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# Distribution of Various Forms of Phosphorus in Coastal Marine Sediments of the Eastern Coast of Thailand

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# Distribution of Various Forms of Phosphorus in Coastal Marine Sediments of the Eastern Coast of Thailand

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## Abstract

Total P and the chemical forms were investigated in coastal marine sediments of the Eastern Coast of Thailand in the dry (April 2001) and wet (July 2001) seasons. The amounts of total P ranged from 55.83 to 2,575.83 and from 30.0 to 2672.50 μg $g^{-1}$ dry sediment for the dry and wet seasons, respectively. The sediments mainly consisted of inorganic than organic P. Sediment inorganic P fractions were determined by a sequential extraction. In riverine sediments, the major form of P was Fe, Al-bound P and the second was organic P, whereas other locations showed different relative dominant P forms. Seasonal changes had an influence on P fractions being available. In the dry season the available fractions derived from organic P whereas those in the wet season were derived largely from Fe, Al-bound P. Release of P from Fe, Al-bound P was mainly from amorphous Mn oxides rather than from Fe oxides.

In this study Fe oxides were the major P sorbent of the sediments followed by clay contents, while organic matter and $CaCO_3$ were less effective in P sorbing. In addition sediment P concentrations decreased with increasing sediment pH and salinity of the overlying water.

Keywords: Phosphorus, Sediment, Fractionation, Bioavailable P, Eastern Coast of Thailand

## Introduction

Phosphorus (P) is an essential element for all life forms (Correll, 1998) and is considered to be one of the major determinants of eutrophication (Gerdes and Kunst, 1998) as well as the key nutrient found to be limiting in natural waters (Reddy et al., 1999). Phosphorus is found in both inorganic and organic forms in sediments where serve as P sinks and sources and play an important role in the P cycling of the coastal marine ecosystem. It enters the rivers and sea in different chemical forms by various sources including point sources and non-point sources, and eventually is incorporated into bottom sediments. Dissolved inorganic P is considered bioavailable, whereas organic and particulate P forms generally must undergo transformation to inorganic forms before being considered bioavailable (Reddy et al., 1999). Phosphorus that is adsorbed to sediments can be released to the overlying water which depends on the chemical forms or fractions in the sediments (Mesnage and Picot, 1995; De Lange, 1992) and the environmental conditions (Matsuda et al., 1989; De Lange, 1992) such as pH, redox potential, microbes, bioturbation etc. The released P may become available to algae and stimulates blooms of phytoplankton and the excess can lead to eutrophication of the water body.

The knowledge of chemical speciation of sediment-bound P is necessary to evaluate the bioavailable P which is the amount of P that is biologically usable, because each chemical forms has its own capacity of release from the sediments (Mesnage and Picot, 1995). Sediment fractionation helps in identifying the chemical forms of P and can highlight the pathways of P into coastal waters (Balchand and Nair, 1994). Phosphorus fractionation is commonly achieved by sequential extractions, in which P is supposed to be selectively removed from different compounds in the sediments (Petterssen et al., 1988) by using a specific reagent preferentially extracting a specific form of P (Balchand and Nair, 1994). The P removed by the first one or two extracting solutions in a sequential extraction method is usually considered bioavailable (Reddy et al., 1999).

The present study was undertaken to 1) investigate the concentrations and chemical forms of sediment P distributed along the eastern coast of Thailand and their relation with selected sediment characteristics including some water qualities, and 2) evaluate the P bioavailability and potential mobility of the sediments. The results obtained will provide the current status of sediment P and a better understanding of P behavior in the coastal sediments which can be used to assess its impacts on water quality and living resources in this area.

The eastern coast of Thailand comprises an area of 5 Provinces: Chachoengsao, Chon Buri, Rayong, Chanthaburi and Trat. It was chosen in this study because the area consists of various activities including agriculture, fisheries, tourism, industry, urban and communities. Since this area is still in a development stage with a high expansion rate of industrialization and urbanization. These activities will substantially increase the amount of wastewater discharges into the coastal area. In addition red tide outbreaks often occur in this area especially in Chon Buri coastal area.

## Materials and Methods

### Sediment Sampling

Sediment samples were collected from twenty stations along the eastern coast. The site and locations are indicated in Table 1 and Figure 1. A triplicate set of surface sediment samples was collected at each station in the dry (April) and wet (July) seasons of 2001 using a modified Petersen grab. The samples were freeze-dried, homogenized and then passed through a 2-mm sieve.

**Table 1** Sediment sampling position

| Station | Location | Latitude | Longitude | Activity |
|---|---|---|---|---|
| BK1 | Bangpakong River (n) | 13° 29' 31.8" N | 100° 59' 46.2" E | Aquaculture |
| BK2 | Bangpakong River (o) | 13° 26' 42.8" N | 100° 56' 41.6" E | Aquaculture |
| AS4 | Angsila | 13° 20' 15.2" N | 100° 55' 05.4" E | Aquaculture |
| BS12 | Bangsaen | 13° 17' 12.3" N | 100° 54' 12.7" E | Recreation |
| SR18 | Koh Loi | 13° 10' 25.7" N | 100° 55' 00.6" E | Aquaculture |
| SR22 | Ao Udom | 13° 07' 26.7" N | 100° 53' 28.2" E | Industry |
| PT28 | Pattaya | 12° 55' 49.0" N | 100° 52' 25.3" E | Recreation |
| MP32 | Nong Fab | 12° 40' 07.7" N | 100° 07' 31.1" E | Industry |
| MP35 | Rayong River (n) | 12° 39' 20.8" N | 100° 16' 48.6" E | Urban |
| MP36 | Rayong River (o) | 12° 38' 54.7" N | 100° 17' 04.0" E | Urban |
| TP38 | Map Ta Phut (TPI) | 12° 37' 58.6" N | 100° 18' 28.8" E | Industry |
| TP40 | Had Mae Rum Phung | 12° 36' 22.6" N | 100° 22' 49.9" E | Natural Park |
| KG45 | Pasae River (n) | 12° 42' 20.9" N | 100° 42' 22.5" E | Aquaculture |
| KG46 | Pasae River (o) | 12° 29' 27.9" N | 100° 42' 29.7" E | Aquaculture |
| CB47 | Chanthaburi River (n) | 12° 29' 05.8" N | 102° 03' 54.8" E | Aquaculture |
| CB48 | Chanthaburi River (o) | 12° 28' 07.1" N | 102° 03' 56.2" E | Aquaculture |
| VR49 | Wen River (n) | 12° 18' 09.6" N | 102° 16' 47.3" E | Aquaculture |
| VR50 | Wen River (o) | 12° 17' 51.7" N | 102° 15' 45.2" E | Aquaculture |
| TD51 | Trat River (n) | 12° 09' 33.1" N | 102° 34' 58.3" E | Aquaculture |
| TD52 | Trat River (o) | 12° 06' 31.4" N | 102° 36' 17.5" E | Aquaculture |

