Mercury in the Chao Phraya River Estuary, Thailand

Sittipun Sirirattanachai[1*] and Wilaiwan Utoomprurkporn[2]

[1] Department of Aquatic Science, Faculty of Science, Burapha University, Chonburi, Thailand
[2] Department of Marine Science, Faculty of Science, Chulalongkorn University, Bangkok, Thailand

Abstract

Mercury distributions in the Chao Phraya River estuary were studied during two cruises one in April (Dry season) and the other in October(Wet season). Concentrations of dissolved reactive mercury [$(Hg\text{-}R)_D$], total dissolved mercury [$(Hg\text{-}T)_D$], and suspended particulate mercury (Hg_P) ranged from <0.15 to 5.29 ng/L, 2.16 to18.12 ng/L, and 0.09 to 3.49 μg/g (dry weight), respectively. These are in a similar concentration range to those found in major estuaries elsewhere. Sediment samples had measured concentrations in a range from 0.2 to 0.77 μg/g (dry weight).

Suspended particulate mercury was the main species of Hg in the estuarine waters. Most of the dissolved Hg was in the non-reactive form [$(Hg\text{-}NR)_D$] and accounted for more than 85% of the total dissolved Hg. The partition coefficients(K_D) between particulate and dissolved forms tend to increase with salinity and were maximum in the high turbidity zone of the estuary.

Seasonal differencies in mercury distribution in the water column were 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. The K_D values of the dry season were higher than in the wet season. The higher K_D for$(Hg\text{-}NR)_D$ in the dry season suggested that the behavior of these species varied with season.

In addition, the Hg concentration in sediments in the wet season were found to be higher than in the dry season. This may be due to the mobilization of soil and sediment particles during flood periods.

Keywords : reactive dissolved mercury, total dissolved mercury, particulate mercury, estuaries, Chao Phraya River (Thailand)

*** Corresponding author.** E-mail: Sitti@buu.ac.th

INTRODUCTION

Mercury contamination in the global aquatic environment has been observed for several decades. The transport and behavior of mercury in rivers and coastal areas has been widely studied by a large number of investigators to identify the sources and the behavior of mercury in aquatic environment (e.g. Figueres et al.,1985 ; Cossa et al.,1988 ; Ferrara et al.,1992 ; Coquery et al.,1995 ; Gagnon et al.,1997). The analytical system for determination of mercury at picomolar levels in natural water was developed in early 1980s, including its determination is by cold vapor atomic fluorescence spectrometry (CVAFS) using a gold amalgamation preconcentration after a reduction with $SnCl_2$ (Bloom and Crecelius,1983 ; Gill and Fitzgerald,1985 ; Gill and Fitzgerald,1987).

Since then reliable concentration data on the mercury contamination in freshwater and seawater have been reported. The variability in concentration of mercury is an indication of source behavior and the dynamics of the coastal zone. Differences in the coastal physical mixing processes, suspended particulate matter (SPM) concentrations, salinity and the inputs associated with the major sources all play a part influencing the concentrations of Hg in the coastal zone (Dalziel,1992). Mercury accumulating in the rivers and estuaries originates from various sources including anthropogenic, as well as direct inputs from the atmosphere and thus may be deposited great distances from the sources areas (Lindqvist,1994).

The Chao Phraya River, Thailand, is heavily affected by a variety of anthropogenic activities along its length. The river runs through Bangkok and several other large cities, encompassing intensive agriculture and the largest industrial area in the country. Concentrations of selected contaminants in the Chao Phraya River have been reported (Menasveta and Chevaporanapiwat, 1981; Chanpongsang, 1984 ; Umnuay, 1984 ; Hungspreugs et al.,1989 ; Pollution Control Department (PCD), 1994). However, the concentration of Hg in aquatic environments of Thailand has not been studied as extensively as other trace metals. In recent years, mercury contamination has been found in vicinity of the gas exploration platforms in the Gulf of Thailand (Hungspreugs et al.,1998) but few other studies of mercury have been reported. Therefore, the distribution and chemical behavior of mercury in the aquatic environment of Thailand is still poorly known. The central focus of this study was related geochemical interaction of mercury species between sediment and water of the Chao Phraya River estuary.

Study site

The Chao Phraya River is the largest river in Thailand, originating from four rivers in the northern mountains which combine to form the Chao Phraya River. The main river from the confluence to the river mouth is 396 km long. The river flows south through Bangkok and several other large cities, the drainage area is about 177,000 km^2. The Chao Phraya River basin is one of the most heavily populated regions of Thailand, where agricultural and industrial activities are 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^3s^{-1} during drought period in April, to more than 1,460 m^3s^{-1} during flood period in October. The mean river discharge is 430 m^3s^{-1} and the high flows can reach about 3,000 m^3s^{-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).

Methods

Samples collection

Surface and near bottom water samples were collected at sixteen stations in the Chao Phraya River in April (dry season) and October(wet season),1999. The location of the sampling stations are shown on figure 1.

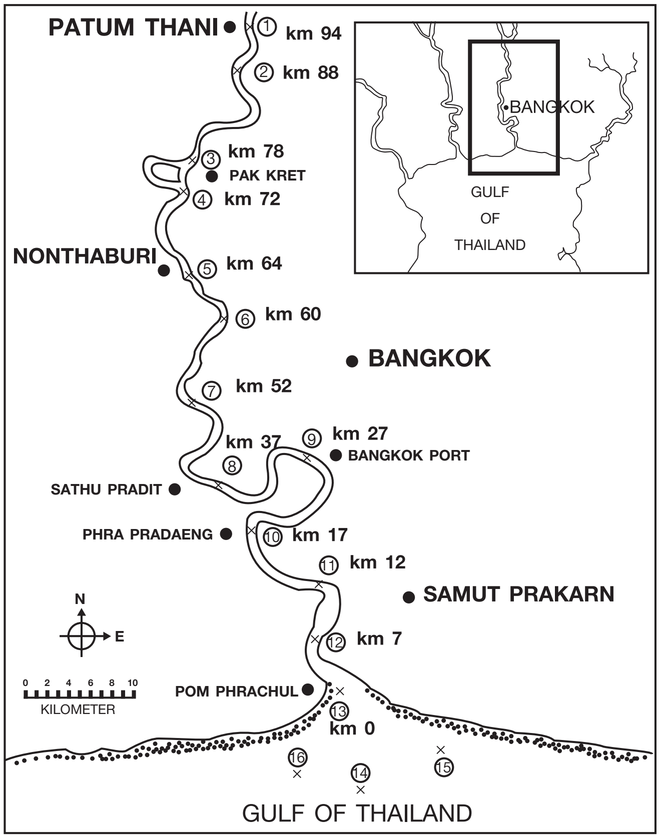

Figure 1 Location of sampling station in The Chao Phraya River estuary.

