	1.97
36	0.8	0.8	6.8	7.0	0.24	0.29	6.72	1.92	0.5	1.19	6.48	1.63
17	0.6	0.4	7.0	7.0	0.41	0.58	6.52	3.62	0.49	0.23	6.11	3.04

Remark Salinity is 0 psu all stations

Table 3-6 Physical and chemical parameters of the Chao Phraya River during a tidal cycle (May,1999).

Time	Salinty(psu.)		DO(mg/L)		pH		SPM(mg/L)		TOC(mg/L)	
(hr.)	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom
0	1.6	2.2	1.05	0.95	6.8	6.9	152	370	1.98	4.38
3	0.8	1.3	1.06	0.92	7.0	7.0	110	588	5.38	4.94
6	1.5	1.6	1.37	1.05	7.2	7.3	52	75	4.18	4.49
9	1.8	5.3	1.85	1.67	7.2	7.3	20	44	2.9	2.16
12	3.3	12.7	1.09	1.00	7.4	7.2	26	163	4.14	1.65
15	1.1	9.3	1.05	0.94	7.2	7.2	58	247	2.94	2.03
18	2.6	16.4	2.61	2.32	7.2	7.3	38	92	4.95	2.83
21	2.8	17.1	1.31	1.66	7.1	7.3	56	65	2.01	*
24	3.6	4.9	1.03	0.93	7.0	6.1	117	1272	*	*

* no sample

Table 3-7 Mercury concentration of the Chao Phraya River during a tidal cycle (May, 1999)

Time	Tidal height	(Hg-R)$_D$(ng/L)		(Hg-T)$_D$(ng/L)		Hg-P(ug/g)		(Hg-NR)$_D$(ng/L)	
(hr.)	(m)	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom
0	0.5	2.01	1.53	20.99	16.92	0.62	0.29	18.98	15.39
3	0.5	0.87	0.41	8.59	13.91	0.88	0.27	7.72	13.5
6	2.3	0.48	<0.15	7.82	4.76	1.08	1.25	7.34	4.76
9	2.6	0.33	<0.15	6.13	2.41	0.68	1.77	5.8	2.41
12	1.7	0.44	<0.15	5.83	2.16	0.66	0.86	5.39	2.16
15	1.5	0.44	<0.15	5.15	4.43	0.73	0.59	4.71	4.43
18	2.4	0.39	<0.15	3.19	1.94	0.7	1.7	2.8	1.94
21	1.9	0.33	<0.15	2.92	2.29	0.76	2.03	2.59	2.29
24	0.5	0.44	<0.15	2.99	4.21	0.45	0.1	2.55	4.21

3.1.2 Dissolved oxygen (DO)

Dissolved oxygen (DO) ranged from 0.2 to 6.0 mg/L and 0.7 to 4.34 mg/L in the dry and the wet season, respectively. DO minima were observed near the front between fresh water and seawater. In the dry season, it was in Bangkok vicinity area (Km 60 to Km 37) while it was near the river mouth area in the wet season, DO concentrations of the bottom water were lower than surface waters. (Fig.3-1 to 3-2)

3.1.3 pH distribution

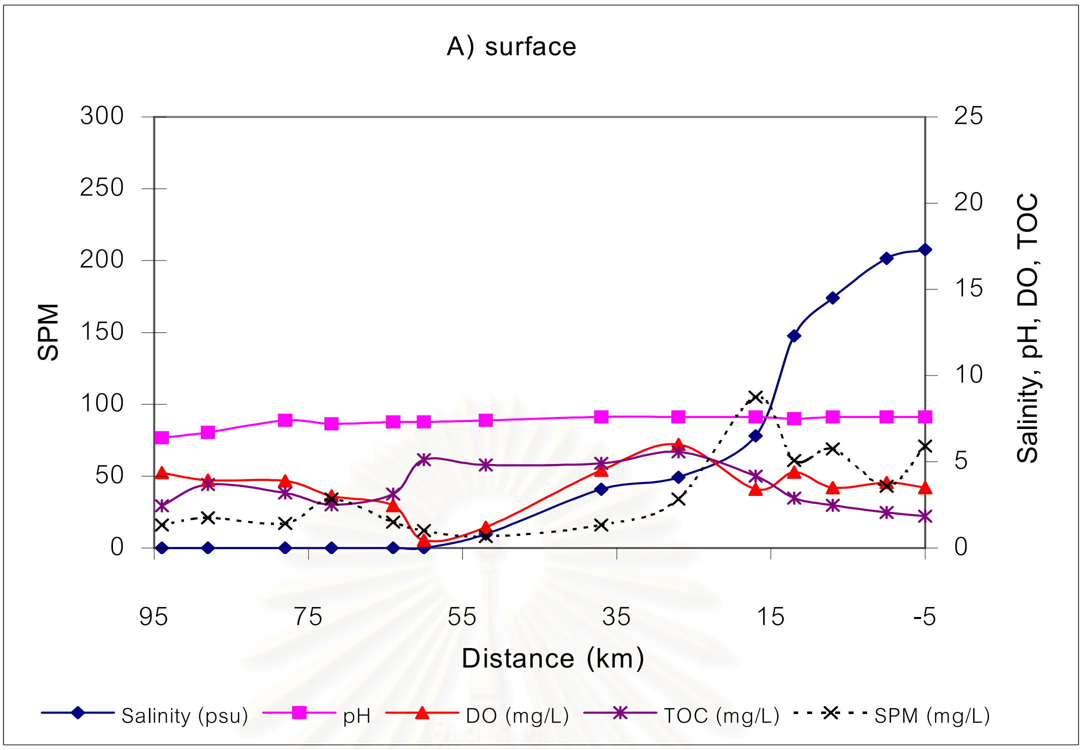
The pH value in the dry season ranged from 6.4 to 7.7 and 6.6 to 7.0 for surface and bottom water, respectively and water in the wet season ranged from 6.7 to 7.2 and 6.5 to 7.3 for surface and bottom, respectively. It increased slightly with increasing salinity toward the river mouth. However, the pH showed no difference between surface and bottom water in both seasons. (Fig. 3-1 to 3-2)

3.1.4 Suspended particulate matter (SPM) distribution

The suspended particulate matter (SPM) concentrations ranged from 8 to 264 and 32 to 194 mg/L in the dry and the wet season, respectively. The concentrations of SPM show slightly higher during the wet season and the bottom concentrations were much higher than the surface water due to mixing with fluid mud during low tide condition. (Fig. 3-1 to 3-2)

3.1.5 Total organic carbon (TOC) distribution

The concentrations of TOC ranged from 1.53 to 5.57 mg/L and 1.89 to 4.49 mg/L in the dry and the wet season, respectively. High concentrations of TOC were observed at the same location as DO minima in the dry season while the estuary seemed to homogeneous in TOC content during the wet season. (Fig.3-1 to 3-2)



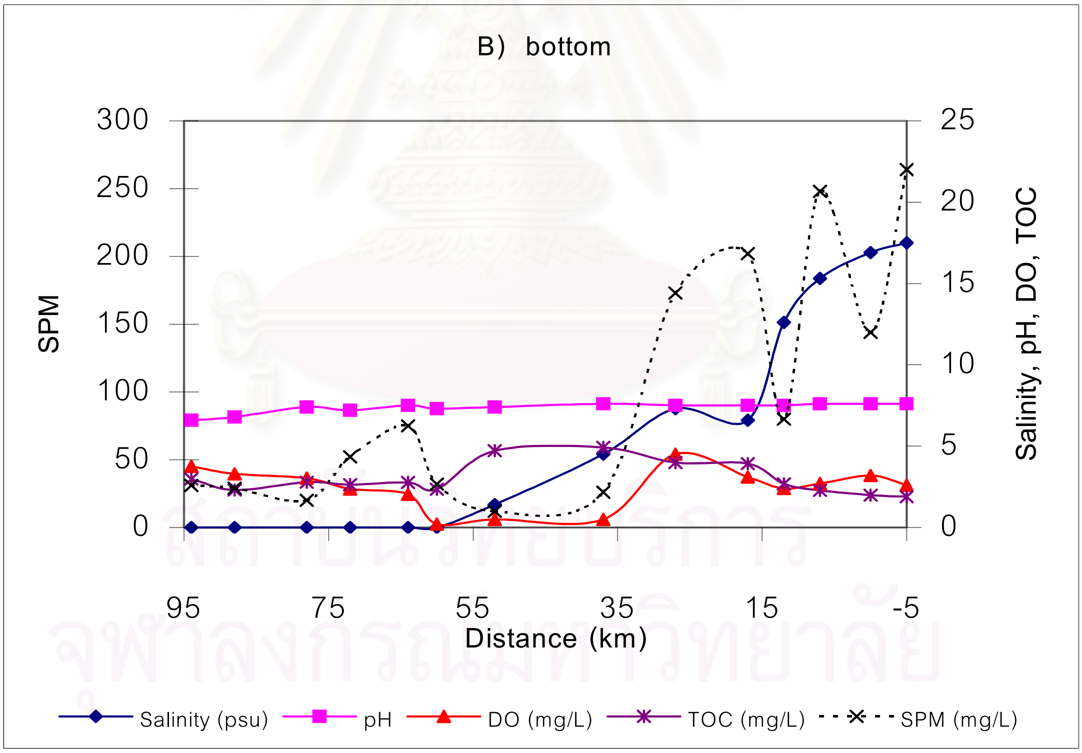
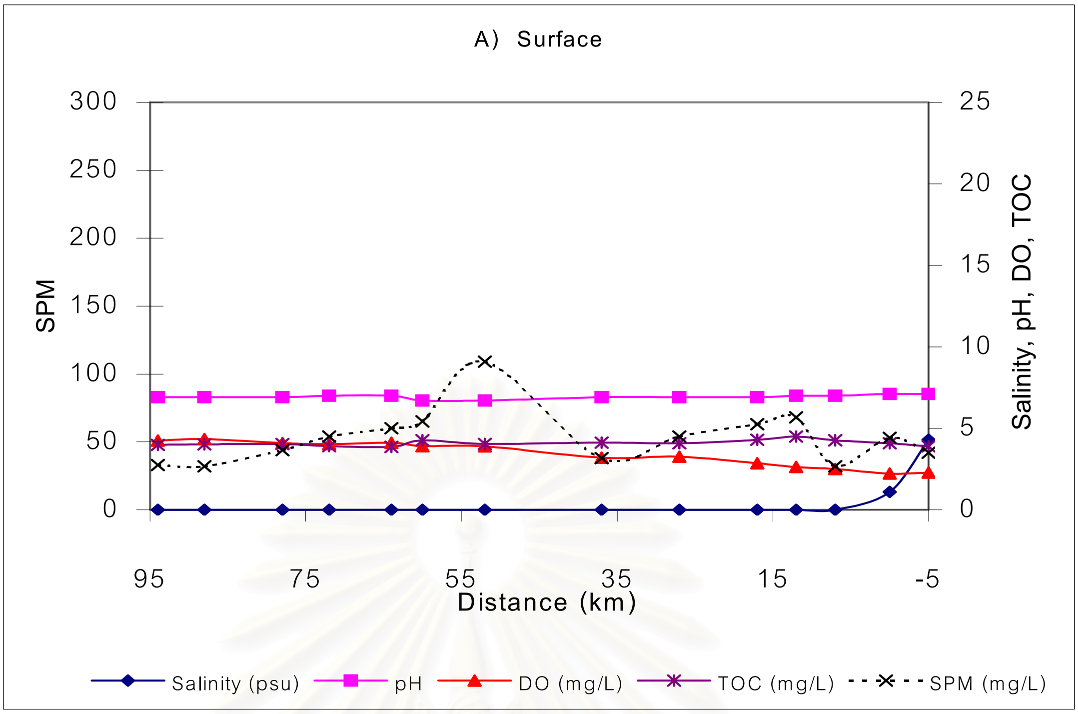


Fig.3-1 Spatial distribution of physical and chemical parameters in the Chao Phraya River estuary in April,1999

A) Surface

B) Bottom


A) Surface

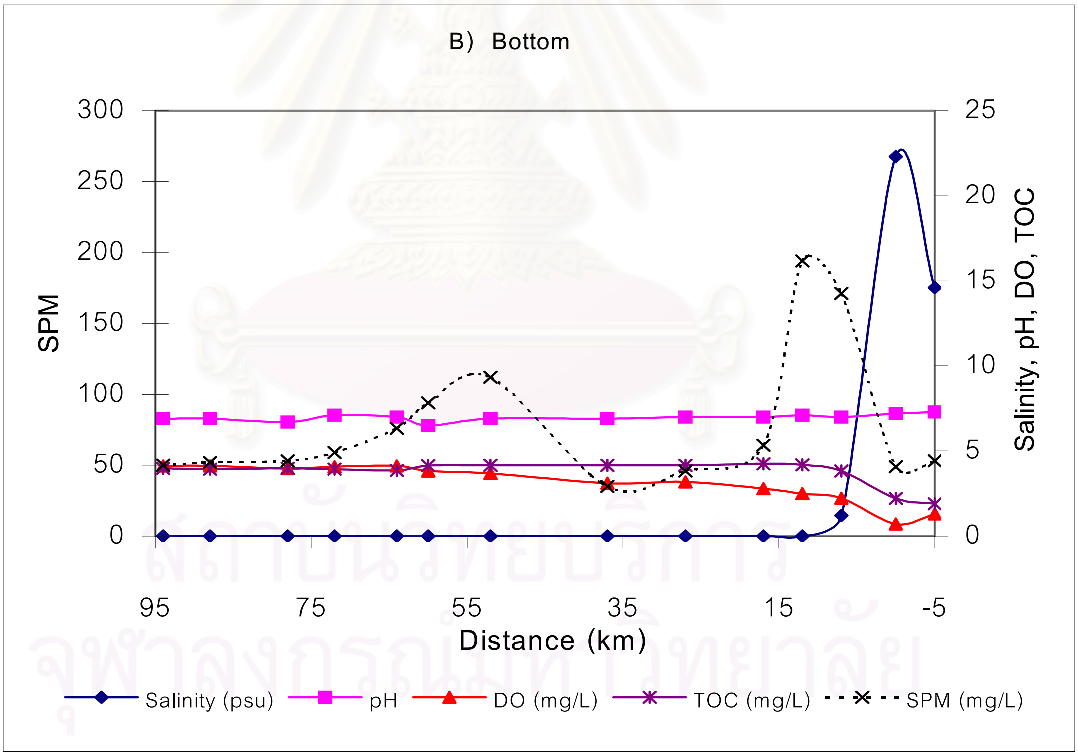

B) Bottom

Fig.3-2 Spatial distribution of physical and chemical parameters in the Chao Phraya River estuary in October,1999

A) Surface

B) Bottom

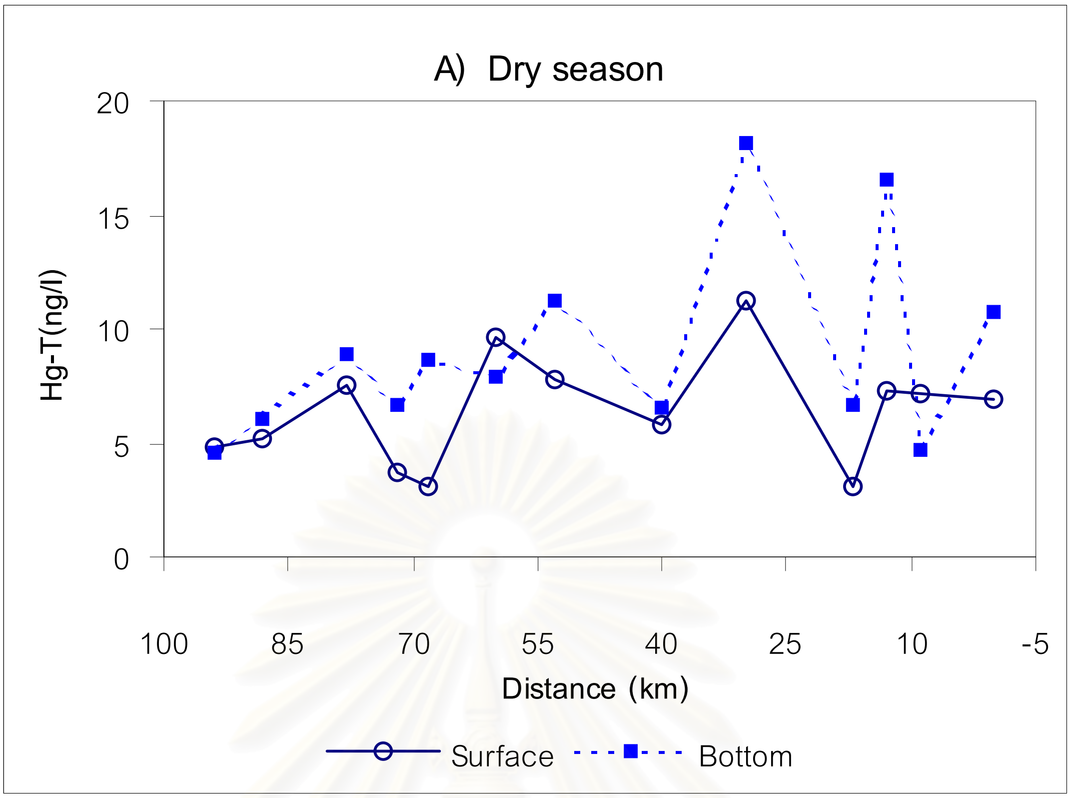
3.2 Dissolved and suspended particulate mercury concentration in the Chao Phraya River estuary

3.2.1 $(Hg\text{-}T)_D$ distribution

In the dry season, $(Hg\text{-}T)_D$ concentrations ranged from 2.16 to 11.21 ng/L and 4.1 to 18.12 ng/L for the surface and the bottom water, respectively (Table 3-3 and 3-4 and Fig.3-3). The surface $(Hg\text{-}T)_D$ concentrations were found to be lower than the bottom water and the values were nearly constant all along the river, while the bottom concentrations found high values at downstream. The high values were observed in the vicinity of industrial area from Km 27 to the river mouth. The $(Hg\text{-}T)_D$ concentrations in the wet season ranged from 4.52 to 17.29 ng/L and 3.88 to 14.03 ng/L for the surface and the bottom water, respectively. The Hg concentration in both the surface and the bottom water were found higher in the upper estuary and decreases gradually towards the river mouth. The Hg concentrations of the surface water were higher than the bottom water.

3.2.2 $(Hg\text{-}R)_D$ distribution

The $(Hg\text{-}R)_D$ concentrations varied between the detection limit <0.15 and 5.23 ng/L. The $(Hg\text{-}R)_D$ concentration in the dry season ranged from 0.23 to 1.92 ng/L and 0.15 to 1.47 ng/L for the surface and the bottom water, respectively (Table 3-3 and 3-4 and Fig.3-4) The $(Hg\text{-}R)_D$ concentrations of surface water were higher in the upstream and decrease gradually towards the river mouth. Similar results were also found in the bottom water excepted at Km 7 where a maximum in concentration was observed (2.3 ng/L). The concentrations of $(Hg\text{-}R)_D$ in the wet season ranged from <0.15 to 5.23 and <0.15 to 2.17 ng/L for surface and bottom water, respectively. The high values of $(Hg\text{-}R)_D$ of the surface water was found at Km 88 and Km 78, high value were 4.09 and 5.23 ng/L.



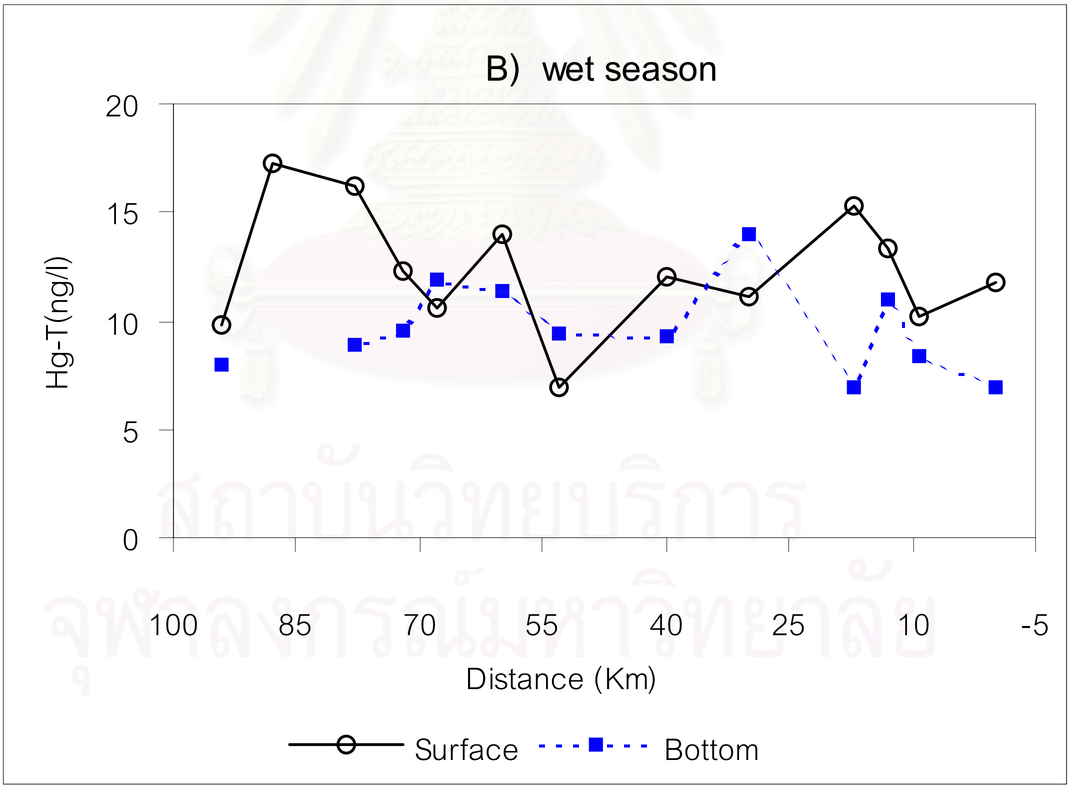


Fig. 3-3 $(Hg\text{-}T)_D$ concentration of The Chao Phraya River estuary in the dry and the wet season (April and October 1999)

A) Dry season

B) Wet season

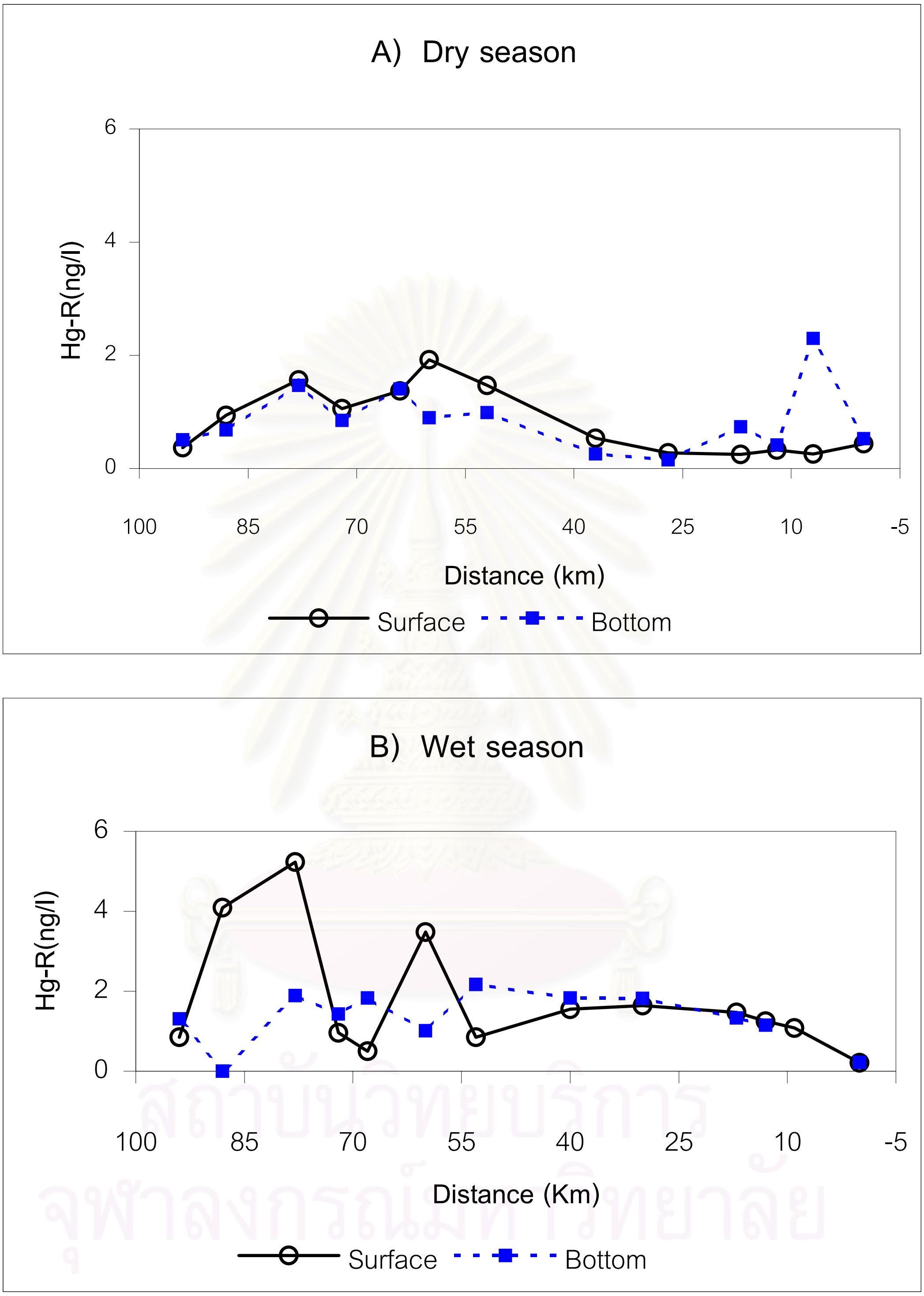


Fig. 3-4 (Hg-R)$_D$ concentration of the Chao Phraya River estuary in the dry and the wet season,(April and October,1999).

