CHAPTER I

INTRODUCTION

Most of the terrigenous material transported through river systems derived from erosion and weathering processes of the watershed are commonly in the form of particulate matter and dissolved species. The material flux may be varied and modified due to the influences of hydrology and biogeochemical processes in the river. The natural watershed characteristics of river systems, such as climate, vegetation, geomorphology, soil and drainage area also affect the chemical compositions and transport of materials (Wolman and Miller, 1960 ; Dickenson and Wall, 1978 ; Webb and Walling, 1984). Furthermore, the anthropogenic inputs may be an important factor of material contamination in the river (Van Bennekom amd Salomons, 1981 ; Meybeck, 1982).

In order to understand the above processes, some material fluxes in the lower area of the Chao Phraya River basin, a tropical climatic zone river in Thailand (Walter and Box, 1976) had been studied to describe typical spatial and seasonal variations of material load in the river.

Influence of Hydrology on material fluxes

There have been several studies of the material fluxes resulting from river transport (Livingstone, 1963 ; Turekian, 1971 ; Stumm, 1973 ; Meybeck, 1979 ; Van Bennekom and Salomons, 1981 ; Degen, 1982 ; Wollast, 1983 ; Walling and Webb, 1986). The chemistry and material flux of a river system are strongly related to its hydrology of the rainfall and run off processes operating in a drainage basin and their interaction with the mechanisms governing the dissolved material fluxes in streamflow (Walling and Webb,1986).

The nature of material transport through river systems is in the dissolved and particulate-associated form. In order to describe patterns and trends in river flux these forms may be isolated due to the different impacts of hydrology and the detailed interaction of solute and flow regimes for a particular river. It is common for dissolved species to have a chemograph (i.e., the plot of chemical constituent with time during an annual cycle) that is a simple inverse of the river hydrograph and this pattern tends to be varied between wet and dry seasons. In contrast, the substances transported in suspended particulate-associated form tends to vary in the river system in a similar manner related to the hydrograph of storm events rather than to any annual climatic or biological rhythm (GESAMP,1987).

The patterns of river flux will reflect the interaction of chemical and hydrological factors. The material transport varies significantly through time as well as over space which depends on the factors of (1) basin size (Wolman and Miller, 1960), (2) flow components (Walling, 1974), (3) seasonal differences (Foster, 1978), (4) climatic conditions (Dickenson and Wall, 1978), (5) catchment topography and (6) the nature of sediment and solute sources in a drainage basin (Webb and Walling, 1984).

Biogeochemical Processes Influencing the Riverine Transport

1. Phosphorus

1.1 Speciation and Sources

Rivers provide major source of phosphorus to the sea (Froelich, Bender, Luedtke, Heath and DeVries, 1982; Graham and Duce,1979). In river water the dissolved reactive phosphorus is derived not only from natural weathering processes but also from the oxidation of urban and agricultural sewage and the breakdown of polyphosphates used in detergents. They are found in the form of orthophosphate (PO_4^{-3}) and orthophosphate ions ($H_2PO_4^{-1}$,HPO_4^{-2}), generally expressed as phosphate-P (PO_4^{-3}-P). In addition, however, dissolved organic and particulate phosphorus have to be considered for comprehensive flux calculations. In the case of polluted rivers receiving untreated domestic waste water, polyphosphate may represent a significant portion of the organic dissolved phosphorus. This component is however rapidly hydrolyzed and transformed into orthophosphate in the river itself.

According to Stumm (1973), on the average, one half of the dissolved phosphorus is in the inorganic form and its concentration corresponds to the solubility of phosphorus-bearing minerals (Ca,Fe or Al phosphates). An equal amount is present as organic phosphorus. It appears impossible to establish a trend between the concentration of phosphorus and environmental factors for unpolluted rivers (Meybeck,1982).

