## Various Forms of Phosphorus in Sediments of the Eastern Coast of Thailand

## Waewtaa Thongra-ar,\* Chaluay Musika, Phaithoon Mokkongpai, Wanchai Wongsudawan and Arvut Munhapol

Institute of Marine Science, Burapha University, Bangsaen, Chon Buri 20131 Thailand.

\* Corresponding author, E-mail: waewtaa@buu.ac.th

Received 1 Dec 2003 Accepted 23 Jun 2004

**Abstract:** The amount of total phosphorus (P) and its chemical forms were investigated in 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 2,672.50 µg g<sup>-1</sup> dry weight for the dry and wet seasons, respectively. The P in sediments was mainly in an inorganic rather than organic form. Sediment inorganic P fractions were determined by a sequential extraction technique. In the estuarine sediments, the major form of P was Fe, Albound P and the second most abundant form was organic P, whereas the other sediments showed different relative dominant P forms depending on the sediment characteristics of each location. The seasonal change had an influence on the chemical form of P available. In the dry season the available fractions were derived from organic P, those in the wet season were derived largely from Fe, Al-bound P. The available concentrations found for both seasons were very similar in terms of the percentage of total P. It was also found that in most samples, the available forms were very low, comprising less than 10 % of total P.

In this study Fe oxides were found to be the major P sorbent of the sediments, followed by clay contents, while organic matter and CaCO<sub>3</sub> were less effective in sorbing P. In addition, the sediment P concentrations decreased with increasing sediment pH and salinity of the overlying water.

Keywords: phosphorus, sediment, fractionation, bioavailability, Eastern Coast of Thailand.

### INTRODUCTION

Phosphorus (P) is an essential element for all life forms<sup>1</sup> and is considered to be one of the major nutrients which, when present in large concentrations, could cause eutrophication<sup>2</sup>, as well as the key nutrient found to be a limiting factor in natural waters<sup>3</sup>. Phosphorus is found in both inorganic and organic forms in sediments where they serve as sinks and sources of P. It enters the rivers and sea in different chemical forms from various sources, including point sources and nonpoint sources. It is eventually incorporated into bottom sediments. Dissolved inorganic P is considered bioavailable, whereas organic and particulate P forms generally must undergo a transformation into inorganic forms before being considered bioavailable<sup>3</sup>. Phosphorus adsorbed onto sediments can be released into the overlying water depending on the chemical forms in the sediments<sup>4,5</sup> and the environmental conditions<sup>5,6</sup>, such as pH, redox potential, microbes, bioturbation etc. The released P may become available to algae and stimulate blooms of phytoplankton, and excess can lead to eutrophication of the water body.

Knowledge of chemical speciation of sedimentbound P, is necessary to evaluate the bioavailable P which is the amount of P that is biologically usable, because each chemical form has its own ability of release from the sediments<sup>4</sup>. Sediment fractionation helps in identifying the chemical forms of P and can highlight the pathways it takes into the coastal waters<sup>7</sup>. Phosphorus fractionation is commonly achieved by sequential extractions, by which P is supposed to be selectively removed from different forms of attachment in the sediments<sup>8</sup> with a specific reagent preferentially extracting a specific form<sup>7</sup>. The weakly-bound P removed by the first one or two extracting solutions in a sequential extraction method is usually considered bioavailable<sup>3</sup>.

The Eastern Coast of Thailand comprises an area of 5 Provinces; Chachoengsao, Chon Buri, Rayong, Chanthaburi and Trat. This area contains various activities including agriculture, fisheries, tourism, industry and urban communities. It is still in a development stage with a high expansion rate of industrialization and urbanization, which will substantially increase the amount of wastewater discharging into the coastal area. In addition, red tide outbreaks occasionally occur in this area, especially in Chon Buri<sup>9</sup>.