A) Dry season

B) Wet season

3.2.3 $(Hg\text{-}NR)_D$ distribution

In order to understand the behavior of Hg species in the Chao Phraya River estuary, information on inorganic and organic speciation of Hg can be obtained using the operationally define labile or reactive and total dissolved Hg forms (Leermakers et al., 1995). The extended of complexation of dissolved mercury in estuarine water vary markedly with the nature and concentration of the inorganic and organic ligands as well as their respective stability constants. Using the general equation:

$$Hg\ (total) = Hg\ (Reactive) + Hg(non\text{-}reactive)$$

$$Hg\ (Reactive) = HgL_{inorganic} + Hg\ (free)^{2+} + Hg^{O}$$

$$Hg\ (non\text{-}reactive) = HgL_{organic} + MeHg$$

$$(Hg\text{-}NR)_D = (Hg\text{-}T)_D - (Hg\text{-}R)_D$$

The $(Hg\text{-}NR)_D$ concentration ranged from 1.73 to 17.97 ng/L and 4.52 to 13.87 ng/L for the dry and the wet season respectively (Table 3-3 and 3-4 and Fig.3-5).

3.2.4 Hg-P distribution

The distributions of Hg-P concentrations are listed in Table 3-3 and 3-4 and shown in Fig.3-6. In the dry season, Hg-P concentrations ranged from 0.18 to 3.49 μg/g and 0.32 to 2.82 μg/g for the surface and the bottom water, respectively. The Hg-P concentrations were higher in the upper part of the estuary and then decreased towards the river mouth except at Km 52 to Km 27 (Bangkok area) where high values were observed. In the wet season, the Hg-P concentrations ranged from 0.11 to 1.67 μg/g and 0.09 to 1.85 μg /g for the surface and the bottom water, respectively. The Hg-P concentrations showed higher values at the upper estuary and then drop almost linearly between Km 72 to Km 7 and elevated concentrations were found near the river mouth.

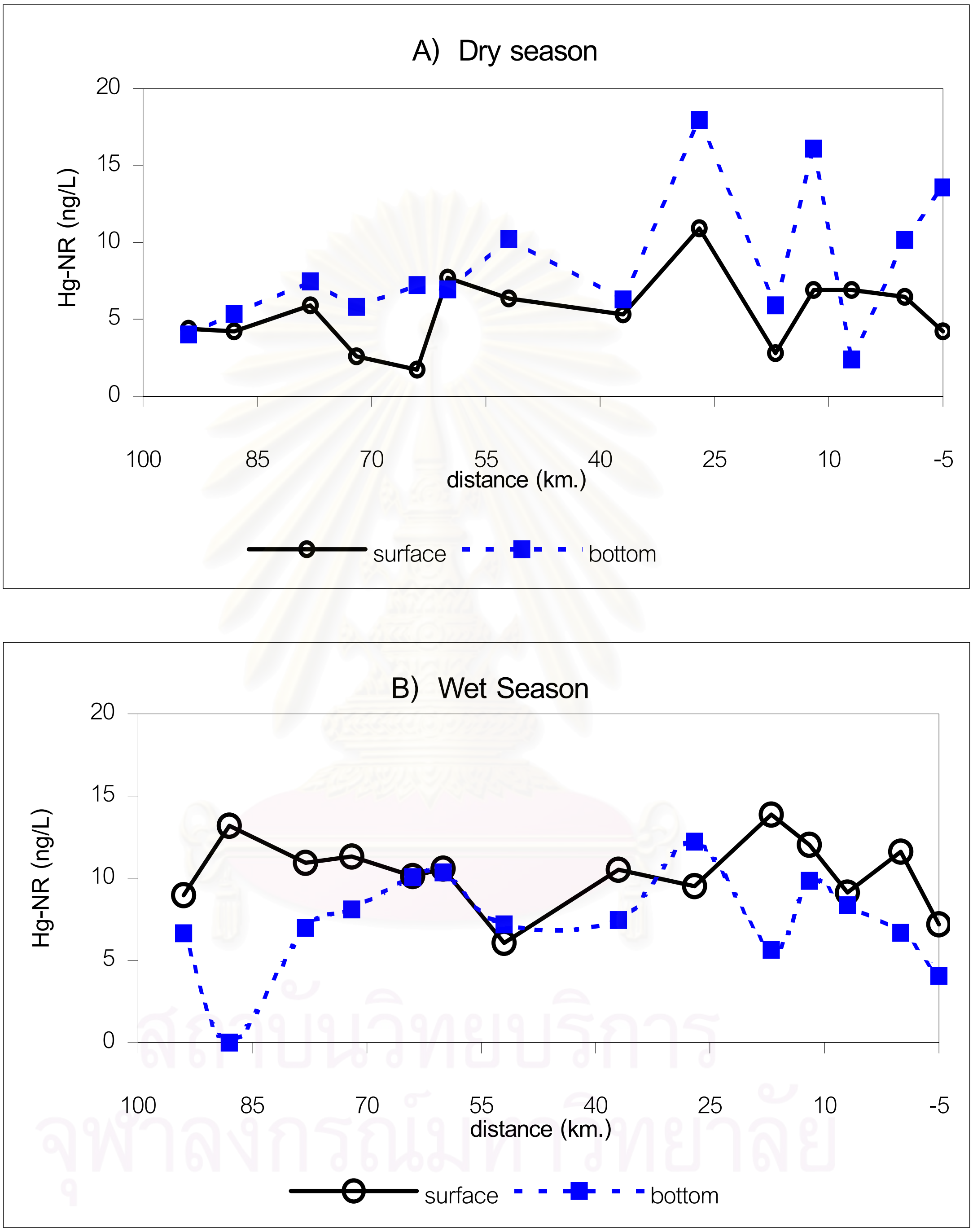
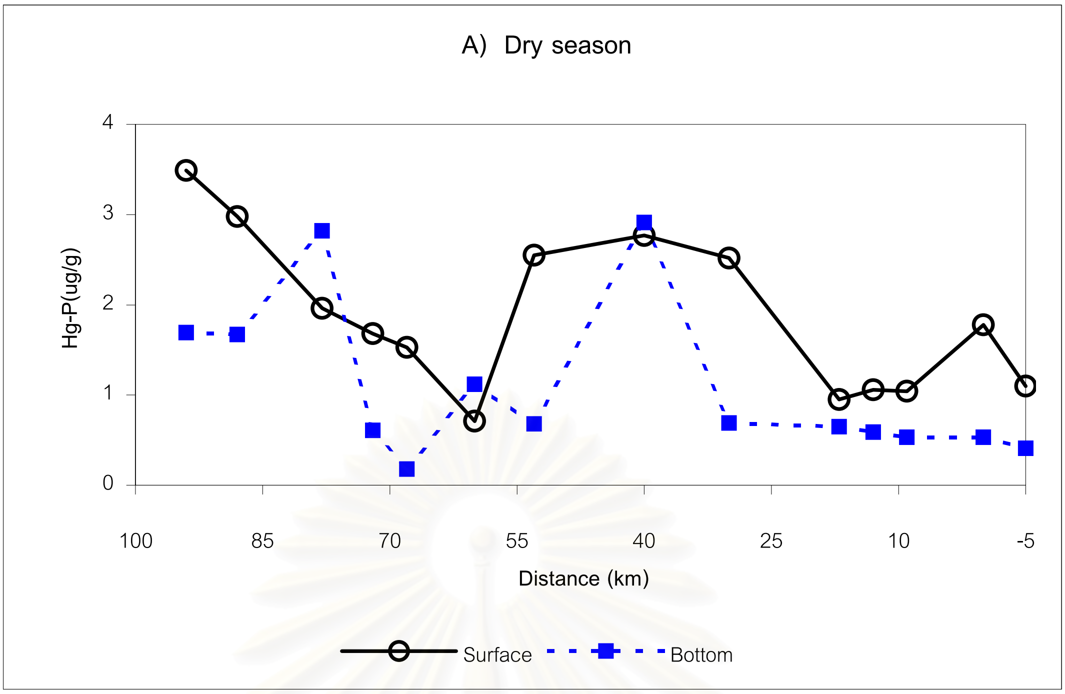


Fig.3-5 (Hg-NR)$_D$ concentration of The Chao Phraya River estuary in the dry and the wet season (April and October 1999).

A) Dry season

B) Wet season



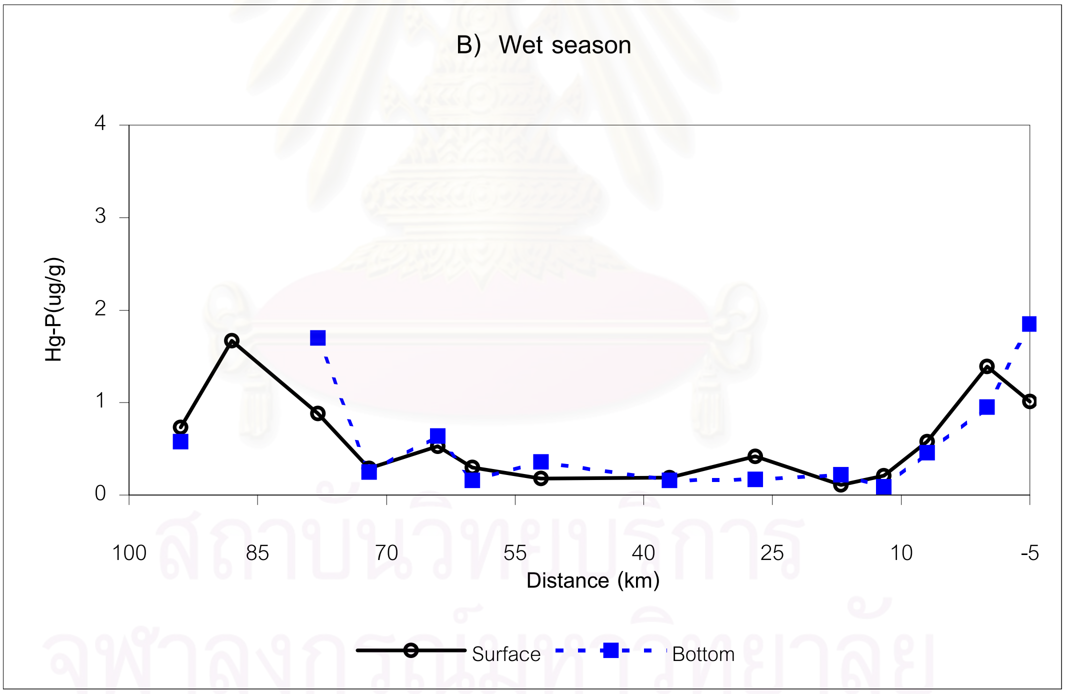


Fig.3-6 Hg-P concentration of The Chao Phraya River estuary in the dry and the wet season (April and October 1999)

A) Dry season

B) Wet season

3.3 Results of field investigation in the dry season (April, 2000)

In order to obtain more data and confirm the results, an extra survey was conducted on one-day field survey in April 2000. The surface and near bottom water samples were collected from the Chao Phraya River estuary at the upstream (Km 96) to downstream (Km 17), which consisted of 7 stations. All physico–chemical parameters were similar to survey in April and October, 1999 (except sediment sample collection). The results are listed in Table 3-5 and Fig.3-7. The Chao Phraya River water during the survey is fresh water (salinity 0) all along the river, from the Km 96 to Km 17 of the river.

The $(Hg\text{-}R)_D$ concentrations ranged from 0.24 to 2.29 ng/L and 0.29 to 4.46 ng/L for the surface and the bottom water, respectively. The $(Hg\text{-}R)_D$ concentrations of the bottom water were observed to be higher than the surface water and higher values were found in the upstream and decreased gradually towards the river mouth. The $(Hg\text{-}T)_D$ concentrations ranged from 6.52 to 18.31 ng/L and 1.92 to 12.85 ng/L for the surface and the bottom water, respectively. The surface $(Hg\text{-}T)_D$ concentrations were higher than the bottom water. $(Hg\text{-}NR)_D$ profile was similar with $(Hg\text{-}T)_D$. While the Hg-P ranged from 0.49 to 2.86 μg/g and 0.23 to 2.79 μg/g for surface and bottom water, respectively. The Hg-P concentrations of bottom water found higher than surface water and both of the surface and the bottom water were high values at the upstream. All concentration of Hg species were high the upstream and decreased towards downstream.

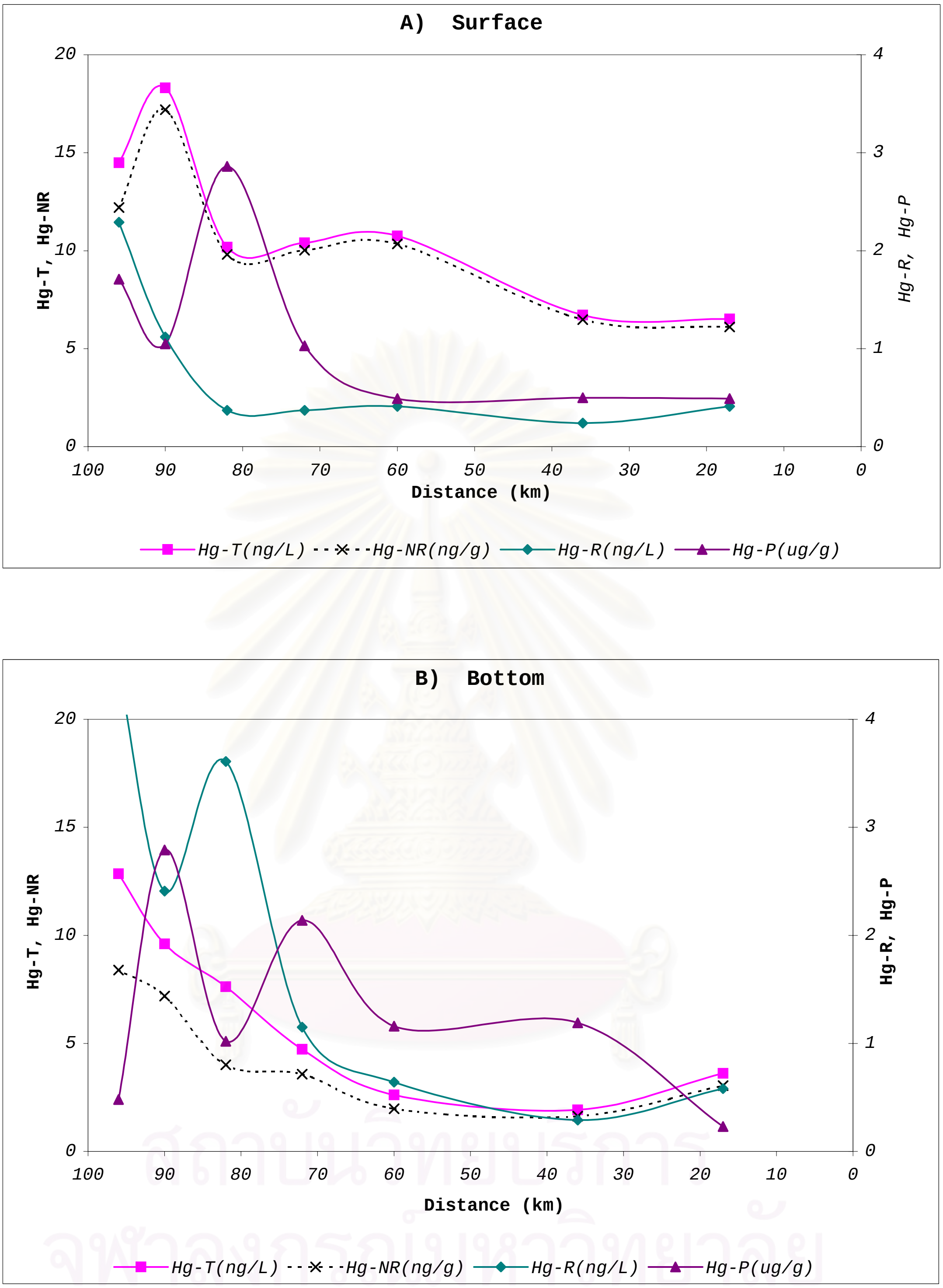
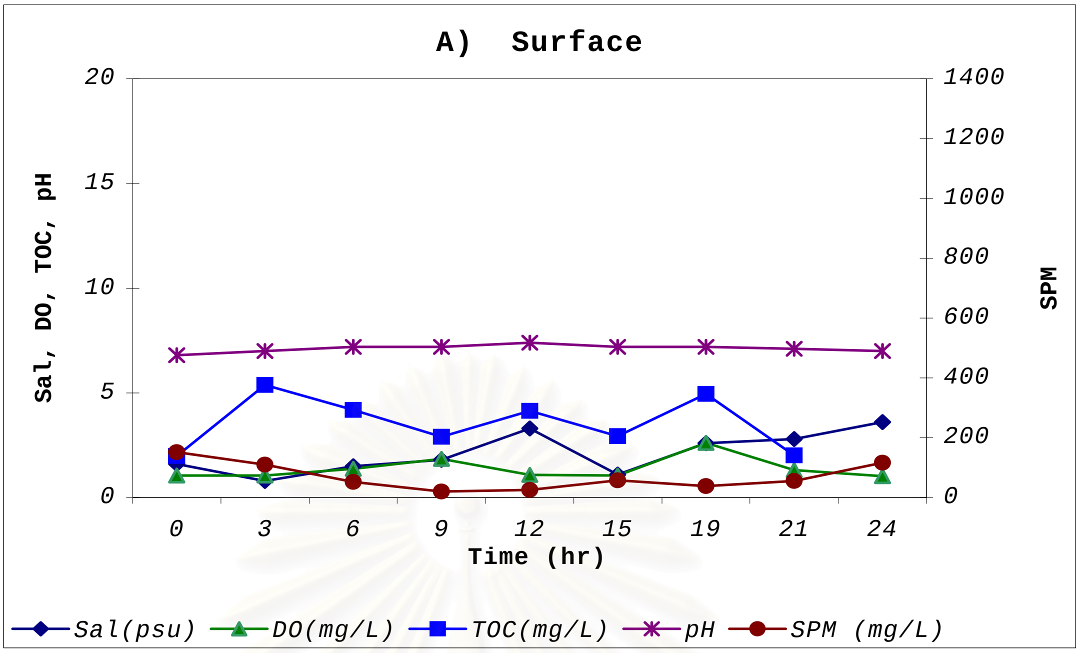


Fig.3-7 Mercury concentration in A) surface and B) bottom water of the Chao Phraya River in the dry season (April 2000)

3.4 Results of field investigation on a tidal cycle

In order to understand the behavior of mercury in the estuary, water samples were collected to determine the concentrations of Hg related to physico–chemical change during estuarine mixing. Water samples were collected at a station near the river mouth (Fig.2-1) over a tidal cycle of the spring tide in May ,1999. The tidal range was 2.4 m, the collection interval was at every 3 hour. Salinity, pH, and DO were determined during the field survey. The concentrations of Hg, SPM and TOC were made in the laboratory. All results obtained over a tidal cycle are shown in the Table 3-6 and 3-7 and Fig.3-8. Surface salinity ranged from 0.8 to 3.6 psu and bottom water ranged from 1.3 to 17.1 psu. Pattern of salinity distribution and DO distribution were similar to tidal range distribution, high values found at high tide. In the other hand, the SPM and TOC show high value at the low tide level. The pH show no evidence of difference over a tidal cycle. While, Hg-R and Hg-T higher concentrations were observed during low tide lower values at the high tide. On the contrary, Hg-P concentrations were observed to be higher at high tide and lower at low tide (Fig.3-9).



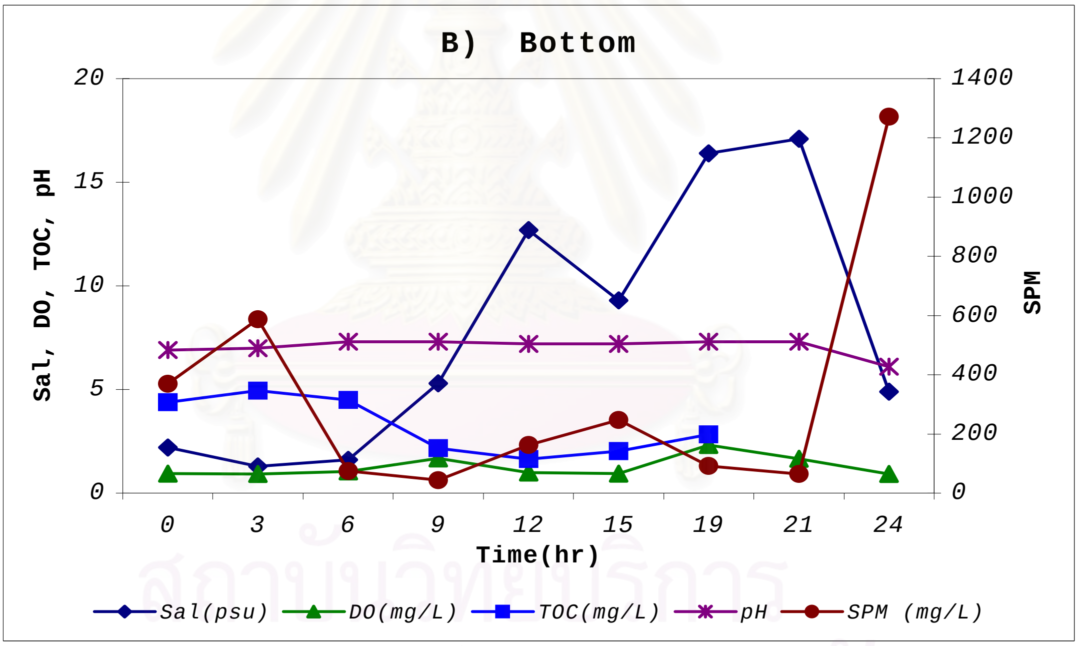
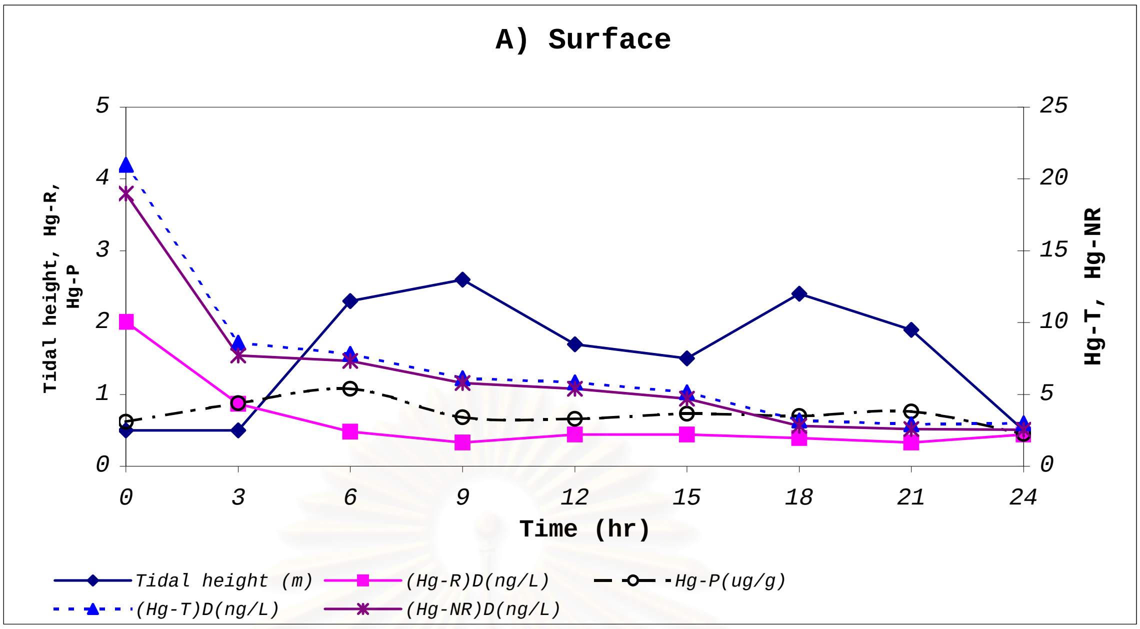


Fig.3-8 Physical and chemical parameters in a tidal cycle (May,1999).

