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Temporal Variability of Nutrient Budgets in a Tropical River Estuary : the Bangpakong River Estuary, Thailand

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Abstract

Water, salt, dissolved inorganic nitrogen (DIN), and dissolved inorganic phosphorus (DIP) budgets in the Bangpakong Estuary were conducted by repeated observations and multiple box modeling. Water samples for inorganic nutrient analyses were collected monthly from June 2000 to May 2001. Flushing time at the estuary depicts high variations ranging from 1.4 (October 2000) to 80 days (February 2001) with an annual mean of 15.2 days. Seasonal variation in salinity gradients and estuarine Richardson numbers show the Bangpakong Estuary was partially stratified during the wet season and a well-mixed estuary in the dry season. Riverine nutrient inputs and distributions of nutrient concentrations within the river estuary varied in space and time. Temporal variations in fluxes were strong within inter-seasonal scales owing to water fluxes and system concentrations. The increase of DIN and DIP fluxes in the estuary may be the results of degradation of particulate organic matter. The Bangpakong Estuary appears to be a heterotrophic system where respiration exceeds photosynthesis (p-r < 0) and a denitrifying system. Seasonal variations in biogeochemical rates were attributable to differences in magnitude of freshwater inputs.

Keywords: nutrients budget; nutrient distribution; nonconservative flux; the Bangpakong River or Estuary, Thailand

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1. Introduction

Estuaries are important regions in the transport and transformation of materials from terrestrial sources and anthropogenic activities. These regions also play an important role in processing nutrients exchanged between land and sea (Eyre and Twigg, 1997). The high nutrient and productivity of estuaries make them rich nurseries and feeding grounds for juvenile fish. Globally, estuarine nutrient loads have steadily increased over recent decades coincident with rises in the human population and industry. Such increases may boost primary production and provide either an additional sink and/or source for carbon, nitrogen and phosphorus (Gordon *et al.*, 1996) in coastal waters.

Nutrient budgets have been prepared for many estuaries and applied as management tools in several watersheds (Howarth *et al.*, 2000; Gazeau *et al.*, 2004; Cao *et al.*, 2005). Research on ecological impacts of altered biogeochemical fluxes in the coastal zone has advanced to the point where fluxes of biogeochemically important elements for environmental management applications can be estimated and predicted (Nixon *et al.*, 1995; Humborg *et al.*, 2000). In order to access efficient coastal zone management, we need to know the magnitude of changes and controlling feedback mechanisms, for example, the natural and anthropogenic nutrient sources and sinks. This involves a description of disturbed and undisturbed biogeochemical cycles on the relevant spatio-temporal scales (Humborg *et al.*, 2000) and an estimation of fluxes and budgets.

However, it is difficult to obtain carbon and nutrient budgets through direct measurement (Hung and Kuo, 2002). A model to estimate nutrient and carbon budgets was developed by Gordon *et al* (1996) and referred to as LOICZ (Land-Ocean Interactions in the Costal Zone). This model has been widely used for C-N-P budget calculations in estuarine and coastal ecosystems (Dupra *et al.*, 2000; Wattayakorn *et al.*, 2001; Hung and Kuo, 2002; Ngusaru and Mohammed, 2002; Wosten *et al.*, 2003; Camacho-Ibar *et al.*, 2003; Zhang *et al.*, 2004; Cao *et al.*, 2005). However, a number of the budgets for tropical estuaries derived from time-averaged concentrations of nutrients and salinity may have particularly large errors, when data from only two contrasting seasons (such as wet and dry seasons) are averaged (Hung and Kuo, 2002 and Webster *et al.*, 2000).

In the present study, non-conservative N and P fluxes, net ecosystem production; [*p*-*r*], and the balance between nitrogen fixation and denitrification (*nfix*-*denit*) were estimated for the Bangpakong River Estuary using the LOICZ biogeochemical model. This large river estuary is situated in a tropical coastal zone of the Gulf of Thailand. Measurement and calculation of water flow and nutrient concentrations were conducted during the period of 2000-2001 and served as data sources for the budget calculations.

2. Materials and methods

2.1. Study area

The Bangpakong River, one of the four major rivers flowing into the inner Gulf of Thailand, is situated on the northeast corner of the Gulf (Fig. 1). In contrast to other major rivers in Thailand, the Bangpakong River flows naturally into the Gulf without dam regulation. This river system gathers water mainly from the Nakorn Nayok and the Prachinburi Rivers. Drainage basin and length of the Bangpakong River are 18,570 km^2 and 125 km (Boonphakdee *et al.*, 1999), respectively. Major sources of nutrients to this drainage include municipal communities, agricultural soils, poultry and aquacultural practices located in the river basin (Kasertsart, 2000; Bordalo *et al.*, 2001).

Saline water extends approximately 120 km upstream from the river mouth during the dry season (December 2000 to May 2001). The river estuary becomes mostly fresh during the wet season (June to November 2000). The tide is diurnal mixed with a moderate range of about 1-2.5 m (Sojisuporn and Jirasirilert, 1991).

2.2. Sampling and chemical analyses

Water sampling and measurement of water parameters were carried out monthly from June 2000 to May 2001 at 25 stations located along the Bangpakong River estuary. Salinity, pH and temperature were measured at 0.5 m depth intervals *in situ* by multi-parameter probes (YSI Sonde 6820) with proper calibrations prior to use. Water samples were collected at a depth of 0.5 m using a Kitahara water sampler within the main channel during neap tide to minimize tidal effects.

One liter of each sample was filtered immediately through GF/C filtered paper. Filtered water was kept frozen until analyses. Three replicate analyses were made for each chemical constituent. Dissolved inorganic nitrogen (NO_3+NO_2+NH_4, hereafter DIN) and dissolved inorganic phosphate (PO_4-P, hereafter DIP) were determined colorimetrically (Strickland and Parson, 1972). In terms of quality control, the precision and the relative standard deviation for the triplicate DIN and DIP analyses selected from several samples were approximately ± 5.0 % and 3.4 %, respectively.

2.3. Steady-state box model calculations

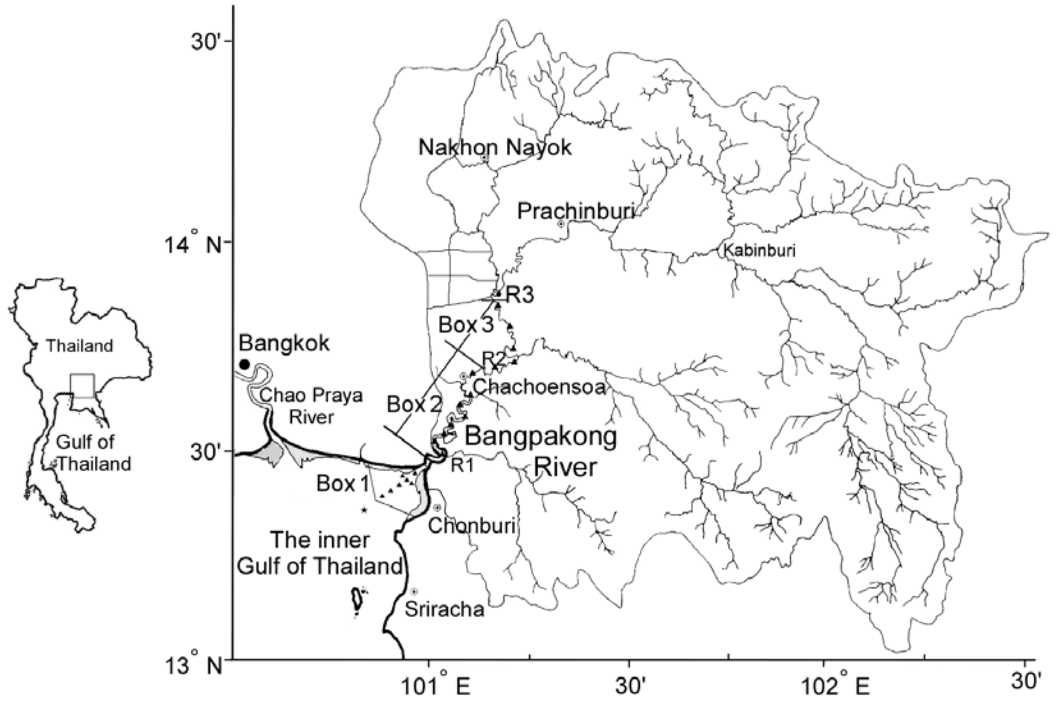

Figure 1. Location of sampling stations in the Bangpakong River Estuary and boundaries of each box. R3, R2 and R1 represent the location where river water ends in the dry season, November and wet season, respectively. The star symbol identifies the offshore station.

and lowest peaks in September 2000 and January 2001, respectively. River discharge and precipitation was highly correlated (r=0.87) with a time-lag of about one month.