The present study was undertaken to 1) investigate

212

Station	Location	Latitude	Longitude	Main Activity in the Area
BKI	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	13º 17' 12.3" N	100° 54' 12.7" E	Recreation/Beach
SR18	Koh Loi	13º 10' 25.7" N	100° 55' 00.6" E	Urban Community
SR22	Ao Udom	13º 07' 26.7" N	100° 53' 28.2" E	Industry
PT28	Pattaya	12° 55' 49.0" N	100° 52' 25.3" E	Recreation/Beach
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 Community
MP36	Rayong River (o)	12° 38' 54.7" N	100° 17' 04.0" E	Urban Community
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	Prasae River (n)	12° 42' 20.9" N	100° 42' 22.5" E	Aquaculture
KG46	Prasae 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	Weru River (n)	12° 18' 09.6" N	102° 16' 47.3" E	Aquaculture
VR50	Weru River (o)	12º 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



Fig 1. Map showing sampling locations.

the concentrations and chemical forms of sediment P distributed along the Eastern Coast of Thailand and their relation with some sediment characteristics, 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 sediments, which can be used to assess its impact on water quality and living resources in this area.

#### MATERIALS AND METHODS

#### Sediment Sampling

Sediment samples were collected from twenty stations along the Eastern Coast of Thailand from the locations 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. A Garmin GPS-12 global positioning system was used for accuracy in locating the stations. The samples were freeze-dried, sieved through a 2-mm mesh and then homogenized.

During the sediment sampling, salinity, pH and dissolved oxygen at the bottom of the water (1 m depth above the sediment layer) were also measured using a Multi-Parameter System (YSI 650 MDS). Also included was a bottom water sample collection for P analysis.

 Table 2. Sequential chemical extraction method used in this study (De Lange<sup>5</sup>).

Fraction	Extractant	Form of inorganic P
F1	2 N NH <sub>4</sub> Cl	Loosely adsorbed P (exchangeable + carbonate)
F2 F3	0.1 N NaOH 0.5 N HCl	Fe, Al-bound P Ca-bound P, apatite

#### Fractionation of Phosphorus

A sequential chemical extraction method described by De Lange<sup>5</sup> (which is similar to the method of Hieltjies and Lijklema<sup>10</sup>) was used to fractionate the inorganic forms of P in the sediments (Table 2). The difference between total P and the sum of the extracted inorganic P, referred to as residual P, was assumed to be organically bound<sup>10</sup>.

Each sediment sample was also analyzed for total P by the ignition method at 550 °C followed by extraction for 16 h with 1 N HCl, whereas un-ignited samples were prepared for total inorganic P<sup>11</sup>. The total inorganic P was also compared to the sum of the sequentially extracted inorganic P. The organic P was indirectly

obtained by the difference between the total P and inorganic P.

The available P was also extracted from the sediments by direct chemical leaching with a dilute acid-fluoride solution, a combination of HCl and NH<sub>4</sub>F, according to the method of Olsen and Sommers<sup>12</sup>. Phosphorus in all extracts was analyzed by the ascorbic acid method of Strickland and Parsons<sup>13</sup> and the concentrations were measured with a UV-Vis Spectrophotometer Model UV 300 Unicam.

#### Sediment Characterization

Selected sediment characteristics were determined as follows: pH in water at a sediment to solution ratio of 1:2.5, calcium carbonate by the approximate gravimetric method for loss of carbon dioxide<sup>14</sup>, organic matter by the acid-dichromate oxidation method<sup>15</sup>, particle size distribution by the hydrometer method<sup>16</sup> and sediment texture was classified according to the U.S. Agriculture texture triangle<sup>17</sup>. Extractable iron (Fe) and manganese (Mn) oxides were also examined in the sediments. The total (free) and amorphous oxides were extracted by a dithionite-citrate solution and an acid ammonium oxalate solution respectively, according to the method of Ross and Wang<sup>18</sup>. Total oxides were refered to as "cystralline and amorphous oxides". The concentrations of these Fe and Mn oxides in the extracts were measured with a flame atomic absorption spectrophotometer Model AAnalyst 100 (Perkin Elmer, Connecticut, USA).