A) Surface

B) Bottom



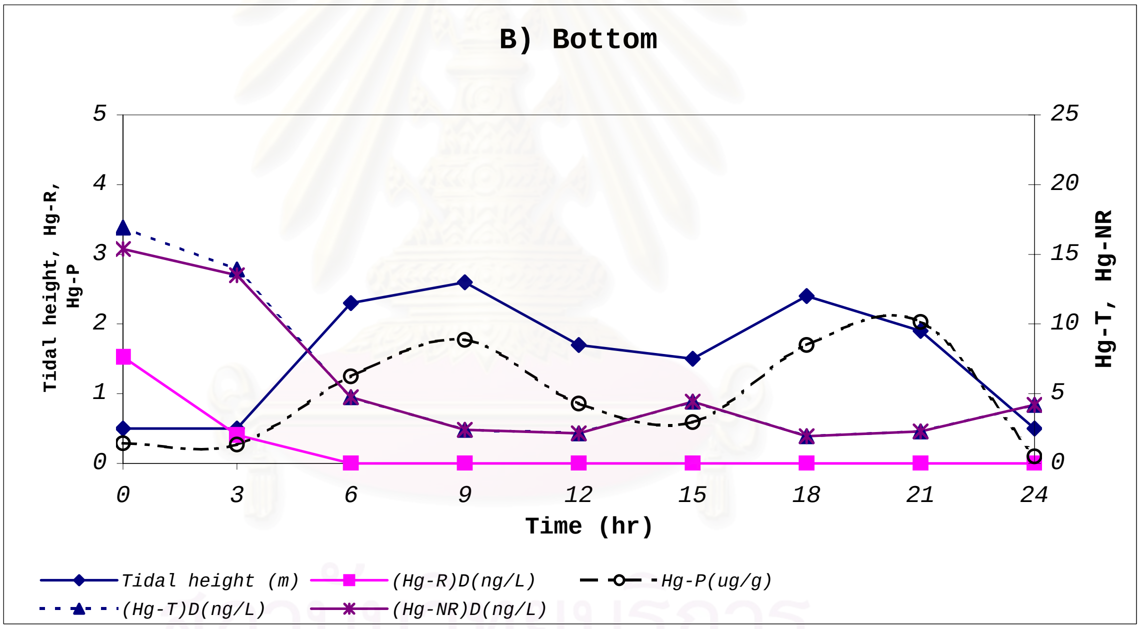


Fig.3-9 $(Hg\text{-}R)_D$, $(Hg\text{-}T)_D$, Hg-P and tidal height in a tidal cycle (May,1999).

A) Surface

B) Bottom

3.5 Sediment

The sediment in the Chao Phraya River estuary originates mainly from the riverine input. Physico-chemical of sediments are listed in Table 3-8 and 3-9. Sediment grain–size distributions are mainly clay and silt fraction (more than 60% of which was <63 μm). The percentage of >63 μm fraction ranged from 15.2 to 58.4 % and <63 μm fraction ranged from 41.6to86.6 % in the dry season, while the >63 μm fraction ranged from 17.9to 44.4 % and <63 μm fraction ranged from 55.6 to 82.1 %. The sediments were slightly coarser upstream and fine grain fraction were increased downstream in both seasons and high amount of <63 μm fraction were found near the river mouth. The concentrations of organic carbon (OC) were determined in sediment grain size <250 μm ranged from 0.67 to 2.62 % and 0.96 to 2.71 %(dry wt.) for the dry season and the wet season, respectively. Hg concentrations in surface sediment were determined in both <250 μm and <63 μm grain size fraction.(Fig.3-10). The Hg concentrations in the dry season ranged from 0.2 to 0.49 μg/g(dry wt.) and 0.21 to 0.59 μg/g(dry wt.) for <250 μm and <63 μm grain size fraction, respectively. In the wet season, Hg concentrations ranged from 0.3 to 0.77 μg/g(dry wt.) and 0.3 to 0.69 μg/g (dry wt.) for sediment grain size fraction of , 250 μm and <63 μm, respectively. There was no difference in concentration of Hg accumulation between <250 μm and <63 μm grain size fraction. The Hg contents of sediments in the dry season were observed increased gradually from the upper estuary towards the river mouth. The high Hg concentrations were found at vicinity of populated area (Bangkok area) and the major industrial area in the vicinity of Km 52 to river mouth. The Hg concentrations in the wet season were found higher than in the dry season.

Al, Fe and Mn were determined in both <250 μm and <63 μm grain size fractions (Fig.3-11 to 3-13). The concentration of Al in the dry season ranged from 49.47 to 70.44 and 49.48 to 72.95 mg/g for sediment grain size <250 μm and <63μm, respectively, and the wet season ranged from 46.15 to 79.63 and 50.36 to 80.18 mg/g for sediment grain size <250 μm and <63 μm respectively. The concentrations of Fe in the dry season ranged from 19.78 to 55.09 mg/g and 31.5 to 55.05 mg/g in sediment grain size <250 μm and <63 μm, respectively. While, in the wet season ranged from 30.57 to 47.14 mg/g and 35.38 to 52.54 mg/g in sediment grain size <250 μm and <63 μm, respectively. The Mn concentrations in the dry season ranged from 613.8 to 958 μg/g and 796.7 to 1028.8 μg/g for sediment grain size fraction <250 μm and <63 μm, respectively. While, in the wet season, the Mn concentrations ranged from 681.6 to 1059.4 μg/g and 676.4 to 1026.6 μg/g for grain size <250 μm and <63 μm, respectively.

Table 3-8 Hg ,Al, Fe ,Mn, OC(%) and grain size of sediment of the Chao Phraya River estuary in the dry season (April 1999)

Distance	% grain size		OC (%)	Hg (ug/g)		Al (mg/g)		Fe(mg/g)		Mn (ug/g)	
(km)	>63 um	<63 um	<250um	<250um	<63um	<250um	<63um	<250um	<63um	<250um	<63um
94	58.4	41.6	0.67	0.20	0.31	50.71	63.47	19.78	31.50	613.8	796.7
88	41.3	58.7	1.03	0.47	0.30	56.56	69.30	27.39	36.28	633.7	829.6
78	50.8	49.3	0.74	0.21	0.29	55.37	58.57	22.88	37.23	692.3	828.6
72	39.9	60.1	1.35	0.30	0.31	70.44	69.60	34.05	41.06	887.2	1028.8
64	57.4	42.6	*	0.31	0.21	54.08	64.59	55.09	55.09	600.5	838.0
60	23.7	76.4	1.02	0.39	0.31	49.77	58.83	29.28	33.93	715.6	858.0
52	55.5	44.6	2.30	0.50	0.59	49.47	57.89	34.76	37.04	797.4	848.4
37	57.7	42.3	2.62	0.21	0.21	59.80	59.61	37.64	39.69	860.6	907.6
27	40.3	59.7	1.84	0.31	0.50	59.13	63.65	36.70	41.67	918.9	836.3
17	26.9	73.1	1.98	0.21	0.40	58.57	64.51	37.14	36.36	882.2	919.1
12	50.6	49.4	1.34	0.49	0.40	57.95	56.42	30.29	36.69	798.9	812.4
7	31.7	68.3	1.95	0.40	0.56	51.47	64.09	32.87	37.73	777.4	954.9
0	27.3	72.7	1.47	0.38	0.47	51.18	49.48	30.91	33.37	808.0	745.7
-5	15.2	84.8	1.50	0.38	0.51	62.80	60.26	34.79	35.56	958.0	930.4
-5	13.4	86.6	2.05	0.40	0.40	64.27	72.95	34.13	35.98	958.0	933.4
-5	24.7	75.3	1.49	0.21	0.40	56.27	60.29	32.46	34.94	777.9	847.8

Note : Concentration in dry weight basis

Table 3-9 Hg ,Al, Fe ,Mn, OC(%) and grain size of sediment of the Chao Phraya River estuary in the wet season (October 1999)

Distance	% grain size		OC (%)	Hg (ug/g)		Al (mg/g)		Fe(mg/g)		Mn (ug/g)	
(km)	>63 um	<63 um	<250um	<250um	<63um	<250um	<63um	<250um	<63um	<250um	<63um
94	35.7	64.3	1.23	0.60	0.69	50.99	55.36	34.89	35.82	806.3	832.7
88	27.4	72.6	1.27	0.67	0.68	46.15	71.33	30.57	37.45	795.4	886.7
78	27.6	72.4	1.23	0.77	0.59	58.16	74.25	39.86	44.46	832.4	933.4
72	34.7	65.3	1.30	0.49	0.48	68.29	67.44	42.38	44.43	1059.4	956.7
64	37.8	62.2	1.79	0.50	0.31	72.84	57.67	40.14	35.38	877.5	676.4
60	39.6	60.4	1.21	0.68	0.40	72.96	69.73	39.55	45.03	833	955.3
52	23.9	76.1	0.96	0.59	0.68	69.84	73.21	41.09	44.11	681.6	963.4
37	42.4	57.6	2.45	0.50	0.39	64.77	63.32	44.33	42.47	834.9	763.1
27	44.4	55.6	1.68	0.49	0.60	74.64	78.49	47.49	46.51	913.8	881.7
17	31.1	68.9	1.67	0.59	0.60	72.75	80.18	43.47	43.04	900.1	1026.6
12	37.2	62.8	1.80	0.40	0.40	73.31	72.08	46.78	45.29	869.5	921.1
7	21.9	78.1	2.66	0.49	0.40	54.56	61.48	42.72	48.03	691.8	770.6
0	35.0	65.0	2.71	0.30	0.40	59.25	65.58	43.08	44.13	765.6	769.1
-5	17.9	82.1	1.61	0.31	0.30	79.63	72.53	47.14	52.54	905	886.6
-5	19.9	80.1	1.72	0.40	0.40	74.93	69.65	46.61	46.78	900.4	1024.7
-5	29.0	71.0	1.69	0.59	0.45	63.72	65.11	46.78	44.21	819	753.9

Note : Concentration in dry weight basis

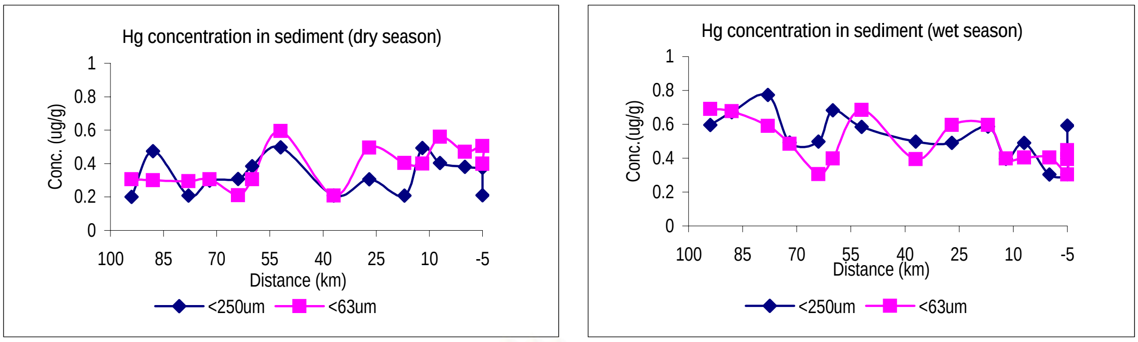


Fig.3-10 Hg concentration in sediment of the Chao Phraya River estuary in the dry and the wet seasor

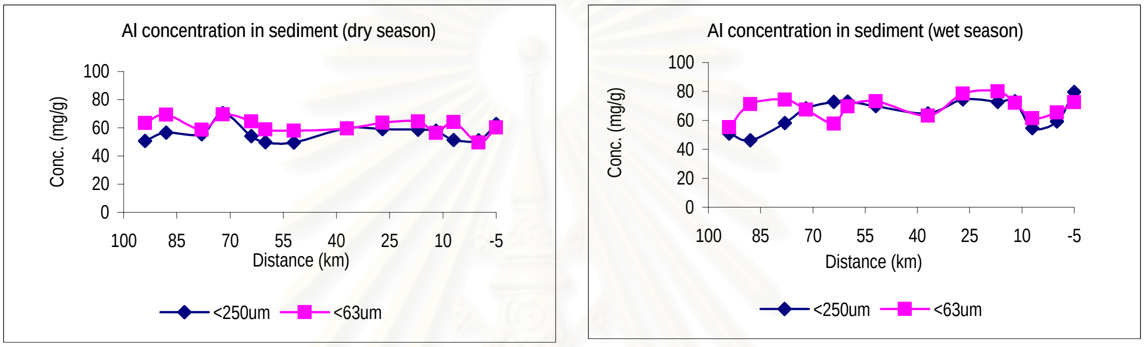


Fig.3-11 Al concentration in sediment of the Chao Phraya River estuary in the dry and the wet seasor

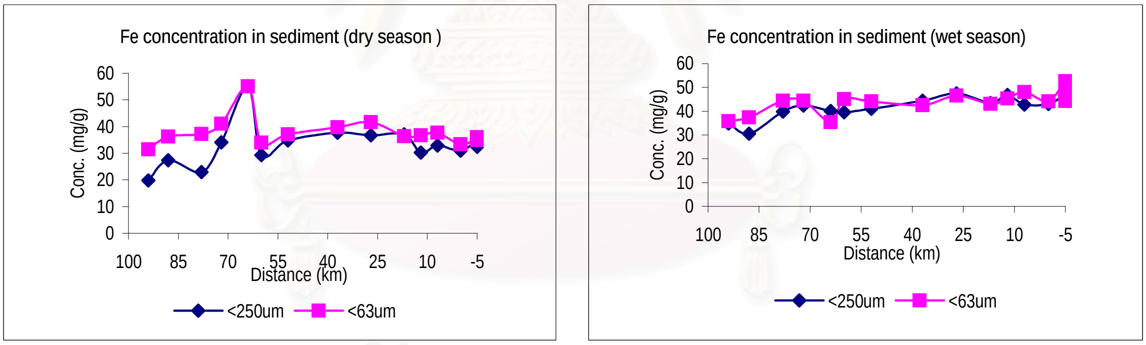


Fig.3-12 Fe concentration in sediment of the Chao Phraya River estuary in the dry and the wet seasor

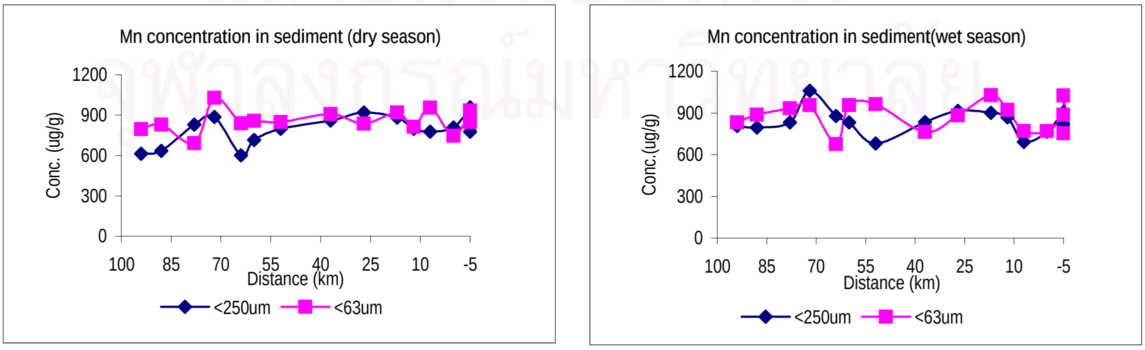


Fig.3-13 Mn concentration in sediment of the Chao Phraya River estuary in the dry and the wet seasor

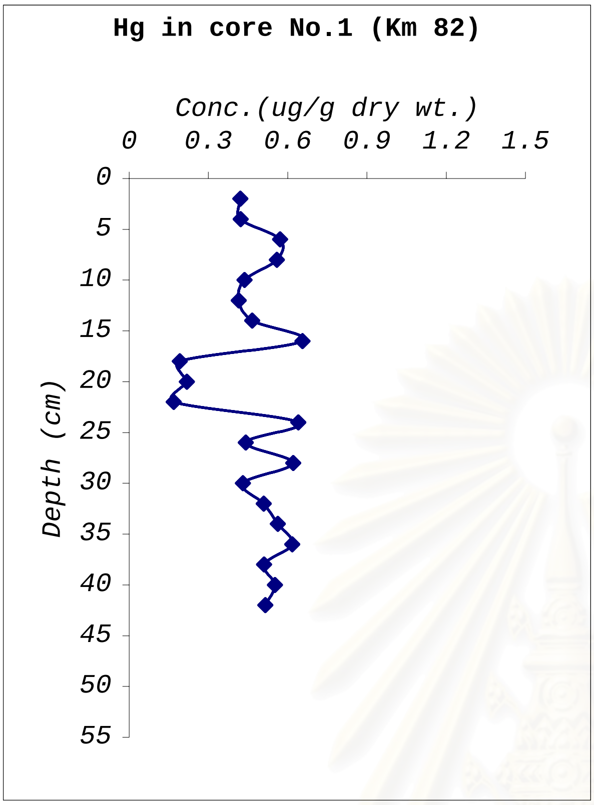
3.6 Sedimentation rates and vertical distribution

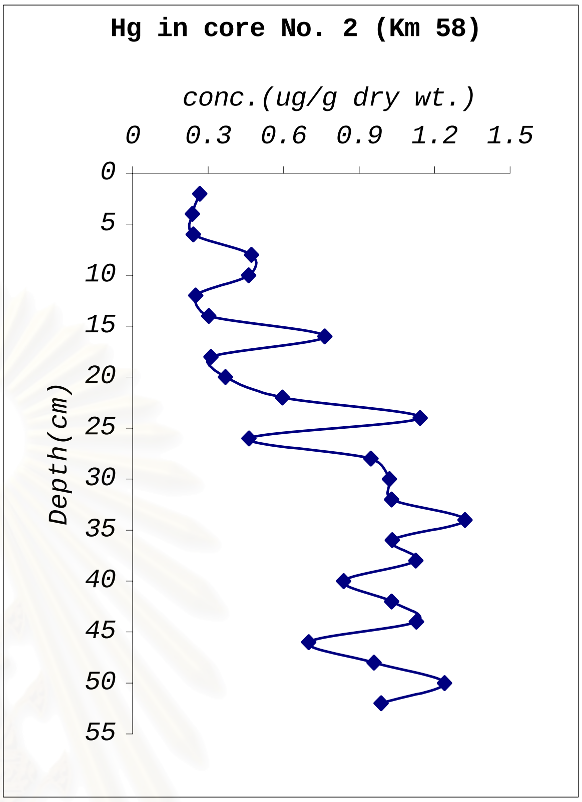
Sediment cores were taken from 3 locations in the Chao Phraya River estuary(Fig.2-1). Each sediment core was subdevided into 2-cm intervals, dried and sieved through a 250 μm sieve. Sedimentation rate at core No.1 be Pb-210 (Farmer, 1978; Nittrouer et al., 1979; Carpenter et al., 1982) was 1.6 cm/year, ie. at 40 cm deep corresponded to about 25 years accumulation. The vertical profiles of Hg concentrations on 3 cores were shown in Fig.3-14.

3.7 Results of laboratory experiments

3.7.1 Result of resespension of sediment experiments

The experiment was set up by mixing of filtered river water (Chao Phraya River) with seawater (Sri Chang Island) in different proportions giving the salinity of 0, 5, 10, 15, and 30 psu. These solutions were stored in 250-ml Teflon bottles and about 0.2 gram wet weight of fresh riverine sediment was added. These solutions were thoroughly shaken and the solutions were left to stand for 0.5, 1, 3, 6, 12 and 24 hrs. The subsamples from each bottle were filtered, acidified with 0.3 % HCl (Suprapur). All experiment was setup in clean room and the whole procedure was carried out under laminar flow hood. The experiment result was shown in Fig.3-15.





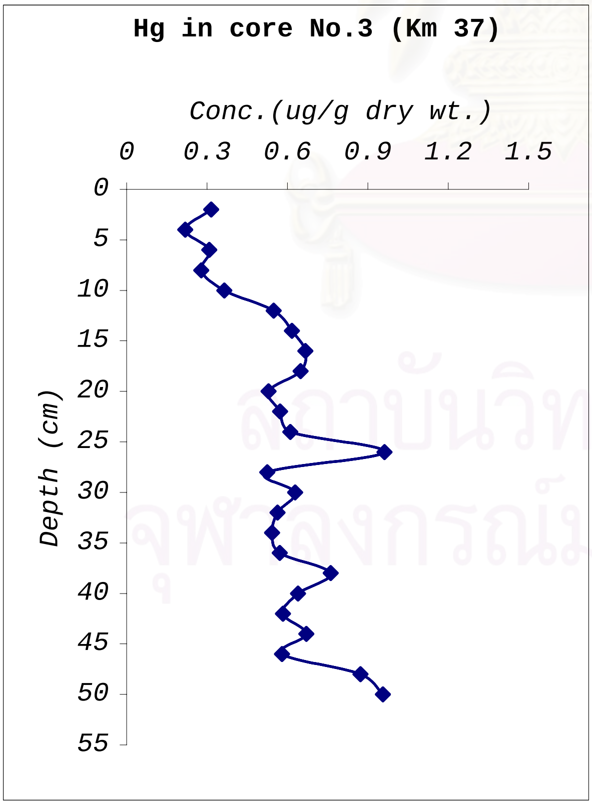


Fig.3-14 Vertical distribution of Hg in core sediment from the Chao Phraya River estuary in April 2000.