Three longitudinal salinity distributions of the Bangpakong River estuary are depicted in Figs. 4 (a, b and c) showing a quasi-synoptic view for August 2000, November 2000 and February 2001 representing the wet season, an intermediate period between wet and dry seasons, and the dry season, respectively. These were selected to illustrate the three principal regimes of the Bangpakong river estuary. In August 2000 [Fig. 4(a)] river discharge was 531 m^3/sec, and strong enough to keep water fresh in almost all parts of the river channel. Seawater was restricted to the vicinity of the river mouth (salinity < 5), and the difference in salinity between surface and bottom was about 5. In November 2000, average river discharge was 165 m^3/sec, salt water intruded 35 km upstream and the entire estuary was vertically well-mixed. In February 2001 survey [Fig.4(c)] discharge at 4 m^3/sec was at a monthly minimum and there was evidence of salt water (>1) 120 km upstream. Mean salinity of the lower estuary (Box 1) approached offshore water salinity.

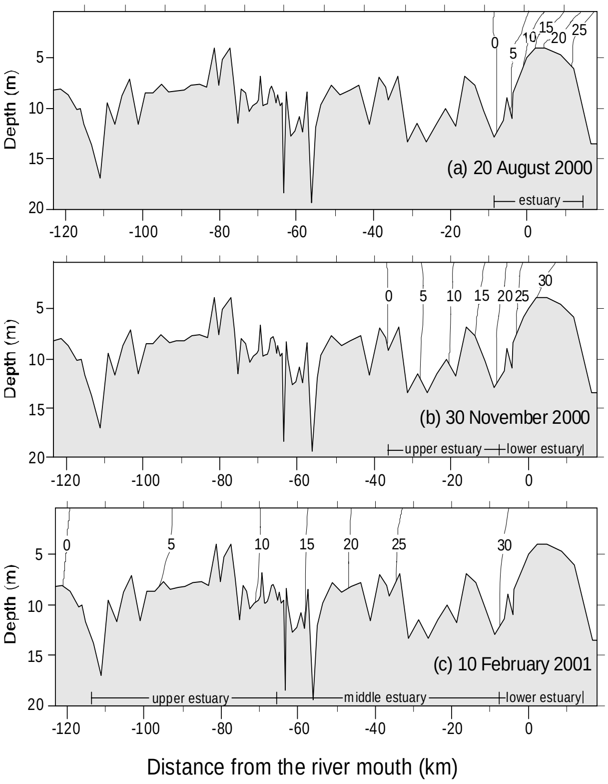

Figure 4. Longitudinal distributions of salinity in the Bangpakong River Estuary under different discharge regimes. (a) 20 August 2000 river discharge 531 $m^3.s^{-1}$ (b) 30 November 2000, 135 m^3 s^{-1} and (c) 10 February 2001, 4 m^3 s^{-1}. The distance is positive seaward from the river mouth. The boundaries of the lower, middle and upper estuary are indicated.

Freshwater inputs, residual flows and mixing volumes were calculated according to Equation 1 and 3. Calculated results are shown in Table 1 and 2. The difference between total freshwater inputs (e.g. June 2000, 50.3x10^6 m^3d^{-1}) and evaporative outflow (0.65x10^6 m^3d^{-1}) was balanced by residual flow (49.8x10^6 m^3d^{-1}). For June 2000, water exchange was calculated as 110.9x10^6 m^3d^{-1}, which is approximately twice the annual mean of residual flow. Similarly, water budgets and flushing times for all surveys are listed in Table 1 and 2. The flushing time (τ) of the system determined by Equation 4, varied temporally from 1.4 day in October 2000 to 80 days in February 2001 with an annual mean of about 15 days. Examples for budgetary calculations in November 2000 are shown in Fig 5.

3.2. Nutrient distributions

DIN and DIP concentrations exhibited spatial and temporal variations within the river estuary (Fig. 6). Concentrations of both nutrients were obviously low in the uppermost reach (>100 km upstream from the river mouth) and offshore water (located at 17.5 km seaward from the river mouth) whereas concentrations in the middle and lower reach (covering from 66 km upstream to 17.5 km seaward from the river mouth) were high. Concentrations of DIN and DIP along the river estuary during the wet season (especially from August to October, 2000) were significantly lower (p<0.05) than those in the dry season. However, at the beginning of the wet season, June 2000, concentrations of DIN and DIP in the middle and lower reaches were higher than those of other surveys, indicating additional inputs of these nutrients.

DIP and DIN concentrations as a function of salinity for the four selected sampling periods are shown in Figs 8 and 10. In general DIP and DIN exhibited linear distributions during a short flushing time in the wet season and increasing non-linearity when flushing time was longer. DIP showed removal at low salinity and additional input at higher salinity during the long flushing time in the dry season whereas DIN received additional inputs in low salinity region. However, a strong input of DIP occurred in the upper estuary during February 2001. Generally the majority of DIN occurred as NO_3 with only a small amount as NH_4, except for the February samples.

3.3. Nutrient budget

Budgets and production of DIP and DIN are summerized in Table 3. Non-conservative fluxes of into Box$_i$, respectively.

Assuming steady state and neglecting groundwater flux, V_{Ri} of the uppermost Box$_i$, with subscript "*i*" depends upon period of samplings, was obtained from:

$$V_{Ri} = - (V_Q + V_{Pi} - V_{Ei}) \quad (1)$$

For the other boxes; V_{Ri} was calculated from:

$$V_{Ri} = - (V_{Ri+1} + V_{Oi} + V_{Pi} - V_{Ei})$$

Assuming steady state, we calculated water exchange V_{xi} from equation of salt balance.

$$0 = V_{Ri}S_{Ri} + V_{Xi}S_{i-1} - V_{Xi}S_i \quad (2)$$

where V_{Xi} is a mixing volume exchanged between Box$_i$ and Box$_{i-1}$. S_i is mean salinity in Box$_i$; S_{Ri} is the salinity of water flowing from Box$_i$, assuming that S_R is the average salinity between Box$_i$ and Box$_{i-1}$. Re-arranging Equation 2, V_{Xi} can be obtained as: $V_{Xi} = - V_{Ri}S_{Ri} /(S_{i-1} - S_i)$ (3) The total water exchange time of the entire estuary (τ) in days can be calculated as

$$\tau = V_{sys}/(V_{X1} + |V_{R1}|) \quad (4)$$

where V_{sys} is the total volume of the entire estuary (sum of the volume of all boxes). Hereafter we refer to the entire estuary as the system.

2.4.2. Nutrient balances

Assuming steady state, mass balances of nutrients (DIN and DIP) were calculated. Flux of nutrients by advection and mixing can be calculated by using V_R and V_X, which were already obtained from Equations 1 and 3. The nutrient fluxes by precipitation and evaporation were negligible. Fluxes from tributaries and sewage were calculated by multiplying discharge volume (V_O) by the concentration of nutrients in tributaries (Kasertsart, 2000) and sewage, which was obtained from Chonburi Municipality (per. comm.).

Since we are assuming steady state, mass of nutrients in a box does not change with time. Thus, it is assumed that production of nutrients in a box by non-conservative processes is equal to the loss of nutrients by conservative processes, such as advection and mixing exchanges.