1.2 Behavior in River and Estuarine System

The behavior of phosphorus is strongly controlled by the production and respiration of organic matter. It is often considered as the limiting nutrient in river system if light is sufficiently available (Taft and Taylor, 1976; Fox, Sagar and Wofsy, 1985). Phosphorus is also a very chemically active element and orthophosphate may be involved in various dissolution, precipitation or adsorption/desorption reactions. These chemical reactions seem to be reversible and have rather fast reaction rates. Stumm and Morgan (1981) have shown that orthophosphate is adsorbed on hydrous oxide surfaces, especially Fe_2O_3 and Al_2O_3 and that this reaction is reversible. At higher concentrations, apatite may be precipitated as coating on calcite surfaces (Morse and Berner, 1979).

In some river inputs, significant amounts of dissolved phosphates, as defined by conventional filtration procedures, can be associated with colloidal material and be subjected, like " dissolved " iron, to destabilization and aggregation in the early stages of estuarine mixing (Bale and Morris, 1981). There is evidence that the behavior of phosphate is at least partly decoupled from that of iron in such processes. Within the estuary there is also a tendency for phosphate to be converted to particulate form by association with iron-rich oxide coatings or mineral particles. In a few estuaries, exchanges with suspended or bottom sediments appear to regulate the concentrations of dissolved phosphorus within a relatively narrow range, around 1 uM (Liss, 1976). More generally, some degree of phosphate scavenging by particles under oxygenated conditions and releasing under anoxic conditions, either in the water column or in sediments may be observed. The behavior of phosphorus has been studied by several authors using laboratory simulation of estuarine mixing. These experiments show clearly that the removal of phosphate is favored in the presence of colloidal iron especially under high pH conditions and in the absence of humic acids (Sholkovitz, 1976; Bale and Morris, 1981; Carpenter and Smith, 1984). Desorption of phosphate in solutions low in dissolved phosphorus has also been demonstrated in laboratory experiments.

The behavior of phosphorus in an estuary is illustrated, for example, by the case of Zaire where observed a maximum of PO_4 in the salinity range 0 to 25 ‰, whereas the concentration of phosphate in particulate phases decreased with increasing salinity (Van Bennekom, Berger, Helder and DeVries, 1978). The increase of dissolved phosphate may be the result of a desorption mechanism. At salinities above 25 ‰ the concentration of PO_4 decreases as a result of mixing process and phytoplankton growth.

2. Silicon

2.1 Speciation and Sources

Silicon in solution in natural waters is mainly in the form of silicic acid $Si(OH)_4$. Opal which is a biological fraction of silicon is usually a minor mineralogical constituent of suspended matter transported by rivers. This creates a problem if the fluxes of biogenic and non-biogenic particulate silicon are to be differentiated. Silicon fixed in biogenic solid phases is more easily mobilized than in lithogenous mineral particles such as quartz and aluminosilicates. There is a major problem in detecting the fluxes of biogenic silica against the large background of the more inert material. In this case, information is needed on the mineralogical form rather than on a particular fraction defined analytically.

Silicon is a mojor dissolved constituent and represents about 10% of the dissolved solids in average river water. It results from the weathering of a variety of silicate minerals. The role of weathering of these minerals is strongly dependent on temperature, rainfall and relief. According to Meybeck (1979) 74% of the dissolved silica transported by rivers originates from the tropical zone which represents only 35 % of the drained continental surface area. The humid regions with high relief (12.5 % of the drained continental surface area) are responsible for 43 % of the dissolved silica transport. In contrast to nitrogen and phosphorus, anthropogenic sources of dissolved silicon are unimportant relative to natural weathering. On the contrary, it is well possible that the eutrophication of rivers and the construction of artificial lakes have resulted in a decrease of the natural river flux of dissolved silicon.

2.2 Behavior in the River and Estuarine System

Mayer and Gloss (1980) found that the riverine dissolved silica shows a buffering effect by sorption reactions between the aqueous phase and suspended sediment in a turbid water. Evidence for the buffering of silica in river systems has been summarized by Edwards and Liss (1973). The dissolved silica in river water is present in a polymeric, colloidal form which could undergo flocculation as the electrolyte concentration increases during estuarine mixing (Krauskopf, 1956).