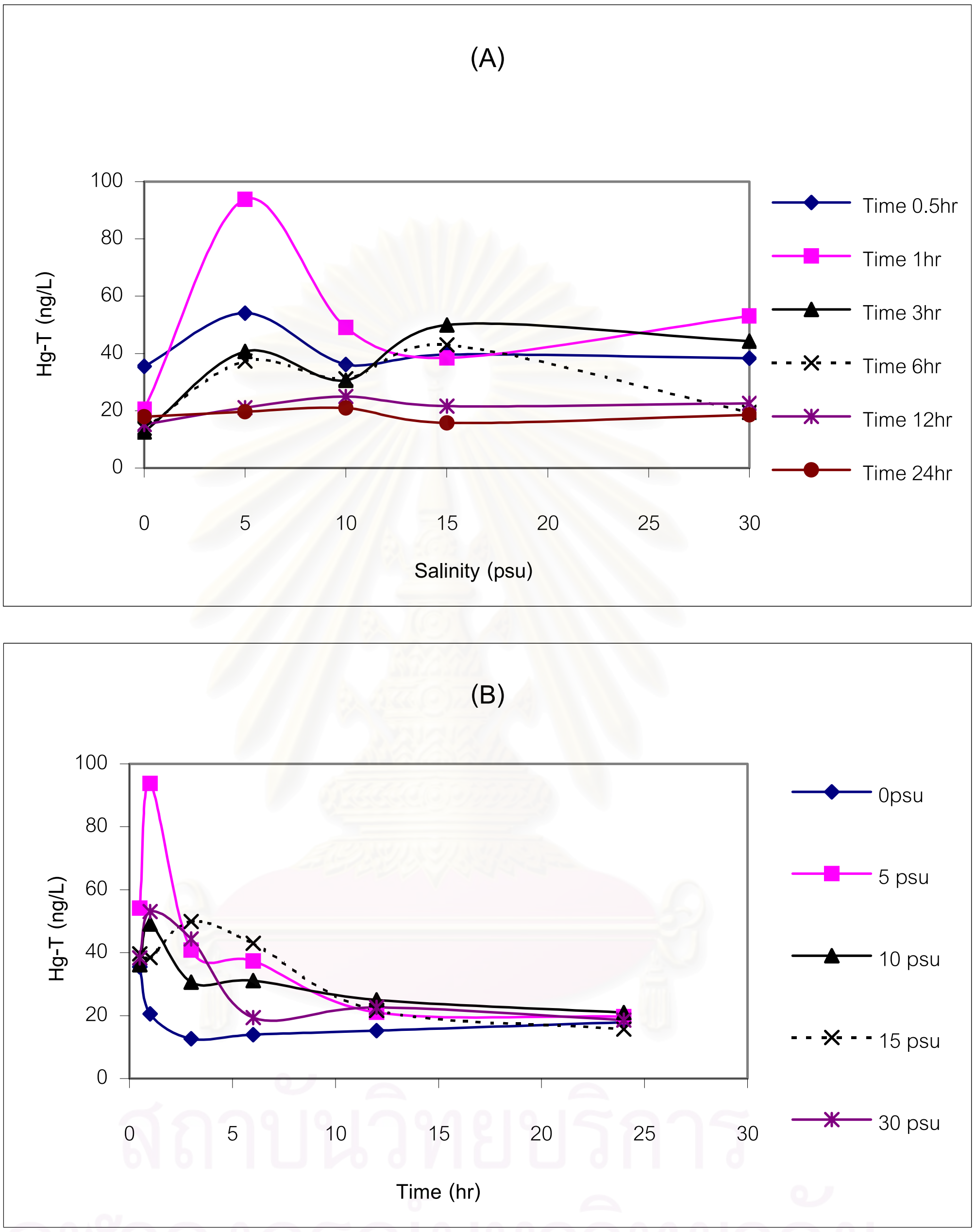


Fig.3-15 The Hg concentrations resuspension of mixing sediment (experimental work)

A) as a function of Salinity

B) as a function of time

3.7.2 The result of mixing experiment

The unfiltered river water from the Chao Phraya River was mixed with seawater off Si-Chang Island in different proportions to give salinity of 0, 5, 10, 15, 20, and 30 psu. These solutions were stored in 250-ml Teflon bottles, which had been acid-washed and rinsed thoroughly many times with Milli–Q water prior to use. These solutions were allowed to stand for 0, 0.5, 1, 3, 6 and 12 hrs. After shaking, filter each sample and follow the procedure as described in Section 2.1. All experiments were setup in a clean room and the whole procedure was carried out under laminar flow hood. The results of these experiments are plotted as a function of time (Fig.3-16).

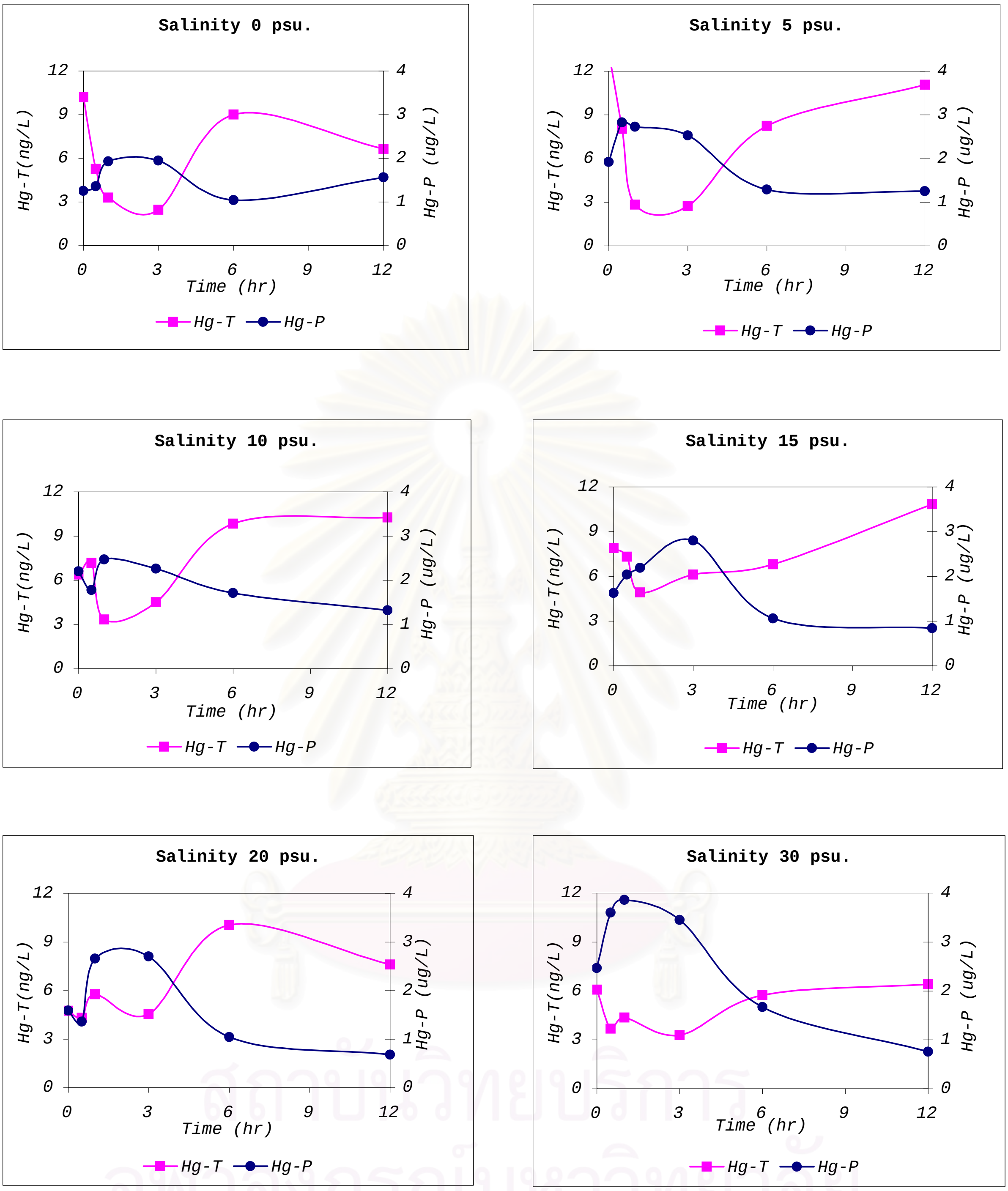


Fig.3-16 (Hg-T)$_D$ and Hg-P as a function of salinity in difference times(experiment work).

Chapter 4

Discussion

4.1 Distribution of dissolved mercury in the Chao Phraya River estuary

The $(Hg\text{-}T)_D$ concentration in both the surface and the bottom water were higher in the upper estuary and decrease gradually towards the river mouth. The concentrations of the surface water in the dry season were observed higher than the bottom water while, the concentrations of surface water were higher than the bottom water in the wet season. A comparison of the $(Hg\text{-}T)_D$ concentration between in the dry and the wet season shown that the values of the wet season were higher than in the dry season. These were due to sources from the river flood and rain driven during rainy season. Coquery et al. (1997) who studied the Loire River, suggested that, during the flood, mercury concentrations were increase with the surficial runoff (direct rainfall and over land flow). Furthermore, the high Hg concentration of surface water could result from mixing as a result of high freshwater flow (Mason et al., 1999). Higher in total Hg concentrations during high flow was also observed in the Wisconsin River (Hurley et al., 1995). The $(Hg\text{-}T)_D$ concentrations of the surface water in the dry season were observed higher than the bottom water. These concentrations may be due to sediment resuspension and mixing with fluid mud bed by the tidal energy are the potential sources of Hg concentrations to the water (Mason et al., 1999) or probably release from the suspended particulate matter during high turbidity mixing at that area (Leermakers et al., 1995). While, the $(Hg\text{-}T)_D$ concentrations of surface water were higher than the bottom water in the wet season. These were due to sources from the river flood and rain that mention above.

The concentraions of $(Hg\text{-}T)_D$ in the Chao Phraya River estuary 2.16 to 18.12 ng/L) were the same order of these found in the Mekong River where concentration of $(Hg\text{-}R)_D$ were 0.28 to 4.37 ng/L and $(Hg\text{-}T)_D$ were 0.88 to 11.5 ng/L (Hungspreugs et al., 1998). Moreover, these concentration are in the same concentration range of what found in major rivers and other regime, e.g. Ferrara et al. (1996) reported for total dissolved mercury range 1.4 to 19.7 ng/L in the Tyrrhenian Sea and Bloom et al. (1990) reported total mercury concentration in water from the sewage out fall (16.1 ng/L) and the industrial discharge stream (10.2 ng/L). Ferrara and Maserti (1992) on the Adriatic Sea (2.03 to 6.75 ng/L), Leermakers et al (1995) on Scheldt estuary (0.5 to 5.2 ng/L) and Guentzel et al. (1996) on the Ochlockonce estuary (1 to 6 ng/L).

Furthermore, in order to see a general picture of Hg concentration in the rivers and coastal areas of Thailand, random samplings were collected for one ot two time situations in selected areas as shown in Table.B-12 and B-13 in Appendix B). The $(Hg\text{-}R)_D$ and $(Hg\text{-}T)_D$ concentration of the rivers ranged from 0.31 to 6.47 and 1.59 to 32.7 ng/L, respectively while concentration of the coastal area ranged from 0.56 to 4.68 and 1.54 to 21.9 ng/L , respectively. Rain water also collected to measure the Hg concnetraions and found that the concentration range were <0.15 to 4.96 ng/L for $(Hg\text{-}R)_D$ and 1.34 to 19.24 ng/L for $(Hg\text{-}T)_D$ (Table B-14 in Appendix B).

The $(Hg\text{-}R)_D$ concentration in both the surface and the bottom water were higher in the upper estuary and decrease gradually towards the river mouth. The $(Hg\text{-}R)_D$ concentration in the Chao Phraya River estuary from this study was only 12% of total dissolved Hg. This may be due to its rich in dissolved organic and particulate matter and Hg was strongly bound to organic compound. Therefore, large fraction of the dissolved Hg was not “easily reducible”. Similar result was observed in the Loire and Seine River varied from less than 5 to 24% of Hg were in reactive form and the explanation was also due to associated with organic compound (Bloom et al., 1991: Mason et al., 1993: Cossa et al., 1997). However, the variability in the levels of Hg reported in coastal water is an indication of the dynamic character of the coastal zone (Dalziel, 1992). Gill and Fitzgerald (1978) reported that most of Hg in open ocean water (>80%) is reactive Hg, while 25-50% of reactive Hg was found in the coastal water (Dalziel and Yeats, 1985).

Most of dissolved Hg form is non-reactive Hg [$(Hg\text{-}NR)_D$], which account for more than 85% of the total dissolved Hg. The seasonal variation of dissolved Hg was observed between the dry and the wet season. The dissolved Hg phase was about 30% of the total dissolved Hg in the wet season while its was only 15% of the total dissolved Hg in the dry season.

4.2 Distribution of suspended particulate mercury

The distributions of Hg-P concentrations calculated in ng/L unit were shown in Fig.4-1. In the dry season, Hg-P concentrations had higher values in the upper part of the estuary and then decreased towards the river mouth excepted at Km 52 to Km 12 where high values were observed, this area was also high turbidity zone. Therefore, the high Hg-P concentration may be due to resuspension from sediment or may be sources from urban sewage of the populated area. The Hg-P concentrations decreased gradually from the upper estuary towards the river mouth in this season can be explanation as the mixing of river water with and seawater (Leermakers et al., 1995) or probably a dilution with less contaminated particles (Figueres et al., 1985).

In the wet season, the Hg-P concentrations were higher at the upper estuary and then drop to low concentration between Km 72 to Km 7 and then elevated concentrations were found near the river mouth at the high turbidity zone (Fig.4-2). These high concentrations were probably from a mixing of particulate from different sources bearing more mercury in that area. Hg-P concentrations show the same pattern in both the surface and the bottom water. Maximum values of Hg-P were observed in the dry season in both the surface and the bottom water and the concentrations in the dry season were found higher than in the wet season. These may be due to the river discharges in April, 1999 are lower than those of October, 1999 (76 m^3s^{-1} and 1,824 m^3s^{-1}) and results in a much longer water residence time in a storage of pollutants and potential remobilization during the dry season (Figueres et al., 1985). The association of mercury with particulate matter by adsorption or coprecipitation onto organic solid phases (Leermakers et al., 1995) during low flow conditions can be important factor

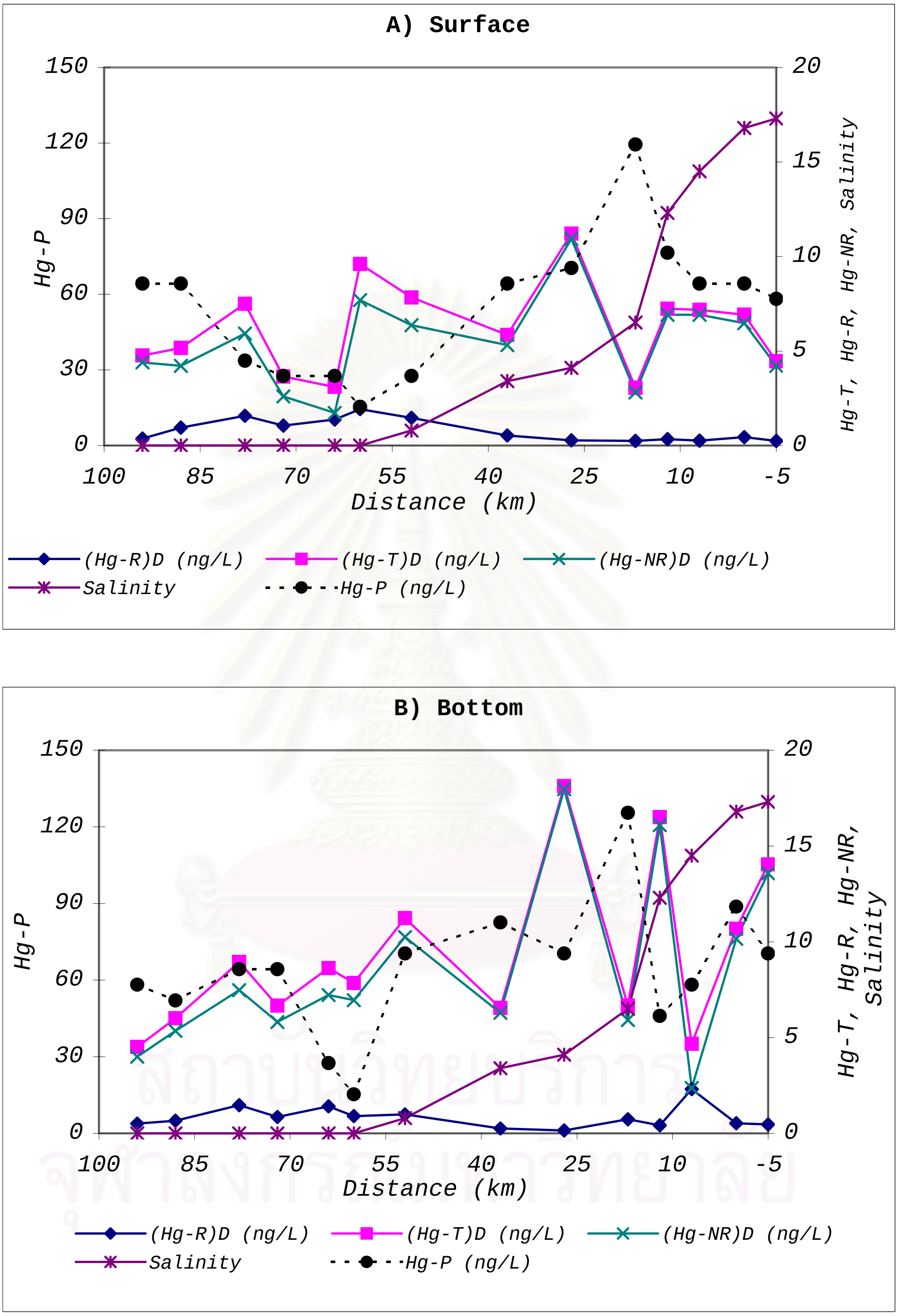


Fig.4-1 Hg concentration and salinity as a function of distance of the Chao Phraya River estuary in the dry season (April 1999)

A) Surface

B) Bottom

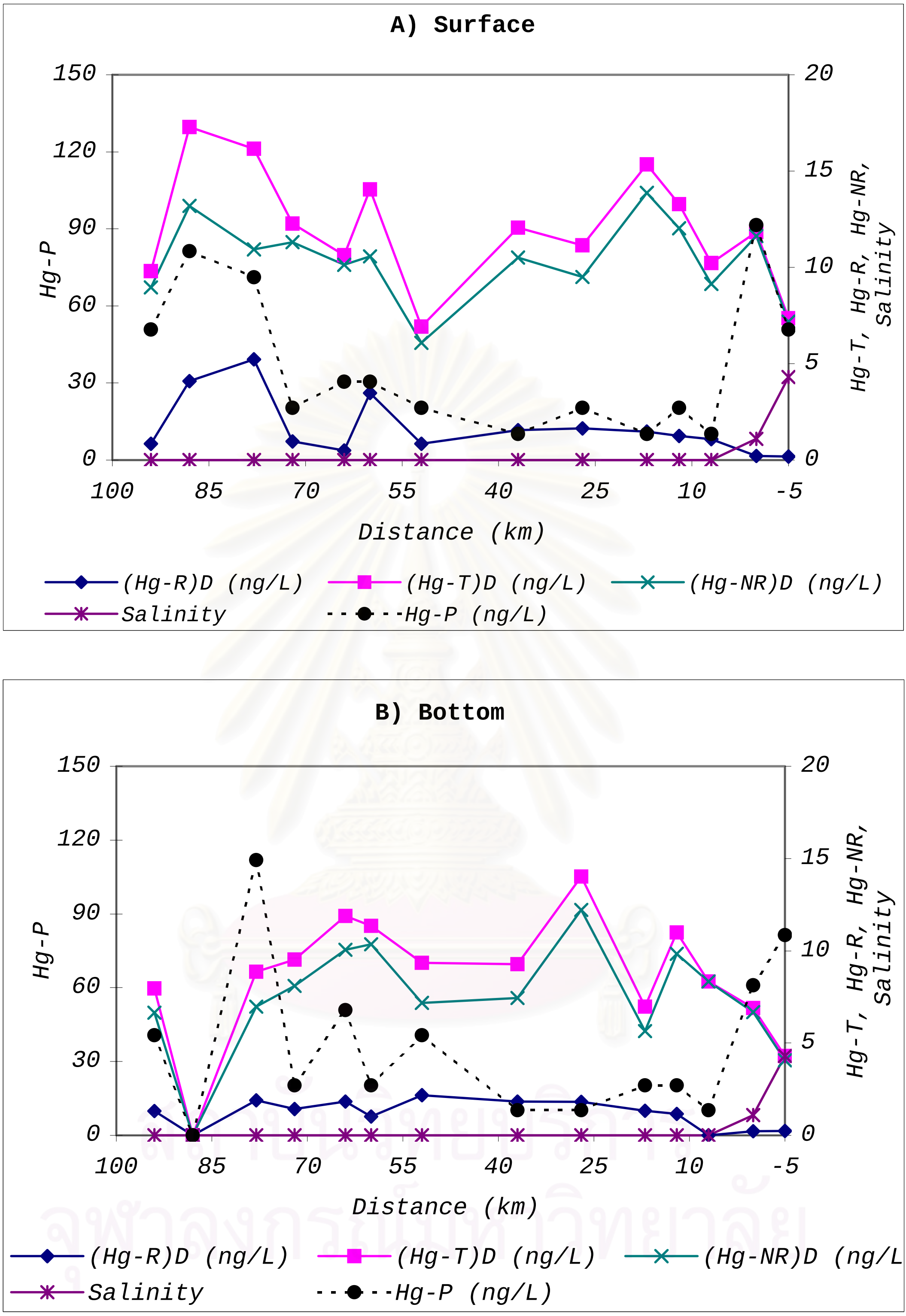


Fig.4-2 Hg concentration and salinity as a function of distance of the Chao Phraya River estuary in the wet season (October 1999)

A) Surface

B) Bottom

since the Hg-P was the dominant Hg species in the estuary during the dry season. Suspended particulate mercury can account or more than 90% of the total mercury, as has been reported in the Scheldt estuary in summer (Leemakers et al., 1995). The suspended particulate mercury being the main fraction of mercury as found in many estuaries e.g. 64% in the Lena, 79% in the Ob and 59% in the Yenisei River (Conquery et al., 1995; Coaas et al., 1997). Compared with this study, the Hg-P was 86% of total mercury in the dry season and was 67% in the wet season. A comparison of the Hg-P concentration in μg/g unit of The Chao Phraya River estuary are the same order with other estuaries e.g. Cossa and Martin (1991) on the Rhone River (1.12 -1.26 μg/g) and Coguery et al., (1997) on the Loire estuary (1.08 ± 0.5 μg/g : 5.4 ± 2.6 n mol /g). However, the higher Hg-P concentrations have been reported, in the Thames suspended detritus contains on average about 5 μg/g Hg (Aston and Chester, 1976) and median values 4.5 μg Hg /g was found in the French estuaries (Figueres et al., 1985). Gagnon et al., (1997) have been reported on preliminary analyses of total Hg in SPM along the main axis of the Saguenay Fjord gave a range of concentrations between 0.25 and 7 μg/g.

4.3 Partitioning of mercury in the Chao Phraya River estuary

The partitioning coefficient (K_D) is defined as the ratio of particulate and dissolved concentration (Chapter 2, Eq.1). The relative affinity of Hg for dissolved and particulate phase is measured by the coefficient: (K_D = Particulate concentration/dissolved concentration) (Turner et al., 1993; Coquery et al., 1997)

In this study, K_D values for $(Hg\text{-}R)_D$ ranged from 128 to 9432 L/g in the dry season and 75 to 10615 L/g in the wet season (Fig.4-3). The K_D for $(Hg\text{-}R)_D$ was observed higher than $(Hg\text{-}NR)_D$ in both seasons. While the K_D values for $(Hg\text{-}NR)_D$ and $(Hg\text{-}T)_D$ were the same order and the values found higher in the dry season (Fig.4-4 and 4-5). These indicated that Hg has the greatest affinity for particulate phase in the dry season. The comparison of K_D values between the Chao Phraya River estuary and other shows in Table 4-1.

