Evaluation of fresh groundwater contributions to the nutrient dynamics at shallow subtidal areas adjacent to metro-Bangkok

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Abstract Both submarine groundwater discharge (SGD) and the Chao Phraya River are major agents of nutrient supply into the Gulf of Thailand. With the development of the city of Bangkok, however, lowered groundwater levels due to over-pumping suggests a decrease of the fresh groundwater flux into the sea. In this study, time-series resistivity monitoring under the seabed adjacent to Bangkok city did not actually show any evidence of fresh groundwater fluxes, and δD and $\delta^{18}O$ signatures in porewater also followed this phenomenon. Consequently, the observed upward water flux can be mainly attributed to recirculation of the overlying water. $\delta^{15}N$ and $\delta^{18}O$ values in nitrate suggested that nitrate was mainly supplied via the river, and rapidly reduced in the surface suboxic sediment, while re-mineralized ammonium and phosphate were substantially released into the overlying water. River water-derived nutrient could be still important as original sources of organic matter, even at the area where high amounts of SGD is observed.

Key words groundwater; resistivity measurement; stable isotopes; Thailand; Chao Phraya River

INTRODUCTION

Groundwater is a fundamental resource providing reliable and low-cost water for domestic, industrial and agricultural purposes. Thus many Asian cities have depended on groundwater for sustenance and used the resource to facilitate economic activity. Furthermore, fresh groundwater is an important pathway for bringing land-derived nutrients to coastal waters (e.g. Umezawa *et al*., 2002).

During the progress of urbanization and intensive dwelling in city areas, however, discharge of septic and industrial wastes has caused severe groundwater contamination by nutrients such as nitrate, and several toxic metals. These contaminants are a potential threat to human health through drinking water, and also affect the primary production of adjacent coastal ecosystems.

Burnett *et al.* (2007) reported that the seepage of fresh groundwater with high dissolved inorganic nitrogen (DIN) concentrations could have important implications for the magnitude and type of productivity in the coastal waters in Upper Gulf of Thailand, because this area was nitrogen-limited from the viewpoint of the Redfield ratio. A complicating factor, however, is over-pumping of groundwater from deep aquifers lying underneath the cities. In Bangkok, continuous groundwater pumping of over 1.5 million m^3/day during recent decades has caused severe subsidence throughout the city areas (e.g. Phien-wej & Nutalaya, 2006), and has dramatically changed hydraulic potentials in the aquifers. Therefore, intrusion of saltwater into the aquifers along the coastal area is another significant impact (e.g. Das Gupta, 1985).

The objectives of this study were: (a) to confirm whether fresh groundwater fluxes exist along the coastal line, where groundwater pumping has been intensively conducted, and (b) to better understand related nutrients dynamics at shallow inter- and sub-tidal areas. At shallow coastal areas, the term ''groundwater'' includes both fresh-water with land-derived nutrients, and recirculated seawater with marine-borne nutrients, including mineralized ones from sediments. To separate each source of groundwater, conductivity is efficiently used in the case of areas where river input is minor (Taniguchi *et al.*, 2006). In the Gulf of Thailand, however, about half of the river flow to this system was provided through the Chao Phraya River, and so salinity in the water column is very low around the river mouth, especially in the rainy season (Burnett *et al.*, 2007), suggesting that conductivity is unlikely to be an effective tool to separate fresh groundwater from the brackish water. In this study, therefore, we tested the use of stable isotopes in water to separate them, in combination with other physical approaches such as resistivity monitoring. The coupled N and O isotopes of nitrate with/without nitrite were also analysed to identify the source of nitrate and to understand its transformation at the shallow estuary.

MATERIALS AND METHODS

Study site and equipments settings

The Bangkok metropolitan area is located about 25 km to the north of the Gulf of Thailand, on the flood plain of the Chao Phraya River. Dry and wet seasons clearly exist, and river discharge in the wet season amounts to 10 times of that in the dry season (Dulaiova *et al.*, 2006). Although subsidence in the centre of the city area mostly stopped after the regulation of groundwater pumping, the largest subsidence rate is still observed around the industrial southeast suburb areas in 2005.