The net export fluxes of DIP and DIN (DY) from Box 1 to the inner Gulf of Thailand were calculated from the LOICZ model as

$$Q_{R1}(Y_1+Y_0)/2 + Q_{X1}(Y_1-Y_0) \quad (5)$$

Where, Y_1 and Y_0 are concentrations of DIP and DIN in Box 1 and offshore water, respectively.

2.5. Estimates of net ecosystem metabolism and net nitrogen production

Net Ecosystem Metabolism (NEM=*p*-*r*), which is difference between primary production and respiration [*p*-*r*] in the system, was evaluated in carbon base, and estimated stoichiometrically from non-conservative flux of DIP (ΔDIP) and a carbon-phosphorus ratio (C:P):

$$[p\text{-}r] = -\Delta\text{DIP (C:P)}_{\text{particulate}} \quad (6)$$

where $(\text{C:P})_{\text{particulate}}$ is the carbon to phosphorus ratio of organic matter being produced or consumed in the system. In this study, we assumed the major primary producer was phytoplankton and applied the Redfield ratio $(\text{C:P})_{\text{particulate}} = 106$ to stoichiometric calculations.

Net nitrogen production *(nfix-denit)*, defined as net result of nitrogen fixation and denitrification, is evaluated by the difference between non-conservative flux of DIN (DDIN) and expected nitrogen removal through biological uptake. In turn, expected amount of nitrogen uptake, the last term of the right side in Equation 7, is related to phosphorus uptake and the N:P ratio of organic matter in the system. Therefore,

$$[nfix\text{-}denit] = \Delta\text{DIN} - \Delta\text{DIP(N:P)}_{\text{particulate}} \quad (7)$$

where ΔDIN and ΔDIP are obtained from nutrient balance and the N:P ratio is also obtained from the Redfield ratio (16:1). This calculation indicates whether the system is a source or sink for fixed nitrogen.

3. Results

3.1. Salinity distributions and water budget

There were large monthly differences in river discharge and precipitation as shown in Fig. 3, with relatively high values during the wet season (June – November 2000) and low values in the dry season (December 2000-May 2001). Differences in river discharge were up to 200-fold between the maximum in September 2000 and minimum in February 2001. A similar trend was found in precipitation with a 25-fold difference between the highest

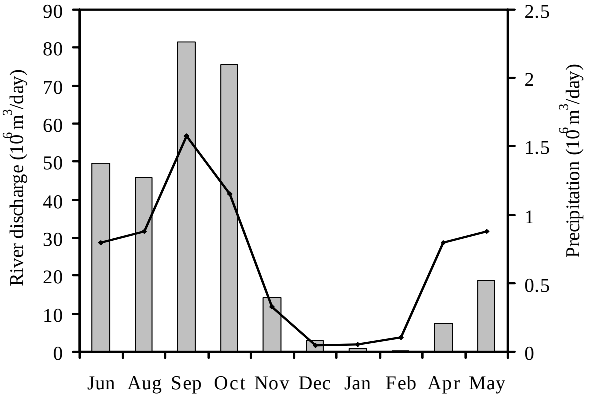

Figure 3. Calculated river discharge (vertical bars) at the Bangpakong river mouth and precipitation (line) of the Bangpakong river basin during the period of June 2000 – May 2001.

In order to determine the non-conservative fluxes of DIP and DIN, a multi-box model was applied as shown in Fig. 2. Details of the model are available in Gordon *et al*., (1996) and on http://www.nioz.nl/loicz.

The boundaries of each box in our model were determined based on the salinity distributions in the Bangpakong Estuary during the dry season when saline water reached 120 km upstream from the mouth (see Results). We divided the whole estuary into three adjoining boxes as shown in Fig. 1 and Fig. 2(a). Box 1, 2 and 3 correspond to lower, middle and upper estuary, respectively. The boundary between Box 1 and Box 2 occurs at the Bangpakong Bridge, which is the first bridge from the seaside. The offshore boundary of Box 1 where concentrations were nearly equal to those of offshore water was determined by nutrient distributions from a previous study (Boonphakdee *et al.*, 1997).

The area and volume of each box is shown in Table 1. Initially, Box 3 represents the region where salinity was < 5; Box 2 was the region where salinity was >5 and <25; and Box 1 was the area where salinity was >25 and < offshore water. A simple box model was applied for the wet season as Box 1 [Fig. 2(b)]. However, two box models [Box 1 and Box 2 in Fig. 2(c)] were used for November 2000 as saline water intruded further upstream than during other months of the wet season. Therefore, river water end-member samples for the wet season, November 2000 and the dry season samplings were not taken from the same station due to a difference in distance of salt intrusion.

In order to calculate the volume of each box, the surface area of Box 1 was divided into 590 bins, each 0.25 km^2. Depth of each bin was obtained from a navigation chart, which represents depths at the lowest low tide. The volumes of Box 2 and 3 were estimated by integrating the mean river cross sectional areas, obtained from bottom topography charts of the Bangpakong River produced by Thai Harbor Department, along the river axis at 2.0 km intervals.

Monthly freshwater inputs for each box were the sum of river discharges, calculated as described by Boonphakdee *et al*., (1999), and direct precipitation to the water surface minus evaporation from the water surface. Estimates of river discharge were made primarily on the basis of monthly measurements at Kabinburi gauge station (Royal Irrigation Department - pers. comm.) that provided an estimate of fresh water inputs from 42 % of the watershed.

2.4. Modeling approach

2.4.1.Water and salt balance

Water and salt balance for each box in the estuary in the Bangpakong estuary was evaluated following Gordon *et al*., (1996) as shown in Fig. 2.

Notations, V_i indicates volume of Box$_i$; S_i, S_0 and S_{Ri} are salinities in Box$_i$, offshore water and average salinity between Box$_i$ and Box$_{i-1}$, respectively. V_Q is river discharge flowing into the uppermost box. V_{Ri}, V_O, V_{Pi} and V_{Ei} are volumes of residual flux, other flows (i.e. tributaries and sewage discharges), precipitation and evaporation flowing

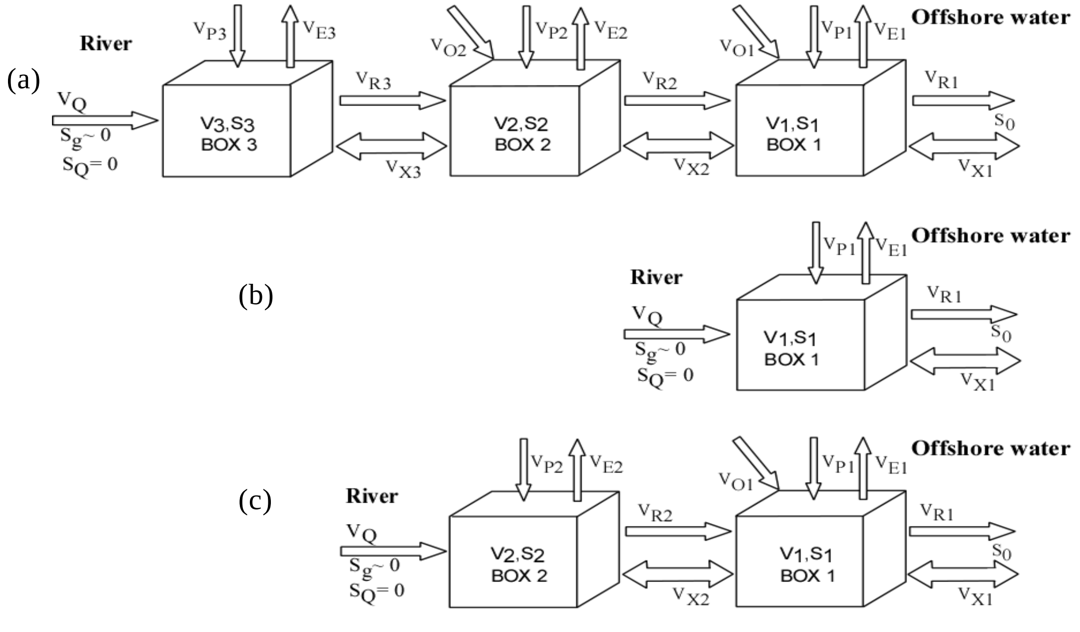

Figure 2. Multi-box model for water and salt budgets in the Bangpakong estuary during (a) the dry season, (b) the wet season and (c) November 2000. V: volume in the box; S: mean salinities in the box; V_Q, V_O, Q_R and Q_X represent river discharge, other flows, residual flow and mixing exchange flow, respectively. See further explanations in the text.