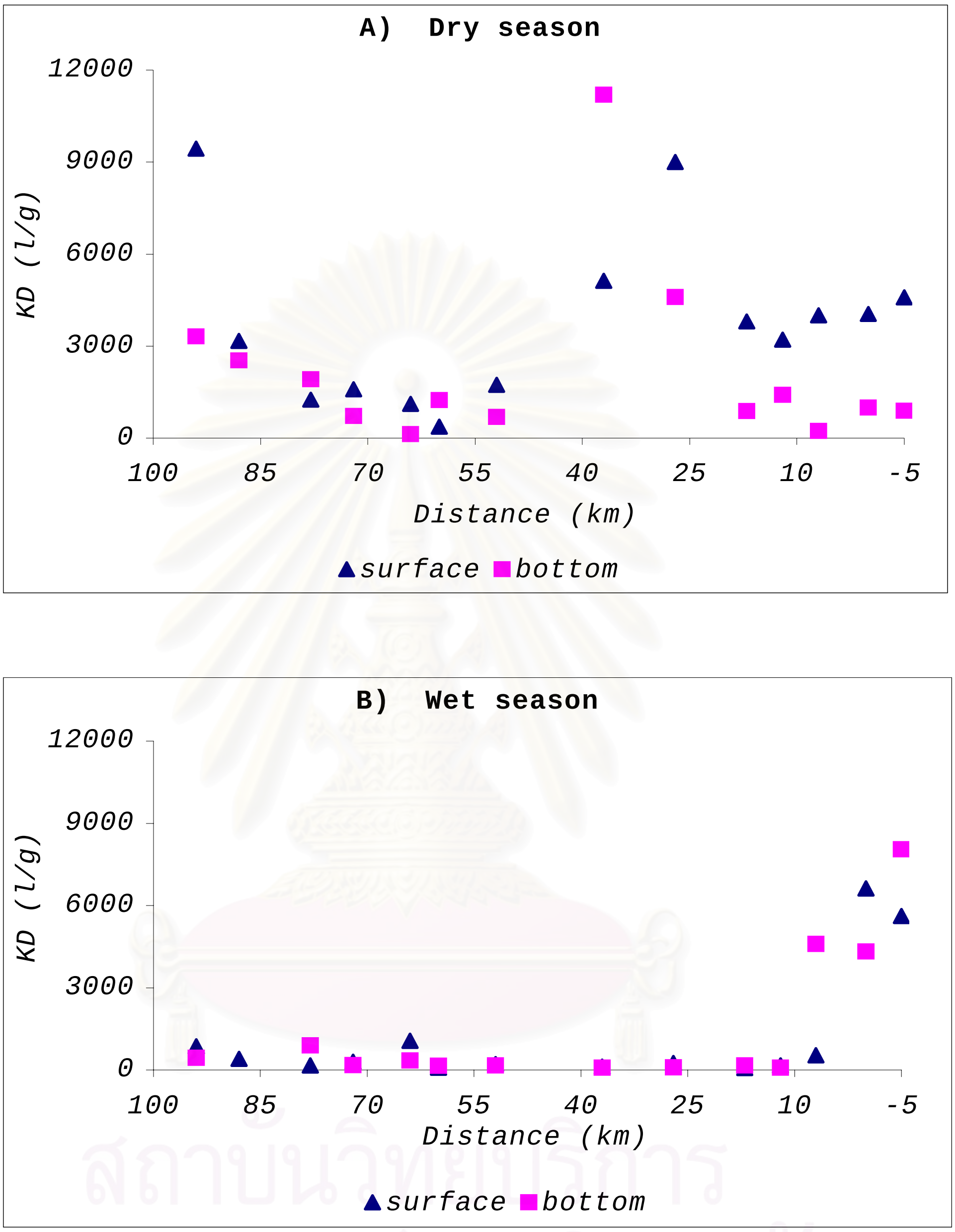


Fig.4-3 K_D [Hg-P/(Hg-R)$_D$] distribution as a function of distance of the Chao Phraya River estuary.

A) Dry season

B) Wet season.

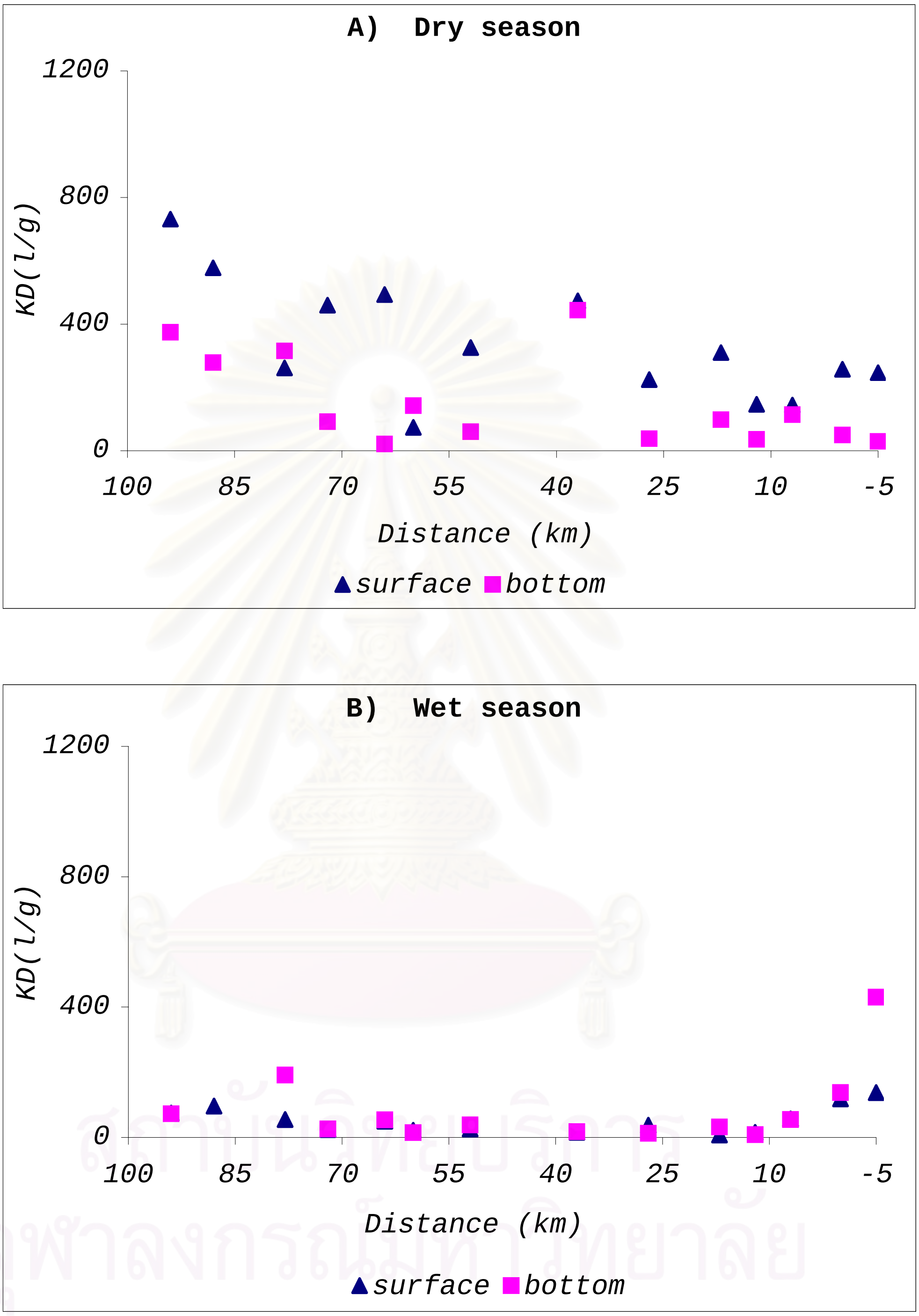


Fig.4-4 K_D [Hg-P/(Hg-T)$_D$] distribution as a function of distance of the Chao Phraya River estuary

A) Dry season

B) Wet season

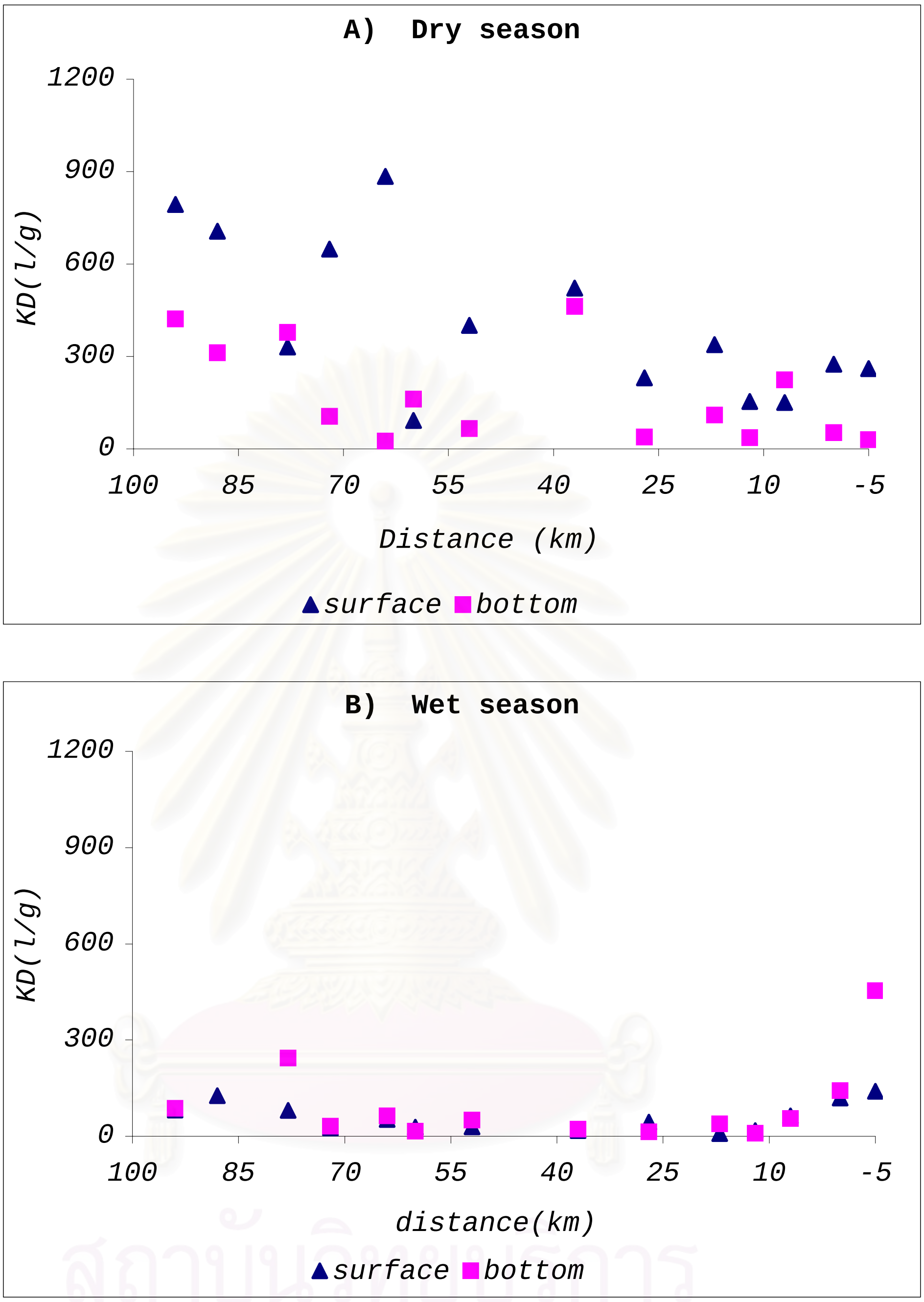


Fig.4-5 K_D [Hg-P/(Hg-NR)$_D$] distribution as a function of distance of the Chao Phraya River estuary.

A) Dry season

B) Wet season

Table 4-1 Comparison of K_D between the Chao Phraya River and other rivers.

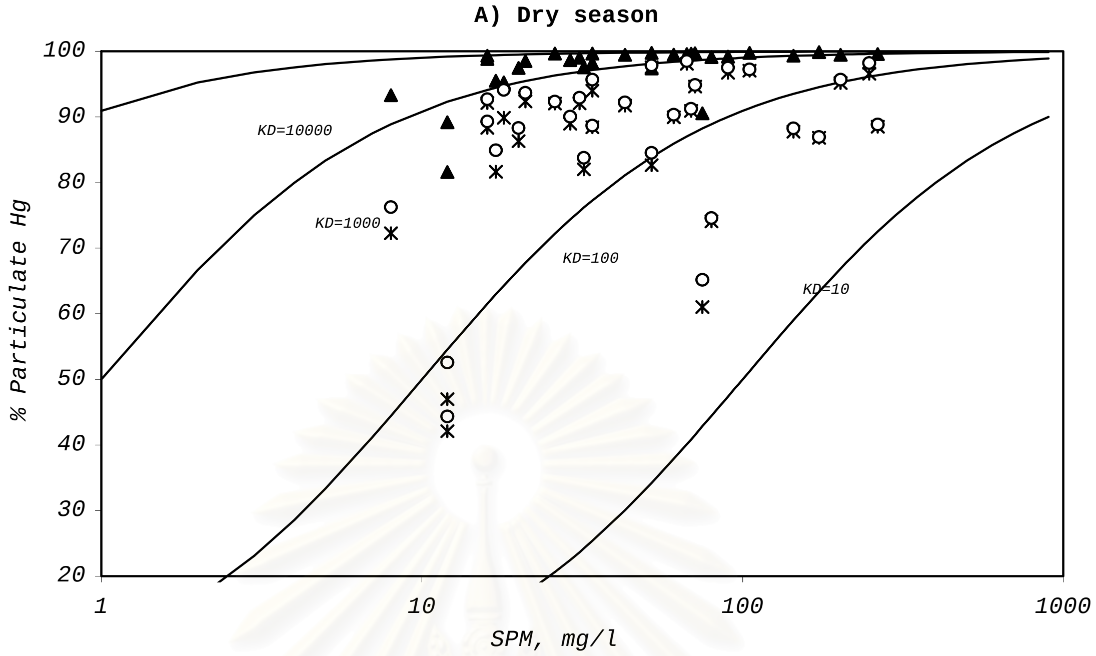
River	$(Hg\text{-}T)_D$ (ng/L)	Hg-P (ug/g)	K_D (l/g)	Reference
Arctic River				
Lena (Russia)	1.00	0.12	120	Coquery et al (1995)
Ob (Russia)	0.56	0.05	89	Coquery et al (1995)
Yenisei (Russia)	0.30	0.04	133	Coquery et al (1995)
American River				
St.Lawrence (Canada)	0.30	0.16	541	Quemerais et al. (1996)
European River				
Rhone (France)	1.06	0.48	541	Cossa et al. (1996)
Loire (France)	0.82	0.19	232	Coquery (1994)
Seine (France)	2.81	1.22	435	Cossa et al. (1994)
Scheldt (Belgium)	2.33	1.46	628	Leermakers et al. (1995)
Asia River				
Chao Phraya River(Thailand)	5.77 (2.16-11.21)	1.87 (0.71-3.49)	324	This Study

To describe the non-reactive Hg fraction were introduced into the model by which has the percentage of the total Hg concentration in the particulate phase versus the suspended particulate matter (SPM). Concentration, by the following equation: (section 2.4, Chapter 2)

The seasonal variability of Hg speciation was shown in Fig.4-6. The results as % particulate Hg, have been incorporated into mass balance sorption models in order to explain the extent of Hg speciation removal and desorption during estuarine mixing. The $(Hg\text{-}R)_D$ or labile Hg concentrations were observed to be high in K_D 1000- 10000 in both seasons, these suggested that considerably high amount of $(Hg\text{-}R)_D$ is particle active, most of them favor adsorption onto the particulate phase, especially during the dry season. While, the non-reactive Hg are present at more than 85 % of total dissolved Hg, the K_D value ranged between K_D 100–1000 in the dry season and in the wet season was found in the range of K_D 10–1000. Therefore, the transported preferentially between dissolved and particulate phases are less, these may be due to type of organic-bound mercury in the dissolved phase and the particulate phases are the same component.

Moreover, the nature of organic content seems to be different type in each season. The K_D value lower than 10 has been found in the wet season which mean the particulate Hg are dominant in dissolved form and presented in non-reactive form. Therefore, in the wet season, non-reactive Hg concentration at 8.8 ± 2.8 ng/L, were found to be higher than the value, 6.6 ± 3.9 ng/L, for in the dry season.

In addition, the K_D values were decreased gradually from the upper estuary towards the river mouth. The K_D values were decreasing with salinity increased, may be due to less organically-bound Hg in seawater. However, the increased Hg sorptions onto the particles with salinity increasing were observed in this study (Fig.4-7). Mercury partition coefficient (K_D) increasing with salinity increased have been reported from Plym and Beaulieu estuaries (Le Roux et al., 2001). The increase in K_D with increasing salinity could be explained by relative hydrophobic and lipophilic $HgCl_2^0$ complex, which subject to salting out. However, speciation calculations indicate that $HgCl_2^0$ comprise


A) Dry season

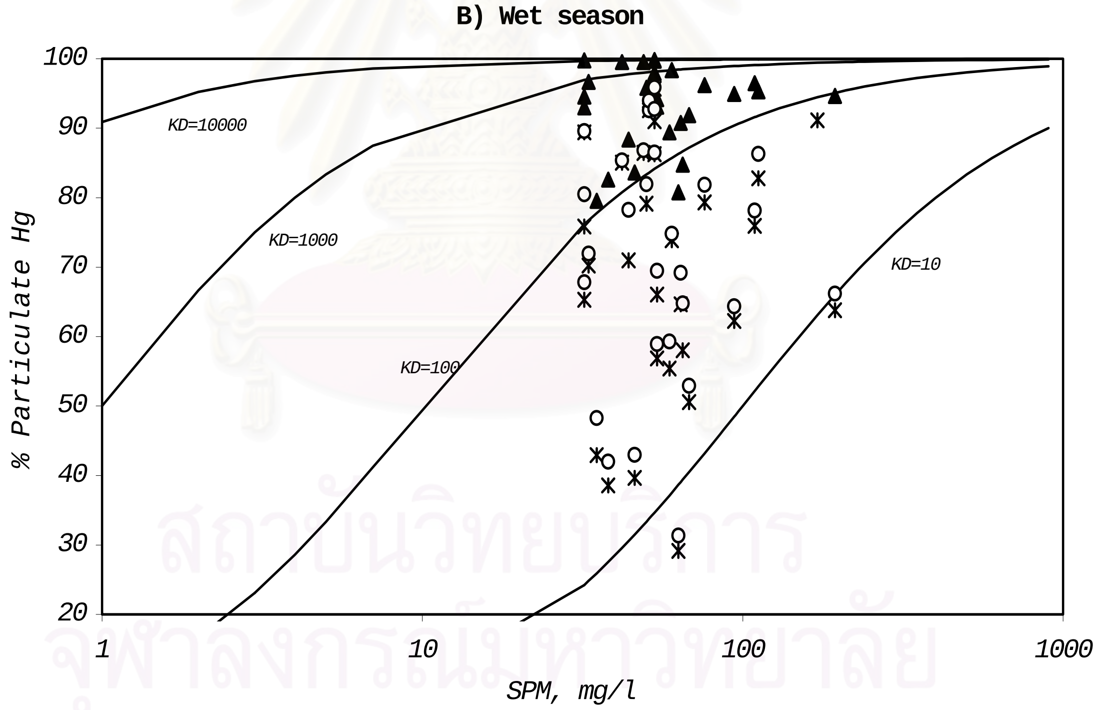

B) Wet season

Fig. 4-6 The variation in percentage of particulate Hg with suspended particulate matter (SPM)

A) Dry season

B) Wet season

The symbols represent samples where; $(Hg\text{-}R)_D$, Δ ; $(Hg\text{-}T)_D$, * ; Hg-NR, O.

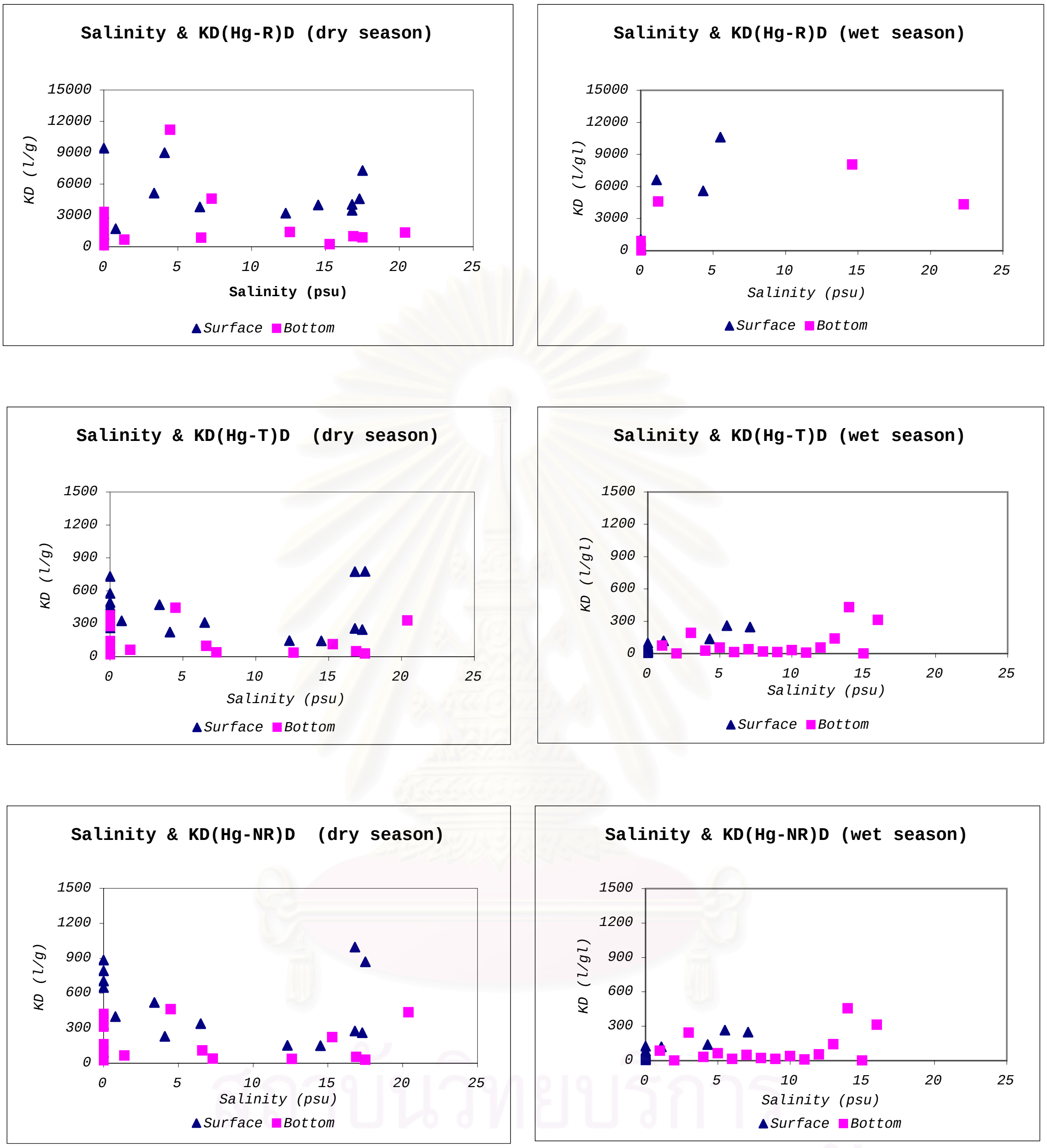


Fig.4-7 K_D of $(Hg\text{-}R)_D$, $(Hg\text{-}T)_D$, and $(Hg\text{-}NR)_D$ as a function of salinity of the Chao Phraya River estuary in the dry and the wet season only about 20% of total chlor-complexes in seawater, and the greater abundance of the more soluble $HgCl_4^{2-}$ complex above salinity of about 10 were predicted to conceal or even offset any salting effects of the neutral complex (Turner et al., 2001).

4.4 Experimental results : sediment resuspension

River sediment was added to mixture of seawater of different proportion salinity of 0, 5, 10, 15, and 30 psu. the results showed that desorption of Hg from sediment occur within the first hour, after that re-adsorption occurred. However, 1-2% of dissolved Hg concentrations is persisted in the water. This replied that resuspension of sediment by physical processes (tide, flow and storm), cause some release of Hg to the water column and then re-adsorption occurs, only 1-2% may be left in water. However, the waters movement is dynamic processes, therefore Hg in the water column and surficial sediment can be inter-change depended on less or strong turbidity and other factors.

