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Elemental composition of suspended particulate matter in Bangpakong River Estuary, Thailand

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Abstract: The elemental composition of various suspended matters in a large river estuary was investigated. Chlorophyll *a* (Chl *a*) concentration, particulate organic carbon (POC), particulate organic nitrogen (PON) and particulate phosphorus (PP) were determined in the Bangpakong River Estuary, Thailand, in November 2002 and November 2004. The latter observation included the upstream sites (salinity varied from 0–27). Moreover, the particulate phosphorus was determined by dividing into particulate organic phosphorus (POP) and particulate inorganic phosphorus (PIP). Good correlations between Chl *a* and POC, PON, PP (or POP) were observed. The average stoichiometric ratio of suspended matter (organic C : N : P) calculated from each slope of linear regression was consistent with the Redfield ratio. It showed that the major composition of organic particulate matter in the estuary predominantly originated from the phytoplankton—derived material. However, the PIP contribution to total PP (11–48%) in the estuary can not be ignored. Additionally, PIP contributions in the mixing zone between fresh and saline waters were particularly high (up to 75%). PIP decreased gradually toward the offshore likely, because inorganic phosphorus was released from suspended matter and PIP was also diluted with an increase of salinity.

Keywords: *estuary, suspended matter, Bangpakong River, biophilic element, phosphorous*

1. Introduction

In estuaries, phytoplankton production is very high due to sufficient nutrient supply from riverine run off. Also, the biogeochemical processes are active in the estuarine environment due to the dramatic change in salinity and high phytoplankton production. On the other hand, suspended matter, contains many kinds of allochthonous materials, including nutrients, organic materials and heavy metals, is transported from river to marine environments autochthonous materials are also produced within ecosystem (TURNER and MILLWARD, 2002). Therefore, the estuaries play an important role in material exchanges and biogeochemical processes between the land and marine environments. Suspended matter is studied widely in estuarine environments in order to characterize and better understand the nutrients and organic materials supplied in the form of suspended matter from riverine input which can greatly influence coastal environments. Previous studies reported that the changes of salinity are able to regulate the adsorption and desorption of nutrients, especially phosphorus (FANG, 2000; SUZUMURA *et al.*, 2000).

Unlike carbon and nitrogen, the chemical nature and forms phosphorus has been poorly characterized in aquatic biogeochemical processes thus far, but recent studies have demonstrated that phosphorus plays a great role in limiting global primary productivity (SUZUMURA and INGALL, 2004 and references therein). Hence, it is necessary to better

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understand the characterization and behavior of phosphorus in aquatic environments.

In the present study, the biophilic elemental constituents (C, N and P) of suspended matter as well as Chlorophyll *a* (Chl *a*) were investigated in a large river, the Bangpakong River Estuary, Thailand in order to more understand about the behavior and characteristic of suspended matter in estuarine area. Moreover, we showed that the contribution of particulate inorganic phosphorus to total particulate phosphorus can not be ignored as well as the abundance and distribution of chemical fractions of phosphorus contained in suspended matter was also quantified along the Bangpakong River to the estuary.

2. Materials and Methods

2.1 Study area

The Bangpakong River is one of the most important large rivers that discharging fresh water into the head of the Gulf of Thailand and is considered to be an important source of inorganic nutrients and organic materials loaded into the eastern part of the upper Gulf of Thailand. Additionally, the Bangpakong River Estuary is a eutrophic embayment where phytoplankton bloom often occurs in the surrounding area (BURANAPRATHEPRAT *et al.*, 2002). The watershed covers 18,500 km^2, and the river runs from the conjunction of two smaller rivers, the Ha-nu-man and the Praprong, 220 km upstream of the river mouth. The Bangpakong River is strongly influenced by the wet Southeast monsoon from late May to October-mid November and the dry Northeast monsoon, during the late November/February period, thus generating two well-marked seasons. Usually, the wet season lasts from June to November and the dry season from December to May. Air temperatures ranged from 23.8℃ to 32.6℃, with a yearly average of 27.9 ℃. Annual rainfall averaged 1315mm for the period 1961–1991, and the number of rainy days covered one third of the year. Usually September has the maximum rainfall. About 96% of the annual river discharge occurs during the wet season (BORDDALO *et al.*, 2001). Recalculating the data from BOONPHAKDEE *et al.* (1999) for the period 1993–1996, the total annual freshwater discharge into the inner Gulf of Thailand averaged 8.44km^3 (512m^{3}s^{-1}during the wet season and 21m^{3}s^{-1}during the dry season). In the estuarine area, the tidal current plays an important role in transporting particles out of the estuary in a short time, and the seasonal variation in residence time depends on the variation of wind-driven circulation (BURANAPRATHEPRAT and YANAGI, 2003). Recently, the Bangpakong River Estuary is eutrophicated and the red tide (e.g., *Ceratium furca*) has often occurred. According to the large supply of inorganic nutrients from riverine input, dissolved inorganic nitrogen (DIN), phosphate and silicic acid concentration up to 75.5, 4.85 and 66.0 μM were observed in Bangpakong Estuary (MEKSUMPUN S., Kasetsart Univ., personal communication)