n = inside the river mouth
o = outside the river mouth

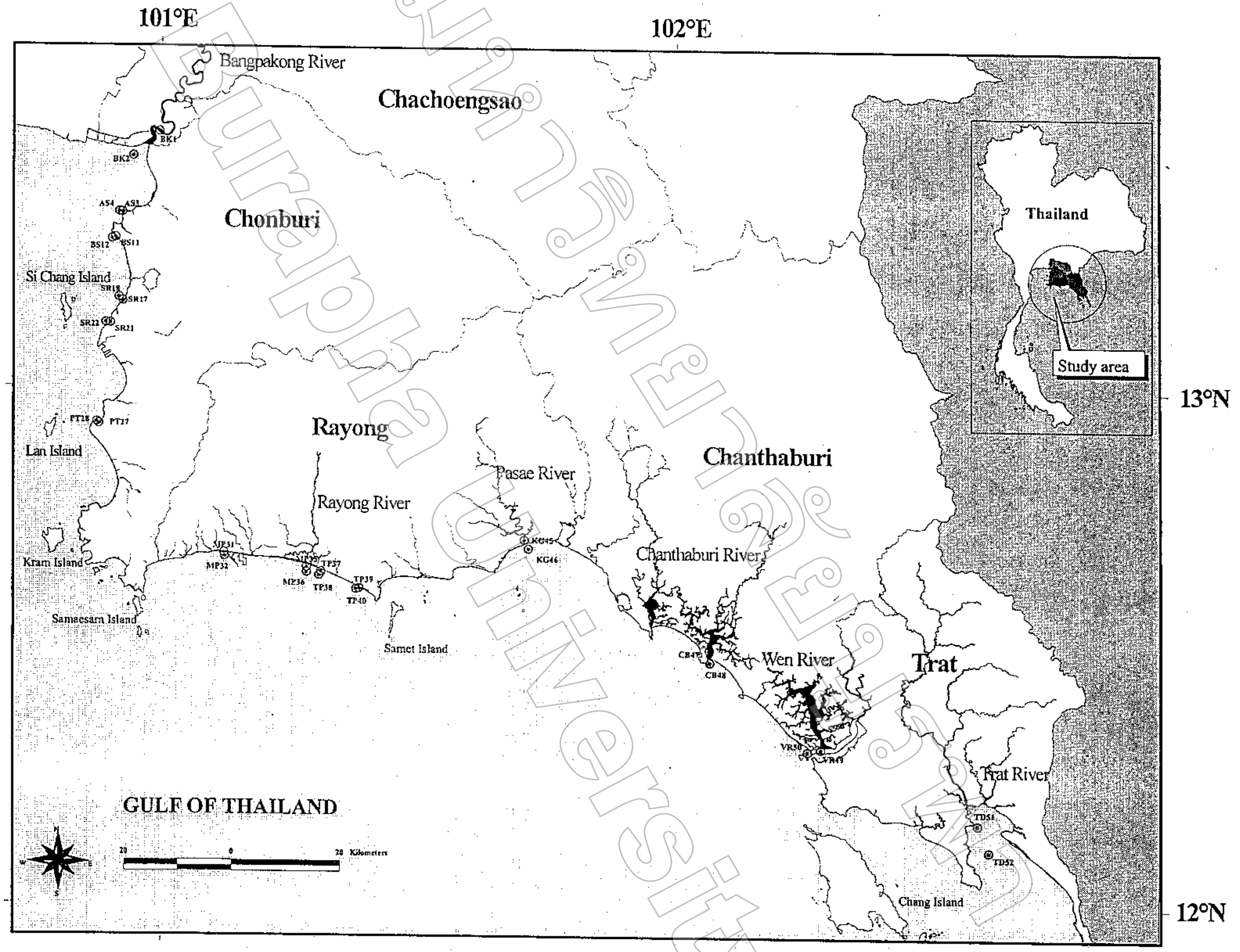

Figure 1 Map showing sampling locations

## Fractionation of Phosphorus

A sequential chemical extraction procedure described by De Lange (1992) which is similar to the procedure of Hieltjies and Lijklema (1980) was used to fractionate the inorganic forms of P distributed in the sediments (Table 2). The independently determined total inorganic P was also made for comparison with the sum of extracted inorganic P forms. The difference between total P and sum of extracted inorganic P referred to residual P, which is assumed to be organically bound.

Total P was determined by ignition method at 550 °C followed by extraction for 16 h with 1 N HCl whereas un-ignited samples prepared for total inorganic P and organic phosphorus was obtained by the difference between total P and inorganic P (Aspila et al., 1976).

The available P was also extracted from the sediments by direct chemical analysis with a dilute acid-fluoride solution, the combination of HCl and $NH_4F$, according to a method of Olsen and Sommers (1982). Phosphorus in all extracts was analyzed by ascorbic acid method of Strickland and Parsons (1972) and the concentrations were taken on an UV-Vis Spectrophotometer Model UV 300 Unicam.

**Table 2** Sequential chemical extraction procedure used in this study

| Fraction | Extractant | Form of P extracted |
|---|---|---|
| F1 | 2 N $NH_4Cl$ | Loosely adsorbed P (exchangeable + carbonate) |
| F2 | 0.1 N NaOH | Fe, Al-bound P |
| F3 | 0.5 N HCl | Ca-bound P, apatite |
| Residual P | Total P- (F1+F2+F3) | Organic P |

## Sediment Characteristics Analysis

Selected sediment characteristics were determined as follows: pH in water at a sediment to solution of 1:2.5, calcium carbonate by approximate gravimetric method for loss of carbon dioxide (Goh et al., 1993), organic matter by acid-dichromate oxidation method (Nelson and Sommers, 1982), particle size distribution by hydrometer method (English et al., 1994) and sediment texture was classified according to the U.S. Agriculture texture triangle (Hillel, 1998). Two extractable iron (Fe) and manganese (Mn) oxides were also determined in the sediments. The total (free) and amorphous oxides were extracted by dithionite-citrate solution and acid ammonium oxalate solution, respectively according to Ross and Wang (1993). Total oxides refer to as "cystralline and amorphous oxides". The concentrations of these Fe and Mn oxides in the extracts were measured by flame atomic absorption spectrophotometer Model AAnalyst 100 Perkin Elmer.

Three replicates of the sediment samples were used for all P extractions and the selected sediment characterization.

## Results and Discussion

### Sediment Characteristics

Selected sediment characteristics are presented in Tables 3 and 4. The sediments were slightly alkaline with pH ranging from 7.0-8.3 and 7.3-8.5 for the dry and wet seasons, respectively. High organic matter content (> 4%) was mainly found in estuarine sediments, especially in the dry season at Chanthaburi and Wen estuaries. $CaCO_3$ content was very high at Angsila where is an oyster farm both in the dry and wet seasons. The texture of the sediments was not much different between the two seasons. High clay contents were found in the riverine estuaries especially Bangpakong estuary. High total and amorphous Fe and Mn oxides were mainly found in the riverine estuaries with the highest concentrations found at Trat estuary. Normally dithionite-citrate solution is assumed to remove all free (total) Fe and Mn oxides, both cystralline and amorphous while oxalate removes the amorphous fraction only. Tables 3 and 4 showed, however, that in some samples the amount of amorphous oxides was higher than that of total oxides. This was also reported elsewhere in other literatures (McCallister and Jogan, 1971; Shukla et al., 1971) and the possible explanation was that some sediments had been subject to processes causing changes in their structure especially an alteration between aerobic and anaerobic conditions. Upon reoxidation, Fe will precipitate and may form amorphous, highly hydrated solid phase with the structural Si and Al. Thus, most of Fe extracted by dithionite-citrate in those sediments was also oxalate-extractable and, in addition, oxalate may be extracting some Fe-carbonate forms such as siderite (McCallister and Jogan, 1971). Also, Ross and Wang (1993) reported that oxalate can extract poorly crystalline oxides.