All manipulations were performed using rigorous clean trace metal protocols adopted from Loring and Rantala (1992) ; and Quemerais and Cossa (1997). Surface water samples were taken directly by hand using polyethylene gloves with 500 ml Teflon (PFA) bottles. All sample bottles were acid washed and rinsed thoroughly with Milli-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 (Marine Science Department, Chulalongkorn University). Near bottom water samples were collected using a 2.5 L Go-Flo bottle which had been thoroughly cleaned prior to use and was drained immediately to 500 ml Teflon (PFA) bottles.

Immediately after return to laboratory, the water samples were filtered through 0.4 μm pore size pre-weighted Nuclepore membrane previously acid - washed and rinsed with Milli-Q water. The whole procedure was carried out under a 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 Cossa et al.(1996). The filtered water for $(Hg\text{-}R)_D$ analysis was unacidified and stored in acid-cleaned 250 ml Teflon (PFA) bottles and kept in the dark at $4^{\circ}C$ until analysis, within 8-12 hours of collection. The samples for $(Hg\text{-}T)_D$ were acidified with 0.5 % HCl (Suparpur,Merck) and stored in double bagged until analysis. The filters were individually kept in tightly sealed plastic Petri dishes and stored frozen prior to determination of particulate mercury (Hg_P).

Sediment samples were collected by a Van Veen grab sampler. Only the uppermost layer (0-3 cm) was collected with minimal disturbance and compaction (Regnier and Wollast,1993). The sediments were transferred to polyethylene bag and kept frozen prior to the determination of Hg.

Parallel water samples were collected separately for the measurement of suspended particulate matter (SPM). Salinity and temperature were determined by a calibrated Conductivity - Temperature-Depth (CTD). Dissolved oxygen and pH were determined by calibrated probes during the field survey.

Water sample analysis

Water samples were analyzed for dissolved reactive mercury $(Hg\text{-}R)_D$, total dissolved mercury $(Hg\text{-}T)_D$, and suspended particulate mercury (Hg_P). All the Hg species were detected by CVAFS after transformation to Hg^0 using methods described by Quemerias and Cossa (1997). In this study, the water samples for Hg-R determination were unacidified before analysis (Mason et al.,1993; 1995). The analysis of the filtered water was performed by a gold amalgamation procedures after reduction with $SnCl_2$. The Hg volatilized from the trap was carried out with Ar (99.999 %) to the detector at the flow rate of 80ml min^{-1} and then measured using Tekran CVAFS Mercury Detector 2500. Analysis of $(Hg\text{-}T)_D$ involved (a) wet - oxidation with BrCl for decomposition of organic complexes, (b)reaction with hydroxylamine to neutralized BrCl, reduced to its elemental form using $SnCl_2$ and (c) measured by CVAFS, using the same method as in Hg-R determination.

Concentrations of Hg_P were determined after HNO_3: HCl (9:1/ v/v) mineralization of the particulate matter in Teflon (PFA) vessels, in the oven at 90 °C for 90 minutes (Quemerias and Cossa ,1997). The resulting clear solutions were diluted with Milli-Q water and mercury concentrations were measured by a Flow Injection Analysis - Mercury Hydride System (FI - MH - AAS, Perkin Elmer).

Sediment sample analysis

Sediment samples were freezed dried lightly crushed, and sieved with 250 μm and 63 μm nylon sieves. Both fractions (<250 μm and <63 μm) of sediment were determined for mercury concentration by total digestion using the same method as Hg_P determination.

Concentrations of SPM were determined gravimetrically after filtration of water samples on pre-weighed Nuclepore membrane filters(0.4 μm pore size).

Analytical Quality Assurances

Detection limits, defined as three times the standard deviation of the blank, were 0.1 ng/L for Hg-R, 0.5 ng/L for Hg-T, and 0.01 μg/g for Hg_P . A certified reference material (CRM) Buffalo River sediment was also analyzed. The recovery (%) was $95.08\pm7.3\%$ for the certified reference material.

Results and discussion

Physico-chemical characteristics

Physico-chemical characteristics of water in the Chao Phraya River estuary are shown in Figures 2 and 3. The salinity front varied widely 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) at only 10 km from the river mouth. The Chao Phraya River estuary was classified as a well mixed estuary. The temperatures of river water during two cruises survey ranged from 28.8 to 31.8 °C and 30.4 to 31.4 °C in the dry and the wet season, respectively. Dissolved oxygen 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. Dissolved oxygen minima were observed in the dry season in the vicinity of Bangkok (km 60 to km 37) while a low level of dissolved oxygen was observed at the river mouth area in the wet season. The pH values ranged from 6.4 to 7.7 in the dry season and 6.7 to 7.3 in the wet season. It increased slightly with increasing salinity toward the river mouth. However, the pH showed no difference between surface and bottom water in both seasons. The SPM concentrations ranged from 8 to 264 mg/L 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 conditions.

