



## AN ASSESSMENT OF BIOGEOCHEMICAL CYCLES OF NUTRIENTS IN THE INNER GULF OF THAILAND

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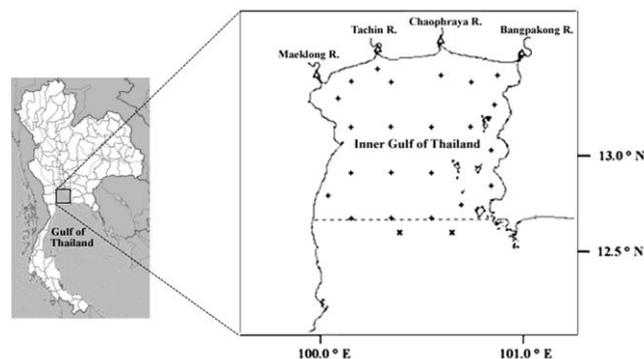
The nutrient dynamics of the Inner Gulf of Thailand were studied using a simple steady-state budget model, according to the Land–Ocean Interaction in the Coastal Zone modelling guidelines. Two sampling campaigns were carried out during the wet (October 2011) and the dry (February 2012) seasons. For each season, budgets for water and salinity, dissolved inorganic phosphate (DIP) and nitrogen (DIN) were determined. The study indicates that the Inner Gulf exports water at the rate of 133–562 MCM.day<sup>-1</sup> in the form of residual flux ( $V_R$ ) at the inner-outer Gulf interface. This results in supply of salt to the inner-outer Gulf interface at the rate of  $4.3 \times 10^3$ – $17 \times 10^3$  ton.d<sup>-1</sup>. Exchange between the Inner Gulf water and the adjoining seawater replaces this salt loss. Mass balance calculations indicate that the Inner Gulf is a net source for DIP and DIN to the adjacent outer Gulf water at the rate of  $4.0 \times 10^4$ – $3.4 \times 10^6$  molP.d<sup>-1</sup> and  $4.1 \times 10^6$ – $20.5 \times 10^6$  molN.d<sup>-1</sup>, during the dry and wet season respectively. The high DIP and DIN exports during the wet season probably reflect the inputs coming from the agricultural, domestic and industrial wastes during the severe flooding over Thailand in 2011. Stoichiometric analysis yields the values of net ecosystem metabolisms (NEM; p-r) and net nitrogen production (nfix-denit) in the Inner Gulf at the rate of  $4.4 \times 10^3$  tons C.d<sup>-1</sup> and  $0.7 \times 10^3$  tons N.d<sup>-1</sup>, indicating that the Inner Gulf is an autotrophic (sink of nutrients) and net nitrogen fixing (nfix-denit >0) ecosystem during the wet season. However in the dry season, the Inner Gulf remains to be autotrophic (p-r = 47 tonsC.d<sup>-1</sup>) but shifted to be a net denitrifying ecosystem (nfix-denit = -88 tonsN.d<sup>-1</sup>). Results from the nitrogen and phosphorus biogeochemical cycling revealed the importance of river discharges in the transport and transformation of these substances within the Inner Gulf of Thailand.

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**Figure 1.** Map of the Inner Gulf of Thailand.

### Introduction

The Gulf of Thailand is a semi-enclosed shallow coastal sea located in a tropical area at latitude 13°N and longitude 100°30'E (Fig. 1). It is situated immediately to the northwest of the South China Sea, from which it is separated by two sills. Monsoon seasons and the intrusion of seawater from the South China Sea are the major factors which have profound effects on the oceanographic conditions within the Gulf.<sup>1</sup> In addition, strong seasonal variations in precipitation and river discharges lead to seasonal variations in water column conditions. Geographically, the Gulf of Thailand may be divided into the Upper and Lower Gulf. The Upper Gulf is the catchment basin of four large rivers namely, the Chaophraya, the Tachin, the Bangpakong and the Mae Klong River on the northern side. Among these, the Chaophraya is the largest river contributing about 49% of the Gulf's surface water, with the discharge of  $22 \times 10^3$  MCM.yr<sup>-1</sup>. Primary production prevailing in the Gulf of Thailand is known to be relatively high, as the result of high nutrient input through rivers and from agricultural fertilizers, household sewage and shrimp farms along the coast, as well as urban runoff from the City of Bangkok.<sup>1</sup> Widespread eutrophication is a growing problem, ranking as the most severe threat to the Inner Gulf due to increasing input of nutrients from the land-based sources. Water quality is generally lower than acceptable standards in the Inner Gulf region, especially at the river entries.<sup>2-7</sup>

