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Nutrient Diagenesis in Sediments of the South China Sea, Area II: Sabah, Sarawak, and Brunei Darussalam waters

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ABSTRACT

Study on nutrient diagenesis and physico-chemical characteristics of bottom sediments of the Sabah, Sarawak and Brunei Darussalum waters had been carried out under the ongoing SEAFDEC Collaborative Research Project. The results indicated that organically enriched offshore sediments consisted high levels of pore water nitrate and phosphate concentrations. For the whole study area, the levels of nitrate and phopsphate concentrations in pore water were in the ranges of 0.05 to 77.12 µg at NO_3^--N/L and 0.07 to 13.13 µg at PO_4^{3-}-P/L, respectively. Upward diffusive fluxes of pore water nitrate widely changed in stations. At the nearshore area, the fluxes of pore water nitrate had an average of 26.5 mg at NO_3^--N/m^2/d and were about one order of magnitude higher than those of phopsphate. However, phosphate upward fluxes were apparently high at deep areas off Sabah. Pore water ammonium concentrations were commonly very low but tended to be more accumulated at nearshore organically enriched areas. The ammonium concentrations for the whole study area ranged from non-detected level to 81.76 µg at N/L. The nearshore stations showed very high upward fluxes of ammonium, which were nearly 10 times higher than those of nitrate and phosphate. Sedimentary organic levels were comparatively high in two distinct regions; (I) a shallow nearshore region of Sarawak, and (II) a deep offshore region of Sabah amd Brunei Darussalum. The sources of organic materials settled in Regions (I) and (II) were suggested to be derived from different origins. The Northeast monsoon can somewhat enhance organic accumulation in the nearshore region. Overall our results obtained from this study had been used to characterize the bottom sediments into three distinct regions and discussed for further fishery resource development and management.

Key words: sediments, pore water nutrients, upward diffusive fluxes,
             total organic carbon and nitrogen

Introduction

A knowledge of the properties of the sediment-water interface, as well as of the kinetics of the chemical reactions taking place in the sediments, is essential for describing and understanding the mass transfer processes between sea water and marine deposits (Vanderborght *et al*. 1977*a*). Besides the effluent and the internal production, the release of nutrients from bottom sediments is one of the major causes of production and organic pollution in the sea. Such processes cause great influence to the seawater quality and interact complicatedly each other. The release of nutrients from sediments is important for algal growth (Ryding and Forsberg 1977, Hosper 1984, Søndergaard *et al.* 1990, Meksumpun *et al*. 1998). An indication of the importance of the sediment release is an increase in the phosphate concentration in summer which is far greater than can be explained by external loading (Sas 1989). In the South China Sea, the boundary conditions at the sediment-water interface are often poorly known.

The research study on nutrient diagenesis in sediments of the South China Sea (Area II) is a part of the ongoing project "the Interdepartmental Collaborative Research Project of the South China

Sea" which is supported by the Southeast Asian Fisheries Development Center (SEAFDEC) and aims to collect up-to-date information on the marine fishery resources and the present oceanographic conditions of the South China Sea for further establishment of appropriate scheme of fishery resource development and management. Here we report the results of porewater and bottom sediment analyses. Objectives of this study are listed as the following items.

1) To investigate the levels of biological important nutrients (nitrate, phosphate and ammonium) in sediment pore water and study the nutrient diagenesis characteristics of bottom sediments in the sea area

2) To examine the organic levels (e.g. total organic carbon, total organic nitrogen and total organic contents) of the bottom sediments

3) To study the influence of the Northeast monsoon on the alternation of sediment characteristics

4) To extrapolate the upward diffusive fluxses of biological important nutrients at the sediment-water interface and define the relations among the sedimentary organic levels, diagenesis characteristics and upward diffusive fluxes of nutrients of the bottom sediments

The baseline data obtained can be used not only to characterize the sea bottom in an aspect of a potential contribution to material budget and biological productivity of the water column but also to provide a better understanding of the sediments as potential resources for benthic production development of the sea area.

Materials and Methods

Collection of sediment samples

Sediment samples were collected from 79 stations (**Fig. 1**) at the sea area off Sabah, Sarawak and Brunei Darussalam, in the South China Sea, during 4 July to 9 August 1996 (pre-Northeast monsoon period) and 25 April to 31 May 1997 (post-Northeast monsoon period) by M.V. SEAFDEC. Almost of the sediment samples were collected by gravity corers (see **Table 1**). Sediment grab was applied in stead of the corer at some stations where the bottom deposit was mainly composed of sand and gravels and hence it was unable to retrieve by the corer. Prior to subsampling, measurement of sediment surface temperature was immediately conducted (**Table 1**) and the appearances of the sediment core were recorded. The cores was subsampled as soon as possible after retrieval. After the overlying water was gently taken off, the sediment core was extruded from the liner and cut into 1-cm sections for the upper 10 cm depth, 2-cm sections for the depth between 10 to 20 cm, 3-cm sections for the depth between 20 to 50 cm, and 5-cm sections for the depth greater than 50 cm.

Analyses of sediment samples

After subsampling, a portion of the sediment samples were packed tightly in plastic containers and immediately frozen under -60 °C for further analysis of water content. Remaining part of the sectioned sediment samples were extracted for pore water by centrifugation of the sediment for 5 min at 3,500 rpm. The supernatant was then filtered with Millipore HA (0.45 μm) and immediately frozen until analysis on board of M.V. SEAFDEC. The pore water samples were analyzed for nitrate nitrogen (NO_3^--N), phosphate phosphorus (PO_4^{3-}-P) and ammonium nitrogen (NH_4^+-N) concentrations with an auto nutrient analyzer (TRAACS 800, Bran & Luebbe).

Sediments were dried at 70 °C for 3 days and then ground to powder. Chemical analyses of the sediment samples were carried out at laboratory of the Marine Environment Section, Chugoku Natinal Industrial Research Institute (CNIRI), Japan. The ground samples for organic content analysis were freeze-dried again before being weighed in silver cups. In order to remove inorganic carbon, the sediments in the cups were treated several times with 2M-HCl solution, freeze-dried, and packed in tin cups prior to analysis. The total organic carbon (TOC) and nitrogen (TON) contents were obtained using an elemental analyzer (Carlo Erba, NA-1500). Total organic matter (TOM) contents

were determined by measuring the weight loss of dry sediment after ignition in a furnace at 450 °C for 3 hours.

Results and Discussions

Nitrate-N in sediment pore water

Nitrate in sediments is formed from ammonium through nitrification in the aerobic top layer (Smits and Molen 1993). The concentrations of NO_3^--N in the surface sediments of each sampling station are summarized in **Table 1**. The levels of NO_3^--N concentrations in the sampling area range from the minimum value of 0.05 µg at NO_3^-N/L at station 7 (a nearshore station; 32 m depth) to the maximum value of 77.12 µg at NO_3^-N/L at station 65 (an offshore station; 1,457 m depth) and the mean value of 29.09 µg at NO_3^-N/L can be calculated for the whole study area. The levels here were comparatively high when compared to those of the Seto Inland Sea, Japan (Yamamoto *et al*. 1998). Although there has no apparent correlation to the water depth, being considered as a single factor, NO_3^--N concentrations in the surface sediments are generally low in neasrshore stations (e.g. stations 17, 32, and 47) and comparatively high in offshore stations (e.g. stations 24, 40, and 53). The availability of NO_3^--N concentrations in the top layer of the sediments reflects that surface sediments of the study area are rather oxidized. Brown color of oxidized sediment can be observed to be less than 0.5 cm of some nearshore cores but it can extend to more than 4 cm of some deep stations. The thickness of top brownish sediments varies mainly due to the degree of detritus accumulation and oxygen penetration, and the type of deposits. Thus, although NO_3^--N concentrations are somewhat varied in sampling stations, the sediments of nearshore stations are apt to receive more organic loading and have less oxygen penetration than those of the offshore ones.