### **RESULTS AND DISCUSSION**

#### Sediment Characteristics

Selected sediment characteristics are shown in Tables 3 and 4. The sediments for the dry and wet seasons were slightly alkaline with pH ranging from 7.0-8.3 and 7.3-8.5, respectively. High organic matter content (>4%) was mainly found in estuarine sediments, especially in the dry season at the Chanthaburi and Weru River estuaries. CaCO<sub>3</sub> content was very high at Angsila where there are ovster farms through out the year. The texture of the sediments did not vary much between the two seasons. High clay contents were found in the river estuaries, especially Bangpakong. High total and amorphous Fe and Mn oxides were mainly found in the river estuaries, with the highest at Trat. 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 show, however, that in some samples the amount of amorphous oxides was higher than that of total oxides. This was also reported elsewhere in the literature<sup>18,19</sup>. A possible explanation was that some sediments had been subjected to

Station No.	Location	рН	CaCO <sub>3</sub> equivalent (%)	Organic matter (%)	Fe Total Oxides	(mg g <sup>-1</sup> ) Amorp. Oxides	Mn Total Oxides	(mg g <sup>-1</sup> ) Amorp. 5 Oxides	Part Distrik Sand	icle Size oution ( Silt	%) Clay	Texture Class
BK1	Bangpakong River (n)	7.6	0.70	2.22	11.86	10.92	1.84	1.92	30.9	49	19.8	Loam
BK2	Bangpakong River (o)	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	Prasae 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	Prasae 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	Weru 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	Weru 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

Table 3. East Coast sediment characteristics in the dry season (April 2001). Results reported are the mean of three replicas.

processes causing changes in their structure especially an alteration between aerobic and anaerobic conditions. Upon reoxidation, Fe will precipitate and may form an amorphous, highly hydrated solid phase with the structural Si and Al. Thus, most of Fe extracted by dithionite-citrate in those sediments was also oxalateextractable<sup>19</sup>. In addition, oxalate itself can extract poorly crystalline oxides as well<sup>18</sup>.

# Phosphorus in the Sediments and Its Chemical Forms

Total and various forms of P distributed in the sediments in this study 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  $30.0 \text{ to } 2,672.50 \text{ µg g}^{-1} \text{ dry weight for the dry}$ 

and wet seasons, respectively. Statistical analysis (2way ANOVA) indicated that the total P content was significantly different depending on both the station and season (p<0.05). The difference between each station and season is shown in Figure 2. High concentrations were mainly found in the estuarine sediments, especially in the dry season, and the highest concentrations were found in Trat estuary. At most stations in both seasons, the sediment P generally consisted of more inorganic than organic P. This was in agreement with the reports of Syers et al<sup>21</sup>, Fang<sup>22</sup> and Frankowski et al<sup>23</sup> who found that inorganic P constituted the major portion of the total P in their sediment study. From the present study the inorganic P concentrations ranged from 43.33 to 1,358.33 and 11.67 to 1,424.17  $\mu$ g g<sup>-1</sup> dry weight for the dry and wet

Station No.	Location	рН	CaCO <sub>3</sub> equivalent	Organic matter	Fe Total	(mg g <sup>-1</sup> ) Amorp.	Mn Total	(mg g <sup>-1</sup> ) Amorp.	Part Distrik	icle Size oution ('	%)	Texture Class
			(%)	(%)	Oxides	Oxides	Oxides	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 PT28	Ao Udom Pattaya	8.3 8.4	11.83 9.49	0.88 0.99	1.53 1.02	1.19 0.72	0.16 0.09	0.10 0.05	50.1 69.3	40.6 26.1	9.3 4.6	Loam Sandy loam
MP32 MP35	Nong Fab Rayong	8.3 8.5	3.66 3.48	0.90 1.58	0.34 1.25	0.20 0.84	0 0.04	0 0.03	96.4 94.2	0.72 1.4	2.88 4.3	Sand Sand
MP36	River (n) 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	Prasae 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	Prasae 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	Weru River $(n)$	7.7	9.13	3.97	24.47	11.08	0.44	0.29	46.4	31.9	21.8	Loam
VR50	Weru 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	Irat River (o)	7.4	2.05	0.49	51.56	17.81	0.56	0.43	39.7	44.8	15.5	Loam

Table 4. East Coast sediment characteristics in the wet season (July 2001). Results reported are the mean of three replicas.

seasons, respectively, whereas organic P ranged from 12.50 to 1,217.50 and from 18.33 to 1,247.50  $\mu$ g g<sup>-1</sup> dry weight for the dry and wet seasons, respectively.