2.2 Sampling strategies

This study was conducted in 2 observation cruises (November 2002 and November 2004) in the Bangpakong River Estuary, including upstream of the river in the latter observation. Surface water samples were collected from sampling stations (Fig. 1) using a clean bucket and stored in plastic bags in dark and cool conditions until further filtration in the laboratory. Additionally, salinity of surface water was measured onboard using a CTD (YSI 6600).

2.3 Filtration and chemical analysis

Particulate matter measured in this study included Chlorophyll *a* (Chl *a*), particulate organic carbon (POC), particulate organic nitrogen (PON), particulate phosphorus (PP) and particulate inorganic phosphorus (PIP). PIP was not measured on the samples collected in November 2002. For Chl *a* sample, water sample was filtered though glass fiber filters (Whatman GF/F), and then Chl *a* was extracted from the filter with 90% acetone in glass tube, placed in dark at 4℃ for 24 hours and determined following the spectrophotometric method of LORENZEN (1967), as detailed in PARSONS *et al.* (1984). To determine POC and PON, water sample was filtered through a pre-combusted Whatman GF/F (450℃, 2 hours) and rinsed with deionized water after filtration to remove the salt, and then the filtered sample was measured

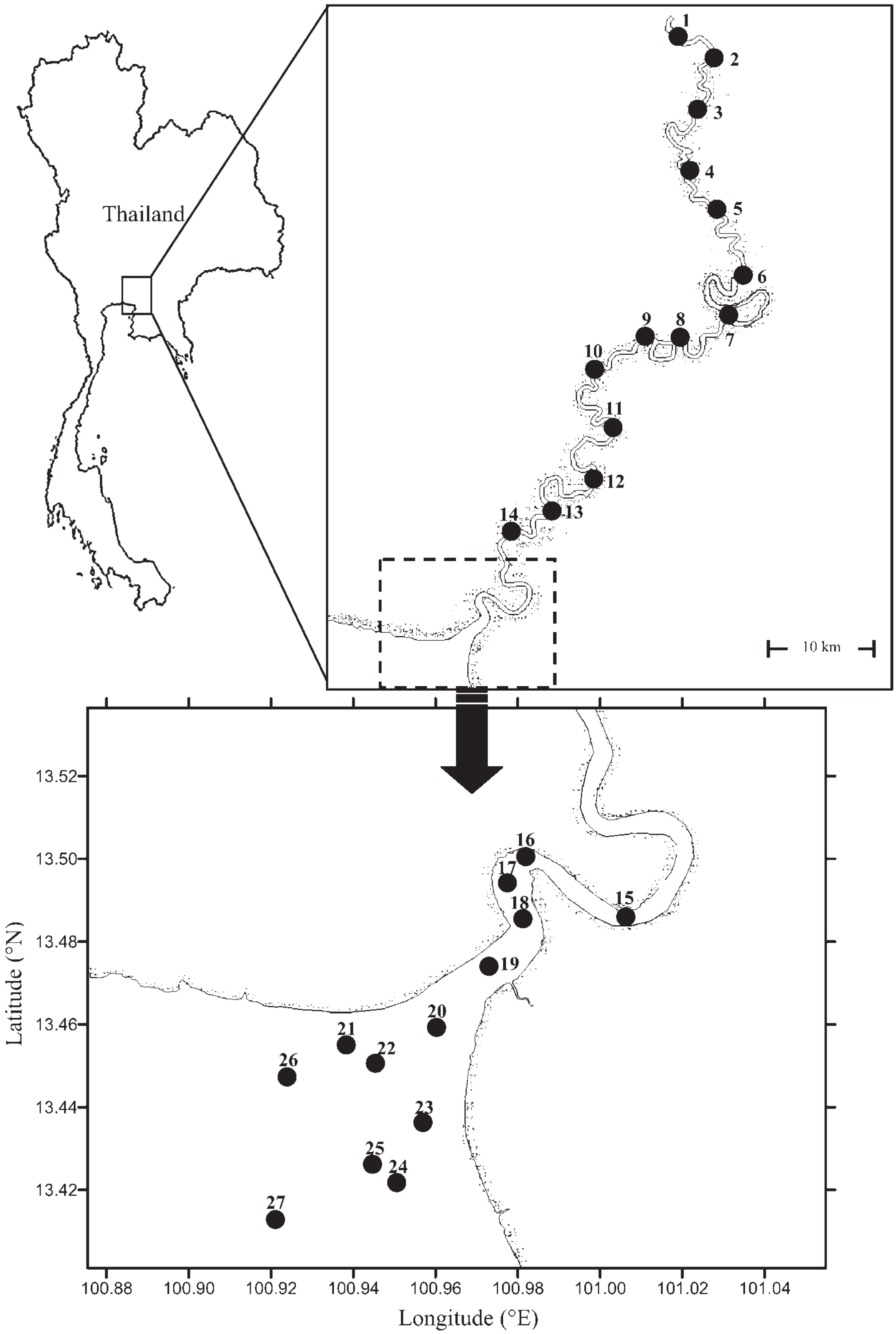

Fig. 1. Location of sampling stations in Bangpakong River and estuary.

Table 1. Salinity and concentrations of particulate biophilic elements in surface water sample from Bangpakong River Estuary (ND = no data).

Station No.	2002					2004						
	Salinity	Chl *a* (μgl^{-1})	POC (μmol-Cl^{-1})	PON (μmol-Nl^{-1})	PP (μmol-Pl^{-1})	Salinity	Chl *a* (μgl^{-1})	POC (μmol-Cl^{-1})	PON (μmol-Nl^{-1})	PP (μmol-Pl^{-1})	PIP (μmol-Pl^{-1})	POP (μmol-Pl^{-1})
15	5.3	2.4	131	14.6	1.55	30.5	2.5	105	13.7	0.43	0.04	0.38
16	3.2	6.7	149	18.1	1.52	30.9	3.6	51	7.5	0.57	0.22	0.35
17	3.4	2.7	143	22.6	1.88	30.9	4.3	62	8.4	0.70	0.26	0.44
18	17.2	17.1	202	30.7	ND	31.0	5.3	92	11.9	0.84	0.16	0.68
19	13.8	40.1	415	61.9	7.33	31.6	11.3	71	7.8	1.91	0.84	1.07
20	29.1	7.5	130	17.4	1.13	31.8	8.0	85	10.8	0.81	0.36	0.45
21	24.1	8.3	194	28.6	ND	31.7	40.1	159	22.3	1.90	0.70	1.19
22	16.6	28.0	279	42.0	4.05	31.8	20.0	119	17.2	1.22	0.52	0.70
23	23.3	28.0	ND	ND	ND	32.1	8.0	67	7.0	0.48	0.14	0.35
24	18.8	17.8	122	15.7	1.38	32.0	2.7	57	6.4	0.43	0.19	0.24
25	22.1	10.7	235	22.1	ND	32.0	4.0	44	4.9	0.35	0.14	0.21
26	23.6	2.0	ND	ND	ND	32.0	10.8	88	10.3	0.76	0.32	0.44
27	28.8	2.1	ND	ND	ND	32.0	2.7	58	6.0	0.40	0.17	0.24