4.5 Experimental results : mixing experiment

The behavior of mercury during estuarine mixing were studied. Unfilter river water was mixed with seawater in different proportions. Therefore, particulate concentration of these mixing water was varied by mixing proportion. The concentration of suspended solid decrease gradually from 59 mg/L in river water to 15 mg/L in seawater (30 psu). The water was subsamples at different time and analyzed for total dissolved and suspended particulate mercury. The experimental result showed that exchange of particulate and dissolved Hg occurred during the estuarine mixing especially during 1-3 hours after the mixing (Fig.3-18). High K_D was observed at low salinity during 1-3 hours. The Hg-P concentration was observed to be dominant form at low salinity and decreased at salinity 10-20 psu while, the $(Hg\text{-}T)_D$ showed dominant form at high salinity in the period of 1-12 hours (Fig.4-8). The experimental results would expect Hg to be preferentially associated with particulate matter in the fresh water while,

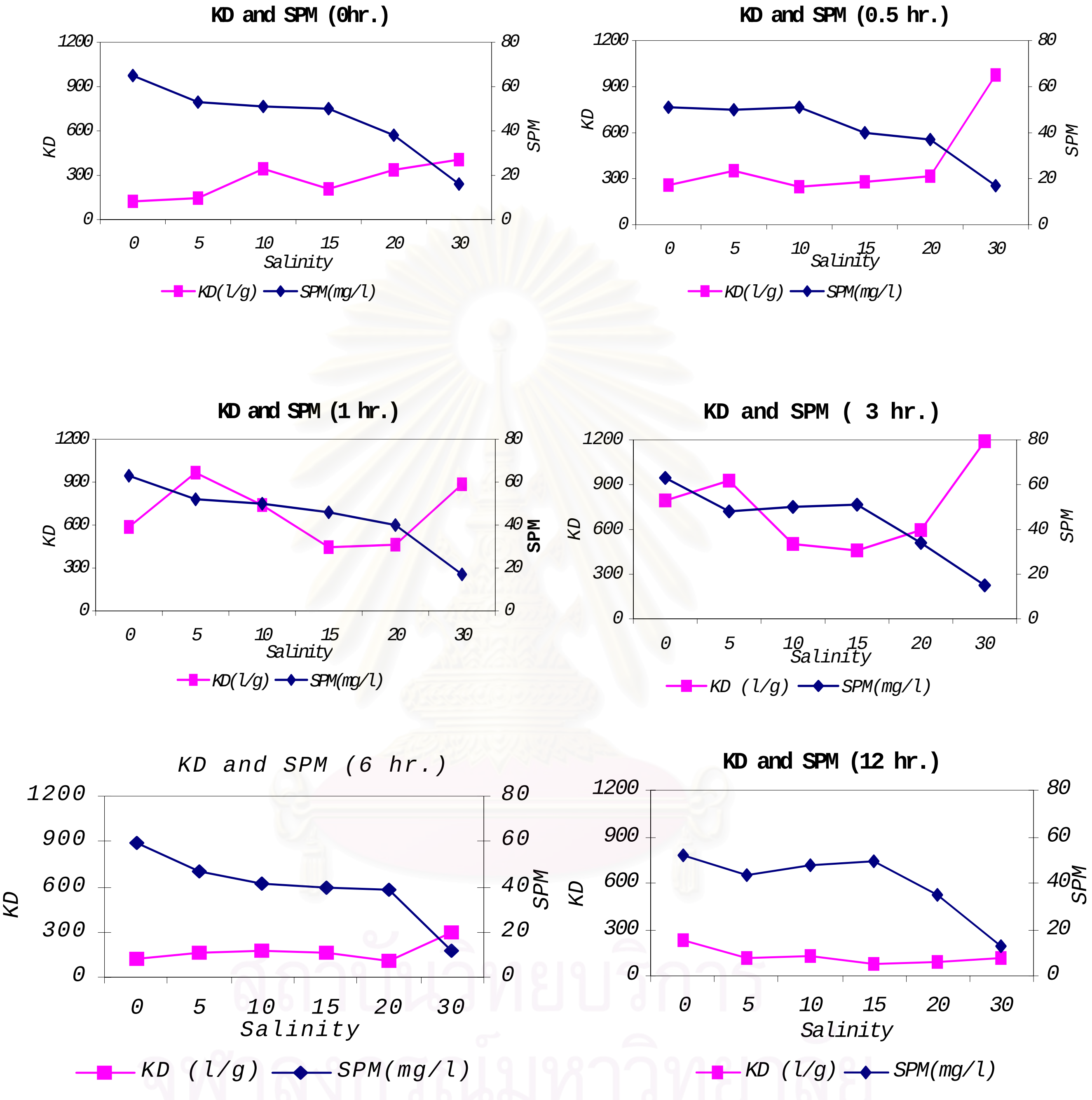


Fig.4-8 K_D and SPM as a function of salinity in difference times (experimental work)

Hg is dominantly in dissolved form in the saline water, these may be due to its existence in the form of chloro-complexes in seawater.

4.6 Mercury in sediment

Mercury concentration in surface sediments of the Chao Phraya River estuary showed no difference in concentration of Hg accumulation between <250μm and <63μm grain size fraction. The surface sediments are mainly clay and silt (<63μm) at approximately 60-70%. The increased percentage of the fine grain sediment (<63 μm) containing higher concentrations of mercury were observed in the dry season, while there was no relationship between Hg concentration and percentages of <63 μm grain size fraction in the wet season. The Hg contents of sediments in the dry season were observed to increase gradually from the upper estuary towards the river mouth. The high concentrations were found at the vicinity of the populated area (Bangkok area) and the major industrial area in the vicinity of Km 52 to river mouth. Removal and transport of contaminated sediments upstream may explain the Hg concentrations in the wet season were higher than in the dry season. During flood periods soil and sediment particles were mobilized. The content in particulate matter is also high in estuaries, where flocculation processes take place at the freshwater – seawater interface (Ferrara et al., 1991). Schultze et al., (1995) suggested that, river sediment contaminated by mercury are distributed over wide areas and are easily transported and released by flows and floods.

4.7 Relationships between Hg and other components

Both of $(Hg\text{-}R)_D$, $(Hg\text{-}T)_D$ and $(Hg\text{-}NR)_D$ concentrations were high in the upper estuary and then decreased gradually towards the river mouth. These may be due to dilution and form chloro-complex in seawater. The concentration of Hg-T decreased with increasing salinity were observed in both the dry and the wet seasons, the result show significant correlation (r= 0.55) only in the wet season (Fig.4-9 to 4-11).

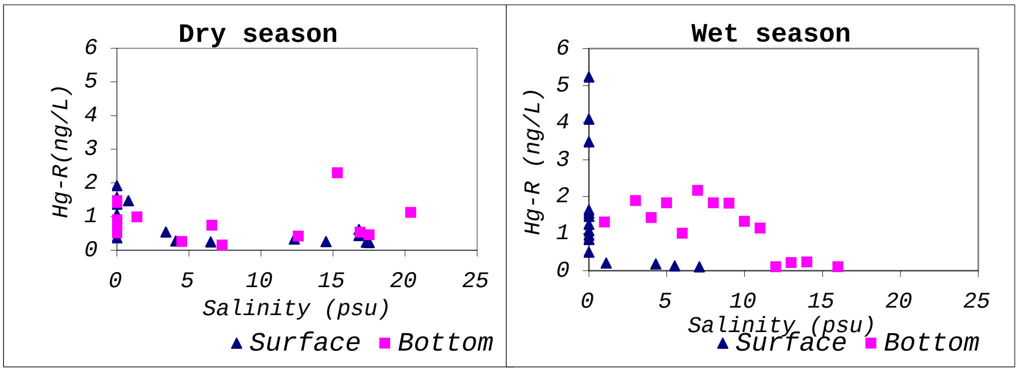


Fig.4-9 $(Hg\text{-}R)_D$ and Salinity correlation in the dry and the wet season

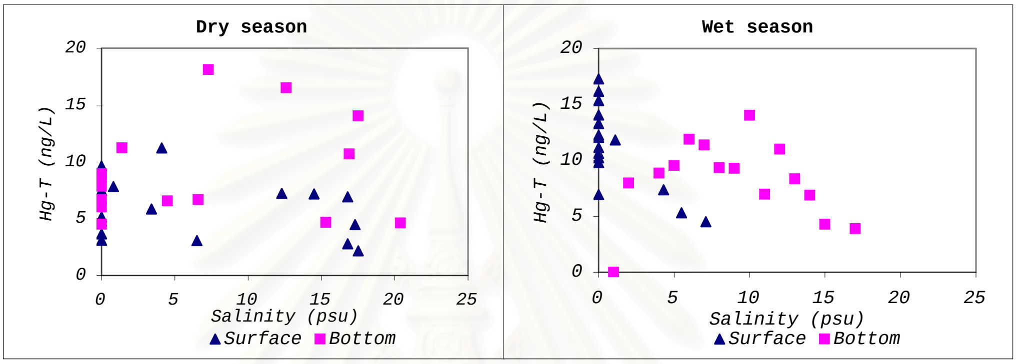


Fig.4-10 $(Hg\text{-}T)_D$ and Salinity correlation in the dry and the wet season

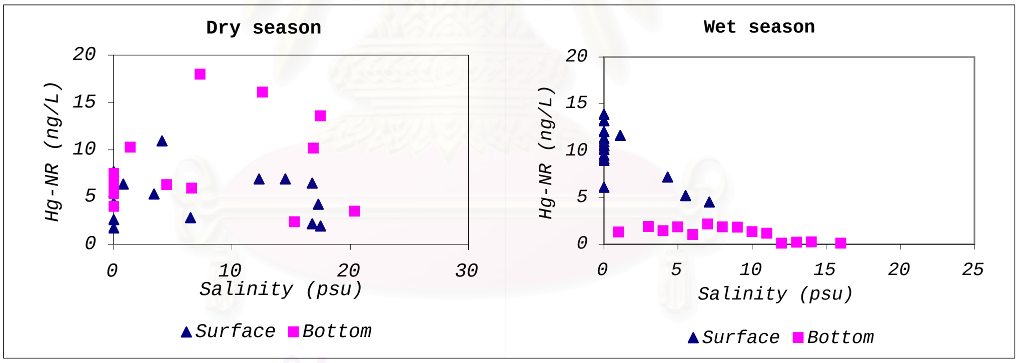


Fig.4-11 $(Hg\text{-}NR)_D$ and Salinity correlation in the dry and the wet season

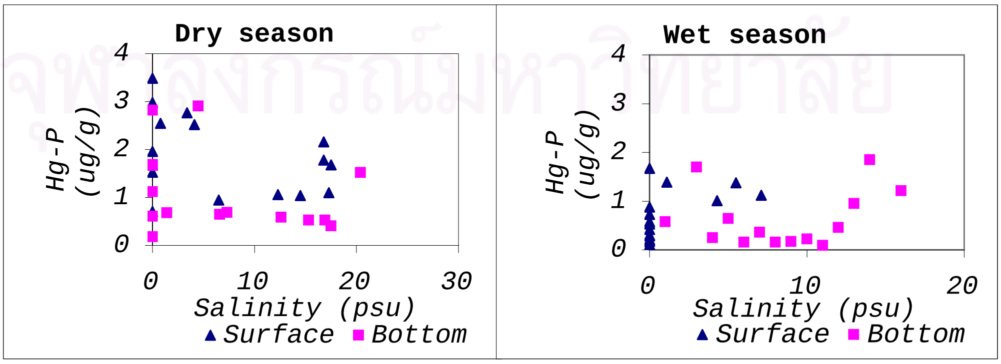


Fig.4-12 Hg-P and Salinity correlation in the dry and the wet season

The Hg concentration decreases with increasing salinity have been observed in the St.Lawrence estuary (Cossa et al., 1988) and the Galveston Bay (Staordal et al., 1996). However, the remobilization of metals bound to particulate matter can occur with increasing salinity. A maxima in dissolved Hg at low salinity has been observed in several estuaries e.g. Schrldt estuary (Leermakers et al., 1995), the Lena, Ob and Yenisei Rivers (Coquery et al.,1995). The Hg-P concentration decreases with increasing salinity observed in both seasons (Fig.4-12). These may be due to less organically bound Hg in seawater. However, a small increase in suspended particulate mercury concentration was observed in the area of salinity increasing. These result could be explained by resuspension and mixing with high suspended particulate mater or salting out effects, that proposed by Turner et al (2001).

In general, the large fractions of the trace elements are mainly concentrated in the fine-grained size fraction of the solid phase (Regnier and Wallast, 1993). Figures et al (1983) found the highest mercury levels in the particulate matter to be associated with the fine-grained sediments. However, they also suggested that the Hg-P decrease with increasing SPM is problably a dilution with less contaminated particles. The results obtained in the Chao Phraya River estuary, Hg-P concentration were decreased with increasing SPM indicated that the distributions of Hg-P along the estuary may be influenced by the strong dilution of the river-bone material and coarser sand carried upstream by bed load transport (Fig.4-13). Forthermore, the association of mercury with particulate organic matters is well documented. A strong correlation was reported between organic matter and Hg in water and sediments (Gobeil and Cossa, 1993; Driscoll et al., 1995; Coquery et al., 1995, and Leermakers et al., 1995), and strong complexes with dissolved organic matter derived principally from freshwater input (Mason et al., 1993). There was no relationship observed between $(\text{Hg-R})_D$ and TOC (Fig.4-14). The $(\text{Hg-T})_D$ concentrations with increase in total organic carbon (TOC) was observed in the Chao Phraya River estuary in the both seasons (Fig.4-15). A comparison of the $(\text{Hg-T})_D$ concentration with TOC showed significant correlation only in the wet season ($r=0.59, p<0.05$) and $(\text{Hg-NR})_D$ correlation with TOC showed similar result with $(Hg\text{-}T)_D$ (Fig.4-16). While the Hg-P concentrations were found to decrease with

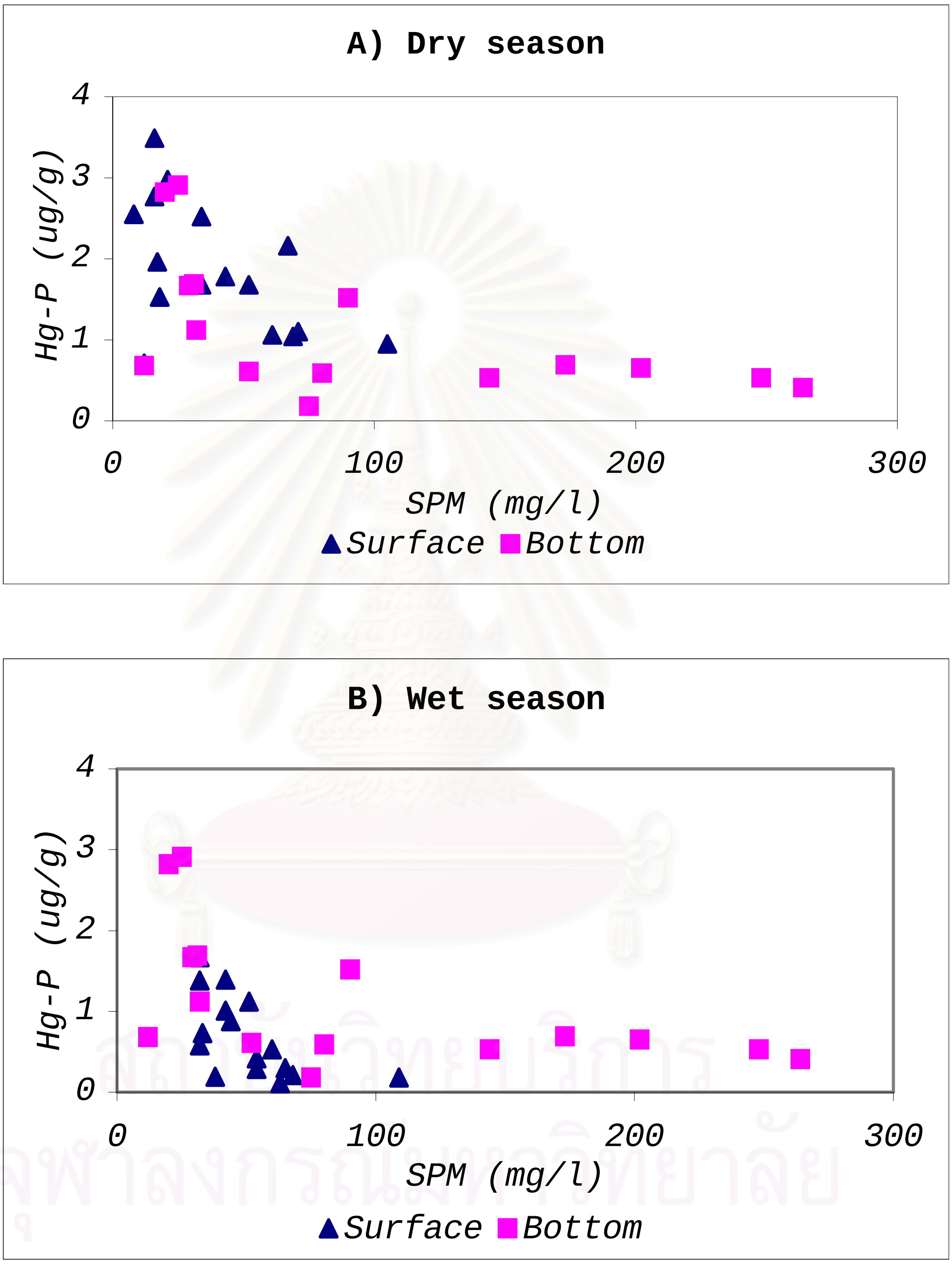


Fig 4-13 Hg-P and SPM correlation in the dry and the wet season

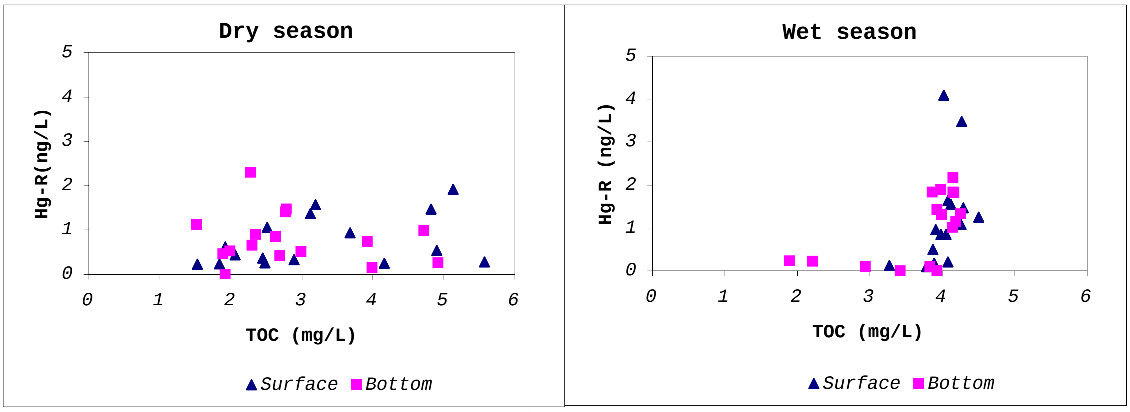


Fig.4-14 $(Hg\text{-}R)_D$ and TOC correlation in the dry and the wet season

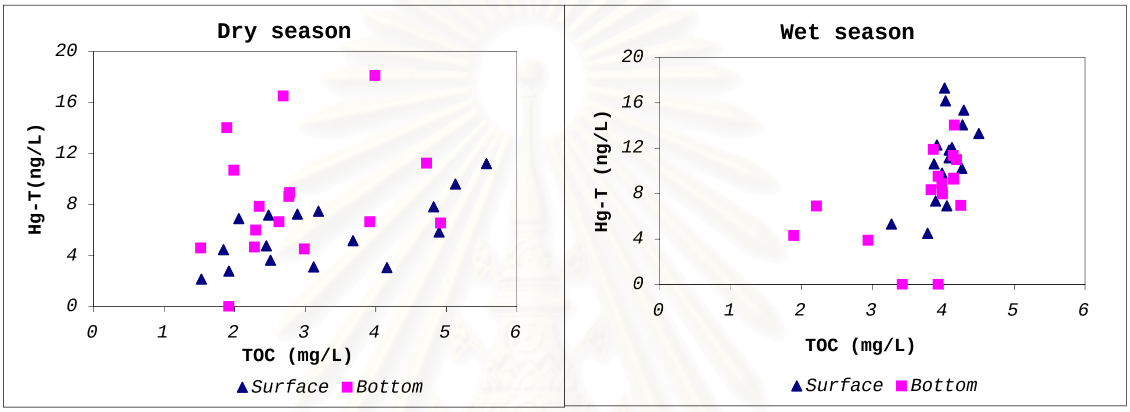


Fig.4-15 $(Hg\text{-}T)_D$ and TOC correlation in the dry and the wet season

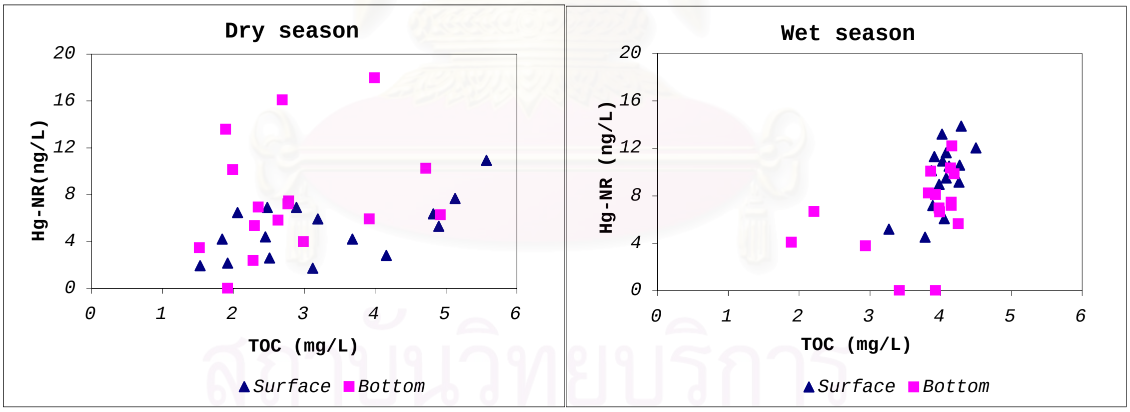


Fig.4-16 $(Hg\text{-}NR)_D$ and TOC correlation in the dry and the wet season

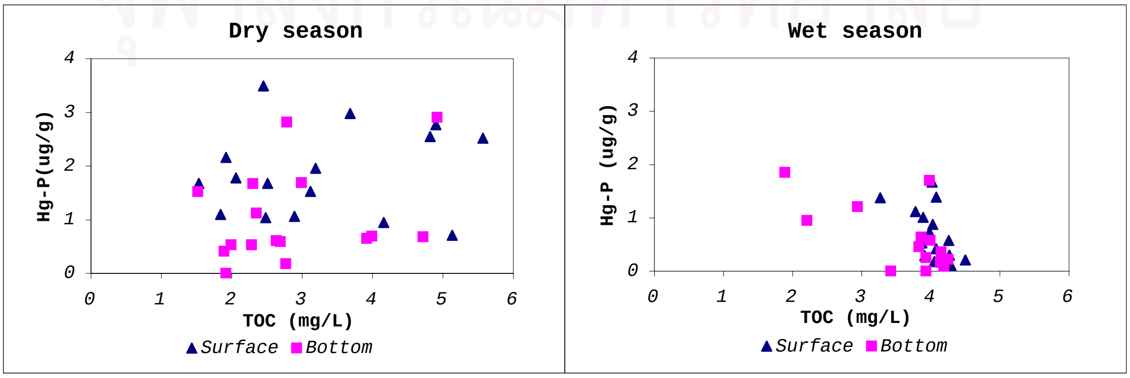


Fig.4-17 Hg-P and TOC correlation in the dry and the wet season

increasing TOC (Fig.4-17), this may be due to the increases in SPM that did not contain very high amounts of mercury concentration as mentioned above.

The association of mercury with organic matter and fine grain was noted by others (e.g. Loring et al., 1983; Figueres et al., 1985; Velinsky et al., 1994; and Gagnon et al., 1997). The concentrations of organic carbon (OC) were determined in sediment <250 μm grain size fraction ranged from 0.67 to 2.62 % and 0.96 to 2.71 % (dry wt.) for the dry season and the wet season, respectively. Eventhough, the percentage of OC concentration in sediments were observed increase gradually from the upper estuary towards the river mouth in both seasons. But, there was no relationship between percentage of OC and the fraction of fine-grain (<63 μm) sediment in both seasons from this study, this result similar with report in the Tidal River in the Washington, D.C. area by Velinsky et al., (1994). In this study, comparison of Hg concentration with percentage of OC in sediment found no correlation (r=0.091) in both season. This probably the concentration of OC content are consider low level (0.67 to 2.71%OC) as compared with those reported by Velinsky et al., (1994) on the Tidal River in the Washington, D.C. area (2.5 and 6.4%OC) or may be the high river flow during the wet season.

Furthermore, the outer part of the Chao Phraya River estuary the sediments are regularly dredged in order to maintain the navigable channel of Bangkok Port. The average annual dredging quantities is about 3,984,915 m^3 at the Bangkok bar channel (Port Authority of Thailand - unpublished data). This may cause fluctuation in the Hg concentration in sediments between the Bangkok Port and the river mouth (>50 Km distances) caused by dredge spoils, while higher amounts of mercury can be released from the sediments (Schultz et al., 1995). In this respect the upper estuary represents a more natural situation and the concentration of Hg accumulation may reflect the input of Hg from the upper estuary. However, there are also several manufacturing industries, including sawmills, battery factory, foodstuff factory and an electricity generation plant situated at the upper estuary along the river (northern part of Bangkok). Even though, with regard to the Hg concentration in the sediments are of the Chao Phraya River estuary found values still lower level as compared with the contaminated estuaries e.g.