Table 1. Freshwater inputs and average salinity of each box and offshore water.

Sampling Period	Fresh water input (10^6 m^3/day)			Salinity			
	Box 3	Box 2	Box 1	Box 3	Box 2	Box 1	Offshore water
Jun 00		-	49.6	-	-	16.7	28.4
Aug 00	-	-	46.0	-	-	8.9	24.5
Sep 00	-	-	81.7	-	-	11.2	25.4
Oct 00	-	-	75.7	-	-	16.7	26.6
Nov 00	-	13.4	14.6	-	5.5	28.5	28.5
Dec 00	2.0	2.8	3.0	0.2	14.2	31.4	32.5
Jan 01	0.4	0.6	0.7	8.5	22.5	31.9	32.5
Feb 01	0.2	0.4	0.5	9.2	22.4	31.0	32.4
Apr 01	4.6	6.6	8.0	1.6	9.5	24.1	31.8
May 01	11.1	16.7	19.7	1.3	6.35	21.6	30.7
			Mean	4.2	13.4	22.2	29.5
Volume (10^6m^3)	41.7	127.2	284.6				
Area (10^6m^2)	6.6	16.3	147.5				

DIN and DIP were derived from the difference between total inputs and outputs for each box and sampling event. Therefore, a positive sign of non-conservative nutrient fluxes in the system indicates nutrient originate from the system. In contrast, a negative sign indicates the system acts as a sink. ΔDIP values for the system were positive with an average of 0.5 and 0.1 mmol m^{-2} d^{-1} for the wet and dry season, respectively. However, ΔDIP values were negative in Box 2 during May 2001 and Box 3 in December 2000 (-1.8 and -0.1 mmol m^{-2} d^{-1}, respectively).

The system was a net source for DIN in both the wet and dry season with average values of 3.6 and 1.3 mmol m^{-2} d^{-1}, respectively. However, inter-seasonal variation of DDIN values in Box 3 was large with a wide range (-27.2 to 37.7 mmol m^{-2} d^{-1}) during the dry season.

The net daily fluxes of DIN and DIP from the Bangpakong estuary to the inner Gulf of Thailand (Fig. 11) in the wet season with an average of 1826 and 141 kmol d^{-1} were higher than those values in the dry season (416 and 31 kmol d^{-1} for DIN and DIP fluxes, respectively). The exported nutrients are important for sustaining high primary productivity in the Gulf of Thailand (Wattayakorn *et al*, 2002).

3.4. Net primary production and net nitrogen production

The estimates of net ecosystem metabolism [*p*-*r*] and net nitrogen production (*nfix*-*denit*) are shown in Table 4. Negative values of [*p*-*r*] in the system indicate that the Bangpakong estuary is a net heterotrophic system throughout the year with a 30-fold difference between the highest and lowest values in June 2000 (-93.6 mmol C m^{-2}d^{-1}) and in February 2001 (-2.7 mmol C m^{-2}d^{-1}), respectively. However, during the dry season, some boxes showed autotrophic with positive values of net production in December 2000, January and May 2001.

Net nitrogen production (*nfix*-*denit*) indicated that the entire estuary is a net denitrifying system with a value of –3.8 mmol m^{-2} d^{-1} during the wet season and slightly net denitrifying system at a rate of -0.3 mmol m^{-2} d^{-1} during the dry season. However, net nitrogen production of the system varied temporally with the lowest and highest values of -7.1 and 1.0 mmol m^{-2} d^{-1} in June 2000 and January 2001, respectively.

4. Discussion

Table 2. Residual and mixing volume exchange flows between Box 1 and the offshore water. Flushing times are for the system (whole boxes).

Sampling period	Residual flow (10^6m^3/day)	Mixing volume (10^6m^3/day)	Flushing time (τ; days)
June 2000	49.8	110.9	1.4
August 2000	46.3	63.9	2.6
September 2000	82.6	106.9	1.5
October 2000	76.3	132.6	1.4
November 2000	14.1	70.7	4.8
December 2000	2.5	41.8	11.5
January 2001	0.3	26.2	17.2
February 2001	0.0	5.7	80.0
April 2001	7.4	14.4	20.8
May 2001	9.2	23.2	10.7
Mean	28.9	60.0	15.2

Table 3. Non-conservative inorganic nutrient fluxes (mmol/m^2/day) in the Bangpakong Estuary. Wet season values are averaged from June to November 2000 and dry season values were averaged from December 2000 to May 2001.

	Area	Jun-00	Aug-00	Sep-00	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Apr-01	May-01	Wet season	Dry season
ΔDIN	Box 1	7.1	2.6	3.7	1.0	3.6	0.3	1.4	0.3	1.1	1.9	3.5	1.0
	Box 2	-	-	-	-	3.8	3.0	1.8	3.0	13.3	9.9		6.2
	Box 3	-	-	-	-		-27.2	-1.7	0.3	2.4	37.7		2.3
	The system	7.1	2.6	3.7	1.0	3.6	-0.5	1.3	0.5	2.3	4.0	3.5	1.6
ΔDIP	Box 1	0.9	0.6	0.6	0.2	0.2	0.2	0.1	0.0	0.1	0.3	0.5	0.1
	Box 2					0.1	0.0	0.0	0.1	0.4	-1.2		-0.1
	Box 3						-0.1	0.0	0.0	0.8	0.3		0.2
	The System	0.9	0.6	0.6	0.2	0.2	0.1	0.1	0.0	0.2	0.1	0.5	0.1

High temporal variations in the Bangpoakong river discharge were closely correlated with precipitation (Fig. 3). Further, the river was assumed to be dominated by large freshwater input during the wet season and little or no flow during the dry season. Variations in river discharge are one of the characteristics of wet and dry tropical river systems (Eyre, 1998; Eyre and Balls, 1999; Hossain and Eyre, 2002). This characteristic is important for the delivery of terrestrial materials to the estuary, estuarine hydrology, salinity structure and potential for departing from their conservative mixing (Eyre and Balls, 1999).

4.1. Salinity distributions

Seasonal variation in flow dynamics in the Bangpakong River Estuary is driven principally by river runoff and tidal fluctuation. Under high discharge, salt water is flushed almost completely out of the river mouth [Fig. 4(a)] and the estuary stratified with a vertical salinity gradient (~5). Following stratification in the wet season, the estuary becomes vertically homogeneous estuary in the dry season because of low discharge and tidal mixing in the dry season. As a result, the salt intrusion distance increases along the river estuary channel in the end of the wet season and the dry season [Figs. 4(b and c)]. Stratifying and de-stratifying largely varied between the wet and dry season, which is one of the characteristics of a wet and dry tropical estuary as described by Eyre (1998), but it is unusual for temperate estuaries in North America and Western Europe even during extreme discharge (Balls *et al.*, 1997; Eyre and Balls, 1999; Vieira and Bordalo, 2000).