with a CHN corder (MT–5, Yanaco, Japan) after acidification with the fumes of concentrated HCl to remove carbonates. Prior to filtration of PP and PIP, a pre-combusted Whatman GF/F (450℃, 2 hours) was sequentially washed with 1M HCl and deionized water and rinsed thoroughly with 0.17 M Na_2SO_4 after filtration (SUZUMURA *et al.*, 2004). PP and PIP were determined based on the protocol of ASPILA *et al.* (1976) as detailed in SUZUMURA *et al.* (2004). Briefly, PIP filtered samples were extracted with 1M HCl as ortho-P at room temperature for 12 hours, while PP filtered sample was combusted at 470℃ in a muffle furnace for 2 hours, kept until they cooled down and were also extracted with 1M HCl, under the same condition as was used for the PIP samples. Aliquots of the supernatant were allowed to determine the ortho-phosphate concentration using the acid molybdate-ascorbic method (PARSONS *et al.*, 1984). Particulate organic phosphorus (POP) was calculated from subtraction of PIP from PP.

3. Results and Discussion

3.1 *Distribution and composition of suspended matter in estuary*

The results of chemical constituents of suspended matter and salinity in the Bangpakong Estuary are given in Table 1. In 2002 observation, salinity generally increased from the riverine sites to the estuarine sites (salinity 3–29) (Table 1). The Chl *a* concentration varied from 2.03 to 40.1 μg Chl *a* l^{-1} with the highest concentration found near the river mouth. As given in the same table, POC and PON ranged from 122 to 415 μmol-C l^{-1} and 15 to 62 μmol-N l^{-1}, respectively. PP varied between 1.13 and 7.33 μmol-P l^{-1}. In Fig. 2, it is apparent that the concentrations of chemical constituents containing of suspended matter showed the highest concentration around the river mouth. Moreover, the distribution of organic particulate matter showed a similar trend to the distribution of the Chl *a* concentration which also increased gradually from inland river area and peaked at the river mouth. Hence, the increase of organic particulate matter in the Banpakong River Estuary associated with the increasing relative phytoplankton biomass. Additionally, good linear correlations were observed between Chl *a* and POC, PON and PP in surface seawater (Fig. 4). In 2004 observation, the high concentration of Chl *a* was also observed near the river mouth (40.1 μg Chl *a* l^{-1}). POC and PON varied from 44.3 to 159 μmol-C l^{-1} and 4.89 to 22.3 μmol-N l^{-1}, respectively. PP and POP ranged from 0.35 to 1.90 μmol-P l^{-1} and 2.27 to 1.19 μmol-P l^{-1}, while PIP ranged between 0.14 and 0.70 μmol-P l^{-1}. The percentage of PIP contributing to PP was between 11% and 48% with an average of 36%. The same as the results of the 2002 observation, the distribution of organic particulate matter