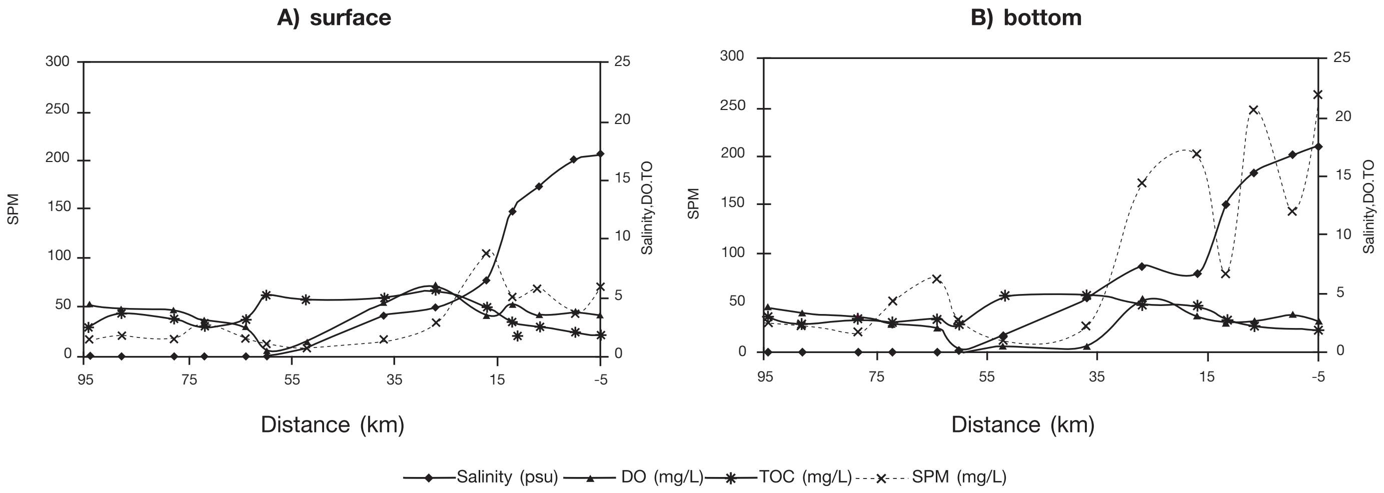

Figure 2 Spatial distribution of physical and chemical parameters in the Chao Phraya River estuary in April, 1999

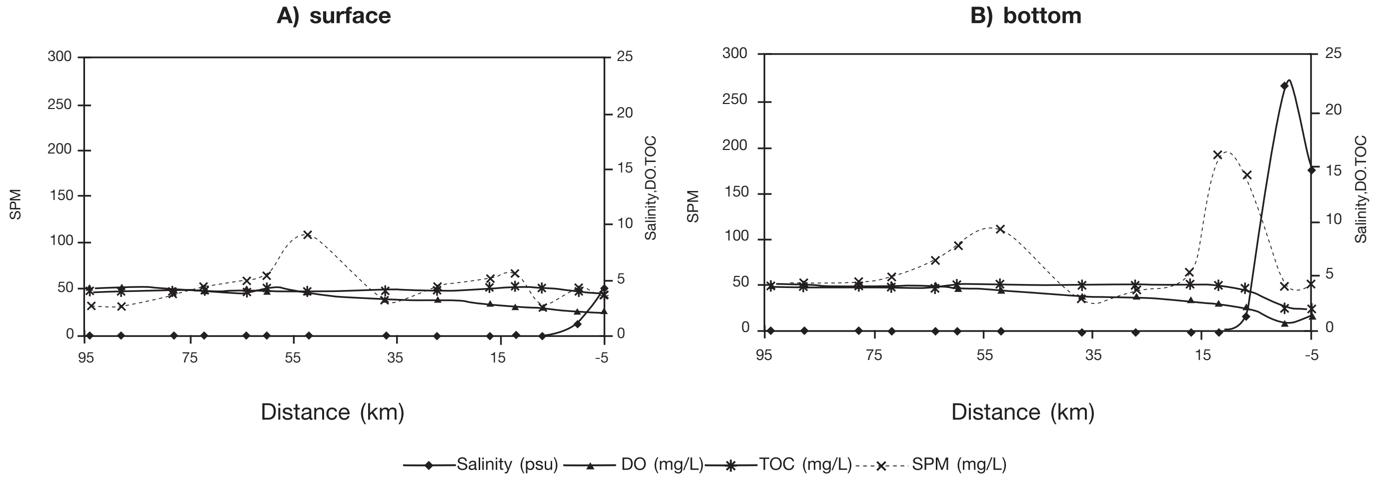

Figure 3 Spatial distribution of physical and chemical parameters in the Chao Phraya River estuary in October, 1999

Dissolved mercury

The distribution of$(\text{Hg-T})_D$ concentrations are shown in Figure 4. In the dry season,$(\text{Hg-T})_D$ concentrations ranged from 2.16 to 11.2 ng/L and 4.1 to 18.1 ng/L for the surface and the bottom water, respectively. Usually, the surface $(\text{Hg-T})_D$ concentrations were found to be lower than the bottom water. The elevated values were observed in the vicinity of industrial area adjacent to km 27 to the river mouth. These concentrations may be due to sediment resuspension or probably release from the suspended particulate matter during high turbidity mixing at that area (Leermakers et al.,1995 ; Mason et al.,1999). The $(\text{Hg-T})_D$ concentrations in the wet season ranged from 4.52 to 17.3 ng/L and 3.88 to 14.03 ng/L for the surface and the bottom water, respectively. The Hg concentration in both surface and bottom water were found to be higher in the upper estuary and decreased gradually towards the river mouth.

The concentrations of mercury in the surface water were higher than the bottom water. A comparison of the $(\text{Hg-T})_D$ concentrations between the dry and the wet seasons indicated that concentration of the wet season were higher which may be due to the sources associated with the river flooding during rainy season. Coquery et al.(1997) who studied the Loire River, suggested that, during flooding, mercury concentrations increase when the surficial runoff increase. Furthermore, the high surface water concentrations could result from mixing as a result of high freshwater flow (Mason et al.,1999). Augmented total Hg concentrations during high flow was also observed in the Wisconsin River (Hurley et al.,1995).