In order to classify the degree of stratification, the estuarine Richardson Number (Ri_E), which represents the ratio of the gain of potential energy due to freshwater discharge to the mixing power of tidal currents (Fisher *et al.*, 1979), was applied:

$$Ri_E = (\Delta\rho/\rho)(gV_O/WU^3_{RMS})$$

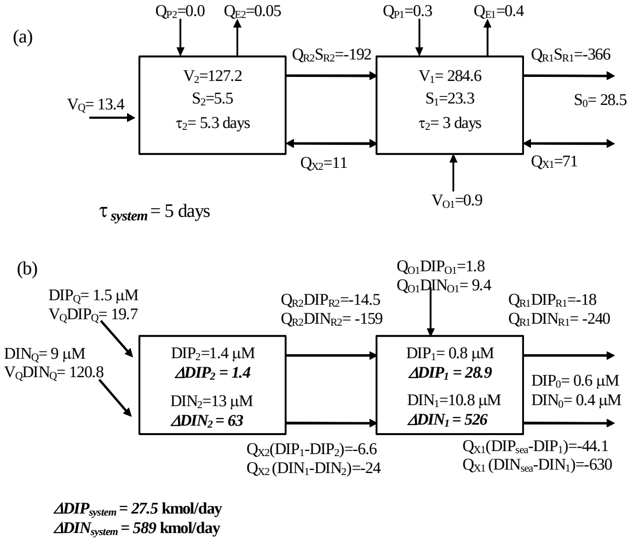

Figure 5. An example of calculations for steady state budgets of; (a) water and salt balance volume in 10^6 m^3, water fluxes in 10^6 m^{3}d^{-1}, salinity in psu and salt fluxes in 10^6 psu m^{3}d^{-1}. The subscript "O" indicates inputs from small branches and sewage whereas "0" means offshore water.(b) non-conservative fluxes of Y(ΔDIN and ΔDIP), for November, 2000. Y_R is the average Y between adjacent boxes. ΔY and Y are in 10^3 mol d^{-1} and µM, respectively.

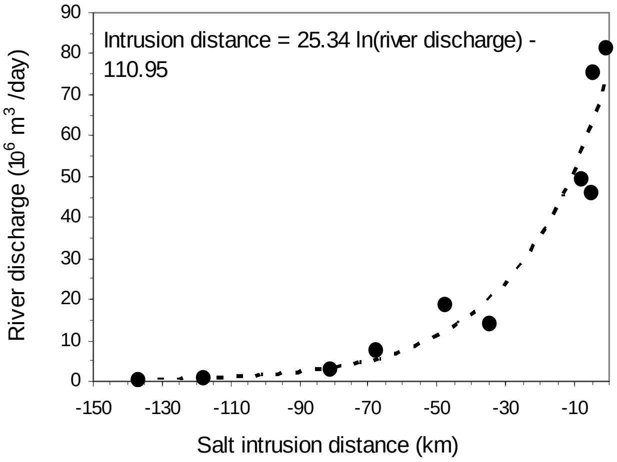

Figure 6. Relationship between salt intrusion distance (upstream from the river mouth;0 km) in the Bangpakong estuary and river discharge at the river mouth. The distance is positive seaward.

Table 4. Stoichiometric calculations of aspects of net ecosystem metabolism [*p-r*] and Net nitrogen production (*nfix-denit*) in the Bangpakong Estuary. Wet season values are averaged from June to November 2000 and dry season values from December 2000 to May 2001.

(mmol /m^2/day)	Area	Jun-00	Aug-00	Sep-00	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Apr-01	May-01	Wet season	Dry season
[*p-r*]	Box 1	-93.6	-63.1	-65.3	-22.0	-20.8	-18.8	-8.7	-2.7	-8.3	-28.7	-52.9	-13.4
	Box 2					-9.4	0.5	0.2	-5.9	-47.3	129.4		15.4
	Box 3						14.2	-1.7	-1.8	-85.0	-33.8		-21.6
	The system	-93.6	-63.1	-65.3	-22.0	-19.6	-14.8	-7.7	-3.0	-19.9	-15.7	-52.7	-12.2
Nfix-denit	Box 1	-7.1	-6.9	-6.2	0.4	-2.5	-2.5	0.1	-0.1	-0.2	-2.5	-4.5	-1.0
	Box 2					2.4	3.1	1.9	2.2	6.1	29.5		8.6
	Box 3						-25.0	-1.9	0.1	-10.4	32.6		-0.9
	The system	-7.1	-6.9	-6.2	0.4	0.6	-2.7	0.2	0.1	-0.7	1.7	-3.8	-0.3

where $\Delta\rho$ is density difference between riverine and offshore water, r is density of the bottom seawater in the estuary, g is acceleration due to gravity, V_Q is river discharge. W and U_{RMS} are estuarine width and the RMS of tidal velocity for the wet and dry season which is obtained from NRCT-JSPS (1999). Ri_E expresses the ratio of the input of freshwater-derived buoyancy per unit width to the tide's mixing capabilities in a particular estuary. An estuary is strongly stratified when $Ri_E > 0.8$, partially stratified when $0.08 < Ri_E < 0.8$, and a well-mixed system when $Ri_E < 0.08$ (Fischer *et al.*, 1979). From the estuarine Richardson Number coinciding with longitudinal salinity distribution in the wet season, the Bangpakong estuary can be classified as a partially mixed estuary with a Ri_E ratio at 0.5, whereas the estuary became a well-mixed estuary ($Ri_E = 0.02$) during the dry season when the salinity difference between surface and bottom along the whole estuary was negligible.

A logarithmic regression between the extent of the salt intrusion length (defined by the upstream position of salinity > 1) and river discharge at the river mouth as shown in Fig. 6 indicated the close relationship ($r^2 = 0.97$, $p < 0.001$). River discharges greater than $70 \times 10^6 m^3 d^{-1}$ did not allow salt intrusion to form and kept the entire river channel fresh. This analysis of data indicates that, during low river discharge in the dry season, tidal straining plays a critical role in the dynamics of vertical mixing of the water column.

4.2. Water budget

Water budgets are critical in deriving nutrient budgets in the box model systems (Gordon *et al.*, 1996; Hung and Kuo, 2002). Based on salt balance, percentage differences between mixing volume and residual flows (Table 2) were higher (84%) in the dry season than those of the wet season (37%). This indicates that water budgets during low flow conditions were dominated by mixing flows. Therefore, variation in mixing volume in the Bangpakong

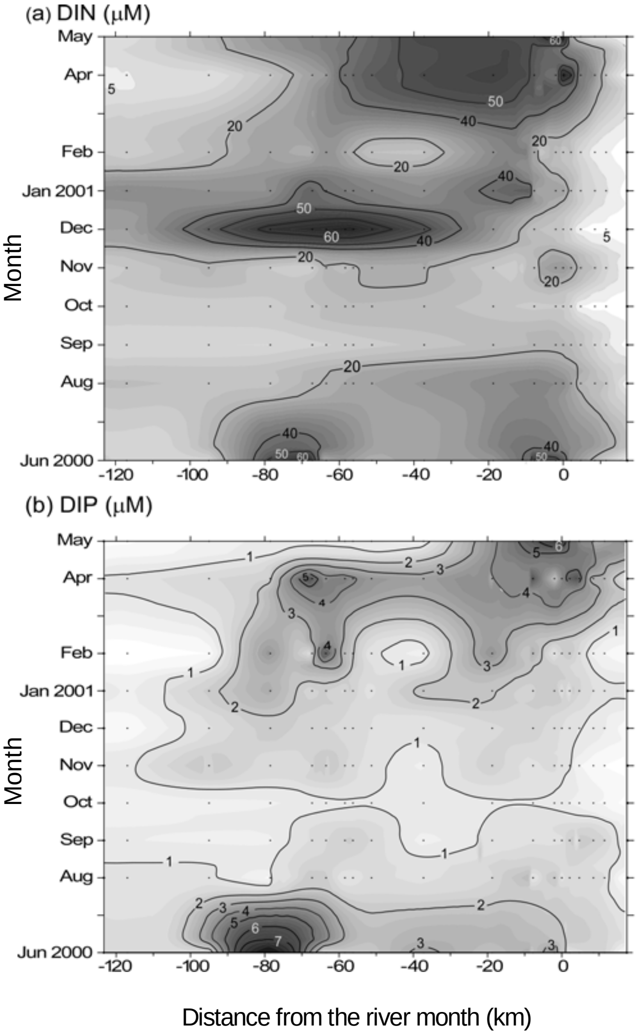

Figure 7. Spatial and temporal distributions of (a) DIN and (b) DIP along the Bangpakong river estuary during the study period (June 2000 – May 2001). The distance is positive seaward from the river mouth.

Estuary was apparently controlled by seasonality in freshwater input similar to water budgets in the Chiku lagoon (Hung and Kuo, 2002) and Bandon Bay (Wattayakorn *et al.*, 2001).