Below the oxidized layer, nitrate reduction can significantly occur. Typical NO_3^--N profiles can be observed in homogeneous, sandy silt cores of stations 60 and 76 (**Fig. 2**). The NO_3^--N concentrations show a maximum in the upper layer. This maximum can be formed by nitrate production and reduction during diagenesis of organic matter (Kato and Terunuma 1995) and related to the activity of autotrophic bacteria in the bulk of the sediments, which in turn strongly depends on the local redox potential (Vanderborght and Billen 1975). The concentrations are subject to vertical transport and denitrification in the zone just below this layer. Below the peak layers, nitrate apparently decreases.

Irregular vertical distribution pattern of NO_3^--N concentrations can be observed in some cores where the deposits alter considerably (e.g. stations 17 and 32, see **Fig. 2, 3**). At nearshore zone, effect of tidal cycle on the removal of combined nitrogen was studied (Usui *et al*. 1998). The tidal current was demontrated to have an inhibitory effect on sedimentary denitrification. Nevertheless, coupling role of NO_3^--N concentration in the overlying water has been emphasized. High NO_3^--N concentration in the overlying water should also be a primary source of nitrate in the sediment. Thus, the irregular pattern of NO_3^--N profiles may be explained by physico-chemical functions of inhibition of nitrate reduction and/or stimulation of nitrification in the circumstance.

Phophate-P in sediment pore water

Phosphate can be liberated from organic matter by bacterial activity just like ammonium. Release of phosphate from sediments is known to be important for algal growth (Hosper 1984, Søndergaard *et al*. 1990). In the study area, the levels of PO_4^{3-}-P concentrations in surface sediments range between 0.07 to 13.31 µg at PO_4^{3-}P/L (**Table 1**), with the mean value of 3.73 µg at PO_4^{3-}P/L. Comparatively high PO_4^{3-}-P concentrations can be observed at some offshore stations (e.g. stations 39 and 41) and at some deep nearshore stations (e.g stations 77 and 78), while very low PO_4^{3-}-P concentrations are commonly found. Such occurrences are considered to be due to the differences in types, organic levels and oxidized condition of the deposits. Since phosphate adsorbs strongly to several components of the sediments, the hydroxides of iron (III) and aluminium in particular, and the adsorptions are stronger in the oxidized layer than in the reduced layer (Berner 1974, Lijklema 1980, Van Raaphorst *et al*. 1988), low PO_4^{3-}-P concentrations (e.g. at station 47, **Fig. 2**) may imply comparatively reduced

condition of the sediments. Correspondingly, the core of station 47 has revealed only thin layer of oxidized zone (**Fig. 3**). The vertical profiles of pore water PO_4^{3-}-P concentrations remain relatively constant in most cores, which should be caused by the buffering capacity of the adsoption and precipitation processes (Horie and Hosokawa 1985, Smits and Molen 1993).

Ammonium-N in sediment pore water

Ammonium is released from the degradation of detritus and nitrified by bacteria under aerobic conditions (Berner 1974, Vanderborght *et al*. 1977*b*). It has been demonstrated that ammonium is taken up by phytoplankton more rapidly than nitrate (Dugdale and Goering 1967). The levels of NH_4^+-N concentrations of surface sediments in the sampling area range from non-detected level to the maximum value of 81.76 μg at NH_4^+-N/L at station 59 (**Table 1**) and the mean value of 15.58 μg at NH_4^+-N/L can be calculated for the whole study area. Such levels of NH_4^+-N concentrations are generally low when compared to other eutrophic sea areas (cf. Yamamoto *et al*. 1998). About one third of the surveyed stations, the surface sediments show no accumulation of NH_4^+-N and thus the sediments here are well oxidized and, consequently, nitrification process should be significantly enhanced. In the sediments, NH_4^+-N concentrations increase with depth (**Fig. 2**). Especially their concentration gradients in the nitrate reduction zone are somewhat greater (see the profiles of stations 60 and 76). In those cores, sharp discontinuities of the nitrate concentration gradients occur at a depth of about 4 cm and 2 cm, respectively. Those depth are well corresponding to the oxidized depths of each core (**Fig. 3**).

In sediment of a long core obtained from station 78, pore water NH_4^+-N concentrations, as contrast with nitrate, show a sharp increase in the upper 10 cm layer (**Fig. 4**). The observed concentrations gradually increase and seem to be constant in the deep layer of *ca* 70 cm. Vertical distribution pattern of all nutrients imply a rather constant depositional process of the deposits. The remaining of nitrate in deep layer, moreover, has revealed the oxidized characteristics of sediment and water overlying in deep region of the surveyed area.

Total organic carbon, total organic nitrogen and C:N ratio of the sediments

Organic carbon content in the sediment is important for understanding the productivity of the ocean. Amount of organic matter deposited in the sediment can reflect bio-productivity of water column, input of organic matter, and sedimentation rate (Kennet 1982). In the study area, the bottom topography changes from a shallow shelf to a deeper zone with increasing distance from the coast of Sarawak (**Fig. 1**). The water depth rapidly changes and a deep valley is situated just off the coast of Sabah, the east part of the survayed area. Such bottom topography, together with the influence of local current, should play a major role controlling the depositional characteristics of the organic matter there. Bottom sediments in the sea off Sabah was studied by Yaacob and Higashikawa (1990). The nearshore sediment ranged from sand to silty loam and were mostly yellowish-grey sandy mud. The grain size changed from fine-grained sand to silt as depth increases. In this study, we defined the sediment types by the water content of the samples (sandy and sitly sediment defined by a water content less and more than 35 % by weight, respectively). The sandy sediments can be observed commonly at nearshore areas of Sarawak (e.g. at stations 1, 8, 9, 15, 17, 18, 30, and 46) and at nearshore stations (stations 77 and 79) of Sabah. In offshore area, only one distinct sandy station was noticed (station 23). The other stations in the survey area almost consist with silty deposits.

Such differences in types of deposits are positively correlated with the levels of organic contents of the sediments. Horizontal distributions of organic contents of carbon and nitrogen of surface sediment showed similar pattern. Low total organic carbon (TOC) content of sediments occurred in neasrshore areas and high TOC content can be found in offshore area of Sabah where the water depth dramatically increases (**Fig. 5**). Very low organic carbon contents (lower than 1.00 mg/g) were found in the sandy zones around station 1, stations 8 and 9, and stations 18 and 30.Å@ The maximum TOC content (17.39 mg/g) was found in silty clay sediment of station 78 (water depth 1,515 m). Average

TOC content for the whole study area is 5.91 mg/g. It is in the same range of the former report by Yaacob (1990) for the Sabah waters (3-13 mg/g). Organic nitrogen (TON) contents in the sediment showed almost the same pattern as that of organic carbon contents (**Fig. 6**). The lowest TON contents of the sediments (less than 0.20 mg/g) were found in the same area as those of TOC. The highest TON contents of the sediments were found around station 78 at the values higher than 2.00 mg/g. Average TON content for the whole study area is 0.97 mg/g.

Horizontal distribution pattern of TOC and TON contents of the sediment in nearshore area may imply a degree of terrestrial impact to the marine environment. **Figures 5** and **6** show increasing organic contents in the area adjacent to riverine sources, e.g. at stations 7 and 17. Sediment particles from the rivers are likely to be settled there. In those stations, nevertheless, such accumulation patterns of TOC and TON may be complicate since the location there should receive more physical effect from water mass distribution and currents. For the whole study area, because the surface current velocity and direction are remarkably influenced by the monsoon, the accumulation patterns of organic carbon and nitrogen were considered to be directly correlated with the bottom topography and the local monsoon. Although the highest organic contents of carbon and nitrogen of surface sediments in some parts of the study area were as high as the high production areas e.g. in the Osaka Bay, Japan (12-22 mg/g for TOC and 1.8-2.4 mg/g for TON) (Montani *et al*. 1991, Mishima *et al*. 1996), the mean values of the organic carbon and nitrogen contents of the whole area were comparatively low. Such low concentrations of benthic organic materials may be one of the causes of comparatively low fishery production in this area.