The inorganic P fractions removable by the sequential extraction are presented in Tables 5 and 6. The results obtained indicated that the sum of the sequential extracted inorganic P of both seasons was in strong agreement with the separately analyzed total inorganic P (r = 0.891, p<0.01) and no significant difference between these values was seen (p>0.05). Similarly, the residual P agreed well with organic P (r = 0.957, p<0.01) and no significant difference between these values was found (p>0.05), indicating the residual P was mainly organic, as was reported earlier by Hieltjies and Lijklema<sup>10</sup>.

The percentage of each chemical form of sediment

P on the basis of total P is presented in Figure 3. In the estuarine sediments, the most abundant fraction of P for both seasons was mainly in the form of Fe, Al-bound P, possibly due to the sediments consisting of higher Fe and Mn oxides than at other locations (Tables 3 and 4), and the second most abundant P in the estuarine sediments was residual P (organic P). For the other locations, Ca-bound P was the major fraction found, e.g. Angsila (AS4), Koh Loi (SR18), Ao Udom (SR22) and Pattaya (PT28), where the sediments consisted of high CaCO<sub>3</sub> content. Statistical analysis showed that the difference of each chemical form of P depended on location and season (p<0.05), which was similar to that of the total P. This may be due to the difference of sediment characteristics of the study area.

Although chemical forms of P taken from sequential

extractions are operationally defined<sup>8</sup>, the results can provide more information on the source or origin of sediment P, its transport and possible remobilization and bioavailability. The first two fractions in sequential extraction schemes (loosely adsorbed P and Fe, Albound P), which can be easily released from sediments by changes of environmental conditions are considered to be potentially bioavailable forms, while Ca-bound P

Ctation	Incontion	Totol D	6	Eractionatio	بر (ارد مرا)		Increase	<u>م</u>			واطوانوسه	0
No.	FOCATION	10141 F (μg g <sup>-1</sup> )	Adsorbed P	Fe,Al-P	Ca-P	Residual P	<u>пюгван</u> (µg g <sup>-1</sup> )	(%)	(µg g <sup>-1</sup> )	(%)	(µg g <sup>-1</sup> )	(%)
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 River (n)	136.67	22.73	21.50	14.00	78.44	51.67	37.8	85.00	62.2	10.75	7.87
MP35	Rayong	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	Prasae 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	Prasae 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	Weru 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	Weru 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

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

Station	Location	Total P	<u>с</u> ,	Fractionatio	n (µg g <sup>1</sup> )		Inorgan	tic P	Organi	сР	Available	Ъ
No.		(μg g <sup>-1</sup> )	Adsorbed P	Fe,Al-P	Ca-P	Residual P	(μg g <sup>.1</sup> )	(%)	$(\mu g g^{-1})$	(%)	(µg g <sup>-1</sup> )	(%)
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	Prasae 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	Prasae 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	Weru 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	Weru 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

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

or apatite, which is the only  $P\ mineral^8\, in\ marine$ sediments, is the least available form or an immobile P form<sup>3,21,24</sup>.

Potential Bioavailability of P in Sediments The available P extracted from the sediments correlated well with the bottom water phosphate for 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). The amount of available P fractions found along the East Coast ranged from 2.73 to 22.15 µg g<sup>-1</sup> and from 3.42 to 72.53 µg g<sup>-1</sup> dry weight for the dry and wet seasons, respectively (Tables 5 and 6). Variation of available P depended on location and season (p<0.05), as indicated in Figure 2; however, in terms of percentage of total P, it ranged from 0.52 to 10.26 % and from 0.55 to 11.4%, for the dry and wet seasons, respectively (Tables

5 and 6).