Eyre (1998) suggested that the quantity of nutrients retained in tropical estuaries was determined by flushing time. Flushing time of an estuary is one of the important determinants of terrestrial materials passing from land to the sea and reflects ecosystem processes of an estuary including denitrification (Norwicki *et al.*, 1997), nutrient cycling and retention (Nixon *et al.*, 1996), phytoplankton bloom development and net production (Nowicki *et al.*,1997; Adams and Bate, 1999). As flushing time in the Bangpakong estuary has a rather wide range varying between 1.4 and 80 days, it is likely long enough to cover and locally mask biogeochemical processes in the estuary (Adams and Bate, 1999).

4.3. Nutrient distributions

Distributions of DIN and DIP in the Bangpakong River estuary show temporal variations due to increasing DIN and DIP with values and flow rising at the beginning of the wet season (e.g. June 2000). Strong correlations between concentrations of particulate nutrients and suspended sediment were reported by Pollution Control Department Thailand (unpublished data, pers. comm.,). An increase in particulate nutrients and suspended particulate matter in the beginning of the wet season reflect an effect of the first flush after a long the dry season as described by Eyre and Balls(1999). Soluble materials accumulated within the catchments through the dry period were transported to the river water by leaching and surface runoff with the first major rainfalls began at the beginning of the rainy season. Such an effect is likely to be magnified in tropical catchments subject to monsoonal rainfall patterns, in which a marked dry season provides an extended period for nutrient accumulation (Lewis, 1986; Eyre and Twigg, 1997; Mitchell *et al.*, 1997).

Given low concentrations of DIN and DIP from the middle and lower reaches of the Bangpakong River estuary during other samplings in the wet season (August - November 2000), it is reasonable to assume that nutrient inputs were diluted by the large volume of river runoff before entering the lower catchments. The apparent trends of longitudinal increases in DIN and DIP concentrations in the middle reach reflect inputs from downstream sections. This pattern is not seen in many estuaries (Eyre and Ball 1999), most likely due to masking by anthropogenic inputs. Bordalo *et al.*, (2001) and Szuster (2001) reported that additional inputs of DIN and DIP in the middle reach of the Bangpakong river estuary could have originated from anthropogenic activities in the river basin such as agriculture, aquaculture, animal husbandry and

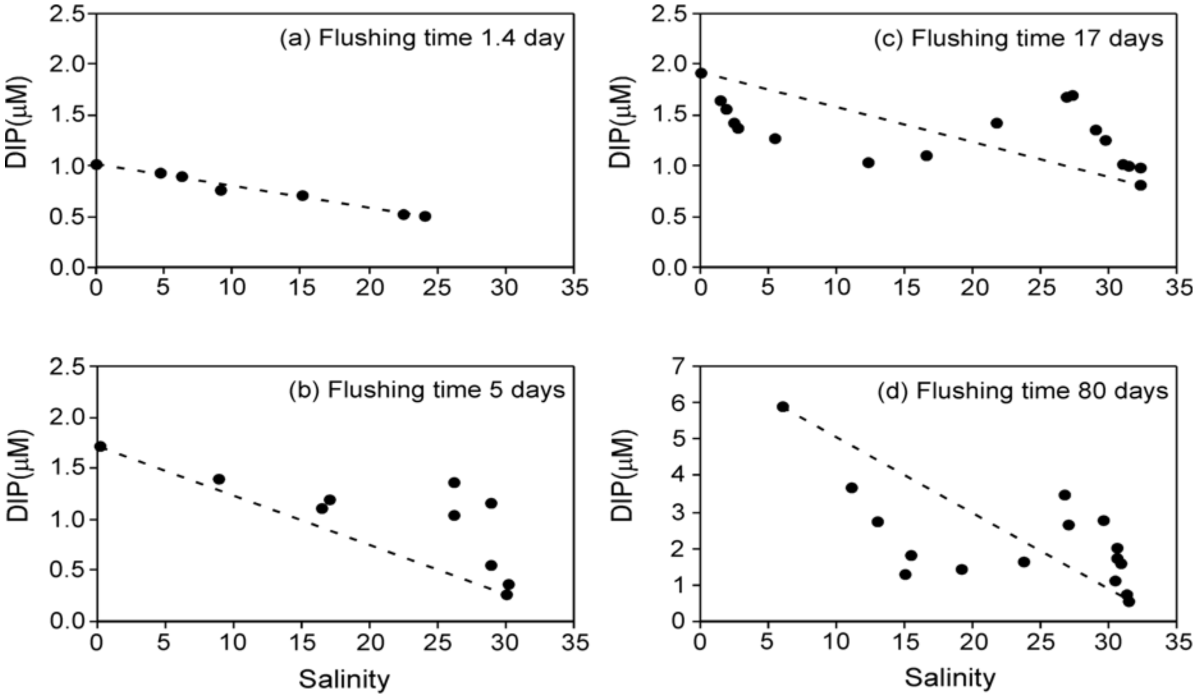

Figure 8. Behaviors of DIP along the salinity gradients of the Bangpakong Estuary (a) during high flow when the estuary is rapidly flushed in October 2000, DIP passes through conservatively, (b, c) as longer flushing time due to lower discharge during the end of the wet season and beginning of the dry season (November, 2000 and December 2000, respectively), DIP shows an increase in departure from conservative mixing and (d) DIP in February, 2001 shows a large departure from conservative mixing (dash lines) and large DIP inputs appear in the upper estuary

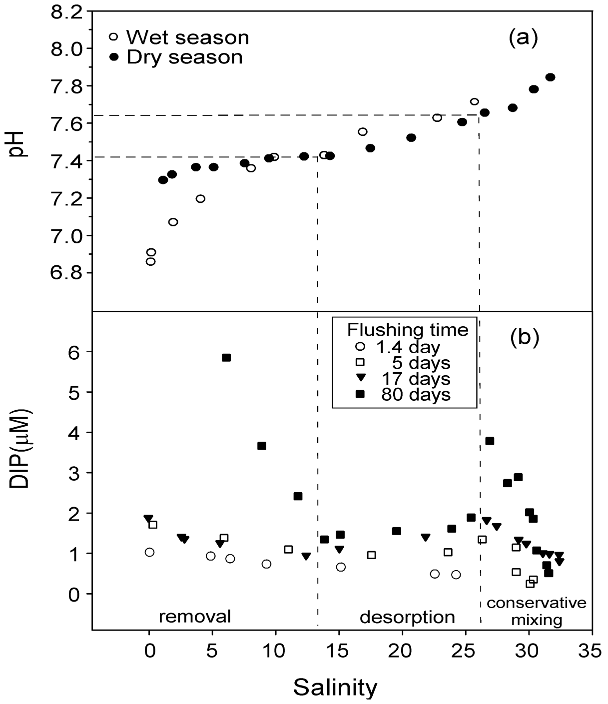

Figure 9. The relationship between pH (a) and DIP concentration (b) as a function of salinity from four different flushing times showing a mixing conservative behavior when flushing time was short (1.4 day) and physico-chemical process (pH control and conservative mixing) when flushing time was longer (5, 17 and 80 days) in the dry season

domestic waste. Therefore, this river estuary receives large inputs from those activities, which may fuel biogeochemical processes in the estuary.

As flushing times in the Bangpakong Estuary are variable (Table 1), it can be expected that materials passing from land to the offshore are likely to deviate from conservative mixing. The non-conservative behaviors of DIN and DIP were evident from their non-linear distributions against salinity. When rapid flushes occur, nutrient retention efficiency in the estuary is low and flushing time in the estuary would be less than the phytoplankton doubling time. In addition, low photic depth (0.4-0.7 m) and poor correlations during the wet season between DIP and nitrate ($r = 0.15$) prohibit phytoplankton blooms. This suggests that removal of DIP from the water column by biological processes is minor. Therefore, mixing of DIP in the estuary was conservative during the short flushing time of about two days in the wet season [Fig. 8(a)].