The atomic ratios of carbon to nitrogen (C:N) have been employed as source indicators of sedimentary particulate organic matter by numerous workers (e.g. Rashid and Reinson 1979, Prahl *et al*. 1980). Generally, high values of C:N ratios (>10) of sediments from mid-latitude areas have been interpreted to be a large effect of terrigenous materials input (Thornton and McManus 1994, Mishima *et al*. 1996). The C:N ratio of the mixed diatoms (50% *Skeletonema costatum*, 20% *Nitzchia seriata* and 20% mixed *Cheatoceros* spp.) in June at Dabob Bay, Washington, have been reported to be 5.4 (Hedges *et al*. 1988). Additionally, the ratios of sediment in the East China Sea, which contain a dominant contribution of marine organic carbon, lie in the range 6.2 to 8.8 (Tan *et al*. 1991). In this study area, the C:N ratios were almost in the range of 6-8 (**Fig. 7**), indicating the marine source. At some nearshore stations (e.g. stations 7 and 17), apparently high C:N ratios (more than 10) can well reflect the impact of terestrial runoff. However, high C:N ratios can also be observed in some offshore stations in the deep waters off Sabah. Such occurrence may suggest high decomposition rate of carbon and/or nitrogen in the surface sediments.

Influence of the Northeast monsoon on bottom sediments

The major circulation in the South China Sea is driven by the monsoon winds (Wyrtki 1961). Winds prior to September are dominated by the Southwest monsoon. The Northeast monsson expands southwards against the diminish of the Southwest monsoon in October, reaching its maximum strenght and covering the entire South China Sea in December. Numerical simulation of the sea level variation indicated that the monsoon winds are the main driving force affecting the sea level around west Malaysia (Azmy *et al*. 1991). The monsoon, therefore, should have more or less effect to the bottom sediments. Numerical simulation of the flow fields at 50 m depth indicated the intrusion current entering the Luzon Strait accelerates along the boundaries of the basin in response to the Northeast monsoon (Chao *et al*. 1995). The southward current off the coast of Vietnam turns cyclonically as it impinges onto the Sundra shelf. Then, a two-layer circulation develop in the shallow Gulf of Thailand; water flowing out of the Gulf at 50 m, to the west part off Borneo, is replinished by a surface inflow (Chao *et al*. 1995). Such a trend of water movement into the west part of the study area may somewhat contribute to the alternation of the bottom deposits.

Evaluation on the influence of the Northeast monsoon on bottom sediments has been carried out by analysis of the change in total organic content (TOM) of the surface (0-1 cm) sediments after

monsoon season (some deep stations off Sabah were omited since the loss of corring apparatus during the post-monsoon survey). The levels of TOM in the surface sediments there ranged between 0.60 to 7.51 % and are significant correlated with those of TOC ($r^2 = 0.76$) and TON ($r^2 = 0.66$) (**Fig. 8**). Such levels were comparatively lower than those usually found in organically enriched area of closed bay. After the Northeast monsoon passes, sedimentary TOM varies from stations to stations. Percentage of changes in TOM (**Fig. 9**) indicate dramatical increases (more than 50 to 160 % of initial TOM) at some nearshore stations that previously consisting with high TOC and TON contents (e.g. station 7) and that previously consisting with low TOC and TON contents (e.g. stations 9, 18, 30 and 69). Such increases should be due to greater discharge of terestrial organic sources enhanced by the monsoon wind. Except for those above stations, other nearshore stations commonly show the decreases of TOM after the monsoon season since those areas receive comparatively strong wind wave effect. In addition, some offshore stations (e.g. stations 12, 13, 22, 23, and 24) demonstrate the increase of TOM (13-24 %). The sources of such increases cannot be clarified yet. Either subsurface outflow circulation from the Gulf of Thailand or resuspension and setlement mechanisms of comparatively high organic matterials can possibly enhance such phenomena. Since suspended matter supplied from rivers or marine productions are transported by the residual flow in the long term, sinks doward and settles at some point of the sea bottom, the sedimentary preocess of the sea area should be more clearly illustrated by further application of 3-dimential numerical model that can reflect the important role of residual flow characteritics of this sea area.

Estimation of upward diffusive fluxes of nutrients at the sediment-water interface

In water quality management, the estimation of nutrient upward fluxes is often beneficial in description of the water system and prediction of the effects of changes such as enahanced nutrient loadings to the productivity of overlying water column. Generally, the properties of surface sediment layer differ considerably from those of deeper layers, and may strongly affect the mass transport across the water-sediment interface. Degree of compaction in the surface layer is low, especially for muddy sediments. The high porosity also favors an increased flux in the pore water of this layer. Thus, the silty sediments of the study area are considered to be most important for the sediment-water interactions. Eighteen silty stations are focused (stations 7, 11, 16, 17, 24, 31, 32, 33, 38, 39, 42, 43, 47, 60, 71, 75, 76 and 78) and the characteristics of the sediments and the chemical properites of pore water of those stations are used for estimation of upward nutrient fluxes of the biological important nutrients.

For flux estimation, assumption of steady state is allowed for these substances, because the changes of their concentrations in the overlying water is slow compared to the mass fluxed of the diffusion and oxidation processes near the sediment-water interface. Dependency on bio-irrigation and pH are ignored since the lack of information. All the rates of conversion processes are temperature dependents. Dispersion in the pore water is set as the result of molecular diffusion. The concentration of dissolved constituents at the sediment-water interface cause the diffusional transport. Thus, nitrate, phospate and ammonium diffuse from the sediments into the seawater because their surficial pore water concentrations are higher than those in the overlying seawater. Based upon Fick's first law and Yamamoto et al. (1998), we estimated the upward diffusive fluxes of thess nutrients by

$$F = -\phi \, D_{sed} \frac{\Delta C}{\Delta Z} \qquad (1)$$

where, F = flux (μg at N or P/cm^2/s), ϕ = sediment porosity, D_{sed} = diffusion coefficient in sediment (cm^2/s), C = pore water nutrient concentration (μg at N or P/L), and Z = depth in sediment (cm). The sediment porosity (ϕ) was calculated by its interrelation to the density, water content and temperature of the sediment, and the density and salinity of porewater as the following equation:

$$\phi = (A/\rho_i)/\{(A/\rho_i)+[(1-A)/\rho_m]\} \qquad (2)$$

where, ρ_i = density of pore water (g/cm³), ρ_m = density of sediment (g/cm³) and the factor A was determined by

$$A = (\omega/100)/[1-(S/1000)] \qquad (3)$$

where, ω = water content of the sediment (%) and S = salinity of the porewater (psu). The diffusion coefficient in sediment (D_{sed}) was calculated according to Nakashima and Nishimura (1986; cited in Yamamoto *et al*. 1998) through the following equations:

$$D_{sed} = (1/F.\phi).D_0^{\ t} \qquad (4)$$

where, F = formation factor and $D_0^{\ t}$ = diffusion coefficient at t °C. F was approximated by

$$F = \phi^n \qquad (5)$$

For marine sediment, the facor n is commonly 2 ~ 4 in which it is about 2 in sandy sediment and becomes greater to 2.5 ~ 3.5 in the muddy deposits (Masuzawa 1985; cited in Yamamoto *et al*. 1998). In this study, we decided n to be 3. In the temperature range of 0 ~ 25°C, the factor $D_0^{\ t}$ can be approximated according to Lerman (1979) as the following equation:

$$D_0^{\ t} = D_0^{\ 0}(1+\alpha t) \qquad (6)$$

where, $D_0^{\ 0}$ = diffusion coefficient at 0 °C and α = ion coefficient. According to Li and Gregory (1974), the $D_0^{\ 0}$ of nitrate, phosphate, and ammonium are 0.978×10^{-5}, 6.1×10^{-6} and 0.98×10^{-5} cm²/s, respectively. The coefficient α for cation and anion are 0.048 and 0.040, respectively (Lerman 1979). By substituting equations (5) and (6) into equation (4), the following equation can be obtained.

$$D_{sed} = D_0^{\ 0}(1+\alpha t).\phi^2 \qquad (4)'$$

Using equations (1), (2), and (4)′ and the concentration gradients at the interface obtained from the regression curve of C as the function of Z, we can culculate the upward diffusive fluxes as F (*SE* $\pm8\%$).