In the dry season, available P did not correlate with any P fractions except residual P (r = 0.297, p<0.05). However, residual P correlated well with organic P, and the two values obtained did not show any significant difference. This indicated that available P fractions in the dry season were derived from the organic forms of P. López-Piñeiro and Garcia-Navarro<sup>24</sup> also reported that organic P was an important fraction in supplying available P. Although organic P is considered as an



Fig 2. Spatial and temporal distribution of (a) total P and (b) available P in the East Coast sediments. Error bars are ± 1 standard error of three replicas. The stations are coded as defined in Table 1.

immobile form in sediments<sup>4</sup>, it may become available for algae growth by a mineralization process involving microbial activity<sup>1,4,6</sup>. Moreover, the results obtained here show negative correlation of available P with organic matter (r = -0.431, p<0.01) and with dissolved oxygen (r = -0.257, p<0.05) (Table 7). This indicates that utilization of oxygen by microbial activity had occurred during organic matter decomposition, resulting in P-release from organic materials in the sediments. Gonsiorczyk et al<sup>25</sup> also reported that the mineralization of organic matter was the driving force of P-release by sediments in eutrophic lakes. Therefore, the role of organic matter was considered a potential source of available P in the dry season of this study. In addition a significant correlation between the available P and clay, as well as Mn oxides, was obtained (Table 7). This was possibly due to organic matter associated with clay content and metal oxides<sup>26</sup>.

In the wet season, available P significantly correlated with loosely adsorbed P (r = 0.322, p < 0.05) and Fe, Albound P (r = 0.267, p < 0.05) (Table 8), indicating the bioavailability of P in the wet season was 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)<sup>4</sup>. Sediment pH is associated with Eh<sup>27</sup>. 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<sup>+2</sup>) and ferrous (Fe<sup>+2</sup>) ions<sup>28</sup>, and allow



**Fig 3.** Different chemical forms of phosphorus distributed in the East Coast sediments in (a) dry season (April 2001) and (b) wet season (July 2001). The stations are coded as defined in Table 1.

 Table 7. Correlation coefficients of various forms of phosphorus, selected sediment characteristics, and some water qualities in the dry season (April 2001) (N = 51- 60).

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**
CaČO,	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)

phosphate to diffuse more freely into the overlying water. Possibly, the release of P in the river estuaries was largely from Fe, Al-bound P, rather than from loosely adsorbed P, because there was a larger portion of the former fraction, which agrees with the reports of Upchurch et al<sup>29</sup> and Gonsiorczyk et al<sup>25</sup>. The available P in 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 a correlation could not be obtained with any Fe oxides, since Fe oxides are more difficult to reduce than Mn oxides<sup>26</sup> resulting in P being strongly held with Fe rather than with Mn. This being the case, the release of P from Fe, Al-inorganic complexes in the wet season was mainly from Mn oxides, especially the amorphous form, rather than from Fe oxides.

## Relationship between Sediment P and Selected Sediment Characteristics

For both seasons, sediment P (both inorganic and organic forms) was most strongly correlated with total and amorphous Fe oxides, followed by clay content (Tables 7 and 8). No significant correlation between total P and organic matter or CaCO<sub>3</sub> could be obtained. This correlation indicated that both cystralline and amorphous Fe oxides were the major P sorbent of the sediments, followed by clay, respectively, while organic matter and CaCO<sub>3</sub> were less effective or may not be 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<sup>26</sup>. They have high specific surface areas and great reactivity<sup>26</sup>, making them a

Table 8. Correlation coefficients of various forms of phosphorus, selected sediment characteristics and some water qualitiesin the wet season (July 2001) (N = 54-60).

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,	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)

powerful sorbent.

For inorganic P fractions, a positive and strong correlation of the two Fe oxides was obtained with the Fe, Al-bound P fraction only. The correlation between organic P and Fe oxides obtained seemed to be indirect, possibly 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, which agrees with the findings of Shukla et al<sup>20</sup> and Börling et al<sup>30</sup>. In addition, Shukla et al<sup>20</sup> reported that CaCO<sub>2</sub> is less effective than amorphous Fe in sorbing added inorganic P in the laboratory and in the lake environment. CaCO<sub>3</sub> also acts to dilute the Fe and Al sites as reported by McCallister and Logan<sup>19</sup>, which agreed with the negative correlation coefficient obtained between Fe, Al-bound P and CaCO<sub>2</sub> content, especially in the wet season (r =-0.426, p<0.01). Also McDowell et al<sup>31</sup> found that the surface areas of CaCO, and organic matter are lowenergy adsorption sites for P sorbing in soils. These reports are all in agreement with the data presented in the study.