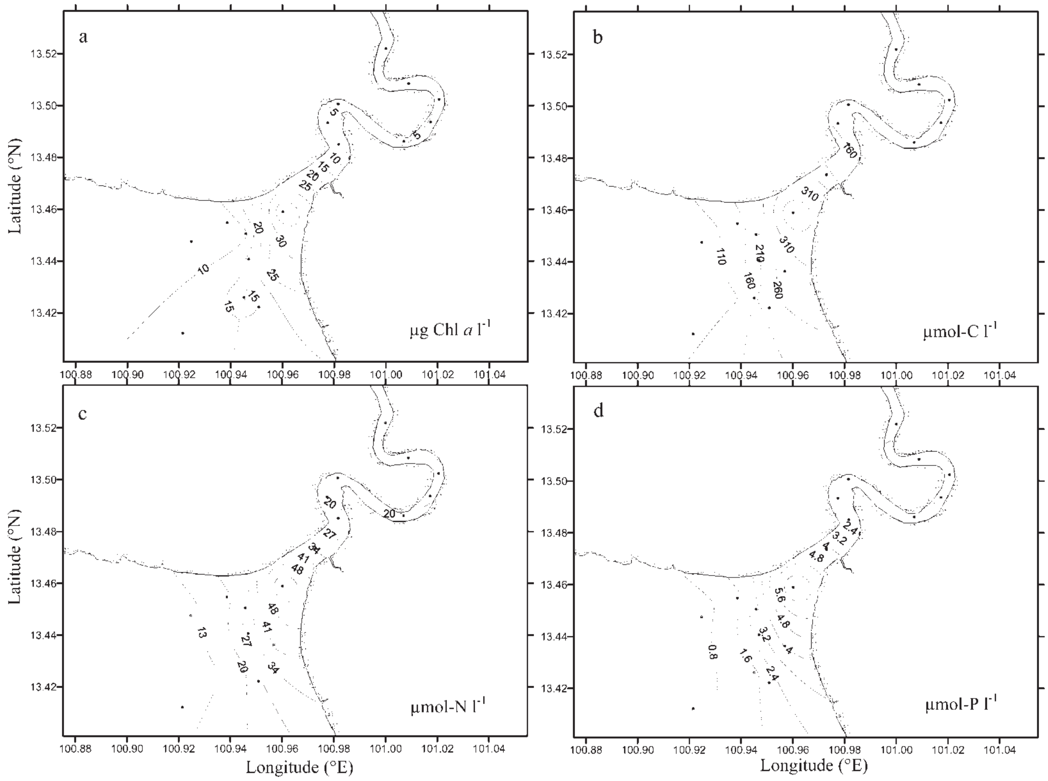

Fig. 2. Distribution of Chl *a* (a), POC (b), PON (c) and PP (d) in Bangpakong River Estuary (2002 observation).

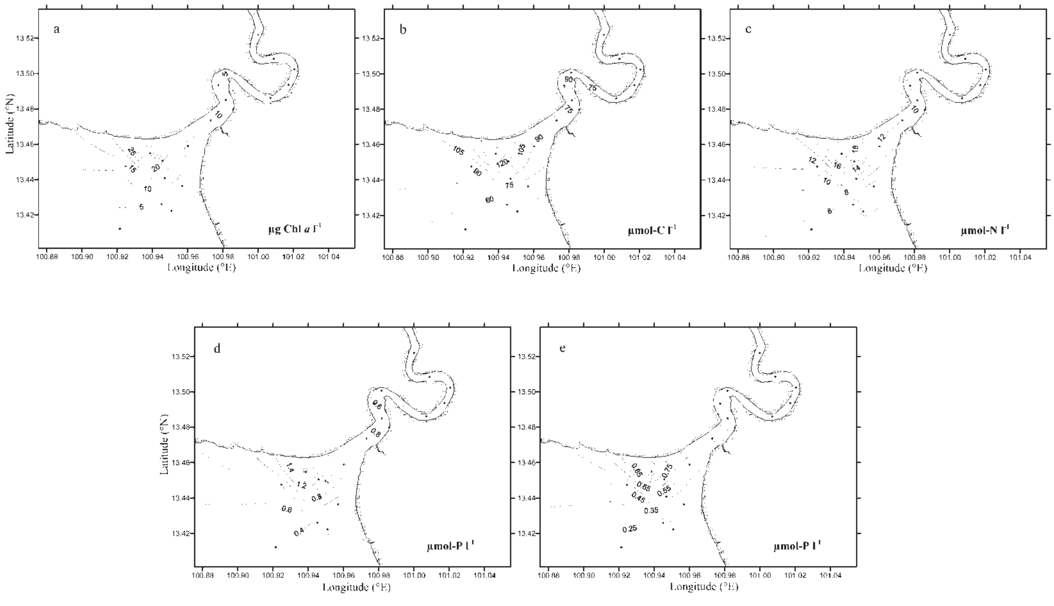

Fig. 3. Distribution of Chl *a* (a) , POC (b) , PON (c) , PP (d) and POP (e) in Bangpakong River Estuary (2004 observation).