The results together with parameters used in the estimations are summarized in **Table 2**. The depths (Z) of sediment layer for upward flux estimation were determined based upon the vertical distribution pattern of each nutrient and depended on stations. The upward diffusive fluxes of NO_3^--N widely change with the average of 26.5 mg at N/m²/d for the nearshore stations. The offshore stations (stations 11 and 39) in which comparatively low and high organic levels show correspondingly low and high values of NO_3^--N fluxes of 5.6 and 88.4 mg at N/m²/d, respectively. The upward diffusive fluxes of PO_4^{3-}-P are slightly lower than those of NO_3^--N. Average PO_4^{3-}-P upward fluxes at the nearshore stations is 2.8 mg at P/m²/d. The values were in similar range to those of the offshore stations in which the sedimentary organic content are low. However, distinguishably high PO_4^{3-}-P upward fluxes are found in the offshore sediment with comaparatively high organic content (e.g. stations 71 and 75). High rate of organic decomposition under comparatively oxidized conditions of the sediment may be the possible cause of such phenomena.

The nutrient fluxes, NO_3^--N in particular, at the sediment-water interface of many stations show a negative trend (see remarks "down-F" in **Table 2**). In those cores, the uppermost layers of the sediments have highest levels of the nutrient concentration with a gradual decrease as the sediment depth increase. To estimate the relaease fluxes of such deposits, the method of Yamamoto *et al*. (1998), which evaluated the upward flux from the concentration gradient between the surface sediment and the overlying water, could be further attempted. However, since NO_3^--N fluxes are often negative, the overlying water might be a possible source of nitrogen to denitrification process in the

Table 1 Sampling date and apparatus, depth of obtained cores, and concentrations of nitrate-N, phophate-P, and ammonium-N in pore water of surface (0-1 cm) sediments (nd = no data)

Date	Station	Apparatus	Core depth (cm)	Nitrate-N (_g at NO$_3$-N/L)	Phosphate-P (_g at PO$_4{}^{3-}$-P/L)	Ammonium-N (_g at NH$_4{}^+$-N/L)
10-Jul-96	1	grab	3	nd	nd	nd
	2	gravity core	19	2.64	1.39	10.22
	3	gravity core	19	13.72	1.55	3.37
	4	gravity core	16	5.25	2.16	34.87
11-Jul-96	5	gravity core	12	2.62	1.98	21.63
	6	gravity core	19	2.75	1.84	21.93
	7	gravity core	18	0.05	0.64	35.79
	8	gravity core	18	nd	nd	nd
12-Jul-96	9	gravity core	7	63.22	2.41	nd
	10	gravity core	14	8.41	1.26	0.00
	11	gravity core	16	0.44	0.81	23.28
	12	gravity core	40	16.13	2.08	0.00
13-Jul-96	13	gravity core	34	11.25	1.87	0.00
	14	gravity core	38	31.05	1.95	0.00
	15	gravity core	38	5.15	1.45	24.08
	16	gravity core	29	3.38	1.66	0.00
14-Jul-96	17	gravity core	18	1.22	1.24	41.30
	18	grab	6	nd	nd	nd
	19	gravity core	20	24.26	1.00	47.88
	20	gravity core	16	7.27	1.28	33.43
15-Jul-96	21	gravity core	70	44.05	2.74	1.67
	22	gravity core	41	45.20	3.90	0.00
	23	grab	8	nd	nd	nd
	24	gravity core	41	66.29	8.70	0.00
16-Jul-96	25	gravity core	25	27.24	3.36	0.00
	26	gravity core	47	16.16	3.52	0.00
	27	gravity core	32	30.80	2.59	0.00
	28	gravity core	38	61.52	3.05	0.00
17-Jul-96	29	gravity core	23	8.43	4.75	0.00
	30	grab	6	nd	nd	nd
18-Jul-96	31	gravity core	18	22.71	2.60	19.48
19-Jul-96	32	gravity core	32	2.09	3.37	43.54
	33	gravity core	85	12.48	6.25	4.81
	34	gravity core	41	73.51	0.07	0.00
	35	gravity core	75	25.99	0.93	0.00
20-Jul-96	36	gravity core	60	30.85	0.60	5.15
	37	gravity core	38	38.51	2.21	10.76
	38	gravity core	70	65.71	2.25	0.00
	39	gravity core	70	18.12	13.31	16.99
21-Jul-96	40	gravity core	14	69.73	0.45	3.41
	41	gravity core	60	16.16	11.55	0.00
	42	gravity core	70	7.07	4.46	19.32
	43	gravity core	90	39.02	4.38	14.48
22-Jul-96	44	gravity core	85	37.24	1.33	0.00
	45	gravity core	29	72.98	1.18	24.99
	46	grab	5	nd	nd	nd
	47	gravity core	35	3.09	0.66	0.00
24-Jul-96	48	gravity core	31	24.37	2.65	0.00
	49	gravity core	20	43.11	2.64	0.00
	50	gravity core	38	17.06	7.08	0.00
25-Jul-96	51	gravity core	26	27.01	3.10	0.00
	52	gravity core	68	25.61	7.03	0.00
	53	gravity core	32	69.28	5.57	1.40
	54	gravity core	26	41.79	7.04	0.02
26-Jul-96	55	gravity core	70	39.70	5.98	11.16
	56	gravity core	60	42.10	6.84	12.62
	57	gravity core	26	57.65	3.82	3.00
	58	gravity core	75	22.62	6.00	10.99
27-Jul-96	59	gravity core	32	2.99	3.08	81.76
	60	gravity core	50	12.13	2.90	7.70
	61	gravity core	50	49.00	4.38	6.03
	62	gravity core	85	56.00	3.50	14.95
28-Jul-96	63	gravity core	35	39.93	4.30	8.32
	64	gravity core	55	35.81	4.81	11.34
	65	gravity core	26	77.12	3.99	11.13
	66	gravity core	29	70.17	4.19	17.35
29-Jul-96	67	gravity core	95	33.84	3.29	20.78
	68	gravity core	65	28.59	3.92	57.27
	69	gravity core	32	26.88	5.01	76.59
	70	gravity core	29	14.63	3.60	69.03
31-Jul-96	71	gravity core	32	25.99	4.39	8.50
	72	gravity core	55	45.50	5.17	22.05
	73	gravity core	26	40.44	4.11	8.69
1-Aug-96	74	gravity core	75	26.82	3.99	8.67
	75	gravity core	75	28.68	5.10	26.58
	76	gravity core	29	10.08	4.02	51.10
2-Aug-96	77	gravity core	26	5.73	8.72	53.76
	78	gravity core	70	21.99	9.04	16.42
	79	gravity core	12	27.54	8.58	41.92

Table 2   Parameters used and the results on estimations of the upward diffusive fluxes at the sediment-water interface of some stations in the study area