We have limited knowledge about the biogeochemistry of the Gulf of Thailand and many processes are not well known, in particular the biogeochemical budgets of carbon and nutrients. The key questions include is the Gulf a source or sink for carbon, nitrogen and phosphorus (CNP) remain unanswered. In addition there are shortcomings in our knowledge of some of the important physical, chemical and biological controls on nutrient biogeochemical cycles. A few processes are affected either by human activities directly or through climate change.

The transformations of these nutrient elements are important because the combination of net fluxes of water, dissolved nutrients and organic matter will determine the role of the system either as a heterotrophic system (source of nutrients) or autotrophic system (sink of nutrients).<sup>8</sup> Although exchange of materials such as water and salt, dissolved nutrients and organic matter in semi-enclosed shallow seas and estuaries has received much attention in recent years,<sup>9-15</sup> The dynamics of nutrients in the Gulf of Thailand have not been well studied so far and information about the sources and processes controlling their

mobilization and fate are still lacking. The present study explores some aspects of the nutrient dynamics in the Inner Gulf of Thailand by using the modelling protocol developed by the Land-Ocean Interactions in the Coastal Zone (LOICZ).<sup>8</sup> The overall aim of the study is to construct biogeochemical budget model for the Inner Gulf of Thailand, in order to understand the processes controlling nutrient dynamics, their stoichiometry and metabolism over a range of temporal and spatial scales.

## Experimental

### Study area

The site of this study is the innermost area of the Upper Gulf of Thailand (Inner Gulf), located at 12°40'–13°36'N and 99°57'–101°00'E (Fig. 1). The Inner Gulf is roughly rectangular in shape, about 100 km long and 100 km wide, with an average depth of 15 m and a volume of  $150 \times 10^9 \text{ m}^3$ . The Gulf is surrounded by highly populated area and some heavily polluting industries. Some untreated effluents have been discharged from industrial sites into the small tributaries that feed into the Inner Gulf. In addition, domestic wastewater generated by residents in and around the area is discharged into open ditches, which ultimately draining into the Gulf.<sup>7</sup> About 50 per cent of the land-based contaminants and nutrients are delivered into the Gulf by the four major rivers at the head of the Upper Gulf, hence frequent algal blooms have become common in the Gulf.<sup>1,2,7</sup>

The average freshwater discharges during 1999–2000 were estimated to be  $8.2 \times 10^3$ ,  $8.1 \times 10^3$ ,  $22 \times 10^3$  and  $6.6 \times 10^3$  MCM.yr<sup>-1</sup> for the MaeKlong, Tachin, Chaophraya and Bangpakong River, respectively.<sup>16</sup> Runoffs from these rivers have produced a strong salinity gradient from about 5 psu near shore to between 31 and 32 psu at the mouth of the Inner Gulf.<sup>17</sup> The average annual rainfall from 1979 through 2006, measured at monitoring stations around the Inner Gulf, was approximately 1,395 mm. Most precipitation occurs during May to October, the highest precipitation is usually received in the month of September, with an average rainfall of 344 mm, which amounts to 20 % of the average annual rainfall. Evaporation over the area is about  $4 \text{ mm d}^{-1}$ .<sup>18</sup>

### Sample collection and analysis

Two cruises were carried out aboard the R/V Chulavijai of Chulalongkorn University, in October 2011 and February 2012. During each survey 15–20 stations (Fig. 1) in the Inner Gulf were occupied at both high and low tide. Coincidentally with each survey, the four major rivers were sampled on the days preceding each cruise. Rivers were sampled at low tide to minimize saltwater intrusion. Sampling was conducted from a bridge or small boat which allowed access to mid-channel. Discrete water samples were collected from the 1.0 m of the surface and 1.0 m of the bottom, stored in 1-L acid-washed polypropylene bottles and were filtered through acid-washed 47 mm diameter Whatman GF/F filters. The filtered water samples were analysed for dissolved inorganic nutrients ( $\text{NH}_4^+$ ,  $\text{NO}_2^- + \text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ) in the laboratory.