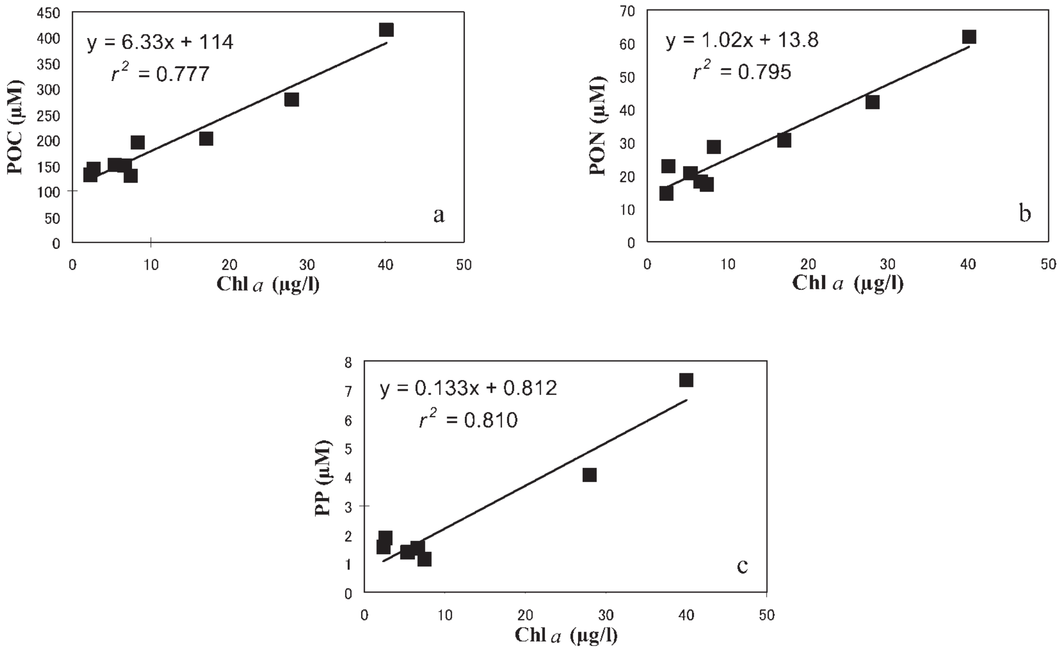

Fig. 4. Linear correlations between Chl *a* and POC (a), PON (b) and PP (c) ($P<0.05$) in 2002 observation.

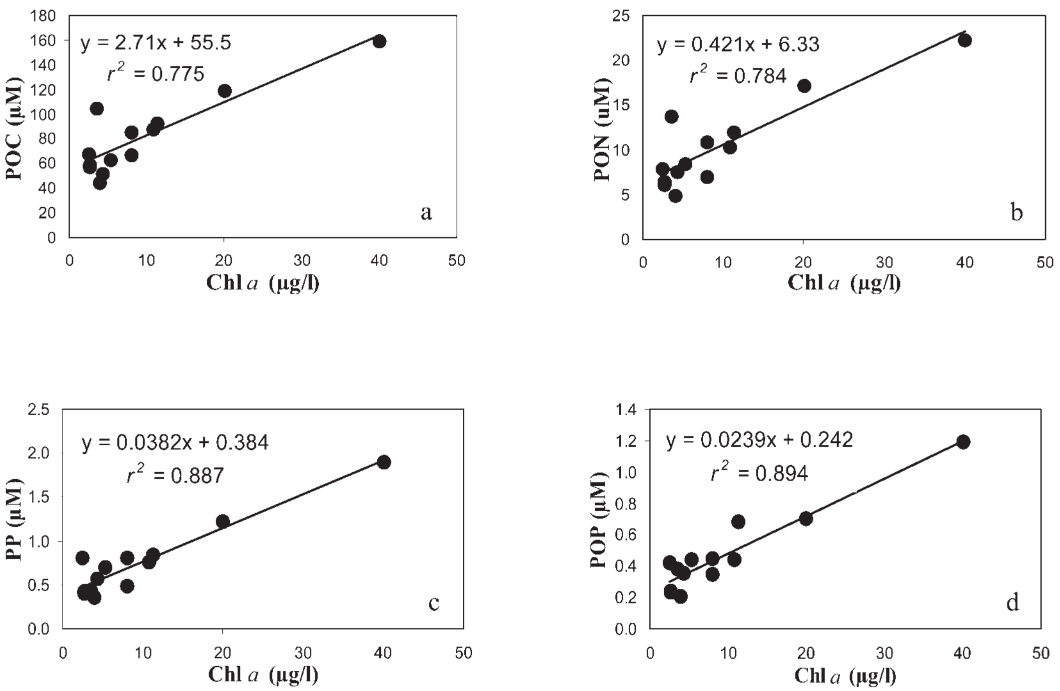

Fig. 5. Linear correlations between Chl *a* and POC (a), PON (b), PP (c) and POP (d) ($P<0.05$) in 2004 observation.