The concentrations of $(\text{Hg-T})_D$ in the Chao Phraya River estuary (2.16 to 18.1 ng/L) were the same order of those found in the Mekong River where concentration of $(\text{Hg-R})_D$ were 0.28 to 4.37 ng/L and $(\text{Hg-T})_D$ were 0.88 to 11.5 ng/L (Hungspreugs et al.,1998). These concentration are significantly higher than the concentration range of that found in major rivers and other regimes, e.g. Bloom et al.(1990), Ferrara and Maserti (1992), Leermakers et al.(1995) and Guentzel et al.(1996).

Reactive Hg concentrations of the Chao Phraya River estuary varied between the detection limit <0.15 and 5.23 ng/L. The distribution of $(\text{Hg-R})_D$ concentrations are shown in Figure 5. The $(\text{Hg-R})_D$ concentration in the dry season ranged from 0.23 to 1.92 ng/L and

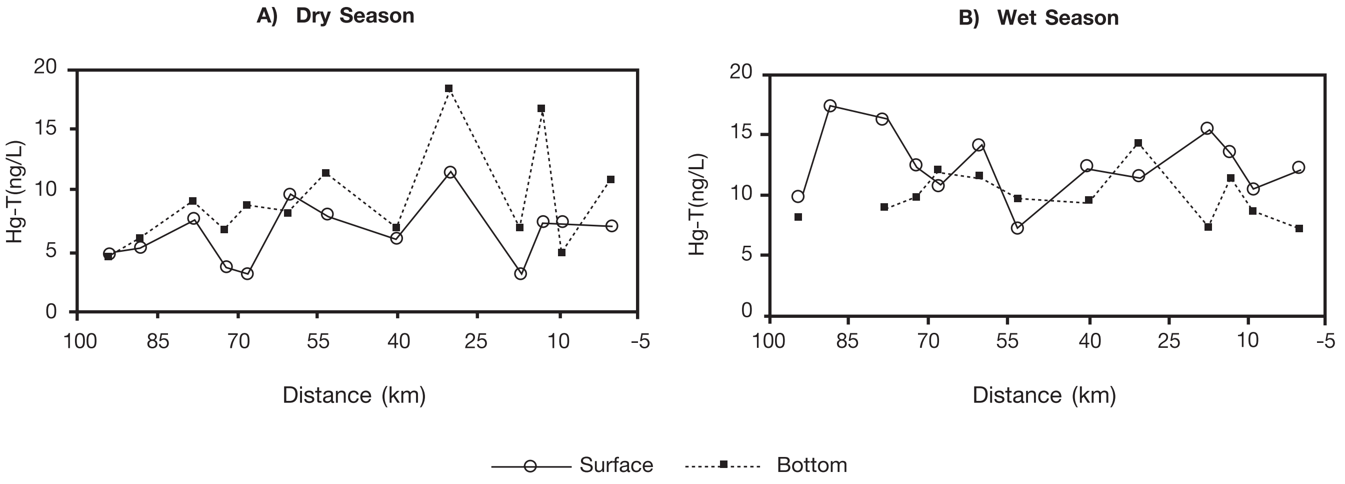

Figure 4 $(\text{Hg-T})_D$ concentration of The Chao Phraya River estuary in the dry and the wet season (April and October 1999)

0.15 to 1.47 ng/L for the surface and the bottom water, respectively. The $(\text{Hg-R})_D$ concentration of surface water were higher upstream and decrease gradually towards the river mouth. Similar results were also found in the bottom water except at km 7, where a maximum in concentration was observed (2.3 ng/L). The concentration of $(\text{Hg-R})_D$ 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 $(\text{Hg-R})_D$ of the surface water were found at km 88 to km 78 and were 4.09 and 5.23 ng/L, respectively.

During the dry season, $(\text{Hg-R})_D$ concentrations in both the surface and bottom waters were higher in the upper estuary (northern part of Bangkok) and decrease downstream (southern part of Bangkok). While the $(\text{Hg-R})_D$ concentration of surface water in the wet season were found to be slightly higher than the bottom water in the upper estuary and both the surface and bottom water concentrations decreased towards at the river mouth to the similar values.

The $(\text{Hg-R})_D$ concentration in the Chao Phraya River estuary from this study was only 12% of total dissolved Hg. This may be due to the dissolved organic matter and particulate organic matter content of the water to which Hg was strongly bound (Turner et al.,2001). Therefore, a large fraction of the dissolved Hg was not "easily reducible". Similar results were observed in the Loire and Seine River, where $(\text{Hg-R})_D$ varied from less than 5 to 24 % of Hg and the explanation was also due to associated with organic compound (Bloom et al.,1991 ; Mason et al.,1993 ; Cossa et al., 1997). Dalziel and Yeats (1985) reported that 25-50% of reactive Hg was found in the coastal water. 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).

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 operationally defined 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 inorganic and organic ligands as well as their respective stability constants. Using the general equation:

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

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

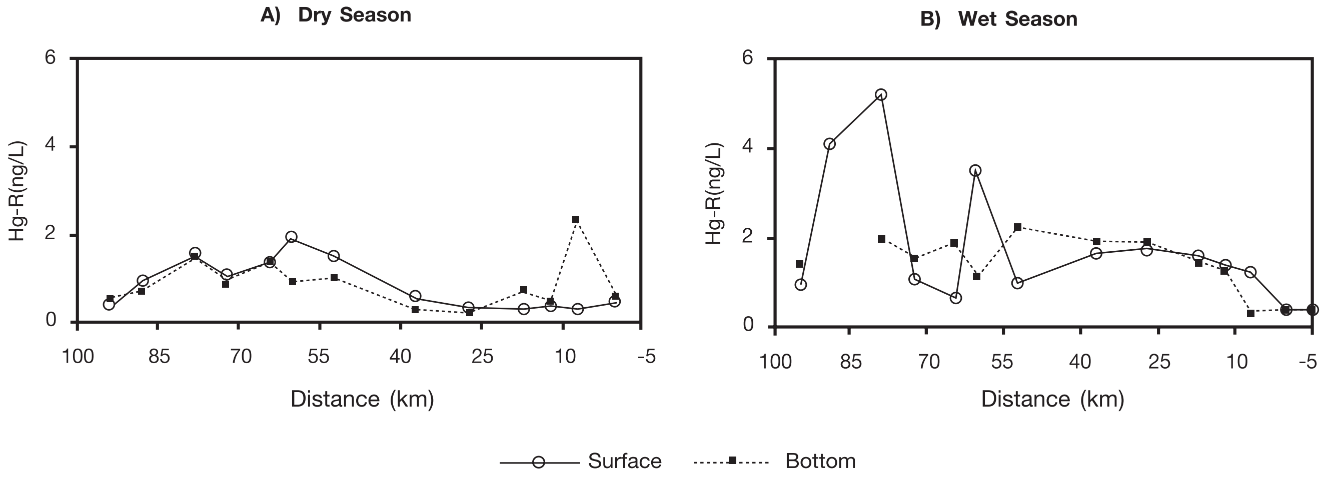

Figure 5 (Hg-R)D concentration of the Chao Phraya River estuary in the dry and the wet season (April and October 1999).

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

Distribution of suspended particulate mercury

The distribution of Hg_P concentrations are show in Figure 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 had higher values in the upper part of the estuary and then decreased towards the river mouth excepted at km 52 to km 27 (Bangkok area) where high values were observed. These may be due to sources from urban sewage. The Hg_P concentrations decreased gradually from the upper estuary towards the river mouth in this season probably a dilution with less contaminated particles.

In the wet season, the Hg_P concentrations ranged from 0.11 to1.67 μg/g and 0.09 to1.85 μg/g for the surface and the bottom water, respectively. The Hg_P concentrations showed higher values at the upper estuary and then declined to a low level between km 72 to km 7 and elevated concentrations were found near the river mouth. The results probably originate from a mixing of particles from different sources bearing more or less mercury in that area. All Hg_P concentrations show the same pattern throughout the estuary in both the surface and the bottom water. However, the remobilization desorption of metals bound to particulate matter can occur with increasing salinity. In this study, a small increase in particulate mercury concentration was observed in the area of salinity increasing. These results could be explained by resuspension and mixing with high suspended particulate matter or salting out effects, that proposed by Turner et al.(2001).

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 trends may be due to the river discharges in April,1999 being lower than those of October,1999 (76 m^3s^{-1} and 1,824 m^3s^{-1}),

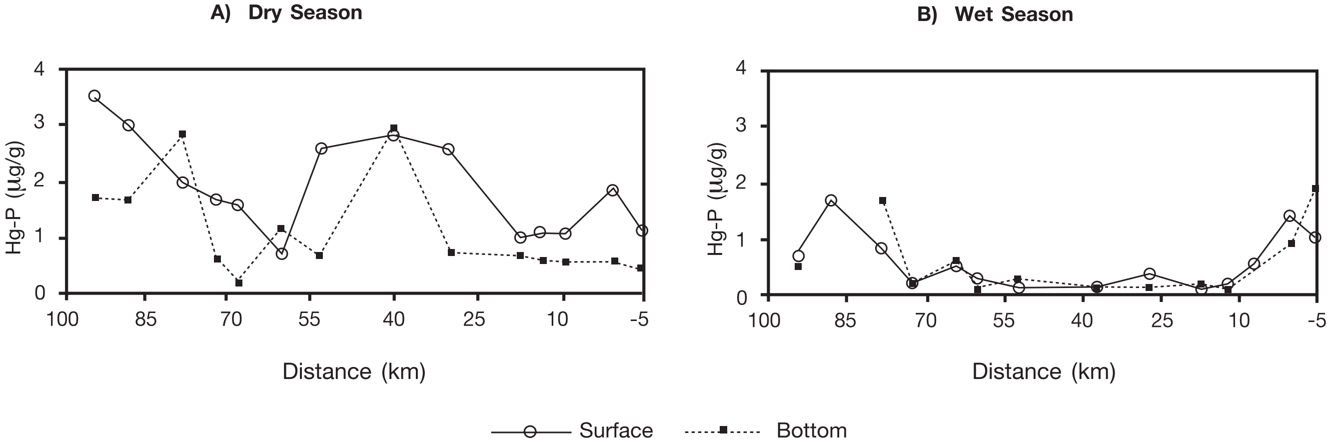

Figure 6 Hg-P concentration of The Chao Phraya River estuary in the dry and the wet season (April and October 1999)

which result in a longer water resident time in a storage of pollutants and potential remobilization during the dry season (Figueres et al.,1985). The association of mercury with particulate matter can occur by adsorption or coprecipitation onto organic solid phases (Leermakers et al.,1995) during low flow conditions. This may be the important factor supported by the fact that the Hg_P is the dominant Hg species in the estuary during the dry season. Particulate mercury accounted for more than 90 % of the total mercury, as has been reported in the Scheldt estuary in summer (Leermakers et al.,1995). In this study, the Hg_P was about 80 % of total mercury. In general, substantial fractions of the trace elements are mainly concentrated in the fine-grained sized fraction of the solid phase (Regenier and Wallast,1993). Figures et al.(1985) 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 probably a dilution with less contaminated particles. Figure 7 shows high (Hg_P) at low SPM concentrations. This indicates that the mercury in associated with permanently suspened SPM. Normally the lower values of (Hg_P) are attributed with resuspension of coarser grained material of lower mercury content.

The Hg_P concentration levels in the Chao Phraya River estuary are higher by one order of magnitude compared to those found in other estuaries e.g. Cossa and Martin (1991) on the Rhone River (1.12-1.26 μg/g). However, Hg_P concentrations higher than those in this study have been also reported, for example in French estuaries the median values were found to be 4.5 μg/g (Figueres et al.,1985).