Dissolved organic nitrogen (DON) and phosphorus (DOP) concentrations were estimated as the difference between the total dissolved nutrient pools and the dissolved inorganic nutrient concentrations.<sup>19,20</sup>

Physical parameters were measured with a conductivity–temperature–pressure instrument (CTD) at a 0.1-m vertical interval. Other water quality parameters were obtained via the YSI 556 multi-probe system during the sampling operation. Rainfall and evaporation data were obtained from Thailand Meteorological Department while discharge data were obtained from the Royal Irrigation Department.

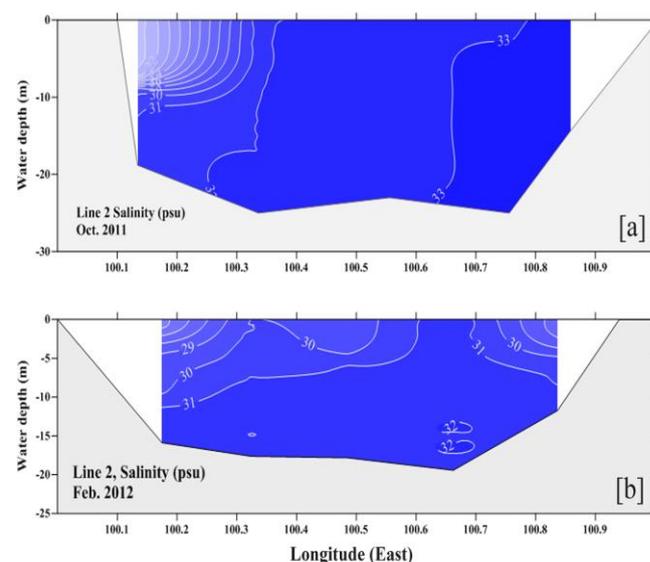
## Results and Discussions

### Data availability

Data used in this budgeting study are shown in Tables 1 and 2. Groundwater discharge and outfalls were assumed to be negligible. Fig. 2 presents a longitudinal transect of water salinity in the Inner Gulf of Thailand during the two sampling periods, revealing some vertical stratification in the region of freshwater influence. Examples of distribution patterns of DIN and DIP in the Inner Gulf are shown in Fig. 3.

**Table 1.** Model input parameters and assumptions

Parameter	October 2011 $10^6 \text{ m}^3 \text{ day}^{-1}$	February 2012 $10^6 \text{ m}^3 \text{ day}^{-1}$
Precipitation	113	27
Evaporation	38	40
Discharge	487	146
Groundwater, other sources	0 (assumed)	



**Figure 2.** Longitudinal transect of water salinity in the study area during [a] October 2011 and [b] February 2012.

**Table 2.** Chemical composition of water samples from rivers (FW), Inner Gulf (System) and adjacent seawater (SW)

Oct-2011	Salinity, psu	NH <sub>4</sub> <sup>+</sup> , μM	NO <sub>3</sub> <sup>-</sup>	DIN	DON	PO <sub>4</sub> <sup>3-</sup>	DOP
FW	0	27.5	11.8	39.4	24.19	3.9	0.47
System	28.5	6.4	0.77	7.1	15.25	0.46	1.22
SW	32.0	8.1	0.24	8.3	9.58	0.86	1.96
Feb-2012							
FW	0	22.2	25.2	47.4	14.8	2.7	1.1
System	31.3	3.65	1.77	5.4	24.34	0.55	0.49
SW	33.8	3.26	0.97	4.2	27.19	0.38	0.39

### Water and salt budgets

Since no significant vertical stratification in salinity was observed in the Inner Gulf (Fig. 2), therefore in this work the one layer single box LOICZ model<sup>8</sup> was applied to calculate nutrient and carbon fluxes, with the model constrained by water and salt budgets. Assuming a steady-state and conservation of mass, water and salt budgets were calculated for the Inner Gulf, for the period October 2011 and February 2012 using daily precipitation, evaporation and river discharge data. Water and salt budgets are calculated by the following equations.