The extent to which dissolved silicon is significantly removed by biological processes depends strongly on the activity of diatoms. This removal is usually limited in unpolluted rivers having a low biological activity. The development of diatoms is favoured in large rivers with low water velocities and in lakes. Opal is relatively soluble and redissolves as soon as the organic coating has been removed from the skeletons. This redissolution process may be an internal source of dissolved silica for the aquatic system. However, if the dissolution of opal occurs after deposition of the skeletons in the sediments the dissolved silicon may react with the clay minerals during early diagenesis (Wollast,1974). Dissolved silica may thus be substantially removed from the water column when the diatom frustules are transferred to the sediments.

In many estuaries, especially in the unpolluted ones, biological processes have little discernible effect on silicon removal. In eutrophic estuaries, increased plankton activity may be responsible for the total removal of dissolved silicon during summer, while in the winter the extent of biological removal is almost absent.

Slight removal, occurring under conditions of low biological activity and generally at low salinity and high turbidity, has been ascribed to chemical processes, mainly reverse weathering reactions of clay minerals (see review in Liss, 1976) or adsorption by amorphous hydroxides of iron and aluminum (Li, 1981). However, the occurrence of these reactions in estuaries has been questioned. For instance in the mixing zone of the Changjiang (Yangtze), under winter time conditions when biological activity is minimal, silicon behaves conservatively even in the presence of suspended matter concentration of several hundred parts per million (Edmond, Spivak, Grant, Hu and Chen, 1984).

The creation of artificial lakes and the eutrophication of large rivers have a drastic effect on the transport of dissolved silicon. For example after the completion of the Aswan Dam on the Nile river, a drop of 5 mg Si/l was observed (Wahby and Bishara, 1981). Also according to Van Bennekom and Salomons (1981) the river Rhine reflects a pronounced seasonal cycle of dissolved silicon: near the river mouth the concentration of dissolved silicon in river water is 7.4 mg Si/l in winter and 3.8 mg Si/l in summer. It should be emphasized that the activity of diatoms in the Rhine and in Lake Constance has been significantly enhanced by the input of excess N and P.

General Setting of the Chao Phraya River

1. Geography

The Chao Phraya River Basin, covers an area of about 162,600 km^2, located between 14^o - 20^o N and 98^o - 101^o E with 980 km of river length in N - S direction. The basin may be divided into three parts; the upper basin of northern highland, the middle basin of the middle flood plain and its surrounding watershed, and the lower basin of the Chao Phraya Delta and its surrounding watersheds.

The upper basin is composed of watersheds of Bhumibol and Sirikit Reservoirs, Wang Basin and upper part of Yom Basin which as large as 56,700 km^2. Its alluvial fans and rolling terraces are good for farming and have almost already been developed.

The middle basin is composed of flood plains north of Nakhon Sawan along Ping, Yom and Nan Rivers and their surrounding watershed and the upper part of Pasak River basin as large as 64,000 km^2. These tributaries meet at Nakhon Sawan to form the Chao Phraya River.

The lower basin is composed of the Chao Phraya Delta and its surrounding watersheds south of Nakhon Sawan as large as 41,900 km^2. The Chao Phraya River distributes Suphan and Noi Rivers at Chainat, but joins Pasak River at Ayutthaya together with Noi River at Bang Sai, then flow out to the Gulf of Thailand.

2. Meteorology

Climate in Thailand belongs to hot and humid tropical monsoon consisting of two seasons; wet season in May to October and dry season in November to April. The annual rainfall varies from 1,200 mm to 1,600 mm in the upper basin. For the lower basin its rain is about 1,200 mm per year in the Northern and West bank areas.

The temperature are usually high in March or April and lower between November and January. The difference of the temperature between the highest and the lowest in one year is about 4^{o} C to 7^{o} C.