The increase in flushing times from 5 to 17 days between the end of the wet season and the beginning of the dry season, and to 80 days during the dry season [Figs. 8(b-d)] illustrates an increase in DIP. A departure from the conservative mixing slope shows an addition input in the mid to high salinity region and removal of DIP in the low salinity region. Furthermore in November 2000, DIP behavior showed combinations of conservative mixing in low and high salinity regions and an additional input in the mid salinity region. This is an evident of intermediate period between the two contrast seasons.

Adsorption of DIP to suspended particulate matter, in particular ferric hydroxides at their subsequence

4.4. Nutrient behaviors

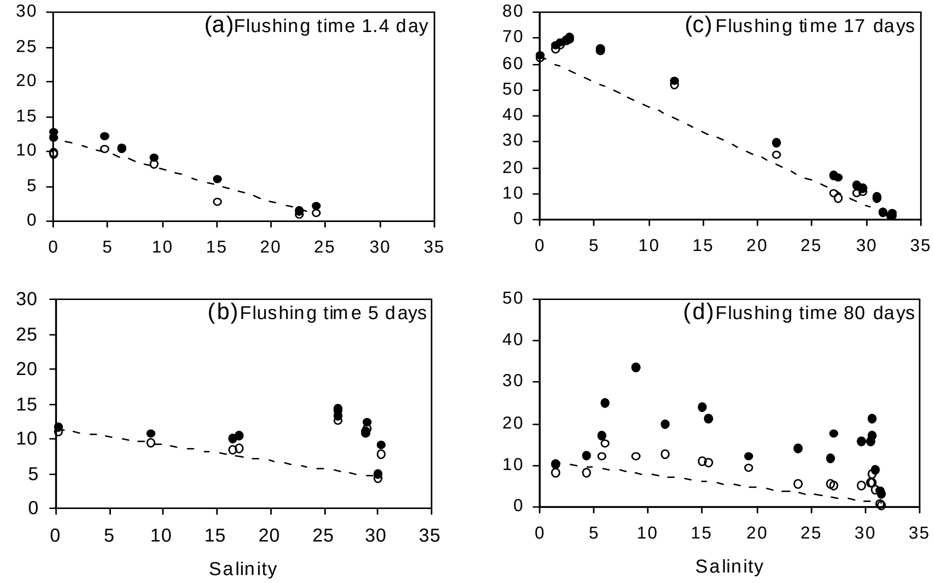

Figure 10. Behavior of DIN (•) and nitrate (o) along the salinity gradient of the Bangpakong estuary (a) during high flow when the estuary is rapidly flushed in October 2000, DIN passes through conservatively, (b, c) as longer flushing time due to lower discharge during the end of the wet season and beginning of the dry season (November 2000 and December 2000, respectively), DIN shows an increase in departure from conservative mixing (dash lines) and (d) in February 2001, DIN shows a large departure from conservative mixing which mainly attributed to ammonia.

sedimentation, has been suggested to explain low ambient concentrations in low salinity regions of sub and tropical estuaries (Balls, 1994; Eyre, 1994; Ayukai and Wolanski, 1997; Eyre and Twigg, 1997; Fang, 2000). However, concentrations of total particulate phosphorus (PCD, pers. comm., 2002) did not related well with DIP removal, suggesting that adsorption to suspended sediment was not an important removal mechanism in the low salinity region. Furthermore, biological uptake was of minor significance due to poor correlation between DIP and nitrate. Eyre and Twigg (1997) suggested that removal of DIP from the water column in low salinity tropical estuaries was likely by adsorption to colloidal-sized iron oxides/hydroxide in a low pH environment. This coincides closely with pH sags in December 2000 and February 2001 as shown in Fig. 9 with removal taking place when pH was <7.4 and desorption occurring above pH 7.4. This suggests that pH plays a role in DIP removal in the Bangpakong estuary. Fox (1990) reported that lowering the pH enhanced removal of estuarine DIP by absorption to suspended sediments. Eyre (1994) explained pH control in the estuarine system that the absorption/desorption processes are regulated by isoelectric point (IEP) of the colloidal oxyhydroxides. Below pH 7.4, the positive charge on the colloidals favors adsorption of anions such as PO_4^{3-}. When the IEP is reached, the charge becomes negative and anions may be desorbed which is supported by a seaward increase in dissolved iron and inorganic iron in the water column and surface sediment along the Bangpakong estuary in dry season (Bordalo *et al*., 2001; Parkpoin *et al*., 2001). As desorption is a slow process (Froelich, 1988), it most likely evident under conditions of long flushing times during the dry season. However, behavior of DIP in the high salinity region (>27) of the estuary where pH > 7.6 was conservative, mixing between low-DIP offshore water and estuarine water. Therefore mixing behavior of DIP in the Bangpakong River estuary during longer flushing time in the dry season was associated with physico-chemical process.

In accordance with DIP distributions, DIN concentrations showed different trends between short and long flushing times. In general, DIN concentration in estuaries fluctuates inversely with salinity (Day *et al*., 1989) indicating no major change within the estuary (Balls, 1994). This situation was in accord with the pattern in the Bangpakong estuary when flushing time was short [Fig. 10(a)]. However, during longer flushing times in the dry season, the estuary acts as a source of DIN [Figs. 10(c) and (d)].

During the dry season when the environment is more stable, DIN concentrations initially increase in the upper estuary where salinity was ~5 and then decreased seawards [Fig. 10(c) and (d)] when salinity was >10. The origin of the additional DIN in the upper estuary was mainly attributed to anthropogenic activities such as agriculture, aquaculture, animal husbandry and domestic waste (Szuster 2001; Bordalo *et al*., 2001). Additional DIN input in the mid salinity region where salinity region >17 in November 2000 [Fig. 10 (b)] may have resulted from nitrification, with a concomitant reduction of dissolved oxygen (NRCT-JSPS, 1999; Bordalo *et al*., 2001).

DIN inputs were observed in the middle and lower estuary as shown in Fig. 10(d). These inputs were dominated by ammonium, which may be derived from external sources, i.e. anthropogenic, or from internal load such as benthic processes. For the middle estuary, there was a huge amount of nitrogen (over 75 tons / day, Boonphakdee, unpublished data) from agricultural practices, in particular shrimp ponds and animal farms. The excess ammonium can be easily produced from mineralization of organic nitrogen (ammonification), a process consuming oxygen. This is consistent with the observed low dissolved oxygen (Bordalo *et al*., 2001) and long flushing time during the dry season.

Maximum ammonium concentrations in the lower estuary were found in the river mouth area where there are extensive mud flats. This reflects the dominance of benthic regeneration in the lower estuary. Total particulate nitrogen deposited during a period of high discharge was then likely to be a source for ammonification in the sediment. Decom-

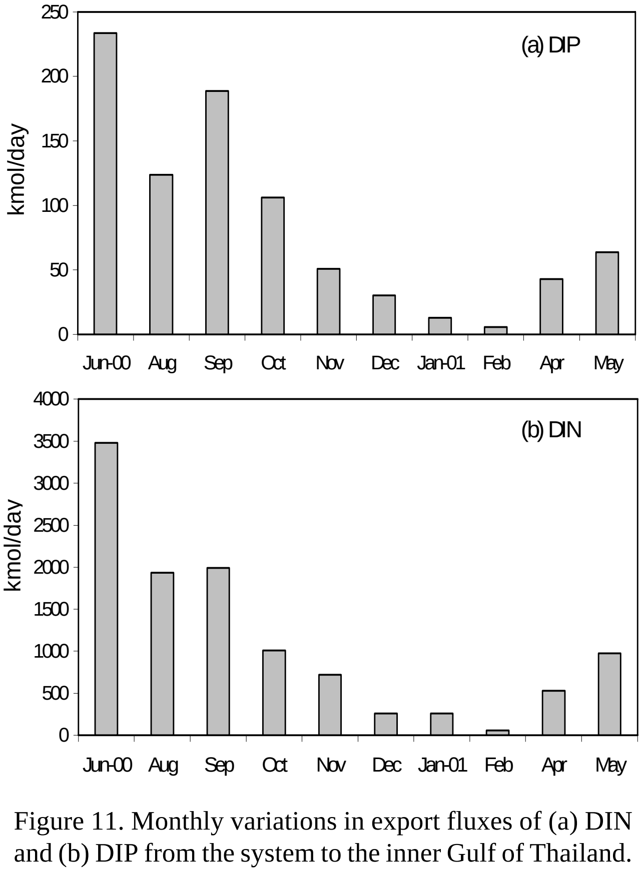

Figure 11. Monthly variations in export fluxes of (a) DIN and (b) DIP from the system to the inner Gulf of Thailand.

position of total particulate nitrogen in the lower estuary may also be enhanced by wind-driven resuspension, which increases the oxidized surface area of the particles. This observation highlights the role of episodic inputs as a driving force behind biological processes along the salinity gradient of tropical estuaries.