**Table 3** Sediment characteristics of the East Coast in the dry season (April 2001)*

| Station No. | Location | pH | $CaCO_3$ equivalent (%) | Organic matter (%) | Fe (mg/g) Total Oxides | Fe (mg/g) Amorp. Oxides | Mn (mg/g) Total Oxides | Mn (mg/g) Amorp. Oxides | Particle Size Distribution (%) Sand | Particle Size Distribution (%) Silt | Particle Size Distribution (%) Clay | Texture Class |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BK1 | Bangpakong River (n) | 7.6 | 0.70 | 2.22 | 12.18 | 10.92 | 1.84 | 1.92 | 30.9 | 49 | 19.8 | Loam |
| BK2 | Bangpakong River (n) | 7.8 | 1.35 | 2.31 | 14.30 | 12.16 | 1.64 | 1.61 | 42.2 | 32.1 | 25.8 | Clay loam |
| AS4 | Angsila | 8.2 | 41.85 | 1.76 | 2.28 | 2.47 | 0.44 | 0.30 | 73.5 | 16.7 | 9.8 | Sandy loam |
| BS12 | Bangsaen | 8.0 | 5.62 | 0.24 | 0.64 | 2.04 | 0.04 | 0.04 | 92.9 | 2.1 | 5.1 | Sand |
| SR18 | Koh Loi | 8.1 | 12.97 | 0.85 | 1.59 | 2.25 | 0.15 | 0.14 | 58.9 | 33.7 | 7.4 | Sandy loam |
| SR22 | Ao Udom | 8.1 | 11.79 | 1.31 | 1.00 | 1.50 | 0.15 | 0.12 | 54.9 | 36.7 | 8.4 | Sandy loam |
| PT28 | Pattaya | 8.3 | 8.89 | 0.40 | 0.88 | 0.89 | 0.06 | 0.06 | 73.8 | 18.7 | 7.5 | Sandy loam |
| MP32 | Nong Fab | 8.3 | 2.06 | 0.27 | 2.99 | 0.49 | 0.03 | 0.03 | 91.8 | 4.4 | 3.9 | Sand |
| MP35 | Rayong River (n) | 8.1 | 2.28 | 0.44 | 1.59 | 1.33 | 0.07 | 0.01 | 89.6 | 3.5 | 6.8 | Sand |
| MP36 | Rayong River (o) | 7.9 | 4.29 | 2.52 | 8.06 | 6.39 | 0.20 | 0.16 | 44.2 | 43.4 | 12.4 | Loam |
| TP38 | Map Ta Phut (TPI) | 7.7 | 1.94 | 0.42 | 1.60 | 1.11 | 0.03 | 0.04 | 57.5 | 21.1 | 21.4 | Sandy clay loam |
| TP40 | Had Mae Rum Phung | 7.9 | 3.43 | 0.10 | 1.31 | 1.97 | 0.01 | 0.02 | 92.9 | 1.3 | 5.8 | Sand |
| KG45 | Pasae River (n) | 7.9 | 3.08 | 3.09 | 13.63 | 12.55 | 0.15 | 0.18 | 60.6 | 23.3 | 16.1 | Sandy loam |
| KG46 | Pasae River (o) | 8.0 | 8.96 | 3.52 | 9.42 | 11.39 | 0.32 | 0.38 | 74.6 | 16.0 | 9.4 | Sandy loam |
| CB47 | Chanthaburi River (n) | 8.0 | 3.66 | 4.59 | 8.60 | 10.46 | 0.14 | 0.20 | 61.9 | 25.1 | 13.0 | Sandy loam |
| CB48 | Chanthaburi River (o) | 8.0 | 3.99 | 5.94 | 14.28 | 16.05 | 0.44 | 0.50 | 41.2 | 46.0 | 12.8 | Loam |
| VR49 | Wen River (n) | 7.9 | 3.10 | 5.03 | 13.91 | 16.77 | 0.50 | 0.50 | 33.9 | 55.6 | 10.5 | Silt loam |
| VR50 | Wen River (o) | 7.9 | 7.61 | 6.55 | 19.92 | 22.59 | 0.74 | 0.50 | 36.9 | 50.7 | 12.4 | Silt loam |
| TD51 | Trat River (n) | 7.0 | 2.22 | 1.12 | 72.19 | 38.77 | 0.41 | 0.37 | 44.9 | 35.4 | 19.8 | Loam |
| TD52 | Trat River (o) | 7.0 | 2.64 | 2.61 | 49.63 | 28.81 | 0.30 | 0.31 | 41.5 | 44.7 | 13.8 | Loam |

* mean of 3 independent samples

**Table 4** Sediment characteristics of the East Coast in the wet season (July 2001)*

| Station No. | Location | pH | $CaCO_3$ equivalent (%) | Organic matter (%) | Fe (mg/g) |  | Mn (mg/g) |  | Particle Size Distribution (%) |  |  | Texture Class |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  | Total Oxides | Amorp. Oxides | Total Oxides | Amorp. Oxides | Sand | Silt | Clay |  |
| BK1 | Bangpakong River (n) | 7.6 | 2.99 | 1.65 | 15.28 | 7.82 | 1.81 | 1.51 | 32.8 | 40.1 | 27.2 | Loam |
| BK2 | Bangpakong River (o) | 7.8 | 2.90 | 2.24 | 15.53 | 8.72 | 1.62 | 1.39 | 44.7 | 35.4 | 19.9 | Loam |
| AS4 | Angsila | 8.1 | 18.42 | 1.74 | 2.76 | 2.06 | 0.47 | 0.32 | 71.2 | 20.4 | 8.4 | Sandy loam |
| BS12 | Bangsaen | 8.1 | 5.71 | 0.10 | 0.50 | 1.34 | 0.04 | 0.05 | 85.5 | 10.0 | 4.5 | Loamy sand |
| SR18 | Koh Loi | 8.2 | 12.25 | 1.01 | 2.27 | 1.74 | 0.17 | 0.12 | 63.0 | 29.7 | 7.3 | Sandy loam |
| SR22 | Ao Udom | 8.3 | 11.83 | 0.88 | 1.53 | 1.19 | 0.16 | 0.10 | 50.1 | 40.6 | 9.3 | Loam |
| PT28 | Pattaya | 8.4 | 9.49 | 0.99 | 1.02 | 0.72 | 0.09 | 0.05 | 69.3 | 26.1 | 4.6 | Sandy loam |
| MP32 | Nong Fab | 8.3 | 3.66 | 0.90 | 0.34 | 0.20 | 0 | 0 | 96.4 | 0.72 | 2.88 | Sand |
| MP35 | Rayong River (n) | 8.5 | 3.48 | 1.58 | 1.25 | 0.84 | 0.04 | 0.03 | 94.2 | 1.4 | 4.3 | Sand |
| MP36 | Rayong River (o) | 7.9 | 3.73 | 0.94 | 6.42 | 3.73 | 0.20 | 0.14 | 41.1 | 44.1 | 14.9 | Loam |
| TP38 | Map Ta Phut (TPI) | 8.2 | 4.80 | 1.01 | 1.66 | 0.80 | 0.04 | 0.03 | 63.4 | 18.7 | 17.9 | Sandy loam |
| TP40 | Had Mae Rum Phung | 8.5 | 5.86 | 0.42 | 0.86 | 0.89 | 0.02 | 0.02 | 96.0 | 0.9 | 3.1 | Sand |
| KG45 | Pasae River (n) | 8.0 | 5.27 | 2.24 | 14.99 | 9.88 | 0.21 | 0.22 | 61.8 | 21.6 | 16.7 | Sandy loam |
| KG46 | Pasae River (o) | 8.0 | 2.09 | 0.97 | 18.13 | 11.99 | 0.28 | 0.27 | 60.8 | 25.7 | 13.5 | Sandy loam |
| CB47 | Chanthaburi River (n) | 8.0 | 5.01 | 3.63 | 11.47 | 9.02 | 0.38 | 0.33 | 63.1 | 28.9 | 8.0 | Sandy loam |
| CB48 | Chanthaburi River (o) | 8.0 | 6.21 | 4.76 | 13.84 | 8.66 | 0.51 | 0.37 | 55.5 | 34.5 | 9.9 | Sandy loam |
| VR49 | Wen River (n) | 7.7 | 9.13 | 3.97 | 24.47 | 11.08 | 0.44 | 0.29 | 46.4 | 31.9 | 21.8 | Loam |
| VR50 | Wen River (o) | 8.0 | 2.58 | 2.75 | 14.92 | 3.07 | 0.71 | 0.49 | 48.0 | 41.8 | 10.2 | Loam |
| TD51 | Trat River (n) | 7.3 | 2.69 | 1.16 | 94.70 | 25.22 | 0.47 | 0.36 | 54.1 | 23.4 | 22.4 | Sandy clay loam |
| TD52 | Trat River (o) | 7.4 | 2.05 | 0.49 | 51.56 | 17.81 | 0.56 | 0.43 | 39.7 | 44.8 | 15.5 | Loam |