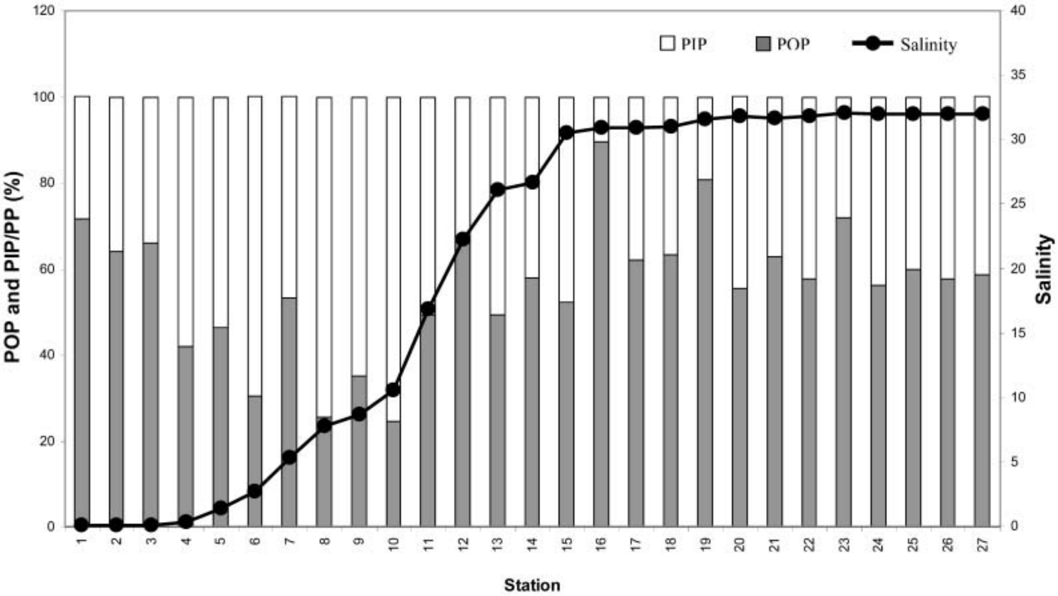

Fig. 6. Distribution of relative abundance of PIP and POP as percentage of PP plotted with salinity along Bangpakong River.

synchronized with the distribution of Chl *a*; they obviously increased around the river mouth (Fig. 3). The Chl *a* increase around the river mouth was probably due to the large supply of inorganic nutrients from riverine runoff and resulted in an increase of phytoplankton biomass at the mouth. Good linear correlations between Chl *a* and particulate biophilic elements were also noted in the 2004 observation (Fig. 5). These results strongly suggested that the particulate organic matter in the Bangpakong River predominantly originated from phytoplankton-derived materials.

Generally, the C : N : P molar ratio is commonly used to indicate chemical constituents in phytoplankton cells and also to provide a better understanding of the importance of suspended matter as a food source for suspension feeders (TANAKA *et al.*, 1998). In the present study, the stoichiometric ratio of organic suspended matter was calculated using the slope value of the linear regression of Chl *a* and POC, PON and PP, respectively. We can assume that the slope in these graphs shows the phytoplankton-derived organic matter, and that parts vary depending on the Chl *a* concentration. On the other hand, we can assume that the y-intercept value shows the detritus-derived organic matter and that parts do not vary depending on the change in Chl *a* concentration. The calculated C : N : P molar ratio of 106 : 17 : 2.2 obtained from 2002 observation was quite similar to the average C : N : P molar ratio in living phytoplankton cells of 106 : 16 : 1 (REDFIELD *et al.*, 1963). Nevertheless, the phosphorous content was 2-fold higher than the Redfield ratio. There are two possible explanations for this result. One is that PIP in the suspended matter can not be ignored and another is that phytoplankton accumulates phosphorus in their cells.