4.5. Nutrient budget

The net quantity of DIN and DIP exported from the system to the inner Gulf of Thailand varied seasonally with higher quantities in the wet season and extreme values in June 2000 (Fig. 11). Values in June, 2000 reflect an influence of high discharge as a consequence of the first flush effect occurring at the beginning of the wet season. Although high nutrient concentrations were observed in the estuary during the dry season (Fig. 6), the export of nutrients was low due to low river discharge. Norwicki *et al.*, (1997) reported that long flushing time in an estuary enhances the completion of biogeochemical processes (i.e. nutrient cycling and adsorption/flocculation) to suggest the Bangpakong estuary plays a dynamic role in nutrient transport to the Gulf of Thailand.

Positive ΔDIP values in the estuary reflect DIP production exceeded its removal from the water column. During the wet season when flushing times were short, biological uptake may not develop well as described previously. In the dry season, when flushing times were long and photic depth deeper(0.8±0.4 m), DIP can be removed by biological uptake and adsorption/desorption to particles (Wattayakorn *et al.*, 2002). During the dry season when the Bangpakong estuary has an average ΔDIP value of 0.1 mmol m^{-2} d^{-1} with only a small inter-seasonal variation, it appears to actively recycle DIP with similar rates of consumption and production ΔDIP~0.1. However spatial variations in ΔDIP values were pronounced showing negative values in the upper estuary in December 2000 and middle estuary in and May 2001. Decomposition of organic matter and adsorption of DIP during these periods exceeded production of DIP.

Inter-seasonal variation in ΔDIP values during the wet season, in contrast to the dry season, were more remarkable with the highest value (0.9 mmol m^{-2} d^{-1}) at the beginning of the wet season (June 2000). This high value is a consequence of the first flush effect in the river basin and is supported by decreasing in ΔDIP values from August to November 2000 with low riverine concentrations of DIP (Fig.6).

The Bangpakong Estuary is a net source of DIN to the Gulf of Thailand with production exceeding removal in both season s similarly to ΔDIP. The first flush and long flushing times also influenced ΔDIN values in the system consistent with the high and low values of ΔDIN in June 2000 and during the dry season (Table 3), respectively. ΔDIN in the upper estuary during long flushing time from December 2000 to April 2001 favored removal with negative averaged value of –6.5 mmol m^{-2} d^{-1}. This represents net respiration and decomposition of organic matter, with nitrification of released NH_4 during the dry season. This is consistent with high concentrations of DIN (Fig. 6) from external inputs in the upper and middle estuary (Box 3 and 2) during the dry season making it a greater source than the lower estuary where there is no major external source.

4.6. Net primary production of organic matter

The carbon budget in an estuarine system, converted from the internal reaction flux of DIP, is assumed to be proportional to production and consumption of organic matter (Gordon *et al.,* 1996). The emphasis of this study has been on net primary production [*p-r*] rather than on gross production. In order for [*p-r*] to be negative, the amount of organic carbon supplied from outside the system must be appropriately reduced.

The [*p-r*] values of the system significantly ($p>0.05$) relied on those of the lower estuary because Box 1 covers ~86 % of the system surface area and mainly distributed > 90% of the excess DIP produced by the system during the dry season. The net heterotrophy in the lower estuary relative to net autotrophy in the middle estuary during May, 2001 was likely related to the high inputs of DIP and DIN into the middle estuary. This is consistent with an imbalance between primary production and respiration along the estuary channel implying that the Bangpakong estuary is very active in breaking down organic inputs and exporting most of these as N and P. The short flushing time and accumulation of a significant DIP gradient ($p<0.05$) between the lower estuary and offshore water suggest that an important fraction of the imported organic carbon (Camacho-Ibar *et al.*, 2003) is probably from a physico-chemical process and sediment detritus in the shallow mud flats.

[*p-r*] values of the system vary seasonally from -53 mmol C $m^{-2}d^{-1}$ in the wet season to -12 mmol C $m^{-2}d^{-1}$ during the dry season (Table 4), likely resulting from recycling of organic material within the system and seasonal variation in terrestrial organic matter input or supply from marine sources. The relatively high net heterotrophy during the wet season can be determined by a huge input of terrestrial organic carbon (Smith and Hollibaugh, 1997).

The Bangpakong estuary is a heterotrophic system in according with many other estuaries (Smith and Hollibaugh 1997; Dupra *et al*., 2000; Middelburg and Nieuwenhuize, 2000 and references therein). They receive high organic loads due to rapid rates of respiration and extensive denitrification. Heterotrophy requires a reduction of accumulated organic carbon or an external source of organic carbon. We suggest that major potential sources of external organic carbon delivered to the Bangpakong River Estuary during the wet season were of terrestrial organic matter. During the dry season, the major sources of organic matter are from offshore water coupled with a large input from anthropogenic activities (Szuster, 2001; Bordalo *et al*., 2001).

The Bangpakong Estuary was a net denitrifying system(-3.8 mmol m^{-2} d^{-1}) during the wet season and only slightly (-0.3 mmol m^{-2} d^{-1}) during the dry season based on results using from Equation 7. Spatial and temporal variations in *nfix-denit* in each sub-system were pronounced, particularly during the dry season. Nitrifying condition and net increments of ammonia in the middle estuary indicated an abundance of external DIN input reflecting anthropogenic inputs and possibly ammonification in this zone (Iriarte *et al*.,1998)

The difference in apparent denitrification among the sub-systems was probably related to differences in lability of the organic matter fueling benthic respiration. Denitrification in shallow coastal ecosystems is a benthic process coupled with benthic and water column nitrification (Camacho-Ibar *et al*., 2003). Middelburg *et al*. (1996) concluded that rate of benthic denitrification is most sensitive to the flux of labile organic carbon arriving at the sediment-water interface. The high apparent denitrification rates in the lower estuary especially at the beginning of the wet season (May-June) are probably favored by the first flush input of labile terrestrial organic matter whereas sediment respiration at the lower estuary during the dry season is fuelled by larger proportions of more refractory terrestrial detritus than retained in sediment.

5. Conclusion

The Bangpakong River estuary is dominated by an episodic, short-lived, large freshwater input during the wet season and little flow during the dry season. The estuary is classified as a wet and dry tropical estuary and represents a partially mixed and well-mixed system in the wet and dry season, respectively. Distributions of DIN and DIP in the Bangpakong river estuary show temporal and spatial variations due to first flush effect, flushing times and anthropogenic inputs. Mixing behaviors of DIP and DIN in the estuary were mainly dominated by conservative mixing during the wet season and physico-chemical processes during the dry season.

Non-conservative fluxes of DIN and DIP indicates that the Bangpakong estuary is the source of nutrients to the Gulf of Thailand and also a very dynamic system due to seasonal variability in net export quantities of DIN and DIP. The system is a net heterotrophic (-32.5 mmol m^{-2} d^{-1}) representing high organic loads from external sources, in particular, from terrestrial source during the wet season and from marine and anthropogenic activities in the dry season. The system was a net denitrifying (-2.1 mmol m^{-2} d^{-1}) with spatial and temporal variations in the middle estuary during the dry season indicating anthropogenic inputs and the system receives large loads of DIN during the wet season with some may retain in the sediment. The seasonality of net metabolism in the Bangpakong estuary is largely controlled by the system-river interactions.

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