Partioning of mercury in the Chao Phraya River estuary

The partitioning coefficient (K_D) is defined as the ratio of particulate and dissolved concentration(mL/g) and expresses the relative affinity of Hg for dissolved and particulate (Turner et al., 1993 ; Conquery et al.,1997). The percentage of particulate Hg can be estimated from K_D and concentration of SPM.

In this study, K_D values 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 of the same order of magnitude and the values found higher in the dry season. These indicated that Hg has the greatest affinity for the particulate phase in the dry season. These were found the higher level of Hg_P in the dry season. The non-reactive Hg fraction were introduced into the algorithm by which the percentage

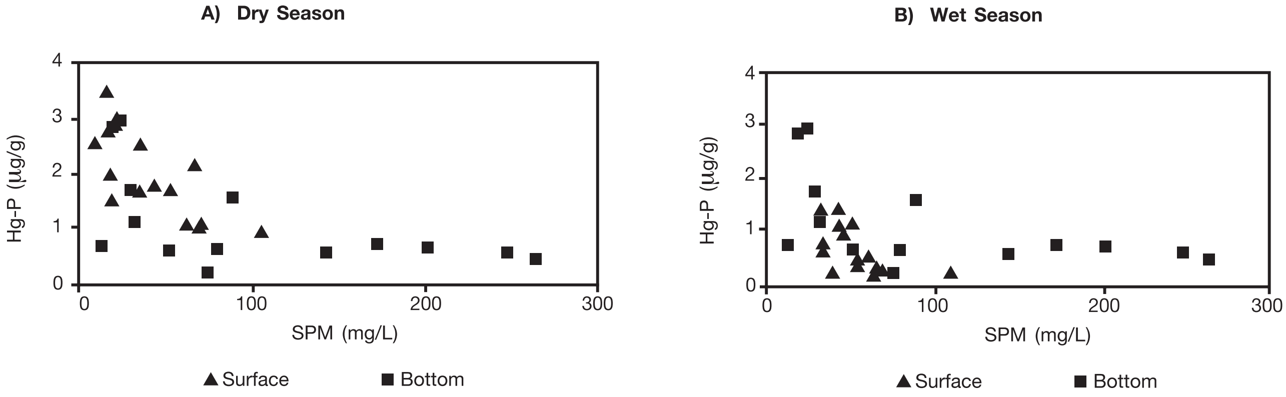

Figure 7 Hg-P and SPM correlation in the dry and the wet season

of the total Hg concentration in the particulate phase may be estimated. The seasonal variability of Hg speciation is shown in figure 8. The results for the percentage of 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 10^6-10^7 L/kg in both seasons, suggesting that a relatively high amount of$(Hg\text{-}R)_D$ is particle reactive, 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 10^5-10^6 L/kg in the dry season and in the wet season was found in the range of K_D 10^4-10^5 L/kg. Therefore, the mercury is transported preferentially in the dissolved are less and these may be due to similar types of organic-bound mercury in the dissolved phase and the particulate phases. Moreover, the nature of organic content seems to be different type in each season. The K_D value lower than 10^4 L/kg 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 decrease of K_D values may be due to less organically-bound Hg in seawater. However, at the river mouth area the increased of Hg sorptions onto the particles with increasing of salinity were observed. Mercury partition coefficients (K_D) increasing with an increase in salinity had also been reported in 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 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 were predicted to conceal or even offset any salting effects of the neutral complex (Turner et al., 2001).

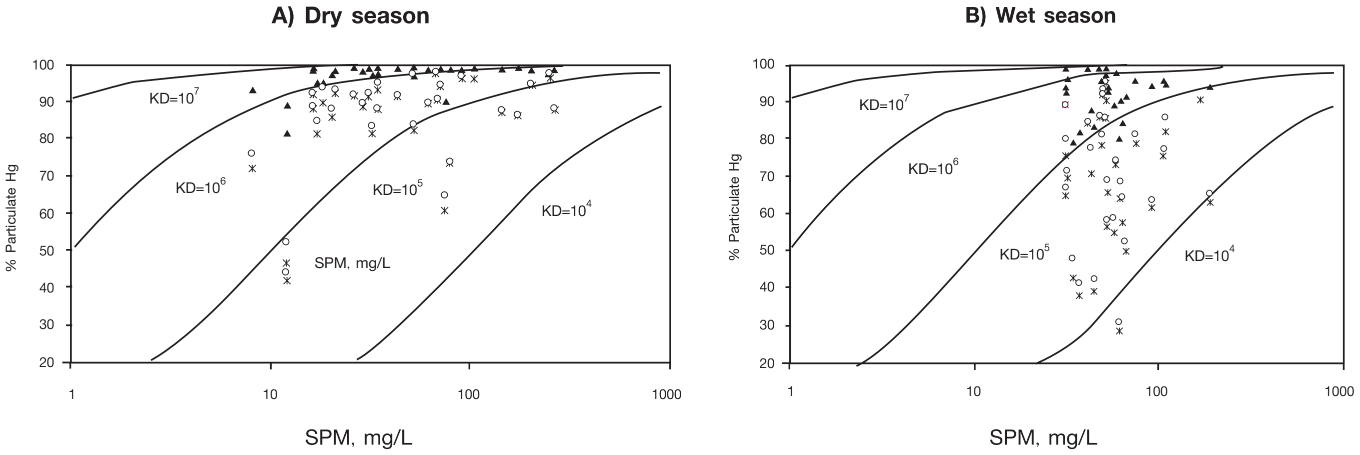

Figure 8 The variation in percentage of particulate Hg with suspended particulate matter (SPM) The symbols represent samples where; $(Hg\text{-}R)_D$, ▲ ; $(Hg\text{-}T)_D$, ⁎ ; Hg-NR, O.