$$dV_S/dt = V_O + V_P + V_E + V_G + V_R \quad (1)$$

$$d(V_S S_S)/dt = V_R S_R + V_X (S_O - S_S) \quad (2)$$

where

$V_S$  denotes the volume of the Inner Gulf,

$V_Q$  the dominant river discharges into the Inner Gulf,

$V_P$  the precipitation,

$V_E$  the evaporation,

$V_G$  the ground water discharge,

$V_R$  the residual volume transport from the Inner Gulf to the adjacent sea area,

$S_S$  the average salinity of the Inner Gulf system,

Therefore, the average salinity of the adjacent sea area,  $S_R = (S_S + S_O)/2$ , and  $V_X$  the water exchange volume between the Inner Gulf and the adjacent sea.

$dV_S/dt$  is estimated from the seasonal variation of mean sea surface of the Inner Gulf,  $V_Q$  is obtained from the Royal Irrigation Department,  $V_P$  and  $V_E$  are obtained from Thailand Meteorological Department; while  $V_O$  and  $V_G$  are assumed to be zero due to no data were available during the study periods.

The water and salt budgets are thus used to calculate the magnitude of all the flows across the system boundaries. Residual volume transport  $V_R$  decreased by about 1/4 as the river discharges  $V_Q$  decreased by about 1/3 from October 2011 to February 2012. The horizontal exchange volume  $V_X$  is estimated from Eq. (2) and the result is shown in Table 3.

$V_X$  in February 2012 is less than 1/4 of that in October 2011 and this is due to the decrease of the strength of estuarine circulation in the Inner Gulf.

Salt must be conserved in the system;<sup>8</sup> hence salt flux out of the system carried by residual flow ( $V_R$ ) must be balanced via mixing ( $V_X$ ). Average residence time of the Inner Gulf water ( $\tau$ ) can be estimated by the following equation.

$$\tau = V_S / (V_X + V_R) \quad (3)$$

The water exchange time ( $\tau$ ) for the Inner Gulf was 28 and 80 days in the wet and dry season respectively (Table 3). Once all the flows are known, the amounts of dissolved inorganic nutrients flowing into and out of the system can be calculated.

### Nutrients budgets

The flux of a nutrient across the system boundary is equal to the average flow volume multiplied by the average concentration of the nutrient in that flow. The difference between the amount flowing in and out is the amount added or removed within the system during the budget period. Nutrient budget of the Inner Gulf is calculated by the following equation.

$$d(V_S C_S)/dt = V_Q C_Q + V_P C_P - V_R C_S + V_X (C_S - C_O) + \Delta C \quad (4)$$

where

$C_S$  denotes the nutrient concentration of the system,

$C_Q$  that of river water,

$C_P$  that of rain,

$C_O$  that of the adjacent sea area and

$\Delta C$  the nutrient flux by the biochemical processes such as photosynthesis, decomposition and release from the bottom in the box.

$C_Q$  is estimated from the observed data and  $C_P$  is assumed to be zero because we have no data. In case of *DIP* budget, positive  $\Delta C$  means that decomposition plus bottom release is larger than photosynthesis but negative  $\Delta C$  means that photosynthesis is larger than decomposition plus bottom release.

**Table 3.** Water fluxes (precipitation  $V_P$ , evaporation  $V_E$ , runoff input  $V_Q$ , residual flow ( $V_R$ ), salinity of the Inner Gulf and adjacent seawater ( $S_{\text{sys}}$ ,  $S_{\text{sea}}$ ), mixing water between Inner Gulf and sea ( $V_X$ ) and water exchange time ( $\tau$ ) in the Inner Gulf in October 2011 and February 2012.