Surveyed stations	Sediment temp (°C)	Nitrate upward fluxes			Phosphate upward fluxes			Ammonium upward fluxes		
		Z	$\Delta C/\Delta Z$	F	Z	$\Delta C/\Delta Z$	F	Z	$\Delta C/\Delta Z$	F
7	30.0	2	2.21	32.43	3	0.23	2.13	3	2.47	40.34
11	23.3	2	0.58	5.64	3	0.48	2.89	3	2.64	28.00
16	24.9	down-F	-	-	3	0.43	3.29	3	0.00	0.00
17	28.5	2	3.38	32.03	down-F	-	-	3	10.11	106.27
24	16.4	down-F	-	-	down-F	-	-	3	0.00	0.00
31	29.8	down-F	-	-	4	0.29	2.64	4	23.89	388.02
32	29.6	2	1.38	20.15	3	0.76	6.86	3	2.15	34.71
33	26.5	down-F	-	-	down-F	-	-	3	10.52	159.96
38	4.9	down-F	-	-	3	0.94	5.05	3	0.00	0.00
39	4.0	2	10.55	88.40	2	3.83	20.02	3	18.47	159.39
42	18.0	down-F	-	-	down-F	-	-	3	4.26	53.10
43	20.0	down-F	-	-	down-F	-	-	3	11.51	151.08
47	29.5	down-F	-	-	2	0.28	2.53	3	21.41	345.60
60	15.2	2	1.99	21.36	3	0.27	1.83	6	4.30	49.79
71	5.1	down-F	-	-	3	2.58	13.99	3	5.05	45.46
75	3.2	down-F	-	-	3	2.17	10.21	3	9.72	74.99
76	19.6	down-F	-	-	down-F	-	-	3	18.55	240.90
78	3.2	down-F	-	-	down-F	-	-	3	4.29	33.09
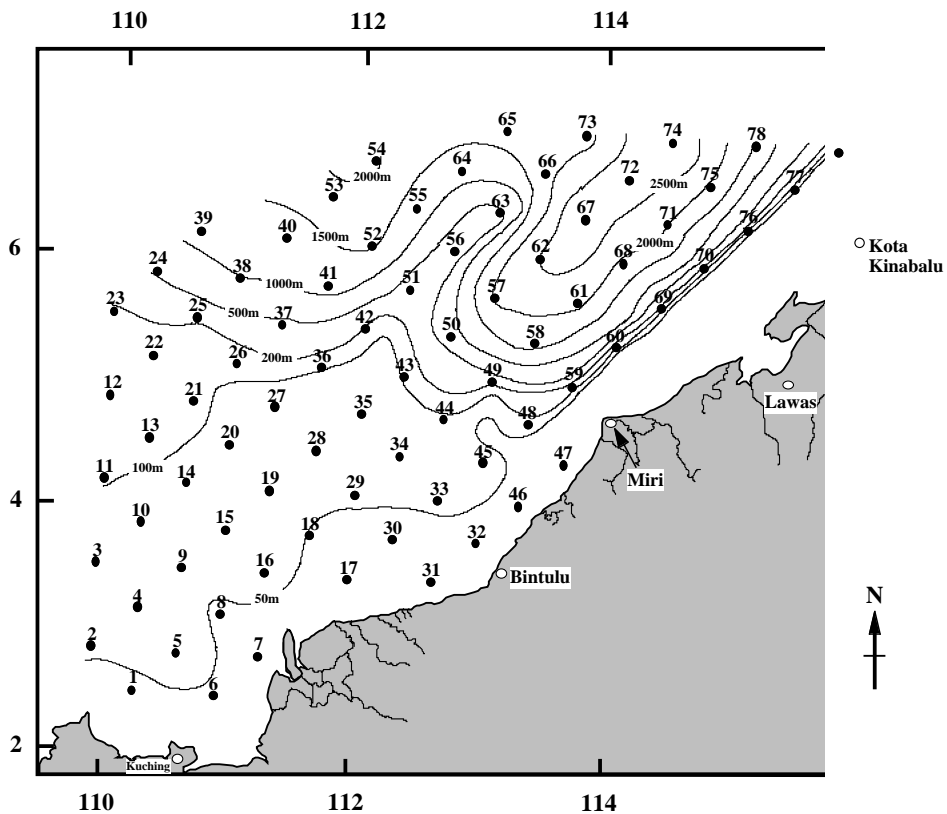
Fig. 1   Sampling stations in Sabah, Sarawak and Brunei Darussalam waters

Nutrient concentra
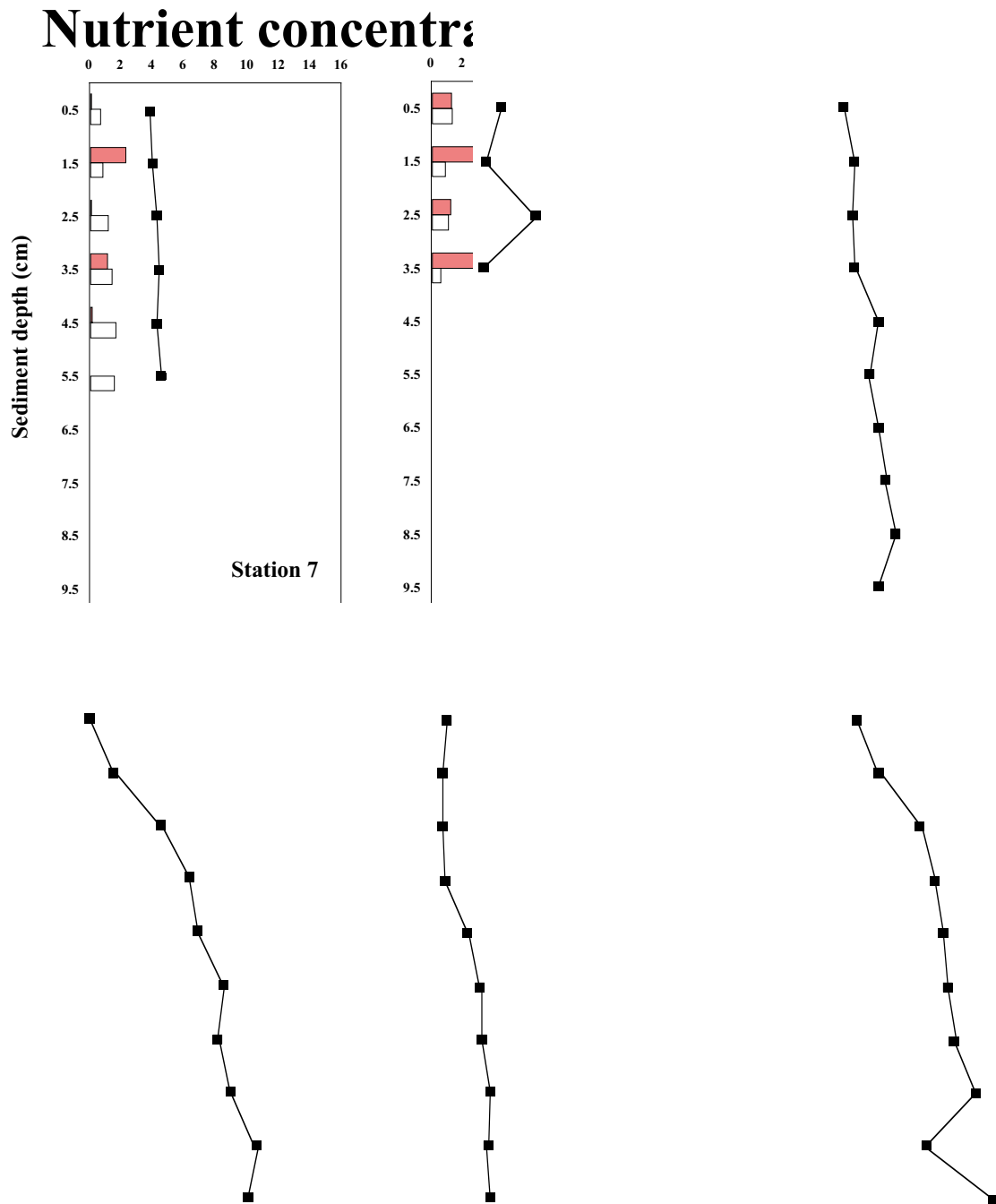
Fig. 2.   Vertical profiles of pore water nitrate, phosphate and ammonium concentrations of the sediments.
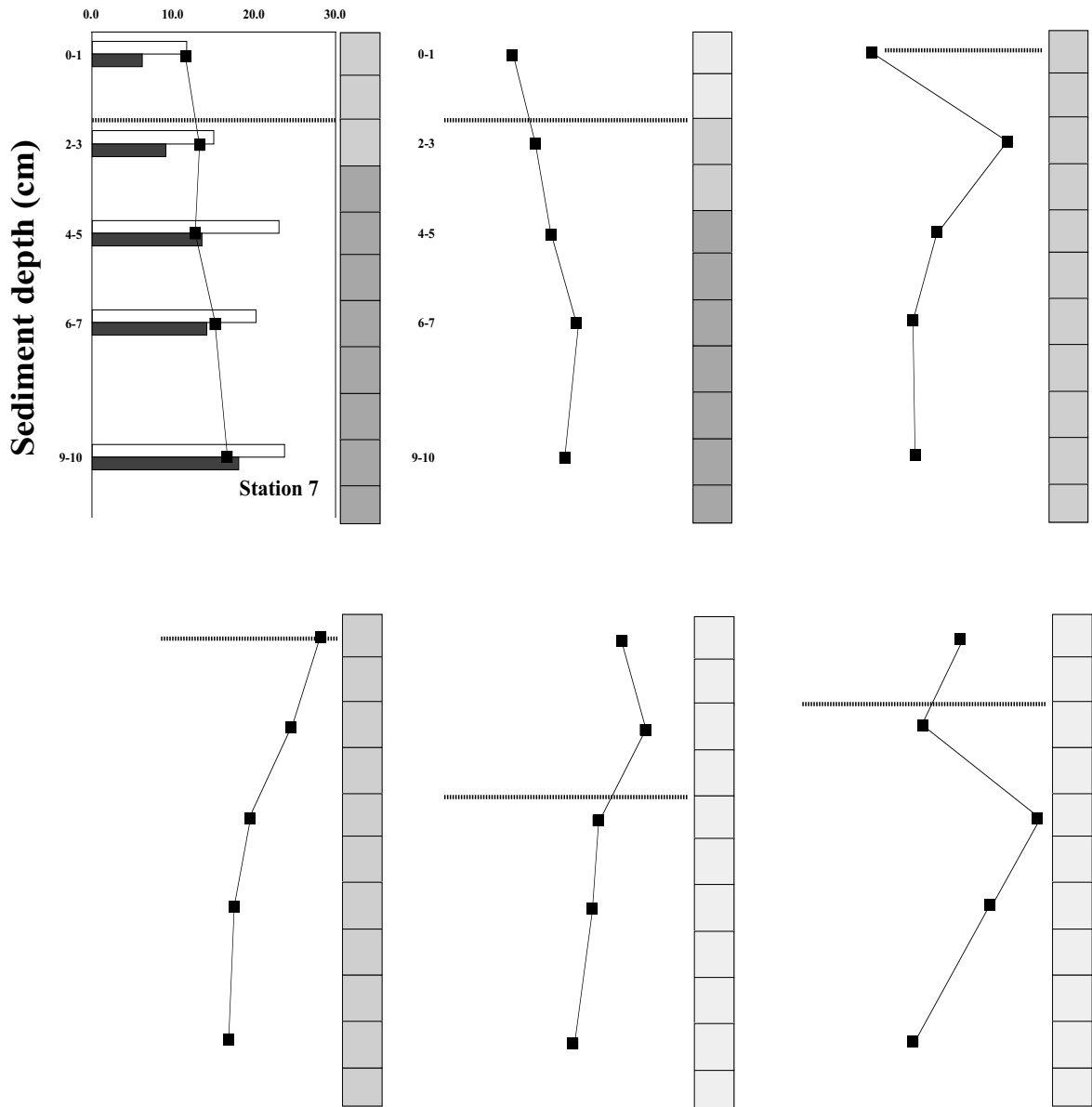
Sed