Mercury in sediment

Mercury concentrations in surface sediments of the Chao Phraya River estuary were determined in both <250 µm and <63 µm grain size fractions. Mercury concentrations in the dry season ranged from 0.20 to 0.50 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, the concentration ranged from 0.3 to 0.77 µg/g (dry wt.) and 0.30 to 0.69 µg/g (dry wt.) for sediment grain size fraction of <250 µm and <63 µm, respectively. The results of Hg concentration in sediment are shown in figure 9. There was no difference in concentration of Hg accumulation were observed between <250 µm and <63 µm grain size fraction. The surface sediments are mainly clay and silt (<63 µm) at approximately 60-70%. The Hg content of sediments in the dry season were observed increased gradually from the upper estuary towards the river mouth. The high concentrations were found at vicinity of the populated area (Bangkok area) and the major industrial area in the vicinity of km 52 to river mouth. The Hg concentration in the wet season were found higher than in the dry season may be explained by resuspension of contaminated sediments upstream. During flood periods soil and sediment particles could be mobilized. The content in particulate matter is also high in estuaries, where floculation processes take place at the freshwater - seawater interface. Schultze et al.(1995) has been suggested that, river sediment contaminated by mercury are distributed over wide areas and are easily transported and released by flows and floods.

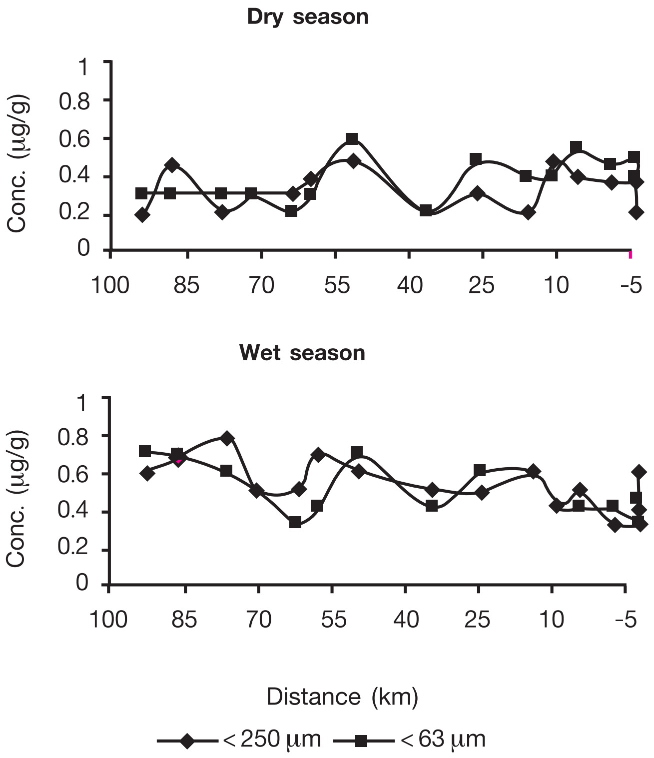

Figure 9 Hg concentration in sediment of the Chao Phraya River estuary in the dry and the wet season

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 3,9 x10^6 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 zone of natural situation and the concentration of Hg accumulating may reflect the input of Hg from the upper estuary. However, there are also several manufacturing industries, including saw-mills, battery production, 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 of the Chao Phraya River estuary, we found values 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 and 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 concentrations 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 0.05 to 2.12 μg/g (dry wt.).

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. 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 transport 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 and the 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.

The Hg concentration of surface sediments in the dry season were observed to increase 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 and transport of contaminated sediments from upstream.

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.

Acknowledgements

We thank Prof. Dr. Manuwadi Hungspreugs for her help and advice during this study. The authors grateful thank Dr. D. Cossa for his helpful comments and suggestion, and thank Dr. G.E. Millward and Dr. M. Foulkes for their helpful suggestion. We also thank Dr. S. Ohde for loaning us some sampling equipment. This study was supported by the Department of Marine Science, Chulalongkorn University and partly supported by IOC/WESTPAC River Inputs Project and Faculty of Science, Burapha University.

References

Bloom, N.S.,and Crecelius, E.A. 1983. Determination of mercury in seawater at sub-nanogram per liter levels. Mar. Chem.14 : 49-59.

Bloom,N.S.; Watras, C.J.; and Hurley, J.P. 1991.Impact of acidification on the methylmercury cycle of remote seepage lakes. Water Air & Soil Pollut. 56 : 477-491.

Cossa, D.; Gobeil, C. and Courau, P. 1988. Dissolved mercury behavior in the Saint Lawrence Estuary. Estuar., Coast and Shelf Sci., 26 : 227-230.

Cossa, D. and Martin, J-M. 1991. Mercury in the Rhone delta and adjacent marine areas. Mar. Chem., 36 : 291-302.

Coquery, M.; Cossa, D.; and Martin, J.M. 1995. The distribution of dissolved and particulate mercury in three Siberian estuaries and adjacent Arctic coastal waters. Wat.Air, and Soil Pollut. 80 : 653-664.

Coquery, M.; Cossa, D.; and Sanjuan, J. 1997. Speciation and sorption of mercury in two macro - tidal estuaries. Mar. Chem.,1458.

Chanpongsang, A. 1984. The distribution of Cd, Pb,Cu and Zn from the Chao Phraya River Mouth to Si Racha. In the Proceeding of the Third Seminar on the Water Quality and the Quality of Living Resources in Thai waters, 26-28 March 1984, National Research Council of Thailand, pp 352-367.

Chongprasith, P.; and Wilairatanadilok, W. 1998. Are Thai waters really contaminated with mercury? Proceeding of the Fourth ASEAN - Canada Technical Conference on Marine Science, October 26-30,1998, Langkawi, Malaysia.

Dalziel, J.A. and Yeats, P.A.,1985. Reactive mercury in the central North Atlantic. Mar. Chem.,15 : 357-361.

Dalziel, J.A. 1992. Reactive mercury on the Scotian shelf and in the adjacent northwest Atlantic ocean. Mar. Chem., 37 : 171-178.

Ferrara, R.; and Maserti B.E. 1992. Mercury concentration in the water, particulate matter, plankton and sediment of the Adriatic Sea. Mar. Chem., 38 : 237-249.