In addition, sediment P in this study showed a strong negative relationship with pH (Tables 7 and 8) indicating that the increase of pH may cause the release of P from the sediments to water, which agreed with the findings of McCallister and Logan<sup>19</sup> and Carpenter and Smith<sup>32</sup>. This was possibly due to the OH- ions competing with  $PO_4^{3-}$  ions associated in the sediments<sup>23</sup>. A similar relationship was also obtained between sediment P and salinity of the overlying water, indicating that P content of sediments decreased with increasing salinity or P desorption occurred as salinity increased, which agreed with the findings of Upchurch et al<sup>29</sup> and Carpenter and Smith<sup>32</sup>. A possible explanation for this is that the adsorbed P is released or displaced by competing anions which predominate in seawater, such as chloride or sulfate<sup>29</sup>. 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.

In conclusion, the total P in sediments of the study area showed broad ranges, possibly due to the difference of sediment characteristics of the study area, especially the amount of Fe oxides, which is considered to be the major P sorbent of the sediments. Fractionation of P can show the nature of P in the sediments of the area. Fe, Al-bound P was the major fraction of P in the estuarine sediments. Reducing conditions in the sediments may increase the solubility of Fe, Al-bound P. Therefore, P may be released from the sediments and at high concentrations can stimulate phytoplankton blooms. The season had an influence on the fractions of P available, which included exchangeable or loosely adsorbed P and Fe, Al-bound P found in the wet season and organic P found in the dry season. The bioavailable P fractions can be used to assess eutrophication in estuaries and coastal waters.

#### **ACKNOWLEDGEMENTS**

Financial support provided by the Institute of Marine Science, Burapha University is gratefully acknowledged.

#### REFERENCES

- Correll DL (1998) The role of phosphorus in the eutrophication of receiving waters: a review. J Environ Qual 27, 261-6.
- Gerdes P and Kunst S (1998) Bioavailability of phosphorus as a tool for efficient P reduction schemes. Wat Sci Tech 37, 241-7.
- 3. Reddy KR, Kadlec RH, Flaig E and Gale PM (1999) Phosphorus retention in streams and wetlands: a review. *Crit Rev Environ Sci Tech* **29**, 83-146.
- Mesnage V and Picot B (1995) The distribution of phosphate in sediments and its relation with eutrophication of a Mediterranean coastal lagoon. *Hydrobiologia* 297, 29-41.
- De Lange GJ (1992) Distribution of various extracted phosphorus compounds in the interbedded turbiditic/pelagic sediments of the Madeira Abyssal Plain, eastern North Atlantic Mar Geol 109, 115-39.
- Matsuda O, Kataoka N and Endo T (1989) A role of microbes in phosphorus cycle in sediments. In: Recent Advances in Microbial Ecology. Proceedings of the 5<sup>th</sup> International Symposium on Microbial Ecology (ISME 5) (Edited by Hattori T, Ishida Y, Maruyama Y, Morita RY and Uchida A), pp 360-4. Japan Scientific Societies Press, Tokyo.
- Balchand AN and Nair SM (1994) Fractionation of phosphorus in the sediments of a tropical estuary. *Environ Geol* 23, 284-94.
- Pettersson K, BostrÖm B, Jacobsen OS (1988) Phosphorus in sediments – speciation and analysis. *Hydrobiologia* 170, 91-101.
- Thongra-ar W, Pinkaew K, Musika C and Wongsuwan W (1998) A baseline study on the occurrence of red tide plankton in the coastal waters from the Bang Pakong River mouth to Sri Racha, Chon Buri province. *Thai J Aqua Sci* 4, 60-77.
- Hieltjes AHM and Lijklema L (1980) Fractionation of inorganic phosphates in calcareous sediments. J Environ Qual 9, 405-7.
- Aspila KI, Agemain H. and Chau ASY (1976) A semiautomated method for the determination of inorganic, organic and total phosphate in sediments. *Analyst* 101, 187-97.
- 12. Olsen SR and Sommers LE (1982) Phosphorus. In: Method of Soil Analysis, Part II. Chemical and Microbiological Properties, 2nd ed (Edited by Page AL, Miller RH and Keeney DR), pp 403-30. American Society of Agronomy, Inc, and Soil Science Society of America, Inc, Publishers, Madison, Wisconsin, USA.
- Strickland JDH and Parsons TR (1972) A Practical Handbook of Seawater Analysis. Fisheries Research Board of Canada, Ottawa, pp 1-310.