* mean of 3 independent samples

## Amounts of Sediment P and the Chemical Forms

Total and various forms of P distributed in coastal marine sediments in the dry and wet seasons are given in Tables 5 and 6, respectively. The concentrations of total P showed broad ranges from 55.83 to 2,575.83 and from 30.0 to 2,672.50 μg $g^{-1}$ dry sediment for the dry and wet seasons, respectively. A statistical analysis indicated that total P content was significantly different depending on the interaction of station with season ($P < 0.05$). The difference between each station and season showed in Figure 2. The high concentrations were mainly found in the riverine sediments especially in the dry than in the wet season and the highest concentrations were found at Trat estuary. Sediment P mainly consisted of inorganic P than organic P of both seasons. This was in agreement with the report of Syers et al. (1973) that inorganic P frequently constitutes the major portion of the total P in lake sediments. From the present study the inorganic P accounted for 43.33 to 1,358.33 and 11.67 to 1,424.17 μg $g^{-1}$ dry sediment for the dry and wet seasons, respectively whereas organic P ranged from 12.50 to 1,217.50 and from 18.33 to 1,247.50 μg $g^{-1}$ dry sediment for the dry and wet seasons, respectively

The inorganic P fractions removed by sequential extraction are presented in Tables 5 and 6. Results obtained indicated that the sum of the sequential extracted inorganic P of both seasons was in good agreement with the independently determined total inorganic P ($r = 0.891$, $P < 0.01$) and their significant difference were not obtained ($P > 0.05$). Similarly, the residual P agreed very well with organic P ($r = 0.957$, $P < 0.01$) and their significant difference were not found ($P > 0.05$) indicating the residual P mainly consisted of organic P as reported by Hieltjies and Lijklema (1980).

**Table 5** Various forms of phosphorus in coastal sediments of the East Coast in the dry season (April 2001)*

| Station No. | Location | Total P (µg g$^{-1}$) | P Fractionation (µg g$^{-1}$) | | | | Inorganic P † | | Organic P † | | Available P † | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Adsorbed P | Fe,Al-P | Ca-P | Residual P | (µg g$^{-1}$) | (%) | (µg g$^{-1}$) | (%) | (µg g$^{-1}$) | (%) |
| BK1 | Bangpakong River (n) | 721.67 | 68.82 | 385.00 | 93.67 | 174.18 | 587.50 | 81.4 | 134.17 | 18.6 | 22.15 | 3.07 |
| BK2 | Bangpakong River (o) | 643.33 | 36.88 | 298.00 | 63.67 | 244.78 | 398.33 | 61.9 | 245.00 | 38.1 | 19.78 | 3.07 |
| AS4 | Angsila | 730.83 | 117.07 | 41.00 | 425.67 | 147.09 | 560.83 | 76.7 | 170.00 | 23.3 | 5.13 | 0.70 |
| BS12 | Bangsaen | 100.83 | 22.12 | 18.00 | 35.33 | 25.38 | 52.50 | 52.1 | 48.33 | 47.9 | 9.95 | 9.87 |
| SR18 | Koh Loi | 528.33 | 94.65 | 39.50 | 315.67 | 78.51 | 410.00 | 77.6 | 118.33 | 22.4 | 8.25 | 1.56 |
| SR22 | Ao Udom | 519.17 | 82.05 | 27.50 | 243.67 | 165.95 | 348.33 | 67.1 | 170.83 | 32.9 | 6.65 | 1.28 |
| PT28 | Pattaya | 310.00 | 76.50 | 20.67 | 155.67 | 57.16 | 187.50 | 60.5 | 122.50 | 39.5 | 9.03 | 2.91 |
| MP32 | Nong Fab | 136.67 | 22.73 | 21.50 | 14.00 | 78.44 | 51.67 | 37.8 | 85.00 | 62.2 | 10.75 | 7.87 |
| MP35 | Rayong River (n) | 172.50 | 25.83 | 25.25 | 14.00 | 107.42 | 60.00 | 34.8 | 112.50 | 65.2 | 17.08 | 9.90 |
| MP36 | Rayong River (o) | 490.83 | 51.93 | 259.67 | 78.33 | 100.90 | 327.50 | 66.7 | 163.33 | 33.3 | 5.55 | 1.13 |
| TP38 | Map Ta Phut (TPI) | 148.33 | 25.82 | 43.17 | 23.00 | 56.34 | 79.17 | 53.4 | 69.17 | 46.6 | 12.73 | 8.58 |
| TP40 | Had Mae Rum Phung | 55.83 | 11.37 | 8.00 | 14.00 | 22.46 | 43.33 | 77.6 | 12.50 | 22.4 | 5.67 | 10.16 |
| KG45 | Pasae River (n) | 400.00 | 22.60 | 188.00 | 89.00 | 100.40 | 284.17 | 71.0 | 115.83 | 29.0 | 2.73 | 0.68 |
| KG46 | Pasae River (o) | 380.83 | 24.88 | 125.00 | 80.67 | 150.28 | 229.17 | 60.2 | 151.67 | 39.8 | 6.22 | 1.63 |
| CB47 | Chanthaburi River (n) | 269.17 | 11.97 | 153.83 | 50.67 | 52.70 | 165.00 | 61.3 | 104.17 | 38.7 | 3.53 | 1.31 |
| CB48 | Chanthaburi River (o) | 452.50 | 51.30 | 196.33 | 111.00 | 93.87 | 315.00 | 69.6 | 137.50 | 30.4 | 3.10 | 0.69 |
| VR49 | Wen River (n) | 497.50 | 62.98 | 172.83 | 108.00 | 153.69 | 319.17 | 64.2 | 178.33 | 35.9 | 2.92 | 0.59 |
| VR50 | Wen River (o) | 560.00 | 42.40 | 233.67 | 162.00 | 121.93 | 386.67 | 69.1 | 173.33 | 31.0 | 4.42 | 0.79 |
| TD51 | Trat River (n) | 2575.83 | 11.68 | 622.00 | 52.33 | 1889.82 | 1358.33 | 52.7 | 1217.50 | 47.3 | 16.85 | 0.65 |
| TD52 | Trat River (o) | 1108.33 | 12.60 | 446.00 | 64.33 | 585.40 | 575.00 | 51.9 | 533.33 | 48.1 | 5.73 | 0.52 |