Figueres, G.; Martin,J.M.; Meybeck,M.; and Seyler, P. 1985. A commparative study of mercury contamination in the Tugus Estuary (Portugal) and major French estuaries (Gironde, Loire, Rhone). Estuar., Coast and Shelf Sci., 20 : 183-203.

Gagnon, C.; Pelletier, E.; and *Mucci, A.* 1997. Behaviour of anthropogenic mercury in coastal marine sediments. Mar. Chem.,59 : 159-176.

Gill, G.A.; and Fitzgerald, W.F.1985. Mercury sampling of open ocean waters at the picomolar level. Deep - Sea Res. 32 : 287-297.

Gill, G.A. and Fitzgerald, W.F., 1987. Piccomlar mercury measurements in seawater and other materials using stannous chloride reduction and two-stage gold amalgamation with gas phase detection. Mar. Chem.,20 : 227-243.

Guentzel, J.L.; Powell, R.T.; Landing, W.M.; and Mason, R.P. 1996. Mercury associated with colloidal material in an estuarine and an open-ocean environment. Mar. Chem. 55 : 177-188.

Hungspreugs, M.; Utoomprurkporn, W.; Dharmvanij, S.; and Sompongchaiyakul S. 1989. The present status of the aquatic environment of Thailand. Marine Pollution Bulletin, 20 : 327-332.

Hungspreugs, M.; Utoomprurkporn, W.; Cossa, D.; and Sirirattanachai, S. 1998. Preliminary Investigation on the mercury distribution in the Mekong Estuary and adjacent sea. In : Proceedings of the International Workshop on the Mekong Delta, February 23-27, 1998, Chiang Rai,Thailand, pp.169-178.

Hurley, J.P., Benoit, J,M.; Babiarzm, C.L.; Shafer, M.M.; Andren, A.W.; Sullivan, J.R.; Hammond, R.; and Webb, D.A. 1995. Influences of watershed characteristics on mercury levels in Wisconsin Rivers. Environ. Sci. Technol. 29 : 1867-1875.

Loring, D.H.; and Rantala R.T.T. 1992. Manual for the geochemical analysis of marine sediments and suspended particulate matter. Earth Science Reviews, 32 (1992): 235 - 283.

Leermakers, M.; Meuleman, C.; and Baeyens, W., 1995. Mercury speciation in the Scheldt estuary. Water Air Soil Pollut. 80 : 641 - 652.

Le Roux, S.M.; Turner, A.; Millward, G.E.; Ebdon, L.; and Apprion, P. 2001. Partitioning of mercury onto suspended sediments in estuaries. J. Environ. Monit. 3 : 37-42.

Lindqvist, O.1994. Atmospheric cycling of mercury : An Overview. In: Mercury polltion integration and synthesis. Watras C.J. and J.W. Huckabee (eds.), the United States of America : Lewis Publishers, pp. 181-186.

Mason, R.P.; Fitzgeral, W.F.; Hurley, J.; Hanson, A.K.; Donaghay, P.L.; and Sieburth J.M. 1993. Mercury biogeochemical cycling in a stratifiled estuary. Limnol. Oceanogr.38 : 1227 - 1241.

Mason, R.P.;Rolfhus, K.R.; and Fitzgerald, W.F.1995. Methylated and elemental mercury cycling in the surface and deep waters of the North Atlantic. Water Air Soil Pollut. 80 : 665 - 677.

Mason, R.P.; Lawson, N.m.; Lawrence, A.L.; Leaner, J.J.; Lee, J.G.; and Sheu, G.-R. 1999. Mercury in the Chesapeake Bay. Mar. Chem., 65, pp. 77- 96.

Menasveta ,P.; and Cheevaporanapiwat, V. 1981. Heavy metals, organochloride pesticides and PCB's in green mussels, mullets and sediments of river mouths in Thailand. Marine Pollution Bulletin 12: 19-25.

Port Authority of Thailand (P.A.T.) 1993. Map of The Chao Phraya River from Pom Phrachul to Memorial Bridge, surveyed by the Marine Survey Division, Marine Department , P.A.T. Bangkok.

Pollution Control Department (PCD) 1994. Water quality monitoring in the Chao Phraya River 1992 to 1993. 26p.

Pollution Control Department (PCD). 1997. Water quality management and master plan for major river basin in the central plain of Thailand project. Pollution Control Department (PCD), Ministry of Science Technology and Environment, PCD 02/ 018, Vol. 6/24. (in Thai)

Polprasert, C. 1982. Heavy metal pollution in the Chao Phraya River estury, Thailand. Water Res. 16 : 775-784.

Quemerais, B.; and Cossa, D. 1997. Procedures for sampling and analysis of mercury in natural waters. Environmental Canada - Quebec Region, Environmental Conservation, St. Lawrence Centre. Scientific and Technical Report, ST- 31 E, 34 p.

Regnier, P.; and Wollast, R.1993. Distribution of trace metals in suspended matter of the Scheldt Estuary. Mar. Chem.,43 : 3-19.

Schultz, T.; Korhonen, P.; and Virtanen, M. 1995. A Mercury model used for assessment of dredging impacts. Wat., Air, and Soil Pollut. 80 : 1171-1180.

Turner, A.; Millward, G.E.; Bale, A.J.; and Morris, A.W. 1993. Application of the KD concept to the study of trace metal removal and desorption during estuarine mixing. Estuar. Coast and Shelf Sci. 36: 1-13.

Turner, A.; Millward, G.E.; and Le Roux, S.M. 2001. Sediment-Water partitioning of inorganic mercury in estuaries. Environ. Sci. & Technol., 22.

Umnuay, G. 1984. The behaviour of some trace elements in the Chao Phraya Estuary. In Proceeding of the Third Seminar on the Water Quality and the Quality of Living Resources in Thai Waters, 26-28 March 1984, National Research Council of Thailand, pp. 304-334.

Velinsky, D.J.; Wade, T.L.; Schlekat, C.E.; McGee, B.L.; and Presley, B.J. 1994. Tidal river sediments in the Washington, D.C. Area. I. Distribution and sources of trace metals. Estuaries, 17 : 305-320.