3. Hydrology

The runoff from the Chao Phraya River Basin is 30,000 x 10^6 m^3/sec on an annual average. The fluctuation in annual runoff is so remarkable that it can be as low as 14,500 x 10^6 m^3/sec in the drought year and 47,500 x 10^6 m^3/sec in the wet year. The tidal effect is extended to near Ayutthaya. The annual volume of water released from the Chao Phraya Dam to the lower basin is controlled based on the purposes of salinity control, irrigation, navigation, industry and domestic consumptions and so on.

Problems in water quality is limited only in the lower delta. Salt intrusion in the Chao Phraya River and Tachin River is controlled by water released for the above purposes from the upper dam/regulator whenever salt concentration exceeds the allowable limit. The water quality is much deteriorated in recent years seemingly due to increasing amount of seweage from factories and population in the Metropolis.

Global River Fluxes

1. Suspended Sediment

Sediment is a general term which is used to describe both suspended and deposited material. All natural water contains varying amounts of suspended sediment. Sediments consist of inorganic and organic compounds, both of which comes from source outside or within the river.

In addition, man-made debris may result in the production of sediments having characteristics similar to those of natural origin. Sediment composition is largely controlled by the composition of the sourse rock from which it is derived by erosion and weathering. It is additionally influenced by climate regime (weathering and hydrological conditions), land form and land use, and time in transit

(Golterman, Sly and Thomas, 1983).

The suspended sediment load of a river depends not only upon its drainage area and discharge, but also upon the geology, topography and climate of the drainage basin. For example, only one large river in Africa (the Orange) has a sediment yield exceeding 100 tons km^{-2}, and most of North and South American rivers have yields of around 100 tons km^{-2}. In contrast, Asian river basins have far greater sediment yields; the Hwang-Ho and Ganges/Brahmaputra both having annual rates in excess of 1,000 tons km^{-2} (Milliman,1981).

2. Phosphorus

The riverine flux of phosphorus may be substantially modified and poorly quantified due to the interactions of two factors: (1) anthropogenic inputs, and (2) inherent complexities in understanding the biogeochemical processes of phophorus in estuarine and coastal waters. Man's influences on surface waters has now greatly increased natural phosphorus levels. These increases were found to be directly proportional to the watershed population and to its energy consumption.

The riverine flux of phosphorus transported to the sea via estuaries and coastal waters. The dissolved phosphorus flux can be modified here in three ways: (1) adsorption/desorption of reactive-P onto/off surface of river-borne suspended clays, (2) biological uptake by estuarine organisms or release of reactive-P from dissolved or particulate organic matter produced upstream, and (3) the transformation (via slow dissolution, desorption and regeneration) of particulate unreactive-P (transported by rivers to estuaries and shelf sediments) to reactive, dissolved-P followed by its eventual released to the overlying water (Froelich et al.,1982).

Several studies of phosphorus behavior in estuaries strongly suggest that rapid desorption reactions with suspended material "buffers" reactive-P at concentrations of about 1 µM over much of salinity mixing range (Pomeroy, Smith and Grant, 1965; Stefansson and Richards, 1963; Butler and Tibbitts, 1972; Parker, Behrens, Calder and Schultz, 1972; Liss, 1976).

In unpolluted rivers the ratio of phosphate-P/ total-P is generally between 0.2 and 0.7 with a median value of 0.4 (Meybeck, 1982). Total phosphorus concentrations in excess of 0.2 mg/l generally indicated that domestic wastes, industrial waste, or fertilizers have been introduced into the water. High levels of phosphorus are believed to be the critical factor in the eutrophication of lakes (McKee and Wolf, 1971).

The specific transport rate in natural waters of phosphate phosphorus is generally between 0.5 and 10 kg P km^{-2} yr^{-1}. Maximum specific transport occurs in wet tropical rivers (Zaire, Indonesia, Amazonia) and minimum in the subarctic rivers (Meybeck, 1982).