- Goh TB, Arnaud RJSt and Mermut AR (1993) Carbonates. In: Soil Sampling and Methods of Analysis (Edited by Carter MR), pp 177-85. Canadian Society of Soil Science. Lewis Publishers, Boca Raton.
- 15. Nelson DW and Sommers LE (1982) Total carbon, organic carbon and organic matter. In: Method of Soil Analysis, Part II. Chemical and Microbiological Properties, 2nd ed (Edited by Page AL, Miller RH and Keeney DR) pp 539-79. American Society of Agronomy, Inc, and Soil Science Society of America, Inc, Publishers, Madison, Wisconsin, USA.
- English S, Wilkinson C and Baker V (1994) Survey Manual for Tropical Marine Resources. ASEAN-Australia Marine Science Project, Living Coastal Resources, Australia Institute of Marine Science, Townsville, pp 1-368.
- 17. Hillel D (1998) Environmental Soil Physics Academic Press, San Diego.
- Ross GJ and Wang C (1993) Extractable Al, Fe, Mn, and Si. In: Soil Sampling and Methods of Analysis. (Edited by Carter MR), pp 239-41. Canadian Society of Soil Science. Lewis Publishers, Boca Raton.
- McCallister DL and Logan TJ (1978) Phosphate adsorptiondesorption characteristics of soils and bottom sediments in the Maumee River basin of Ohio. J Environ Qual 7, 87-92.
- Shukla SS, Syers JK, Williams JDH, Armstrong DE and Harris RF (1971) Sorption of inorganic phosphate by lake sediments. *Soil Sci Soc Amer Proc* 35, 244-9.
- 21. Syers JK, Harris RF and Armstrong DE (1973) Phosphate chemistry in lake sediments. J Environ Qual 2, 1-14.
- 22. Fang TH (2000) Partitioning and behaviour of different forms of phosphorus in the Tanshui estuary and one of its tributaries, Northern Taiwan. Estua Coast Shelf Sci 50, 689-701.
- Frankowski L, Bolalek J and Szostek A (2002) Phosphorus in bottom sediments of Pomeranian Bay (Southern Baltic-Poland). Estua Coast Shelf Sci 54, 1027-38.
- López-Piñeiro A and Garcia-Navarro A (2001) Phosphate fractions and availability in vertisols of south-western Spain. *Soil Sci* 166, 548-56.
- 25. Gonsiorczyk T, Casper P and Koschel R (1998) Phosphorusbinding forms in the sediment of an oligotrophic and an eutrophic hardwater lake of the Baltic lake district (Germany). Wat Sci Tech **37**, 51-8.
- Sparks DL (1995) Environmental Soil Chemistry. Academic Press, San Diego.
- 27. Tan KM (1982) Principles of Soil Chemistry. Marcel Dekker, Inc, New York.
- Olsen CR, Cutshall NH and Larsen IL (1982) Pollutantparticle associations and dynamics in coastal marine environments: a review. *Mar Chem* 11, 501-33.
- 29. Upchurch JB, Edzwald JK and O'Melia CR (1974) Phosphates in sediments of Pamlico Estuary. *Environ Sci Tech* **8**, 56-8.
- Börling K, Otabbong E and Barberis E (2001) Phosphorus sorption in relation to soil properties in some cultivated Swedish soils. Nutrient Cycling in Agroecosystems 59, 39-46.
- 31. McDowell R, Sharpley A, Brookes P and Poulton P (2001) Relationship between soil test phosphorus and phosphorus release to solution. *Soil Sci* **166**, 137-49.
- Carpenter PD and Smith JD (1984) Effect of pH, iron and humic acid on the estuarine behaviour of phosphate. *Environ Tech* 6, 65-72.