Fig. 3. Vertical profiles of total organic carbon (TOC), total organic nitrogen (TON) and C:N ratio of the sediments (dot lines indicating oxidized depth and core logging for each station are illustrated
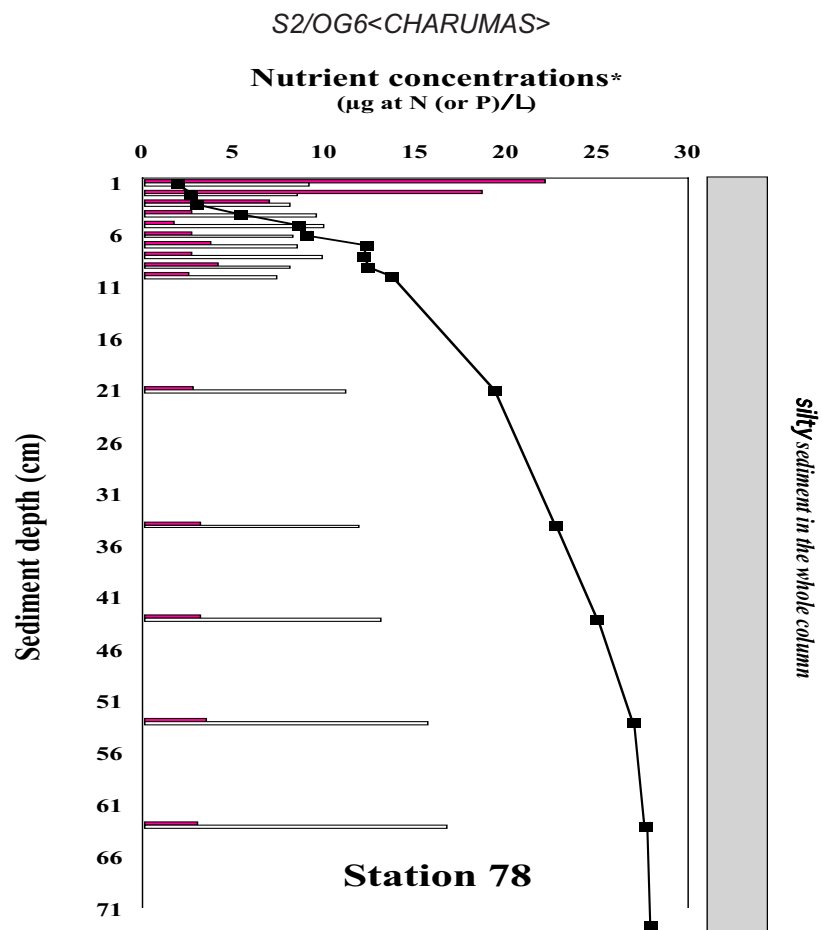
Nutrient concentrations*
(µg at N (or P)/L)