* mean of 3 independent samples
† Independent determination

**Table 6** Various forms of phosphorus in coastal sediments of the East Coast in the wet season (July 2001)*

| Station | Location | Total P | P Fractionation ($\mu g\ g^{-1}$) | | | | Inorganic P† | | Organic P† | | Available P† | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| No. | | ($\mu g\ g^{-1}$) | Adsorbed P | Fe,Al-P | Ca-P | Residual P | ($\mu g\ g^{-1}$) | (%) | ($\mu g\ g^{-1}$) | (%) | ($\mu g\ g^{-1}$) | (%) |
| BK1 | Bangpakong River (n) | 644.17 | 68.33 | 346.33 | 78.00 | 151.51 | 532.50 | 82.7 | 111.67 | 17.3 | 72.53 | 11.3 |
| BK2 | Bangpakong River (o) | 630.83 | 51.67 | 343.67 | 118.00 | 117.49 | 531.67 | 84.3 | 99.17 | 15.7 | 19.48 | 3.09 |
| AS4 | Angsila | 554.17 | 100.83 | 45.00 | 228.67 | 179.67 | 461.67 | 83.3 | 92.50 | 16.7 | 23.65 | 4.27 |
| BS12 | Bangsaen | 74.17 | 19.67 | 13.00 | 19.33 | 22.17 | 48.33 | 65.2 | 25.83 | 34.8 | 6.63 | 8.94 |
| SR18 | Koh Loi | 429.17 | 96.50 | 33.83 | 136.33 | 162.51 | 381.67 | 88.9 | 47.50 | 11.1 | 17.53 | 4.08 |
| SR22 | Ao Udom | 374.17 | 65.67 | 19.50 | 163.67 | 125.33 | 302.50 | 80.9 | 71.67 | 19.2 | 13.10 | 3.50 |
| PT28 | Pattaya | 259.17 | 66.67 | 14.50 | 153.67 | 24.33 | 220.00 | 84.9 | 39.17 | 15.1 | 3.73 | 1.44 |
| MP32 | Nong Fab | 30.00 | 11.50 | 4.50 | 0.33 | 13.67 | 11.67 | 38.9 | 18.33 | 61.1 | 3.42 | 11.4 |
| MP35 | Rayong River (n) | 103.75 | 16.00 | 22.75 | 1.67 | 63.33 | 85.00 | 81.9 | 18.75 | 18.1 | 11.00 | 10.6 |
| MP36 | Rayong River (o) | 477.50 | 37.33 | 225.67 | 35.00 | 179.50 | 263.33 | 55.2 | 214.17 | 44.9 | 13.88 | 2.91 |
| TP38 | Map Ta Phut (TPI) | 129.17 | 30.50 | 35.50 | 13.00 | 50.17 | 70.00 | 54.2 | 50.00 | 38.7 | 13.90 | 10.8 |
| TP40 | Had Mae Rum Phung | 64.17 | 13.00 | 8.50 | 6.00 | 36.67 | 16.67 | 26.0 | 47.50 | 74.0 | 5.93 | 9.24 |
| KG45 | Pasae River (n) | 320.83 | 20.67 | 195.67 | 59.67 | 44.82 | 249.17 | 77.7 | 71.67 | 22.3 | 7.27 | 2.27 |
| KG46 | Pasae River (o) | 385.00 | 7.67 | 274.33 | 66.67 | 36.33 | 335.00 | 87.0 | 50.00 | 13.0 | 7.73 | 2.01 |
| CB47 | Chanthaburi River (n) | 321.67 | 44.83 | 155.50 | 62.50 | 58.84 | 247.50 | 76.9 | 74.17 | 23.1 | 7.70 | 2.39 |
| CB48 | Chanthaburi River (o) | 364.17 | 56.17 | 148.50 | 104.67 | 54.83 | 311.67 | 85.6 | 52.50 | 14.4 | 5.38 | 1.48 |
| VR49 | Wen River (n) | 300.83 | 48.50 | 133.50 | 64.67 | 54.16 | 241.67 | 80.3 | 59.17 | 19.7 | 6.82 | 2.27 |
| VR50 | Wen River (o) | 437.50 | 71.83 | 163.50 | 57.33 | 144.84 | 310.00 | 70.9 | 127.50 | 29.1 | 5.02 | 1.15 |
| TD51 | Trat River (n) | 2672.5 | 10.50 | 1140.33 | 37.00 | 1484.67 | 1424.17 | 53.3 | 1247.50 | 46.7 | 22.62 | 0.85 |
| TD52 | Trat River (o) | 948.33 | 5.50 | 533.00 | 48.33 | 361.50 | 450.00 | 47.5 | 498.33 | 52.6 | 5.22 | 0.55 |