Sampling period	$V_P$	$V_E$	$V_Q$	$V_R$	$S_{\text{sys}}$	$S_{\text{sea}}$	$V_X$	$\tau$
	MCM day <sup>-1</sup>				psu	psu	MCM day <sup>-1</sup>	days
Oct-11	113	-38	487	-562	28.5	32.9	4787	28
Feb-12	27	-40	146	-133	31.3	33.8	1752	80

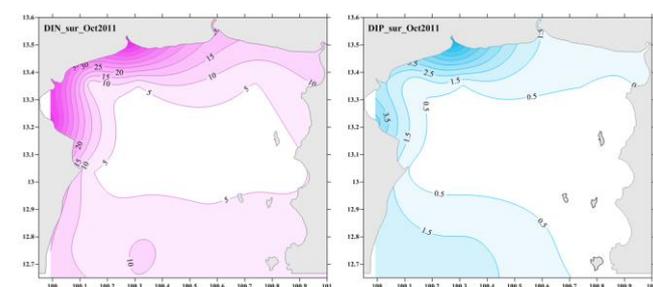
**Table 4** Estimated rates of non-conservative fluxes,  $p-r$  and ( $nfix-denit$ ), unit: mmol m<sup>-2</sup> d<sup>-1</sup>

Sampling period	$\Delta DIP$	$\Delta DIN$	( $p-r$ )	$\Delta N_{\text{obs}}$	$\Delta N_{\text{exp}}$	( $nfix-denit$ )
Oct-2011	-0.34	-2.05	36.5	0.19	-5.51	5.70
Feb-2012	0.004	-0.42	0.39	-0.79	-0.06	-0.73

When we assume that the main primary producer in the system is phytoplankton, we may estimate nitrogen fixation ( $nfix$ ) minus denitrification ( $denit$ ) by the following equation.<sup>8</sup>

$$nfix - denit = \Delta N - 16\Delta DIP \quad (5)$$

Temporal variations of average nutrients concentrations in the system are shown in Table 2. DIN concentration in the system was higher in the wet season as compared to dry season but DIP concentration was lower. DIN/DIP ratio was 16 (Redfield ratio) in the wet season but it was lower than 16 in the dry season. This suggests that the limiting nutrient of photosynthesis in the Inner Gulf was DIP in the wet season but it changed to DIN in the dry season.

**Figure 3.** Spatial distribution of DIN and DIP in the study area in October 2011

For the Inner Gulf of Thailand, model output indicated that total nutrient fluxes from the Inner Gulf to the adjacent outer Gulf region in the wet season are  $-2.9 \times 10^6$  mol d<sup>-1</sup> for NO<sub>3</sub><sup>-</sup>,  $-17.5 \times 10^6$  mol d<sup>-1</sup> for NH<sub>4</sub><sup>+</sup> and  $-3.4 \times 10^6$  mol d<sup>-1</sup> for PO<sub>4</sub><sup>3-</sup>, which are 1, 8, and 93 times higher than those in the dry season. The high nutrients exports during the wet season probably reflect the inputs coming from the agricultural, domestic and industrial wastes during the severe flooding over Thailand in 2011. During the present study, the system showed the removal of DIP at the rate of 0.34 mmol m<sup>-2</sup> d<sup>-1</sup> (October 2011) serving as a sink and almost in balance in February 2012. On the other hand, DIN values in

the Inner Gulf are negative in both sampling periods, which showed the removal of DIN at the rate of 2.05 and 0.42 mmol m<sup>-2</sup> d<sup>-1</sup> in October 2011 and February 2012, respectively, serving as a sink for DIN. Table 4 summarizes the net ecosystem metabolism of the Inner Gulf of Thailand. Negative values of ( $nfix-denit$ ) suggests a denitrifying system in the Inner Gulf during the low flow period.

## Conclusions

The LOICZ biogeochemical modelling results of non-conservative fluxes,  $p-r$  and ( $nfix-denit$ ) indicate that in the Inner Gulf of Thailand photosynthesis was larger than decomposition plus bottom release in the wet season but photosynthesis was nearly the same as decomposition plus bottom release in the dry season. Nitrogen fixation was higher than denitrification in the wet season but denitrification was larger than nitrogen fixation in the dry season. The results presented in this study may help scientists to summarise existing and new data in consistent and rigorous formats that may be more useful to coastal zone managers. It is also assumed that they may assist in the development of more applied models that could be used by managers in the decision-making process. The findings give insight into the way nutrient inputs are modified as they move from the land to coastal waters and how these, in conjunction with internal biological fluxes, affect the system metabolic processes. This may create an interest in the present system to be compared with other shallow coastal systems and to strengthen the understanding of nutrient behaviour to place further these findings in a regional and global context.

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