As described above, the phosphorus content in suspended matter was determined separately into PP and PIP, and POP was calculated as the difference between PP and PIP in the 2004 observation. The elemental C : N : P ratio of 106 : 17 : 0.9 was obtained when POP was employed to assume the stoichiometric ratio of phytoplankton-derived organic matter, while the C : N : P molar ratio of 106 : 17 : 1.5 was achieved when using PP fraction. This means that the phosphorus content in suspended matter was 1.5 times higher than the Redfield ratio that corresponded well with that we found in

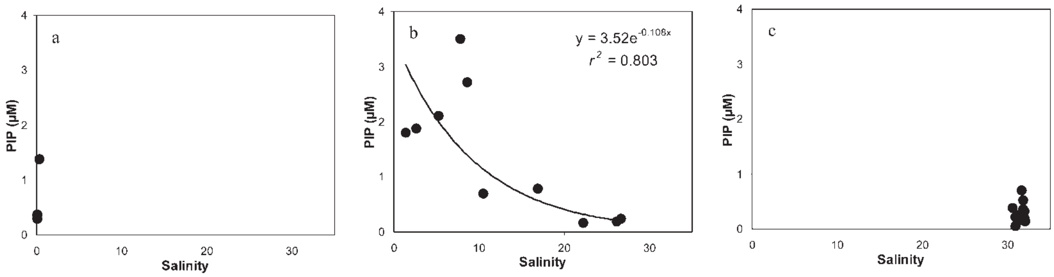

Fig. 7. Relationships between salinity and PIP concentration in different zonation ; fresh water (a), mixing water (b) and saline water (c) ($P<0.05$).

our 2002 observation. The results clearly confirmed that the PIP in suspended particles in surface water can not be ignored in the Bangpakong River Estuary.

3.2 Characterizations of chemical fractionation of phosphorus suspended matter in Bangpakong River

PIP has contributed significantly to the PP pool and can be released into ambient water as soluble ortho-P (LEBO, 1991; SUZUMURA *et al.*, 2004; YOSHIMURA *et al.*, 2007). In this study, the distribution and characteristics of chemical fractions of phosphorus were also investigated along the Bangpakong River. The distribution of the reactive abundance of POP and PP as a percentage of PP along the river and plot against salinity are given in Fig.6. The Bangpakong River was zoned into three sections, namely freshwater (salinity 0–0.5), mixing water (salinity 0.5–30) and saline water (salinity$>$30) by salinity. Generally, the contribution of the PIP fraction was less than that of POP in freshwater with average PIP accounting for 39% of PP. In mixing water, PIP increased gradually and was generally higher than the POP fraction, accounting for 33% to 75% of PP with an average of 56%. Arguably, the contribution of PIP to PP was mostly lower than POP in saline water, for PIP contributed from 11% to 48% to PP. The result suggested that PIP fractions were produced and have contributed significantly to PP in mixing water and maintained a low contribution in saline water. These results also corresponded well with PIP fraction abundance in the Arakawa River, Tokyo Bay. SUZUMURA *et al.* (2004) reported that the relative abundance of PIP as a percentage of PP varied from 12% to 86% in the Arakawa River, the PIP concentration was gradually decreased with increasing salinity, and an 11% to 75% variation was observed in this study (Bangpakong River). Fig. 7 clearly shows the significant correlation between the PIP fraction and salinity ($r^2=0.802$, $P<0.05$) in mixing water. PIP fraction decreased not linearly but exponentially. If PIP fraction is diluted by saline water which contains a low PIP content, PIP fraction should decrease linearly with the increasing salinity. Our result indicates that PIP fraction in mixing water was released from suspended matter into ambient water with an increase of salinity, and PIP was also diluted with saline water with a low PIP content. A few earlier studies including field observations and laboratory experiments have demonstrated that PIP fractions was released from suspended matter as ortho-P into ambient water with increasing salinity (LEBO, 1991; SUZUMURA *et al.*, 2004). The results of the present study corresponded closely with those previous studies, investigating PIP behaviors in coastal environments.

4. Conclusion

In this study, the suspended matter in surface water was characterized in estuarine environment, and the distribution and characteristic of chemical fractions of phosphorus was also investigated along the Bangpakong River. We conclude that (1) the suspended matter in the Bangpakong River Estuary primarily originated from phytoplankton-derived matter; (2) PIP fraction can not be ignored in estuarine water; and (3) PIP has contributed largely to PP in mixing water (salinity 0.5–30), and was released from suspended matter and also diluted with an increase of salinity.

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