* mean of 3 independent samples
† Independent determination

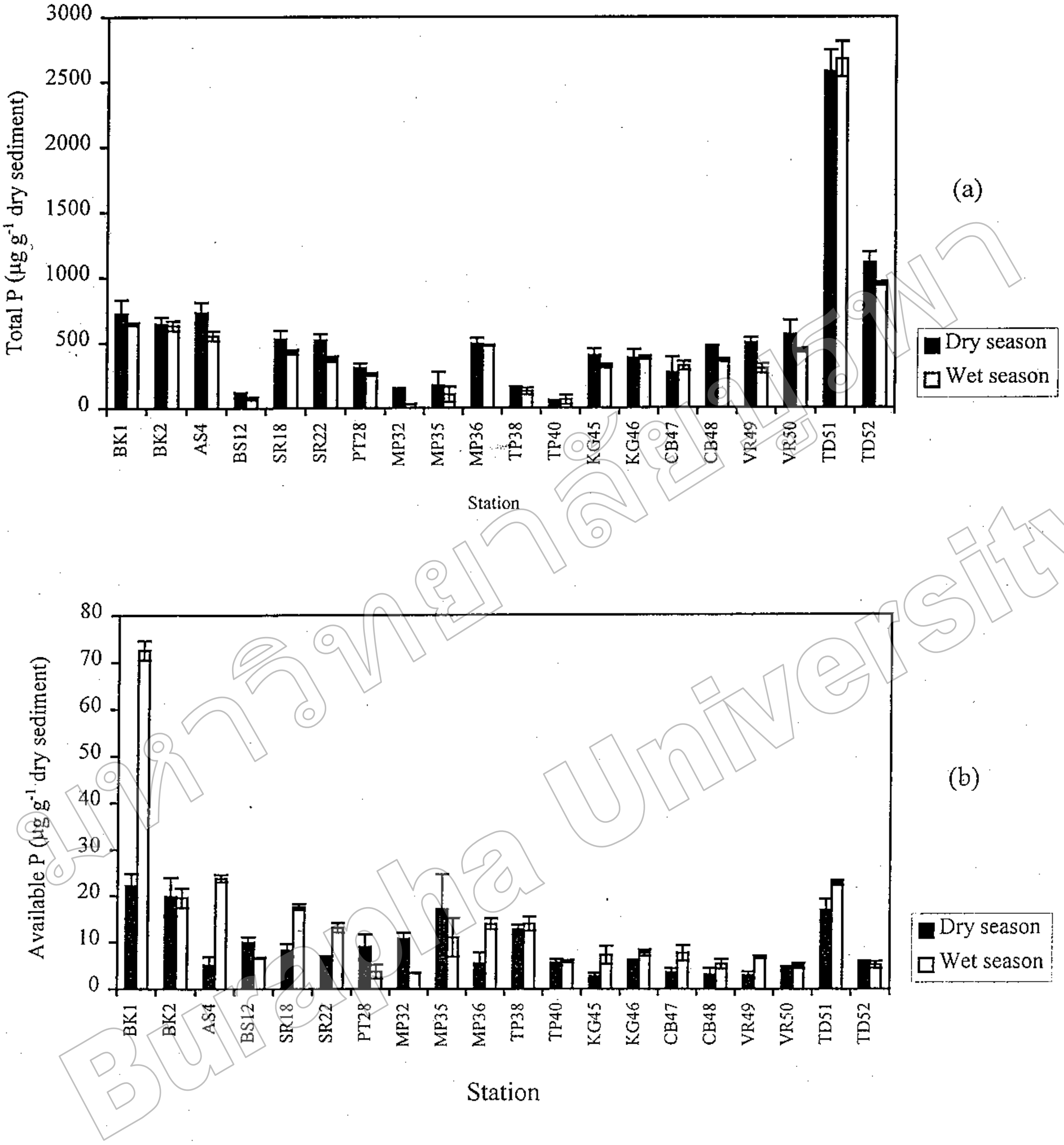

**Figure 2** Spatial and temporal distribution of (a) total P and (b) available P in coastal marine sediments of the east coast. Error bars are ± 1 standard error of three replicates. See table 1 for more details of station codes.

The percentage of each chemical forms of sediment P on the basis of total P is presented on Figure 3. In riverine sediments, the most abundant fraction of P of both seasons was mainly in the form of Fe, Al-bound P because the riverine sediments consisted of higher Fe and Mn oxides than the other locations. And the second P abundant was residual P (organic P). For other locations, Ca-bound P was the major fraction found at Angsila (AS4), Koh Loi (SR18), Ao Udom (SR22) and Pattaya (PT28) where the sediments consisted of high $CaCO_3$ content. A statistical analysis showed the difference of each chemical P form depended on the influence of both station and season ($P < 0.05$) which was similar to that of total P. This may be the results of the geological conditions and weathering processes as well as human activities.

Although chemical P forms taken from sequential extraction are operationally defined (Pettersson et al., 1988), the results can provide much more data on the source or origin of sediment P, the transport and possible remobilization and bioavailability. The first two fractions in sequential extraction schemes (loosely adsorbed P and Fe, Al-bound P) which can easily release from sediments by changes of environmental conditions are considered to be potentially bioavailable forms. While Ca-bound P or apatite which is the only P mineral (Pettersson et al., 1988) is the least available form or an immobile form (Syers et al., 1973; Reddy et al., 1999; López-Piñeiro and Garcia-Navarro, 2001).

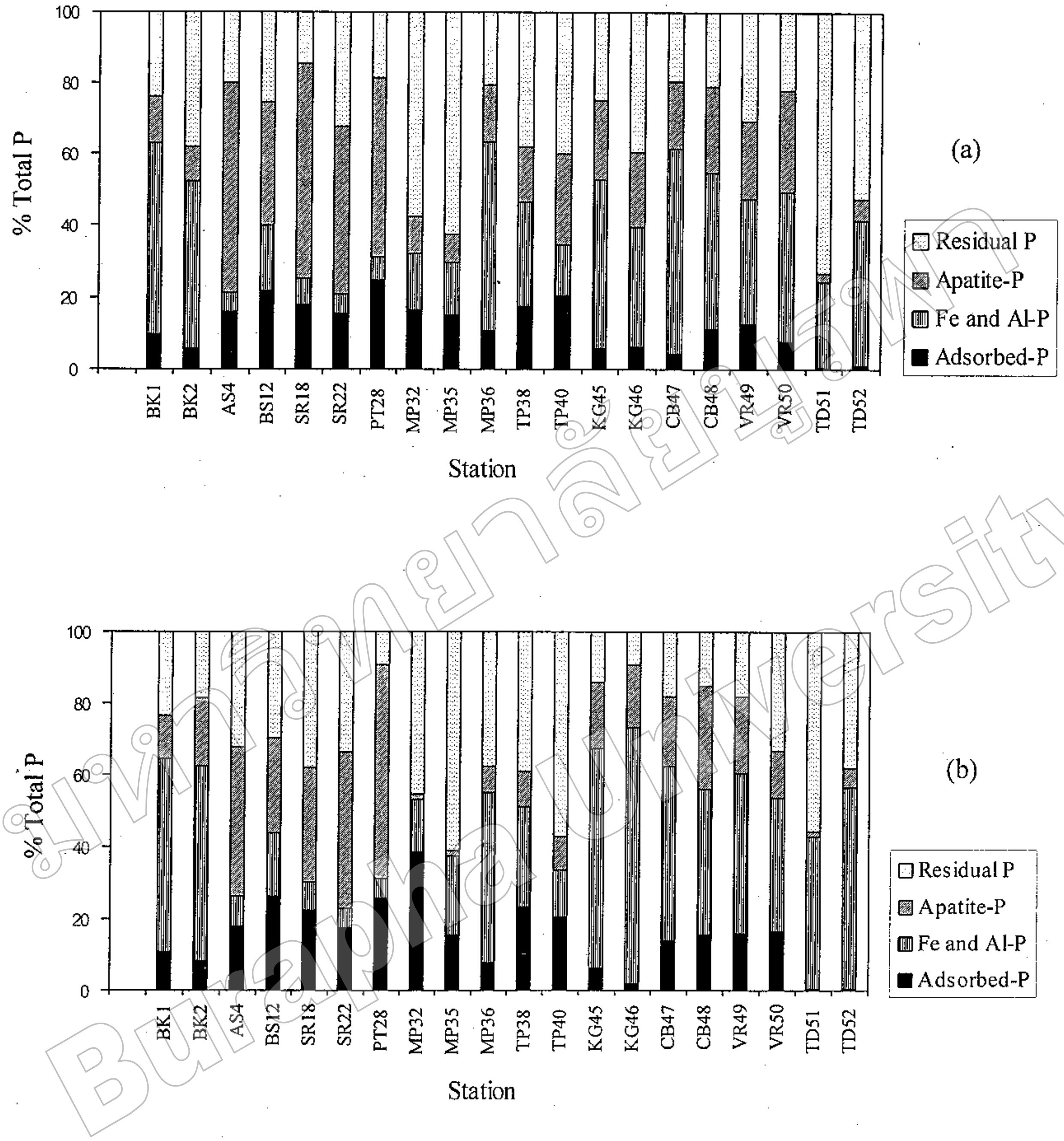

**Figure 3** Different chemical forms of phosphorus distributed in coastal marine sediments of the east coast in (a) dry season (April 2001) and (b) wet season (July 2001). See table 1 for more details of station codes.

## Potential Bioavailability of P in Sediments

The amount of available P fractions found along the eastern coast ranged from 2.73 to 22.15 $\mu g\ g^{-1}$ and from 3.42 to 72.53 $\mu g\ g^{-1}$ based on dry sediment for the dry and wet seasons respectively (Tables 5 and 6). The variation of available P depended on the influence of both station and season ($P < 0.05$) and the results indicated in Figure 2. However, in terms of percentage of total P, it ranged from 0.52 to 10.16 % and from 0.55 to 11.4 %, for the dry and wet seasons respectively (Tables 5 and 6). The available P well correlated with bottom water phosphate of both seasons ($r = 0.701$, $P < 0.01$ for dry season and $r = 0.631$, $P < 0.01$ for wet season) (Tables 7 and 8).