Hg concentration range from 0.02 to 8.63 μg/g in the Adriatic Sea (Ferrara & Maserti, 1992) and 0.13 to 9.2 μg/g in the Tidal River in Washington, D.C. area (Velinsky et al., 1994). Polprasert (1982) reported the mercury cocentrations in sediments of the Chao Phraya River estuary ranged from 0.08 - 1.86 μg/g (dry wt.). Chongprasith and Wilairatanadilok (1998) reported the mercury levels in the coastal of the Gulf of Thailand and the Andaman Sea of 0.047 to 2.135 μg/g (dry wt.).

4.8 Daily material fluxes of total Hg.

The net uptake/release of Hg into each section of the estuary is of the greatest in the analysis of water quality in estuaries. Cities discharged large quantities of waste and a greatly deteriorated and effected estuarine environment. Estimating of time and spatial behaviors of water quality in estuaries is complicated by the effects of estuarine hydrology. Some simplifications can, however, be made to provide some useful results in estimation the net flux (Thomann and Mueller, 1987). The estimated daily flux of total Hg in the Chao Phraya River estuary to the Upper Gulf of Thailand was calculated by following advection equation:

$$F = W \times S \times C$$

Where :

F = Flux (kg/day)
W = Water Discharge (m^3/day)
S = Substance concentration (mg/L)
C = 10^{-6} kg/mg x 10^3 L/m^3

The assumption behind this equation is that only the advective transport is considered. All other hydrological processes including mixing are ignored. The discharge of the Chao Phraya River estuary during the dry season (April 1999) was 6.2×10^6 m^3/day, while the wet season (October 1999) was 142.6×10^6 m^3/day. In order to simplify the analysis, it was also assumed that there was no change of flow between segments. The horizontal flux of total Hg are shown in Fig.4-18. The daily flux of total

Hg in the dry season decreased gradually towards downstream, the decreasing of flux by ~50% was found at Km 60 and then the flux was increased downstream near the high turbidity zone from Km 52 to Km 12. The estimated flux of Hg in the wet season was also higher at the upstream and decreased from Km 78 to Km12, then increased at the river mouth in the vicinity of the high turbidity zone. The daily net flux in the wet season was higher than in the dry season due to high river flow.

The net uptake/release of total Hg in each section of the Chao Phraya River estuary are shown in Fig.4-19. The daily flux in both seasons seemed to be in the similar pattern. The upstream concentration was greater than downstream and the concentration was increased at the high turbidity zone. The increasing concentrations of Hg at the downstream could be due to some new sources. These Hg may be from local point source or from sediment and interstitial water near the high turbidity zone.

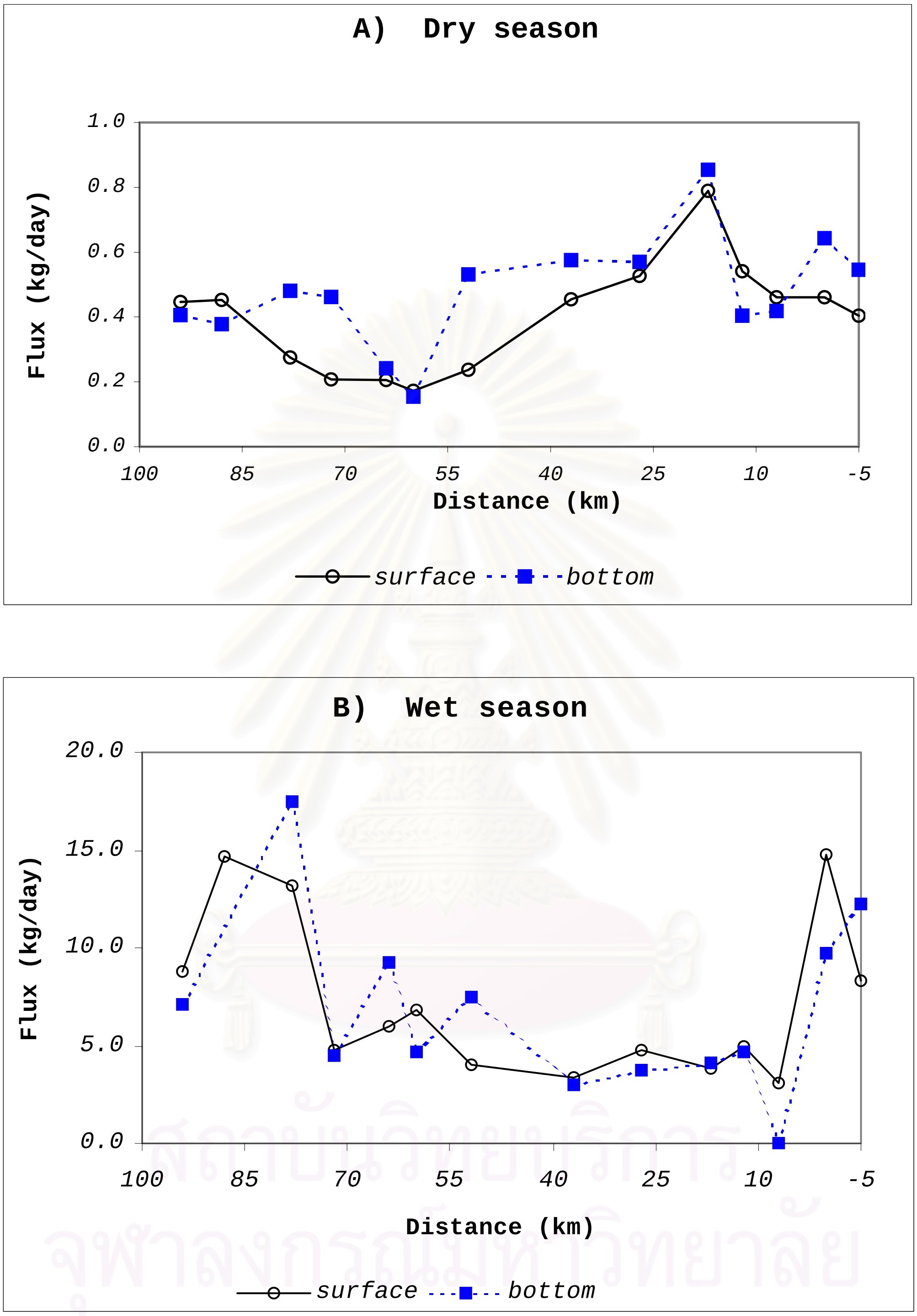
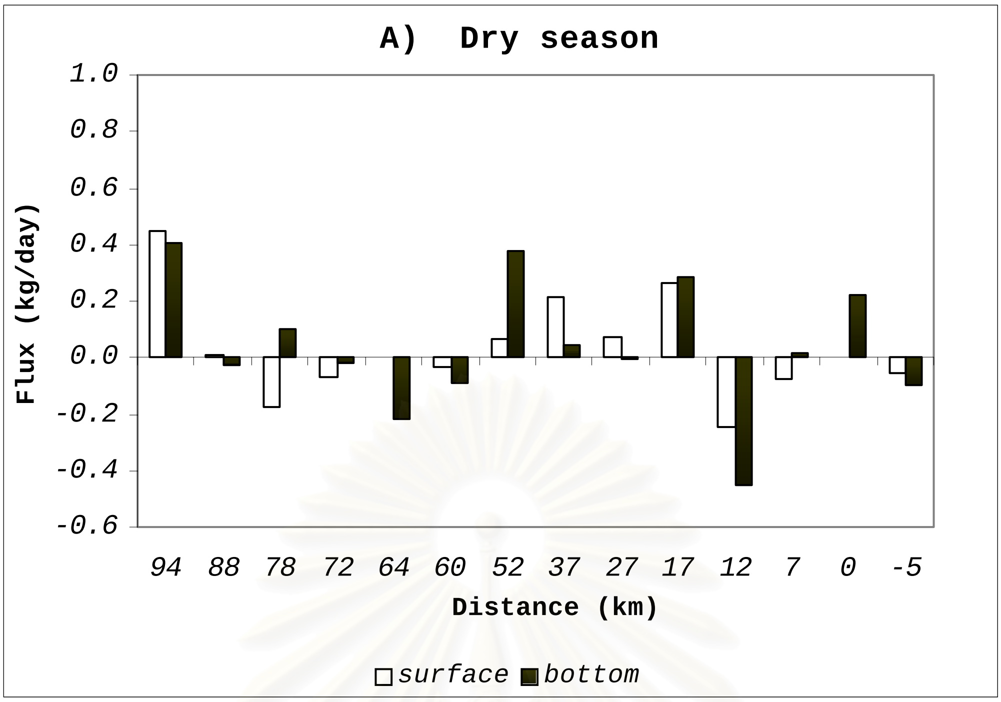


Fig.4-18 Horizontal flux downstream of total Hg in the Chao Phraya River estuary

A) Dry season

B) Wet season



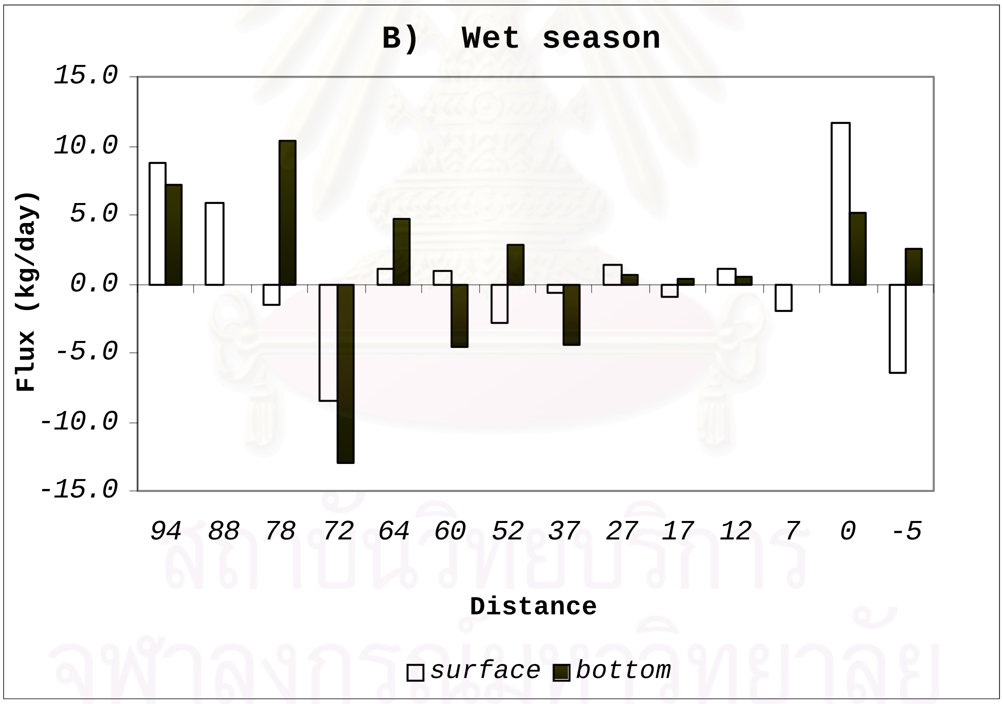


Fig.4-19 Additive and removal of total Hg in each section of the Chao Phraya River estuary,

(+ = added, - = removed)

A) Dry season

B) Wet season

Chapter 5

Conclusion and Recommendations

5.1 Conclusion

The seasonal variation of mercury distribution in the Chao Phraya River estuary was observed between the dry and the wet season. The concentrations of $(Hg\text{-}R)_D$ and $(Hg\text{-}T)_D$ in the wet season were higher than those in the dry season. The dissolved Hg phase was about 30% of the total Hg in the wet season while it was only 15% of the total Hg in the dry season. Most of the dissolved Hg form is non-reactive Hg $[(Hg\text{-}NR)_D]$, which accounted for more than 85% of the total dissolved Hg. In The dry season, $(Hg\text{-}T)_D$ concentrations of the bottom water were higher than the surface water, particularly, the high values were observed in the vicinity of industrial areas. These results indicated that internal processes (adsorption, coprecipitation, remobilization, and resuspension from sediment) were important factors contributing to Hg contamination in the estuary, while the external processes (fresh water river flow, river runoff and precipitation from atmospheric sources) were important factors in the wet season.

The Hg-P phase was the dominant Hg species in the estuary, about 85 % (57-97%) of total mercury was found in the dry season while it was about 70% (38-95%) of the total Hg in the wet season. Hg-P concentrations in the dry season were higher than the wet season. These may be due to the river discharge affect in the dry season are lower than those of the wet season, result in a much longer water residence time in a storage of pollutants and potential remobilization during the dry season.

Hg-P concentrations were higher in the upper estuary and then decreased gradually towards downstream and increasing of Hg-P was observed in the high turbidity zone in both seasons. This may be due to resuspension from sediment and interstitial water.

The observed partition coefficients (K_D) between particulate and dissolved form were higher in the high turbidity zone during both seasons and the K_D value of the dry and the wet season was higher than in the wet season. These indicated that Hg has the greatest affinity for particulate phase in the dry season. The higher K_D for non-reactive dissolved Hg in the dry season suggested that the behavior of $(Hg\text{-}NR)_D$ was different between the dry and the wet season. Increasing of K_D with increasing salinity was also found in the Chao Phraya River estuary.

Laboratory experiment showed that adsorption and desorption of mercury occurred during mixing along salinity gradient. The experimental results would expect Hg to be preferentially associated with particulate matter in the fresh water while Hg is dominantly in dissolved form in the saline water, these may be due to its existence in the form of chloro-complexes in seawater.

The Hg concentration of surface sediments in the dry season were observed increased gradually from the upper estuary towards the river mouth where the higher concentration were found in the vicinity of the major industrial area. While, the Hg concentrations in the wet season were higher than in the dry season, these may be caused by resuspension of contaminated sediments upstream. Resuspension experiments, in the laboratory, showed that mercury desorbed from sediments rapidly. However, the readsorption occurred within 6 hours and 1-2% of Hg concentration is persisted in the water. The vertical profile of Hg in core sediment indicated that Hg concentrations in surficial sediment were about three to five times lower than concentration found 20 years ago due to the use of mercury in the production process of some industries during that period.

A comparison of the Hg concentrations from this study with other major estuaries and coastal areas indicates that concentration of Hg in the Chao Phraya River estuary are in a similar concentration range to those found in major estuaries elsewhere.

5.2 Recommendations

Mercury is widely distributed in the environment. Anthropogenic inputs to the aquatic environment are therefore regarded as important sources of mercury contamination. However, further information to support this study is required. Thus, recommendations from this study are proposed as followed:

1. Mercury contamination study in the Chao Phraya River, other major rivers, estuaries, and other areas in Thailand need to be conducted. For more reliable data, ultra-clean technique to strongly recommended to be used in mercury determination.
2. Contributions of mercury from various sources (e.g., wastewater effluent or direct discharges to water, as well as air deposition from combustion processes, manufacturing operations, and natural sources) needs to be further studied.
3. The mercury distribution during various hydrological conditions and the bioavailability of mercury within the river systems, including other ecological systems should be investigated.
4. Release of mercury from sediments in various conditions should be studied (e.g. sediment texture, pore water, anoxic condition, and effect of burrowing organisms).
5. Relationship between mercury and organic carbon (dissolved organic carbon (DOC), particulate organic carbon (POC), and type of organic matter) should be investigated.
6. The mechanisms that control the transport, transformation, and the fate of mercury in Thai aquatic systems should be focused.

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APPENDICES

APPENDIX A

1. Principle method of the analysis of dissolved Hg (Quemerais and Cossa,1997)

In natural waters, dissolved Hg exists in two different chemical from: Hg^O (elemental Hg) and Hg (II). The divalent form can bind to organic compounds to from such compounds as CH_3Hg^+ (or monomethyl mercury). The elemental form of Hg^O is volatile. In practice, the forms most frequently found are Hg^O, Hg^{2+} and its complexes, and CH_3Hg^+ and its complexes (Fitzgerald,1989). Preconcentration of Hg on gold traps is based on the volatility of the elemental form. As a result, it is necessary to convert all forms of Hg present in the sample to elemental Hg in order to make it volatile so that it can be collected on a gold trap.

The first step is the dissociation of Hg from its organic complexes, followed by the reduction of mono – and divalent forms to Hg^O. BrCl is used for the dissociation of organic complexes. Hydroxylamine is used only to neutralize the BrCl, since traces of bromine interfere with the amalgamation of Hg on to the Au collection column. The Hg is then reduced to its elemental form using $SnCl_2$. Bubbling argon gas through the reagent permits removal of the volatile Hg, which is collected in the " collector " trap.

On the analytical line, the preconcentration trap is heated to 500 °c under a stream of argon (80 ml/min.), the Hg released in the vapor phase crosses the gas cell of and atomic fluorescence spectrophotometer, where it is detected (see Fig.1a).

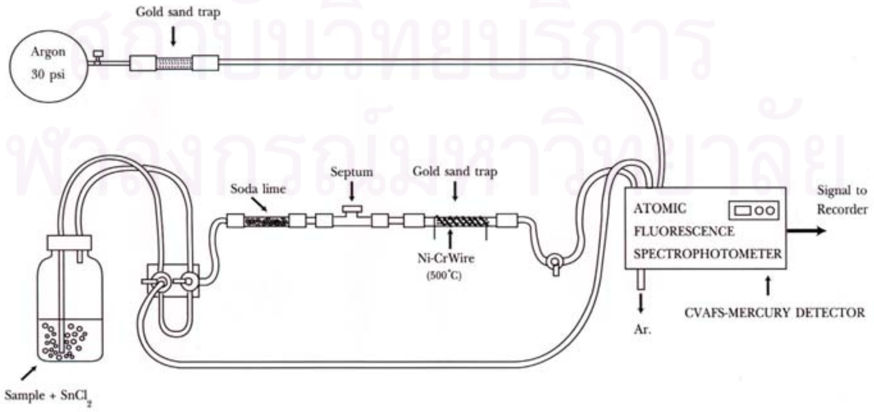

Fig.A-1 Schematic diagram illustating the procedute for Hg-R and Hg-T determination by preconcentration system (BrCl method)

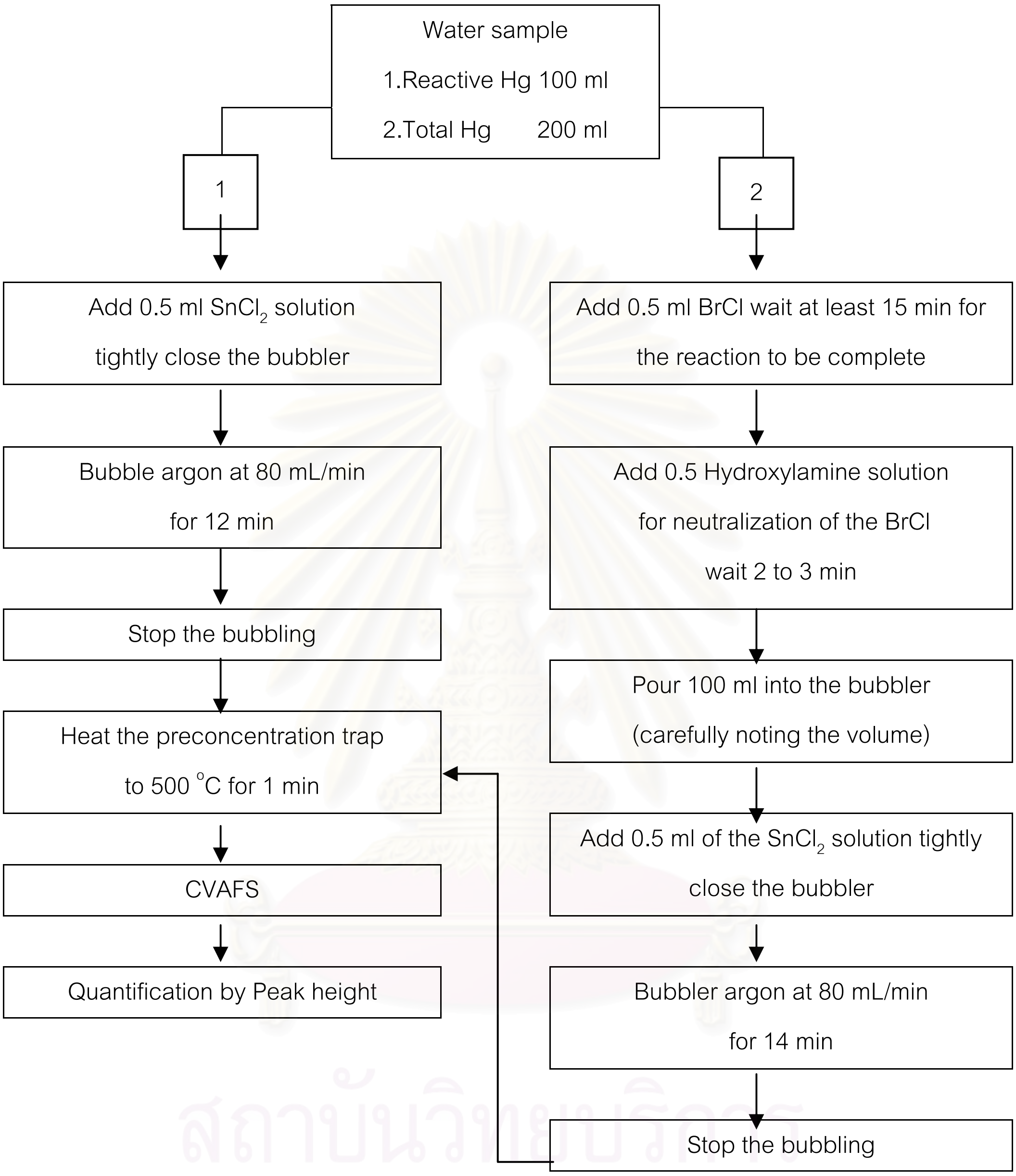

Fig. A-2 Schematic sequence for analytical $(Hg\text{-}R)_D$ and $(Hg\text{-}T)_D$ in water sample.

2. Anslysis of dissolved phase mercure (filtrate)

2.1. Analysis of Hg (BrCl method)

The analysis of Hg must be dune in a Class 100 laminar flow hood or in clean room.

Add 0.5 ml of BrCl solution for 250 ml of filtrate. A persistence yellow colour in obtained. Wait at least 15 minutes for the reaction to be complete. The quantity of BrCl to be added depends on the concentration of organic matter in the sample. Ensure that there is an excess of oxidant after the addition (i.e. the persistence of a yellow colour).

2.1.1 Add 0.5 ml of hydroxylamine solution to make the yellow colour disappear (neutralization of the BrCl); wait two to three minutes.
2.1.2 Pour 50 to 100 ml of filtrate into the bubbler, carefully noting the volume.
2.1.3 Add 0.5 ml of $SnCl_2$ solution, tightly close the bubbler.
2.1.3 Bubble argon at 80 ml/min. for 14 minutes.
2.1.4 Stop the bubbling.
2.1.5 Heat the preconcentration trap to 500 ^{o}c for 1 minutes.

The concentration is calculated by comparing the peak high with the peak height of the standard. The standard is obtained by injecting 20 μL of Hg – saturated air. The air temperature must be noted in order to calculate the quantity of Hg injected. Repeat the analytical cycle with a sample that has already been analysed, (i.e. a sample that should contain no Hg), to determine the quantities of Hg present in the reagents (blanks).

2.2 Preparation of Reagents

2.2.1 Preparation of BrCl solution

Carry out steps under a Class 100 chemical fume hood, being very careful because bromine is highly reactive. Prepare the reagent in a pre-washed 125 ml Teflon bottle.

2.2.1.1. Fill the bottle with 20 ml of Milli – Q water.

2.2.1.2. Add 1.1 g of $KBrO_3$ and 1.5 g of KBr.

2.2.1.3. Add 80 ml of HCl (suprapur).

BrCl can be stored for a very long time in the refrigerator. To prevent contamination, the bottle should be capped as tightly as possible using pliers and stored in well – sealed double polyethylene bags.