Human influences can modify the concentration and material fluxes through river system, as well as the speciation and geochemical processes. Most usually, man's influences increase the flux of dissolved and suspended matter discharge by rivers. Van Bennekom and Salomons (1981) revealed that man's activities have increased five times the phosphorus load of rivers. The natural river inputs to ocean is 0.5 x 10^{12} g P yr^{-1} while the present day inputs is estimated to be 2.3 x 10^{12} g P yr^{-1}. The sudden increase of dissolved phosphorus in the river was due to the introduction of detergent polyphosphate. However, it is difficult to extrapolate the present-day river transport from the existing data and that better estimates may be obtained from an evaluation of the inputs related to various activities. The estimates of the fluxes related to various pollutant sources are summarized in Table 1.

Table 1 Estimations of anthropogenic fluxes of dissolved phosphorus in rivers in 10^{12} g yr^{-1} (GESAMP,1987).

Authors	P
Stumm (1973)	0.6
Lerman et al.(1975)	1.8
Van Bennekom and Salomons (1981)	
domestic	1.7
agricultural (*)	0.35
industrial	1.7
Total	3.75
Meybeck (1982)	1.0
Wollast (1983)	1.7

* Particulate phosphorus fluxes due to land erosion estimated as 10 x 10^{12} g yr^{-1} by these authors.

3. Silicon

Livingstone (1963) estimated a global mean value of 6.1 mg Si/l based on a weighted average river discharge. A more extensive set of data, especially from some large rivers, and the use of specific transport rates for various environments led Meybeck (1979) to propose a slightly lower value 4.85 mg Si/l. This value gives a total gross river input of dissolved silica of 181 x 10^{12} g Si yr^{-1} and corresponds to a mean continental export rate of 1,800 kg Si km^{-2} yr^{-1}. The extreme paucity of the data concerning suspended opal in the aquatic system does not permit any evaluation of the river flux of this component.

Some Characteristics of the Chao Phraya River

The salinity at 10-142.6 km from the river mouth of the Chao Phraya River at low tide on October 1984 as chloride concentration was in the range of 4.9-31.3 mg/l (Onodera, 1985). The report of the National Environment Board (1985) revealed that the pH of the lower area of the Chao Phraya River basin in 1984 ranges from 6.7-7.9, and of the upper basin was in the range of 7.5-7.8.

On the basis of the results of Umnuay (1984), it was suggested that the behavior of phosphorus in the Chao Phraya estuary is conservative in the range of salinity 0-13 ‰. This means the dissolved phosphate concentration does not gain or loss during estuarine mixing in the region of salinity 0-13 ‰, but may be diluted by physical mixing processes. This was similar to behavior of reactive dissolved silicate which also found that it behaves conservatively in the Chao Phraya Estuary. Some material concentrations of the Chao Phraya River were shown in Table 2 .

Table 2 The content of suspended sediment, phosphate phosphorus, particulate phosphorus and dissolved silicon in fresh water (0 ‰) of the Chao Phraya River (Umnuay, 1984).

Parameters	April, 1983	June, 1983	October, 1983
Suspended sediment (mg/l)	15 - 27	9 - 43	28 - 78
Phosphate phosphorus (μg/l)	127 - 207	53 - 110	17 - 86
Particulate phosphorus (mg/l)	0.18 - 0.23	0.13 - 0.49	0.02 - 0.51
Dissolved silicon (mg/l)	1.67 - 7.45	0.80 - 8.43	6.06 - 7.21

In addition, the research of the Environmental Science Section, Environment Health Division, Department of Health (1984), it was found that discharge, suspended sediment, and total phosphorus loads transported by the Chao Phraya River into the Gulf of Thailand during 1981 to 1983 were 174×10^{8} m^{3} yr^{-1}, 1.792×10^{3} tons yr^{-1}, 5.2×10^{3} tons yr^{-1} respectively.

The Objective of the Study

The objectives of this study are as follows;

1. To examine the daily and seasonal variations of suspended

sediment flux, phosphorus flux and silicate flux through the Pak Kret and Bang Sai Transects in the Chao Phraya River.

2. To describe the patterns and trends of suspended sediment flux, phosphorus flux and silicate flux in the Chao Phraya River.

3. To estimate the annual mean fluxes of suspended sediment, phosphorus and silicate through the lower basin of the Chao Phraya River.