In the dry season available P did not correlate with any P fractions except with residual P ($r = 0.297$, $P < 0.05$). However, residual P well correlated with organic P and the two values obtained did not show significant difference as mentioned earlier. This suggested that available P fractions in the dry season derived from organic forms of P. Organic P is considered as an immobile form in sediments (Mesnage and Picot, 1995). However, it may become available for algae growth by a mineralization process involving microbial activity (Matsuda et al., 1989; Mesnage and Picot, 1995: Correl, 1998). There was a report of López-Piñeiro and Garcia-Navarro (2001) that organic P was an important fraction in supplying available P. Normally organic P was associated closely with sediment organic matter as reported by Sommers et al. (1972), but such result was not obtained in the present study. However, results obtained showed negative correlation of available P with organic matter ($r = -0.431$, $P < 0.01$) and with dissolved oxygen ($r = -0.257$, $P < 0.01$). This indicated that utilization of oxygen by microbial activity had been occurred during organic matter decomposition, resulting in P-release from organic materials in the sediments. Gonsiorczyk et al. (1998) also reported that the mineralization of organic matter was the driving force of P-release by sediments in eutrophic lakes. Due to organic matter associated with clay content and metal oxides (Sparks, 1995), a significant correlation between available P and clay as well as Mn oxides was also obtained (Table 7).

In the wet season available P significantly correlated with adsorbed P ($r = 0.322$, $P < 0.05$) and Fe, Al-bound P ($r = 0.267$, $P < 0.05$) (Table 8) suggesting the bioavailability of P in the wet season derived largely from the two fractions. Phosphorus can be released from the two fractions into the overlying water by changes of pH and redox potential (Eh) (Mesnage and Picot, 1995). Sediment pH is associated with Eh (Tan, 1982). The redox potential has an influence on the precipitation of Fe and Mn oxides in oxic sediments (high Eh). When sediments become anoxic (low Eh), Fe and Mn can occur as soluble manganous ($Mn^{+2}$) and ferrous ($Fe^{+2}$) ions (Olsen et al., 1982), and allow phosphate to diffuse more freely into the overlying water. Possibly the release of P was largely from Fe, Al-bound P rather than from adsorbed P because of a larger portion of the former fraction in the riverine estuaries which agreed with the reports of Upchurch et al. (1974) and Gonsiorczyk et al. (1998).

From the correlation coefficient data, available P of the wet season also established a significant and high correlation with total and amorphous Mn oxides ($r = 0.620$ and $r = 0.702$ respectively) (Table 8). Such correlation could not be obtained with any Fe oxides. Since Fe oxides are more difficult to reduce than Mn oxides (Sparks, 1995) resulting in P being strong held with Fe rather than with Mn. In such case release of P from Fe, Al-inorganic complex was mainly from Mn oxides especially amorphous form rather than from Fe oxides.

**Table 7** Correlation coefficients of various forms of phosphorus and selected sediment characteristics and water qualities of the dry season (April 2001)

| Parameter | Total P | Adsorbed P | Fe,Al-P | Ca-P | Residual P | Inorganic P | Organic P | Available P |
|---|---|---|---|---|---|---|---|---|
| Sediment pH | -0.705** | 0.418** | -0.794** | 0.293* | -0.706** | -0.650** | -0.709** | NS |
| Organic matter | NS | NS | NS | NS | NS | NS | NS | -0.431** |
| $CaCO_3$ | NS | 0.285* | NS | NS | NS | NS | NS | 0.348** |
| Clay | 0.363** | NS | 0.606** | NS | 0.333* | 0.412** | 0.288* | 0.275* |
| Total Fe oxides | 0.887** | -0.355** | 0.858** | NS | 0.881** | 0.815** | 0.896** | NS |
| Amorphous Fe | 0.793** | -0.320* | 0.866** | NS | 0.757** | 0.751** | 0.776** | NS |
| Total Mn oxides | NS | NS | NS | NS | NS | NS | NS | 0.401** |
| Amorphous Mn | NS | NS | 0.521** | NS | NS | 0.340** | NS | 0.396** |
| Salinity | -0.792** | NS | -0.731** | NS | -0.834** | -0.772** | -0.752** | -0.430** |
| Bottom Water P | NS | NS | NS | NS | NS | NS | NS | 0.701** |
| DO | -0.292* | NS | -0.304* | NS | -0.284* | -0.262* | -0.302* | -0.257* |
| Water pH | -0.611** | NS | -0.718** | NS | -0.603** | -0.665** | -0.503** | -0.489** |
| Available P | NS | NS | NS | -0.261* | 0.297* | NS | NS | |

*, ** : Significant at $P = 0.05$ and 0.01 respectively
NS : Not significant ($P > 0.05$)

**Table 8** Correlation coefficients of various forms of phosphorus and selected sediment characteristics and water qualities of the wet season (July 2001)

| Parameter | Total P | Adsorbed P | Fe,Al-P | Ca-P | Residual P | Inorganic P | Organic P | Available P |
|---|---|---|---|---|---|---|---|---|
| Sediment pH | -0.705** | NS | -0.824** | NS | -0.611** | -0.651** | -0.661** | -0.305* |
| Organic matter | NS | 0.280* | NS | NS | NS | NS | NS | NS |
| $CaCO_3$ | NS | 0.627** | -0.426** | 0705** | NS | NS | NS | NS |
| Clay | 0.423** | NS | 0.583** | NS | 0.282* | 0.518** | 0.325* | 0.514** |
| Total Fe oxides | 0.903** | -0.337** | 0.963** | NS | 0.858** | 0.848** | 0.892** | NS |
| Amorphous Fe | 0.744** | -0.356** | 0.908** | NS | 0.642** | 0.757** | 0.702** | NS |
| Total Mn oxides | 0.334* | 0.295* | 0.381** | NS | NS | 0.426** | NS | 0.620** |
| Amorphous Mn | 0.314* | NS | 0.357** | NS | NS | 0.391** | NS | 0.702** |
| Salinity | -0.635** | NS | -0.722** | NS | -0.466** | -0.693** | -0.499** | -0.494** |
| Bottom Water P | NS | NS | NS | NS | NS | NS | NS | 0.631** |
| DO | NS | NS | NS | NS | NS | NS | 0.271* | NS |
| Water pH | -0.502** | NS | -0.549** | NS | -0.434** | -0.540** | -0.432** | -0.633** |
| Available P | 0.275* | 0.322* | 0.267* | NS | NS | 0.391** | NS | |

*, ** : Significant at $P = 0.05$ and 0.01 respectively
NS : Not significant ($P > 0.05$)

### Relationship between Sediment P and Selected Sediment Characteristics

For both seasons, sediment P was strongly correlated with total and amorphous Fe oxides followed by clay contents respectively (Tables 7 and 8). No significant correlation between total P and organic matter as well as $CaCO_3$ could be obtained. Such correlation suggested that both cystralline and amorphous Fe oxides were the major P sorbent of the sediments followed by clay, respectively, while organic matter and $CaCO_3$ were less effective or may not responsible for P sorbed in the study area. Fe oxides are quite common in sediments as suspended particles and as coatings on clay mineral surfaces and humic substances in organic matter (Sparks, 1995). They have high specific surface areas and great reactivity (Sparks, 1995) making them as a powerful sorbent. For inorganic P fractions, a positive and strong correlation of the two Fe oxides was obtained with Fe, Al-bound P fraction only. The correlation between organic P and Fe oxides obtained seemed to be indirect due to Fe oxides associated with organic matter forming Fe-organic P complex. In most sediment samples, Fe oxides were in amorphous rather than crystalline form (Tables 3 and 4). Therefore, amorphous Fe oxides would be expected to be the most effective sorbent for P in the study area of the present study which agreed with the other findings of Shukla et al.(1971) and Börling et al. (2001). Comparison of the two oxides (Fe and Mn), a significant, but weak correlation between total P and Mn oxides was obtained only in the wet season suggesting that Mn oxides had a lesser contribution in P sorbing than Fe oxides. This is possibly because Mn oxides are more easily to reduce than Fe oxides (Sparks, 1995) and reducing conditions of the wet season may favor the reaction resulting in P release from this oxides. In addition, Shukla et al. (1971) reported that $CaCO_3$ is less effective than amorphous Fe in sorbing added inorganic P in the laboratory and in the lake environment. $CaCO_3$ also acts as a dilutant to the Fe and Al sites as reported by McCallister and Logan (1978) which agreed with the negative correlation coefficient obtained between Fe, Al-bound P and $CaCO_3$ content especially in the wet season ($r = -0.426$, $P < 0.01$). Also McDowell et al. (2001) found that the surface areas of $CaCO_3$ and organic matter are the low-energy adsorption sites for P sorbing in soils. These reports are all in agreement with the data obtained from the present study.