2.2.2 Preparation of hydroxylamine solution

In a Class 100 fume hood, weigh 30 g of hydroxylamine and add 70 g of Milli–Q water to yield a 30 % solution. The solution must be prepared in a pre-washed 125 ml Teflon bottle. The bottle polyethylene bags then store in the refrigerator.

2.2.3 Preparation of $SnCl_2$

Prepare the $SnCl_2$ in a Class 100 fume hood. Use a pre-washed 125 ml Teflon bottle.

2.2.3.1 Place 75 g of $SnCl_2$, $2H_2O$ in the bottle .

2.2.3.2 Add 12.5 ml of suprapur HCl (conc.) .

2.2.3.3 Heat on a hot plate until it dissolve without boiling.

2.2.3.4 Once cooled add 65 ml of Milli -Q water.

2.2.3.5 Before use, degas the solution for 12 to 24 hrs in the bubbler using ultra-pure argon.

This operation must be carried out in a Class 100 laminar flow hood.

The resulting solution will keep for approximate one month in the refrigerator.

The bottle must be tightly capped and stored in double polyethylene bags.

3. Analysis of solid phase mercury (filter and sediment)

3.1 Digestion of the filters and sediments

Digestion is carried out using Teflon bomb which is placed in a oven at 90 ^{o}c for one and a half hour.

3.1.1 Place the filter on the bottom of the Teflon bomb, with the side with the particles facing downward.

3.1.2 Add 5 ml of the low Hg HNO_3/HCl (9:1) mixture.

3.1.3 Tightly close the cover of the reactor.

3.1.4 Place in the oven at 90 ^{o}c.

3.1.5 Once the oven has reached the desired temperature, leave the bombs for one and a half hour.

3.1.6 Turn of the oven and take out the bombs place it in a Class 100 fume hood and let the bomb cool.

3.1.7 Open the bomb in the fume hood to let the acid vapors escape.

3.1.8 Add 10 ml of Milli–Q water to each reactor to obtain a total volume of 15 ml and transfer the contents into the 100 ml bottle.

3.1.9 Sample is ready for CAVFS analysis.

3.2 Filtration

Filtration of samples must be performed with six hours of sample collection, in a Class 100 laminar flow hood or in a clean room.

3.2.1 Place a Neuclepore membrane filter in the filter holder millipore filter.

3.2.2 Pour an aliquot of pre – homogenized sample in to filter funnel.

3.2.3 Collect the filtrate in a pre-washed Teflon bottle.

3.2.4 Acidify the filtrate to 0.5 % (V/V) with Suprapur HCl (for determine $(Hg\text{-}T)_D$).

3.2.5 Tightly cap the bottle and place it into double polyethelene bags.

3.2.6 The filter place it in a Petri-dish and place it in polyethylene bags.

The filters (particulate fraction) must be placed directly in the frozen. Before use, the filters are dried in a oven at 60 ^{o}c for 6 hours and then weighed on an analytical balance and the new weight is recorded the exact quantity of particulate matter present on the filter. The filters are then stored in a dessicator until digestion.

3.3 Sediments sample

Weight 50 mg sediment sample and transfer to a Teflon bomb, and then follow the same manner as for the filters samples, except the total volume were obtain to 20 ml.

4. Cleaning Procedures

Polyethylene gloves must be worn at all times. All cleaning should be carried out under a Class 100 laminar flow hood in a clean environment.

4.1 Cleaning of filters (Neuclepore membrane filters)

4.1.1 Soak in ultra – pure HNO_3, 10 % (V/V), in a Teflon ware for five days. Thoroughly rinse with Milli–Q water then soak for several days in Milli–Q water, Changing the water regular until the pH is neutral.

4.1.2 Place the filters in a clean Petri-dish.

4.1.3 Dry in a oven at 60 ^{o}c for 6 hours.

4.1.4 Store the filter in a vacuum dessicator.

4.1.5 Weigh the filters on an analytical balance, recording the weight on the Petri-dish.

5. Standard Mercury

The concentration of Hg is calculated by comparing the peak high with the peak height of the standard. The standard is obtained by injecting 20 μL of Hg – saturated air. The air temperature must be noted in order to calculate the quantity of Hg injected. The quantity of Hg (in pg) in the standard is calculated by multiplying the volume of air injected (20 μL) by the mercury vapour density (in ng/cm^3 or pg/μL) at the temperature considered. The mercury vapour density is taken from the table a in Appendix. Given that the laboratory temperature is generally around 21 to 22 ^{O}c, 20 μL of saturated air .vapour contain approximately 300 pg of mercury. The concentrations are calculated on the basis of peak heights. By measuring the peak height of the standard (in cm), the response of the apparatus (in pg/cm) can be determined. The standard may be injected between each sample and the day of analysis, approximately 15 injections can be made. If the apparatus response is very stable, four to five injections per day of analysis is enough.

6. Reagent blank and detection limits

The first test conducted mad in possible to determine the reagent blank the reproducibility of the blank. Typically, a reagent blank of the dissolved fraction is the quantity of Hg present in 400 μL of BrCl + 200 μL of hydroxylaamine + 500 μL of $SnCl_2$. The mean of the blank analyses obtained in the tests is on the order of 100 pg of Hg. The blanks vary depending on the day of analysis, and several blanks must be prepared over the course of a given day. In general, the collection line, particularly the bubbler, becomes contaminated used to clean the bubbler. Analyses of the blanks must be conducted until the signal becomes stabilized.

For elements at the trace level, the factor limiting detection is the blank. The detection limit is defined as three time the standard deviation of the blank. Given that the blanks are variable from one day to another, the detection limit also varies daily. To obtain a good detection limit, it is essential to have a blank that is as weak as possible and highly reproducible. The mean and standard deviation of the blanks and the corresponding detection limits. To obtain a resoluble detection limit, the variability of the blanks should always be less than 10 %. If it exceeds this value, it is possible that leaks occurred in the system (in the bubbler or and the analytical line) or that there was poor reproducibility of the operator is steps. The problem must be identified and resolved before proceeding to sample analysis.

Table A-1 Saturated Elementary Hg Vapor Density at 1 atm and from 20 ^{O} to 30 ^{O}C

T ^{O}C	Vapor density ng/cm^2	T ^{O}C	Vapor density ng/cm^2	T ^{O}C	Vapor density ng/cm^2	T ^{O}C	Vapor density ng/cm^2	T ^{O}C	Vapor density ng/cm^2
20.0	13.18	20.2	13.40	20.4	13.63	20.6	13.86	20.8	14.09
21.0	14.31	21.2	14.56	21.4	14.80	21.6	15.05	21.8	15.29
22.0	15.54	22.2	15.80	22.4	16.07	22.6	16.34	22.8	16.60
23.0	16.87	23.2	17.15	23.4	17.44	23.6	17.73	23.8	18.02
24.0	18.30	24.2	18.61	24.4	18.92	24.6	19.23	24.8	19.54
25.0	19.85	25.2	20.18	25.4	20.51	25.6	20.84	25.8	21.17
26.0	21.50	26.2	21.86	26.4	22.22	26.6	22.57	26.8	22.93
27.0	23.28	27.2	23.67	27.4	24.05	27.6	24.43	27.8	24.81
28.0	25.19	28.2	25.61	28.4	26.02	28.6	26.43	28.8	29.02
29.0	27.25	29.2	27.69	29.4	28.14	29.6	28.58	29.8	29.0
30.0	29.46	30.2	29.94	30.4	30.41	30.6	30.88	30.8	31.36

Table A-2 Description of the mercury species and fractions discussed.

Mercury species	Symbol	Description
Total dissolved Hg	$(Hg\text{-}T)_D$	Sample filtered through Nuclepore membrane filter (0.4 um) Determine by BrCl oxidation, followed by SnCl2 reduction
Dissolved reactive Hg	$(Hg\text{-}R)_D$	Easily reduced Hg species performed on water sample after filtered
Particulate Hg	Hg-P	Measured by digestion of particulate on Nuclepore membrane filters
Dissolved non –reactive Hg	$(Hg\text{-}NR)_D$	Calculate by $(Hg\text{-}T)_D\text{-}(Hg\text{-}R)_D$
Total Hg	Hg-T	Dissloved total Hg + Particulate Hg

APPENDIX B

RAW DATA AND RESULTS

Table B-1 K_D of Mercury species of the Chao Phraya River estuary in the dry season (April 1999).

Distance	K_D (Hg-R)$_D$		K_D (Hg-T)$_D$		K_D (Hg-NR)$_D$	
(km)	Surface	bottom	surface	bottom	surface	bottom
94	9432	3314	732	375	793	423
88	3170	2530	578	278	706	312
78	1248	1918	262	315	331	378
72	1585	718	460	92	649	105
64	1117	128	494	21	884	25
60	370	1244	74	143	92	161
52	1735	687	326	61	401	66
37	5130	11192	474	444	522	463
27	9000	4600	225	38	231	38
17	3800	878	310	98	338	110
12	3212	1405	146	36	153	37
7	4000	230	145	113	150	224
0	4045	1000	258	50	275	52
-5	4583	891	247	29	261	30
-5	7304	1358	778	330	870	437
-5	3484	*	774	*	995	*

Note : K_D = l/g

Table B-2 K_D of Mercury species of the Chao Phraya River estuary in the wet season (October 1999).

Distance	K_D (Hg-R)$_D$		K_D (Hg-T)$_D$		K_D (Hg-NR)$_D$	
(km)	Surface	bottom	surface	bottom	surface	bottom
94	859	443	74	73	81	87
88	408	*	97	*	127	*
78	168	899	54	192	81	244
72	302	175	24	26	26	31
64	1060	350	50	54	52	64
60	86	158	21	14	28	15
52	212	166	26	39	30	50
37	123	87	16	17	18	21
27	256	93	38	12	44	14
17	75	165	7	32	8	39
12	168	78	16	8	17	9
7	537	4600	57	55	63	55
0	6619	4318	117	138	120	142
-5	5611	8043	137	430	141	455
-5	10615	*	259	*	266	*
-5	*	*	248	312	248	312

Note : * = No sample

Table B-3 Mercury species of the Chao Phraya River estuary in the dry season (April 1999).

Distance	Hg-R (ng/L)		Hg-T (ng/L)		Hg-P (ng/L)		Total Hg (ng/L)		% of Hg-P	
(km)	surface	Bottom	surface	bottom	Surface	bottom	Surface	bottom	surface	bottom
94	0.37	0.51	4.77	4.51	64.29	58.16	69.43	63.18	92.6	92.1
88	0.94	0.66	5.16	6.01	64.29	52.04	70.39	58.71	91.3	88.6
78	1.57	1.47	7.49	8.94	33.67	64.29	42.73	74.7	78.8	86.1
72	1.06	0.85	3.65	6.66	27.55	64.29	32.26	71.8	85.4	89.5
64	1.37	1.41	3.1	8.63	27.55	27.53	32.02	37.57	86.0	73.3
60	1.92	0.9	9.61	7.85	15.29	15.3	26.82	24.05	57.0	63.6
52	1.47	0.99	7.83	11.23	27.55	70.41	36.85	82.63	74.8	85.2
37	0.54	0.26	5.85	6.55	64.29	82.64	70.68	89.45	91.0	92.4
27	0.28	0.15	11.21	18.12	70.41	70.41	81.9	88.68	86.0	79.4
17	0.25	0.74	3.06	6.66	119.39	125.51	122.7	132.91	97.3	94.4
12	0.33	0.42	7.24	16.51	76.53	45.92	84.1	62.85	91.0	73.1
7	0.26	2.3	7.18	4.67	64.29	58.16	71.73	65.13	89.6	89.3
0	0.44	0.53	6.91	10.68	64.28	88.78	71.63	99.99	89.7	88.8
-5	0.24	0.46	4.46	14.03	58.16	70.41	62.86	84.9	92.5	82.9
-5	0.23	1.12	2.16	4.6	87.11	96.2	89.5	101.92	97.3	94.4
-5	0.62	*	2.79	*	105.29	*	108.7		96.9	

Note : Hg-P calculate in nanogram/litre

* = No sample

Table B-4 Mercury species of the Chao Phraya River estuary in the wet season (October 1999).

Distance	Hg-R (ng/L)		Hg-T (ng/L)		Hg-P (ng/L)		Total Hg (ng/L)		% of Hg-P	
(km)	surface	Bottom	surface	bottom	Surface	bottom	Surface	bottom	surface	bottom
94	0.85	1.31	9.81	7.96	50.84	40.67	61.5	49.94	82.7	81.4
88	4.09	*	17.29	*	81.35	*	102.73		79.2	
78	5.23	1.89	16.16	8.86	71.18	111.86	92.57	122.61	76.9	91.2
72	0.96	1.43	12.27	9.53	20.34	20.34	33.57	31.3	60.6	65.0
64	0.5	1.83	10.63	11.89	30.51	50.85	41.64	64.57	73.3	78.8
60	3.48	1.01	14.05	11.36	30.51	20.34	48.04	32.71	63.5	62.2
52	0.85	2.17	6.93	9.35	20.34	40.68	28.12	52.2	72.3	77.9
37	1.55	1.83	12.06	9.28	10.17	10.17	23.78	21.28	42.8	47.8
27	1.64	1.82	11.15	14.03	20.34	10.17	33.13	26.02	61.4	39.1
17	1.47	1.33	15.34	6.97	10.17	20.34	26.98	28.64	37.7	71.0
12	1.25	1.15	13.29	10.99	20.34	20.34	34.88	32.48	58.3	62.6
7	1.08	<0.15	10.22	8.34	10.17	10.17	21.47		47.4	
0	0.21	0.22	11.83	6.9	91.52	61.02	103.56	68.14	88.4	89.6
-5	0.18	0.23	7.36	4.3	50.85	81.35	58.39	85.88	87.1	94.7
-5	0.13	*	5.32	*	50.85	*	56.3		90.3	
-5	<0.15	<0.15	4.52	3.88	71.18	81.35			68.1	71.8

Note : Hg-P calculate in nanogram/litre

* = No sample

Table B-5 Experimental result on sediment resuspension $(Hg\text{-}T)_D$, ng/L.)

Salinity/Time	0.5	1	3	6	12	24
0 psu	35.48	20.51	12.64	13.94	15.21	17.87
5 psu	54.11	93.80	40.77	37.40	21.04	19.66
10 psu	36.14	49.10	30.62	31.11	24.98	20.94
15 psu	39.59	38.45	49.95	43.00	21.65	15.74
30 psu	38.34	53.10	44.32	19.40	22.61	18.56

Table B-6 Experimental result on sediment resuspension (% total dissolved Hg)

Salinity/Time	0.5	1	3	6	12	24
0 psu	4.13	2.47	1.59	1.69	1.86	2.24
5 psu	6.35	10.96	4.87	4.29	2.43	2.31
10 psu	4.49	5.95	3.59	3.58	2.88	2.05
15 psu	4.54	4.41	5.95	4.95	2.61	1.76
30 psu	4.54	6.28	5.48	2.33	2.73	2.19

Table B-7 Experimental result of particulate mercury concentration as a function of Salinity & times

Sal./Time	0	0.5	1	3	6	12
0%	1.25	1.36	1.93	1.95	1.04	1.56
5%	1.92	2.83	2.73	2.53	1.29	1.25
10%	2.2	1.78	2.47	2.26	1.71	1.32
15%	1.63	2.04	2.19	2.8	1.06	0.84
20%	1.59	1.36	2.66	2.7	1.04	0.68
30%	2.47	3.6	3.86	3.45	1.67	0.76

* concentration : Hg-P (ug/g)

Table B-8 Experimental result of dissolved mercury concentration as a function of Salinity & times

Sal./Time	0	0.5	1	3	6	12
0%	10.2	5.27	3.29	2.46	9.0	6.65
5%	13.28	8.04	2.83	2.73	8.24	11.07
10%	6.39	7.18	3.34	4.51	9.84	10.25
15%	7.89	7.31	4.92	6.12	6.81	10.84
20%	4.74	4.31	5.76	4.54	10.05	7.6
30%	6.08	3.69	4.36	3.29	5.74	6.41

* Dissolved mercury : $(\text{Hg-T})_D$ (ng/L)

Table B-9 SPM concentration of water samples on mixing experiment.

Sal./Time	0	0.5	1	3	6	12
0%	65.2	51.5	63.5	62.6	58.7	52.2
5%	53.0	50.4	52.2	48.3	47.4	42.7
10%	50.8	51.3	49.6	49.6	41.0	48.3
15%	50.0	40.0	46.5	50.8	40.0	48.7
20%	38.3	31.4	40.4	33.9	39.1	35.2
30%	16.5	16.9	17.4	14.8	12.2	13.0

* concentration : Hg-P (ug/g)

Table B-10 K_D value (Hg-P/(Hg-T)$_D$) of water samples on mixing experiment (K_D = l/g)

Sal./Time	0	0.5	1	3	6	12
0%	123	258	587	793	116	235
5%	145	352	965	927	157	113
10%	344	248	740	501	174	129
15%	207	279	445	458	156	77
20%	335	316	462	595	103	89
30%	406	976	885	1190	291	115

* Dissolved mercury : (Hg-T)$_D$ (ng/L)

Table B-11 Daily flux of total Hg flow through the Chao Phraya River estuary in the dry and the wet season

Distance(km)	Dry Season				Wet Season			
	Total Hg (ng/L)		Flux (kg/day)		Total Hg (ng/L)		Flux (kg/day)	
	surface	bottom	surface	bottom	surface	Bottom	surface	bottom
94	69.43	63.18	0.446	0.406	61.5	49.94	8.773	7.124
88	70.39	58.71	0.452	0.377	102.73		14.654	
78	42.73	74.7	0.275	0.480	92.57	122.61	13.205	17.490
72	32.26	71.8	0.207	0.462	33.57	31.3	4.789	4.465
64	32.02	37.57	0.206	0.242	41.64	64.57	5.940	9.211
60	26.82	24.05	0.172	0.155	48.04	32.71	6.853	4.666
52	36.85	82.63	0.237	0.531	28.12	52.2	4.011	7.446
37	70.68	89.45	0.454	0.575	23.78	21.28	3.392	3.036
27	81.9	88.68	0.526	0.570	33.13	26.02	4.726	3.712
17	122.7	132.91	0.789	0.854	26.98	28.64	3.849	4.085
12	84.1	62.85	0.541	0.404	34.88	32.48	4.976	4.633
7	71.73	65.13	0.461	0.419	21.47		3.063	
0	71.63	99.99	0.460	0.643	103.56	68.14	14.772	9.720
-5	62.86	84.9	0.404	0.546	58.39	85.88	8.329	12.250

Note : River discharge for the dry season ~74 m^3/s (6.2×10^6 m^3/day)

: River discharge for the wet season ~1651 m^3/s (142.6×10^6 m^3/day)

Table B-12 Hg concentration in core sediment of The Chao Phraya River estuary in April 2000.(μg/g dry.wt)

Depth	Hg in Core No.1			Hg in core No.2	Hg in Core No.3
	Conc.1	Conc.2	Mean	Conc.	Conc.
2	0.411	0.432	0.421	0.267	0.315
4	0.411	0.434	0.422	0.237	0.219
6	0.538	0.605	0.571	0.241	0.308
8	0.555	0.564	0.559	0.472	0.278
10	0.427	0.448	0.437	0.461	0.365
12	0.371	0.459	0.415	0.251	0.549
14	0.426	0.507	0.466	0.303	0.617
16	0.555	0.758	0.656	0.763	0.667
18	0.141	0.244	0.192	0.311	0.649
20	0.227	0.209	0.218	0.369	0.529
22	0.174	0.162	0.168	0.595	0.572
24	0.640	0.641	0.640	1.142	0.611
26	0.429	0.454	0.441	0.462	0.962
28	0.685	0.557	0.621	0.947	0.525
30	0.421	0.441	0.431	1.021	0.629
32	0.376	0.643	0.509	1.029	0.563
34	0.460	0.666	0.563	1.32	0.543
36	0.481	0.754	0.617	1.032	0.571
38	0.440	0.581	0.510	1.125	0.761
40	0.548	0.556	0.552	0.838	0.640
42	0.452	0.579	0.515	1.029	0.583
44				1.128	0.671
46				0.699	0.580
48				0.959	0.872
50				1.239	0.956
52				0.987	

Note Core 1 km 82

Core 2 km 58

Core 3 km 37

Table B-13 Mercury concentration of surface water in the coastal and the Gulf of Thailand (1999-2001) (unfillter water).

Location	$(Hg\text{-}R)_D$ (ng/L)	$(Hg\text{-}T)_D$ (ng/L)	Remark
Hua Hin, Prachuapkirikhan (May 7, 1999)	0.56	3.27	Near-shore
Bangsan,Chonburi (August 5, 1999)	1.01	1.59	Near-shore
Bangsan, Chonburi (June 25, 2000)	1.26	3.48	Near-shore
Ko Kang Kao, Chonburi (August 26, 1999)	1.06	2.85	Off-shore
Ko Kang Kao, Chonburi (November 8, 2000)	1.59	2.39	Off-shore
Ko Kang Kao, Chonburi (July 20, 2000)	1.35	11.63	Off-shore
Mae Ram Pung Beach, Rayong (April 12, 2000)	1.41	21.91	Near-hore
Mae Ram Pung Beach, Rayong (April 13, 2001)	0.8	5.29	Near-shore
Sriracha, Chonburi (June 25, 2000)	4.68	10.13	Near-shore
The Gulf of Thailand (August 8-11, 2000)	0.62-1.79	1.54-4.27	Natural gas platform

Table B-14 Mercury concentration of surface water in The Chao Phraya River and other river in Thailland (1999-2001) (unfillter water).

Location	$(Hg\text{-}R)_D$ (ng/L)	$(Hg\text{-}T)_D$ (ng/L)	Remark
Chao Phraya River (July 18, 1999)	0.71	11.14	Si Phraya Bangkok
Chao Phraya River (January 24, 2001)	0.38	3.4	Bang Kra Beu Bangkok
Chao Phraya River (February 2, 2001)	6.47	28.12	Tha Phra Chan Bangkok
Chao Phraya River (June 8, 2001)	4.18	32.7	Si Phraya Bangkok
Chao Phraya River (November 13, 2000)	1.13	3.4	Bang Pa-In Ayuthaya
Chao Phraya River (November 13, 2000)	1.13	3.54	Pa Moke Aung-Thong
Chao Phraya River (July 24, 2001)	0.98	17.6	Bang Pa-In Ayuthaya
Chao Phraya River (July 24, 2001)	0.56	3.51	Pa Moke Aung-Thong
Pa Sak River (November 13, 2000)	1.2	3.33	Tha Ruae Ayuthaya
Pa Sak River (July 24, 2001)	0.37	1.59	Tha Ruae Ayuthaya
Bang Pakong River (August 5, 1999)	0.72	1.93	Cha-Choengsao
Bang Pakong River (August 5, 2000)	0.74	2.44	Cha-Choengsao
Bang Pakong River (July 20, 2001)	0.31	1.92	Cha-Choengsao
Mekong River (February 25, 2001)	0.64	2.97	Golden Triangle Chiang Rai
Sai River (February 25, 2001)	0.67	3.61	Golden Triangle Chiang Rai

Table B-15 Preliminary Study on Mercury Concentration in rain water in Thailand (2000-2001)

Location	Hg-R (ng/L)	Hg-T (ng/L)	Remark
1.Klong San, Bangkok Aug. 24, 2000	<0.15	1.34	Light rain
2.Chulalongkorn Univ., Bangkok Aug. 29, 2000	1.73	4.25	
3.Chonburi Aug. 31, 2000	0.82	2.78	Heavy rain
4.Chulalongkorn Univ., Bangkok Sep. 19, 2000	3.7	9.42	
5.Chulalongkorn Univ., Bangkok Sep. 26, 2000	4.96	19.24	
6.Chulalongkorn Univ., Bangkok July 31, 2001	3.33	11.08	Heavy rain

Hg in precipitation ranged from 5 to 25 ng/L (Porcella, 1994)

BIOGRAPHY

Mr.Sittipun Sirirattanachai was born on January 26, 1951 at Chonburi Province. He received a B.Ed. Degree from Colleage of Education Bangsaen in 1974, M. Sc. (Physical & Chemical Oceanography) from Department of Marine Science, Faculty of Science, Chulalongkorn University in 1980. After graduation, he has worked as a lecturer in the Department of Aquatic Science, Faculty of Science, Burapha University, Chonburi Province, since 1983. Present position is Assistant Professor at the Department of Aquatic Science, Burapha University.