Fig. 4.   Vertical profiles of total organic carbon (TOC), total organic nitrogen (TON) and C:N ratio
of long sedimental core of station No. 78 (Core logging is comparatively illustrated).
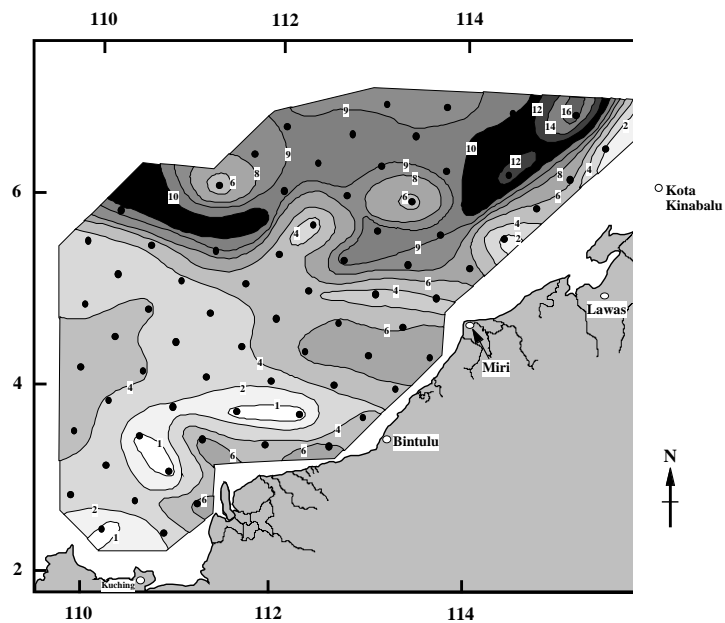
Fig. 5.   Horizontal distribution of total organic carbon ((TOC) contents of the surface (0-1 cm)
sediments
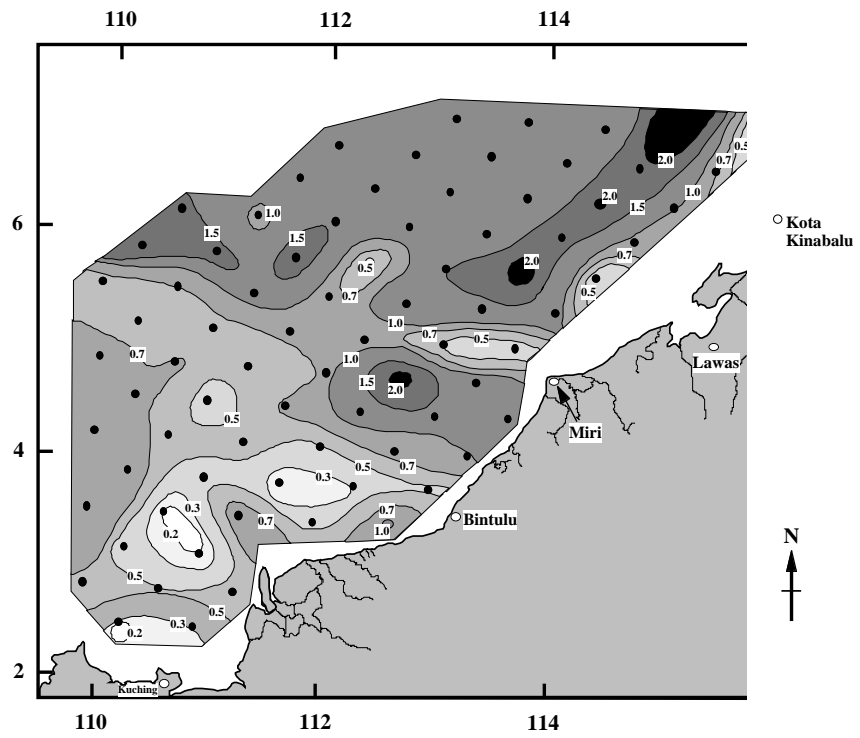
Fig. 6.   Horizontal distribution of total organic nitrogen ((TON) contents of the surface (0-1 cm) sediments
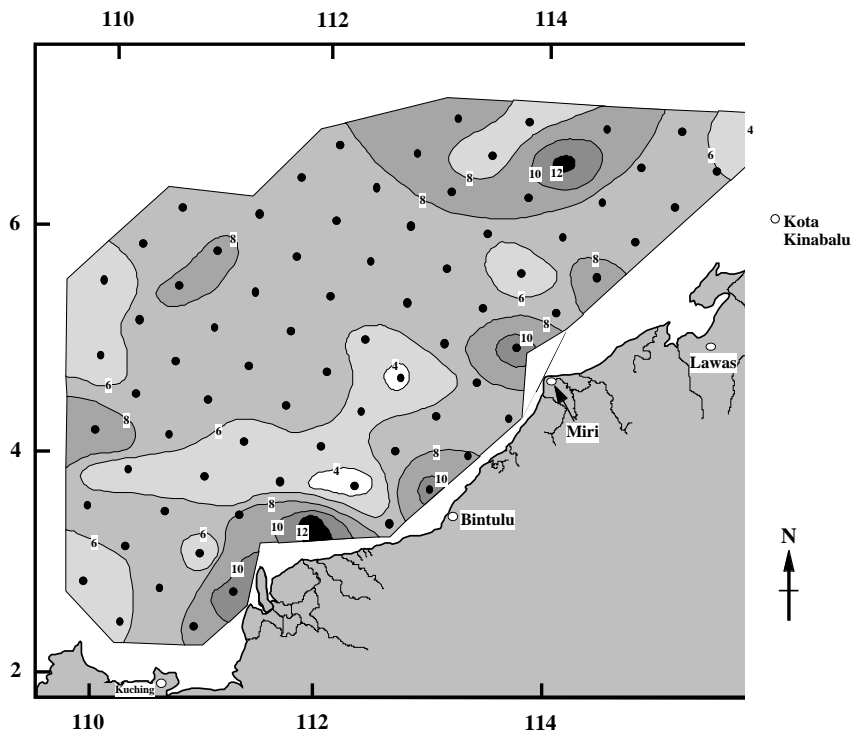
Fig. 7.   Horizontal distribution of C:N ratios of the surface (0-1 cm) sediments
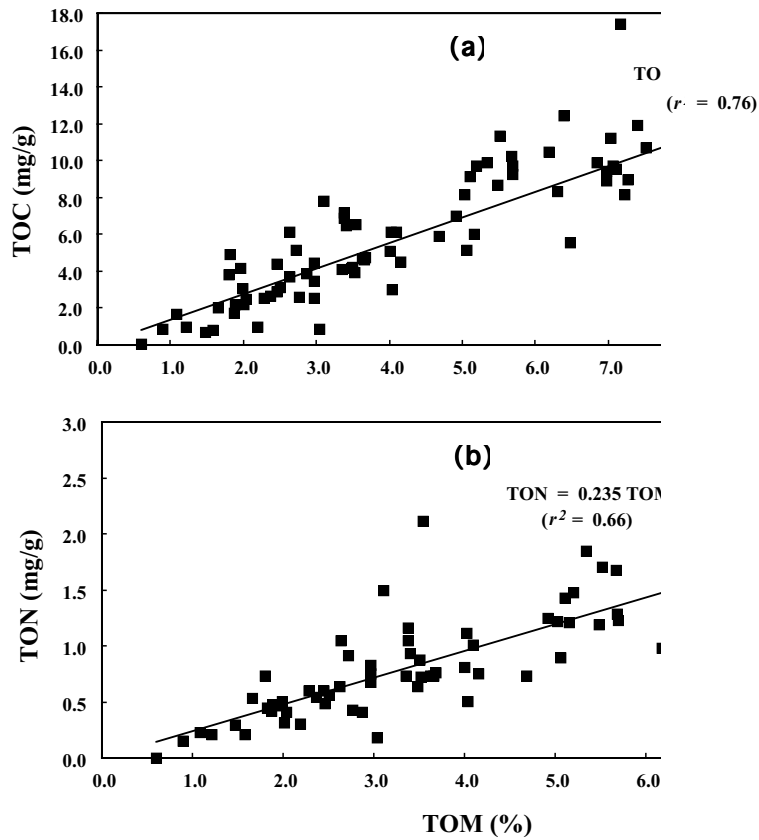
Fig. 8.   Relationships between the levels of total organic contents (TOM) and total organic carbon
(TOC) contents; a) and total organic nitrogent (TOC); b) of the sediments obtained from the
whole study area.
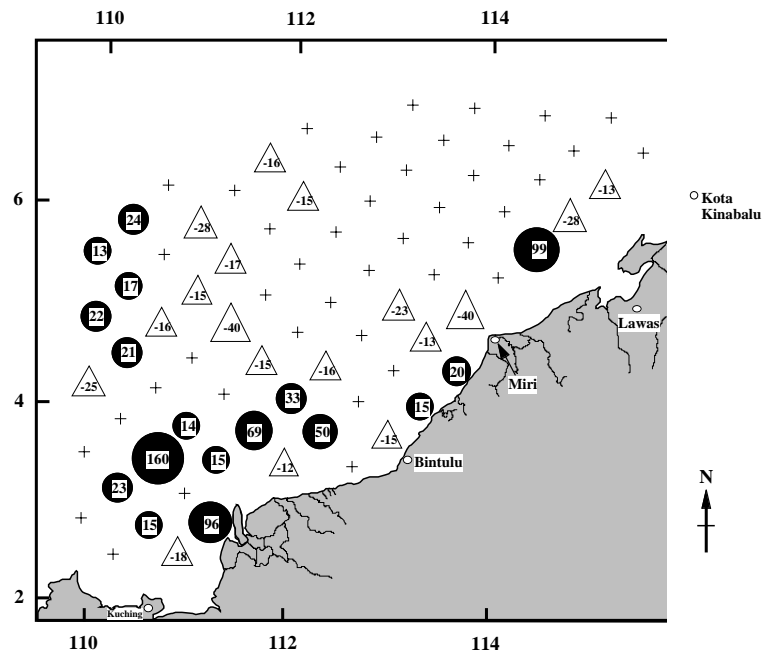
Fig. 9.   Percentage of increases (dull circles) or decreases (open triangles) in the levels of total or-
ganic contents (TOM) of the surface (0-1cm) sediments after the northeast monsoon period
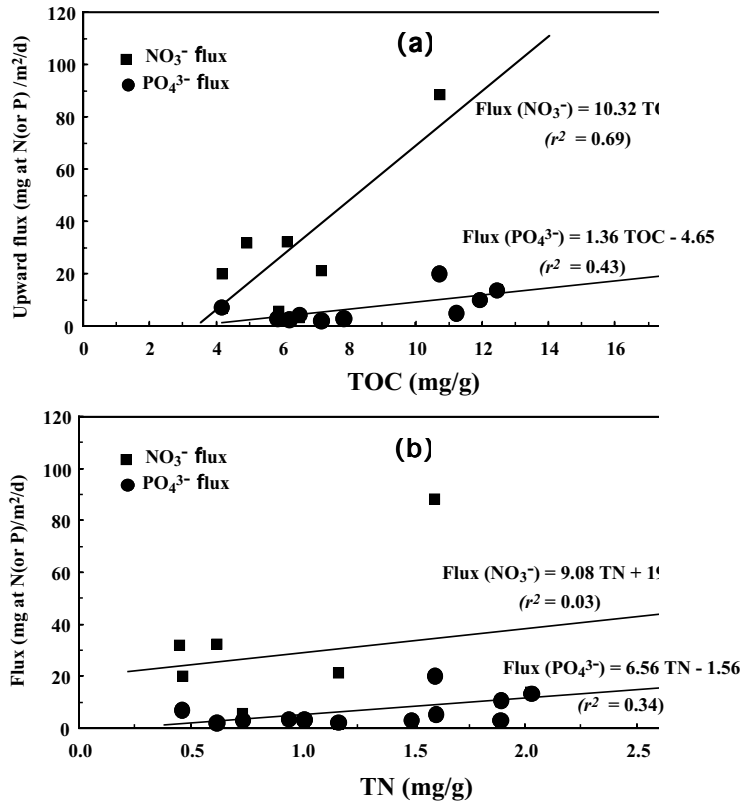
Fig. 10   Relationships between the calculated rates of upward diffusive fluxes of pore water nutri-
ents and the levels of total organic carbon (TOC) contents; (a) and total organic nitrogen
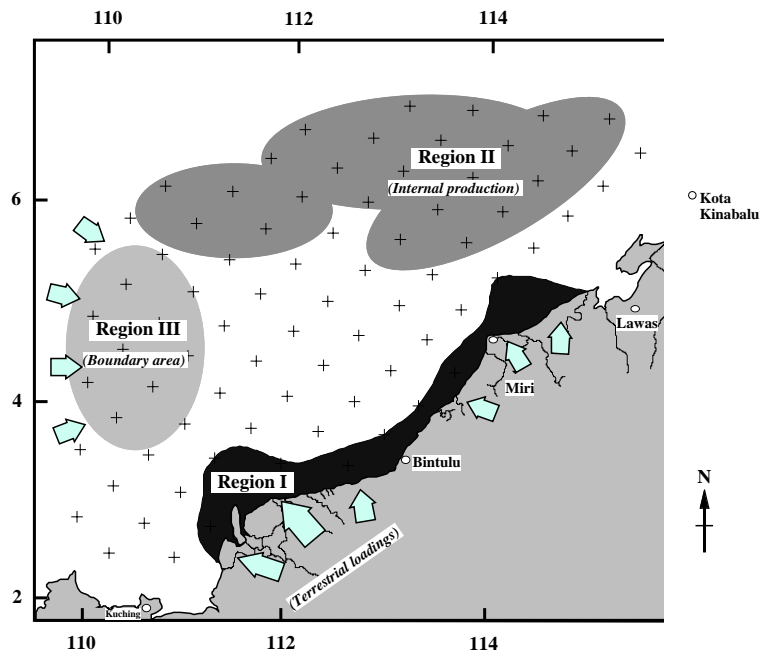(TON) contents; (b) of the surface (0-1cm) sediments.