Sediment P showed negative relationship with pH (Tables 7 and 8) indicating the lower pH sediments showed the higher contents of P. McCallister and Logan (1978) and Carpenter and Smith (1984) also found the similar result. This phenomenon is related to changes in surface charges of organic and inorganic materials in the sediments, which are pH dependent (Sparks, 1995). The $H^+$ and $OH^-$ ions, which cause the development of surface charges are responsible for the electric surface potential (Tan, 1982). Similar relationship was also obtained between sediment P and salinity indicating that P content of sediments decreased with increasing salinity of the overlying water or desorption of P occurred as salinity increase which agreed with the findings of Upchurch et al. (1974) and Carpenter and Smith (1984). The possible explanation for this is that the adsorbed P is released or displaced by competing anions predominated in seawater such as chloride or sulfate (Upchurch et al., 1974). In addition, dissolution of Fe and Mn from the sediments through their complexation with chloride may contribute, in part, to the release of inorganic P complex from the sediments.

## Conclusion

The amounts of total P in the sediments showed broad ranges, possibly due to difference of geological conditions of the area as well as seasonal variation. Fractionation of P can provide the nature of P in the sediments of the area. Fe, Al-bound P was the major fraction of P in the riverine sediments. Reducing conditions in the sediments may increase the solubility of Fe, Al-bound P, therefore the quantity of P may be released from the sediments and the high concentrations can stimulate phytoplankton bloom. Seasonal changes had an influence on the fractions of P being available which included exchangeable or loosely adsorbed P, Fe,Al- bound P and organic P. The bioavailable P fractions can be used to assess eutrophication in estuaries and coastal waters.

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# Appendices

# Appendix 1

## Physico-chemical properties of bottom water of sampling stations in the dry season (April 2001)

| Station No. | Location | Salinity (‰) | Temp. (° C) | pH | DO (mg $L^{-1}$) | $PO_4$-P (mg $L^{-1}$) |
|---|---|---|---|---|---|---|
| BK1 | Bangpakong River (n) | 20 | 34.3 | 7.6 | 5.5 | 0.12 |
| BK2 | Bangpakong River (o) | 25 | 33.9 | 7.8 | 4.6 | 0.11 |
| AS4 | Angsila | 30 | 32.2 | 8.2 | 6.5 | 0.04 |
| BS12 | Bangsaen | 28 | 32.2 | 8.5 | 6.7 | 0.01 |
| SR18 | Koh Loi | 25 | 31.9 | 8.2 | 4.2 | 0.02 |
| SR22 | Ao Udom | 32 | 31.6 | 8.3 | 4.9 | 0.02 |
| PT28 | Pattaya | 30 | 31.8 | 8.3 | 5.9 | 0.01 |
| MP32 | Nong Fab | 35 | 33.3 | 8.4 | 5.6 | 0.07 |
| MP35 | Rayong River (n) | 29 | 33 | 8.2 | 4.5 | 0.06 |
| MP36 | Rayong River (o) | 30 | 32.1 | 8.2 | 4.6 | 0.02 |
| TP38 | Map Ta Phut (TPI) | 30 | 32.0 | 8.3 | 5.0 | 0.02 |
| TP40 | Had Mae Rum Phung | 30 | 32.3 | 8.3 | 5.3 | 0.001 |
| KG45 | Pasae River (n) | 32 | 33.2 | 8.3 | 6.5 | 0.01 |
| KG46 | Pasae River (o) | 33 | 32.6 | 8.3 | 6.3 | 0.01 |
| CB47 | Chanthaburi River (n) | 22 | 32.7 | 7.9 | 5.4 | 0.004 |
| CB48 | Chanthaburi River (o) | 26 | 32.5 | 7.9 | 5.3 | 0.005 |
| VR49 | Wen River (n) | 31 | 32.7 | 8.2 | 5.1 | 0.01 |
| VR50 | Wen River (o) | 33 | 32.8 | 8.3 | 5.7 | 0.01 |
| TD51 | Trat River (n) | 7 | 32 | 7.7 | 4.7 | 0.01 |
| TD52 | Trat River (o) | 23 | 32.2 | 8.1 | 4.8 | 0.01 |

# Appendix 2

## Physico-chemical properties of bottom water of sampling stations in the wet season (July 2001)

| Station No. | Location | Salinity (‰) | Temp. (° C) | pH | DO (mg $L^{-1}$) | $PO_4$-P (mg $L^{-1}$) |
|---|---|---|---|---|---|---|
| BK1 | Bangpakong River (n) | 0 | 31.3 | 7.0 | 6.0 | 0.09 |
| BK2 | Bangpakong River (o) | 0 | 30.9 | 7.8 | 3.2 | 0.08 |
| AS4 | Angsila | 18 | 29.6 | 7.9 | 4.9 | 0.02 |
| BS12 | Bangsaen | 22 | 30.4 | 8.4 | 5.5 | 0.004 |
| SR18 | Koh Loi | 28 | 29.8 | 8.0 | 3.2 | 0.01 |
| SR22 | Ao Udom | 29 | 29.7 | 8.1 | 2.0 | 0.01 |
| PT28 | Pattaya | 31 | 29.5 | 8.0 | 3.1 | 0.01 |
| MP32 | Nong Fab | 33 | 30.5 | 8.1 | 6.8 | 0.01 |
| MP35 | Rayong River (n) | 33 | 31.2 | 8.1 | 5.7 | 0.12 |
| MP36 | Rayong River (o) | 33 | 30.4 | 8.1 | 5.2 | 0.01 |
| TP38 | Map Ta Phut (TPI) | 33 | 30.5 | 8.1 | 4.4 | 0.01 |
| TP40 | Had Mae Rum Phung | 32 | 29.7 | 8.0 | 5.2 | 0.01 |
| KG45 | Pasae River (n) | 25 | 29.7 | 8.1 | 0.42 | 0.01 |
| KG46 | Pasae River (o) | 27 | 29.8 | 8.2 | 0.12 | 0.01 |
| CB47 | Chanthaburi River (n) | 22 | 29.1 | 8.0 | 0.34 | 0.01 |
| CB48 | Chanthaburi River (o) | 23 | 29.1 | 8.1 | 3.0 | 0.01 |
| VR49 | Wen River (n) | 13 | 29.4 | 7.9 | 6.9 | 0.01 |
| VR50 | Wen River (o) | 16 | 29.6 | 8.1 | 7.9 | 0.002 |
| TD51 | Trat River (n) | 0 | 28.1 | 6.5 | 6.4 | 0.01 |
| TD52 | Trat River (o) | 2 | 28.4 | 7.0 | 6.8 | 0.01 |