Fig. 11   Schematic zoning of the bottom sediments in the Sabah, Sarawak and Brunei Darussalam
waters for fishery resource development and management purpose.

surface sediment. In the case of NH_4^+-N, the upwad fluxes range widely from 0 to 388.0 mg at N/m^2/ d. Very high NH_4^+-N upwad fluxes are about one order of magnitude higher than those of NO_3^--N and PO_4^{3-}-P, and generally observed in nearshore stations with high organic content (e.g. stations 31, 47, and 76). However, such values fluctuated greatly in stations and thus may reflect the variations in macrofaunal activity, detrital inputs to the sediment-water interface, and the oxygen content of the bottom water.

In this study area, fairly high rates of nutrient upward fluxes have been demonstrated. They are comparable to the estimated benthic flux at very high productivity areas (e.g upwelling area of Chile; Farias *et al*. (1996) and organically enriched area of the Seto Inland Sea; Yamamoto *et al*. (1998)). The sediment here should thus be able to provide an important nutrient sources for phytoplankton in the water column with respect to other sources, such as inputs from salt marshes and rivers. Release flux from the sediment is known to be affected by sediment property, temperature, dissolved oxygen, deposited substances supplied from seawater, etc. (Kato and Terunuma 1995) Examination on the relations between the rates of nutrient upward fluxes and sedimentary organic levels (TOC and TON) by linear regression method (**Fig. 10**) indicates remarkable correlations of NO_3^--N and PO_4^{3-}-P upward flux rates to TOC ($r^2 = 0.69$ and 0.43, respectively) but less correlations to TON ($r^2 = 0.03$ and 0.34, respectively). These correlations indicate that the accumulated organic matter tends to be biogenically metabolized and thus enhance the exchange between the sediment-water interface of the water region.

GENERAL CONSIDERATION

Organically enriched bottom sediment is important either as habitats and direct food sources for benthic production or as potential nutrient source for biological productivity of the water column. For further fishery resource development and management of the sea areas of Sabah, Sarawak and Brunei Darussalum, the overall information obtained from this study have been used to characterize the bottom sediments into three distinct regions (**Fig. 11**):

(I) a shallow, nearshore organically enriched region, in which the high organic materials accumulated are mostly land-derived sources,

(II) a deep, offshore organically enriched region, in which the high organic materials accumulated are marine-derived sources and,

(III) a boundary-offshore region, with moderate organic levels, receiving more affect of outside water mass movement.

These three regions are different in diagenesis characteristics of the sediment and related pore water nutrient constituents. Region (I) should be the most appropriate area for benthic production development. However, since this region is temporal impacted from terrestrial organic loadings and apt to be organically polluted, monitoring of both magnitude and direction of the organic loadings may be of future importance. Correspondingly high upward diffusive flux of NH_4^+-N at the sediment-water interface is also a distinct characteristic of this region. At Region (II), highest sedimentary organic contents are observed. This region is an important "sink" area of internal production in adjacent waters and thus could provide a potential source of nutrient, PO_4^{3-}-P in particular, into overlying seawater. Here, possibility of upward movement of bottom water should deserve more in depth study since it may occasionally enhance primary production in the water column. Region (III) is the conjunction zone which can receive more influence of the whole water circulation regime of the South China Sea. This area directly faces comparatively strong current and thus future attempt in clarifying depositional characteristics of the bottom sediment may provide a better understanding of precise current pattern of the sea area.

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