To monitor fresh groundwater discharge from the shallow coastal areas adjacent to the metro-Bangkok area, a transect line was selected about 10 km eastward from the river mouth (Fig. 1(b)).

Continuous heat-type automated seepage meters (i.e. vented benthic chambers to automatically measure water flow), were deployed on the subtidal seabed at each of four stations (A to D; Fig. 1(c)) from 20 to 23 June 2006. The average depth of the

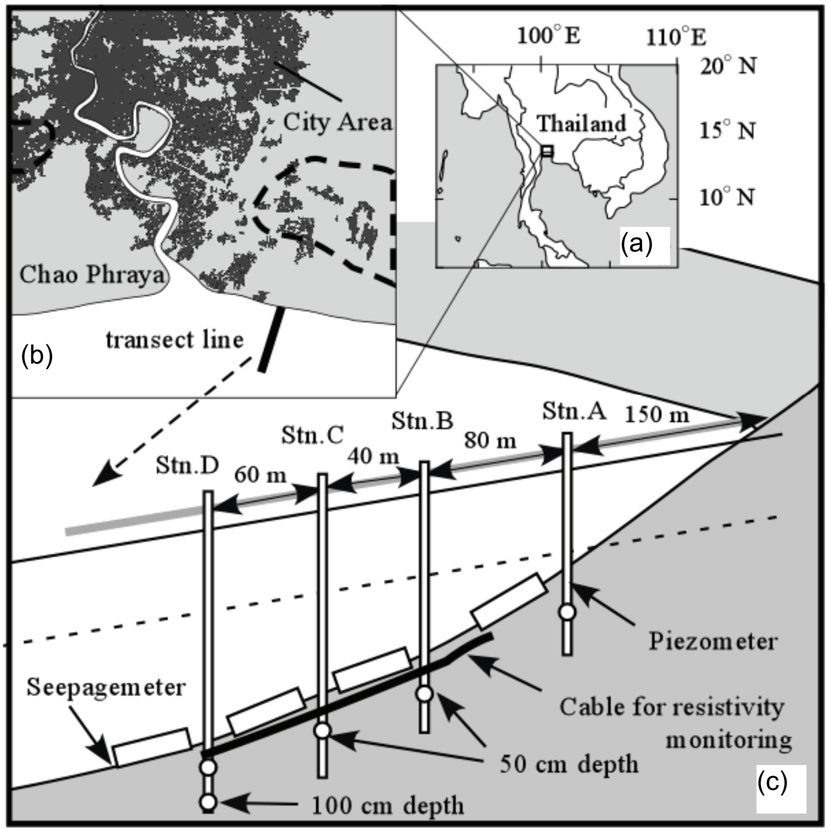

Fig. 1 Location of study area, and setting design of instruments (piezometers and seepage meters) along the transect line. In (b), enclosed areas with a broken line indicate the areas, where subsidence of over 30 mm/year is currently observed, probably due to groundwater pumping (Phien-wej & Nutalaya, 2006).

seepage meter during the observation period was about 1.4, 1.6, 1.7 and 1.9 m at Stations A, B, C and D, respectively. Two set of piezometers (ϕ = 12 mm; vinyl chloride), each of which had an intake with a strainer at 50 cm and 100 cm depth, respectively, were also installed at each station. The water accumulated inside the piezometric tube was discarded using tygon tubing and a plastic syringe 1 hour before the sampling. The porewater sample recharged during the subsequent 1-hour period was collected every 3 hours (low, flood and high tide) on 23 June, and individually stored for the analysis of each chemical component (see below). Seawater overlying the sediment at each station, several river water samples and one offshore water sample (13°19′55″N, 100°49′54″E) were also collected for chemical analysis.

Resistivity under the seabed was measured along the transect line using a Sting R1 IP/Swift (American Geophysical Instrument) every 1 hour from low tide (08:00 h) to high tide (16:00 h) on 22 June. About 14 probes were installed along the 140–m transect (interval length between probes was 10 m). The Schlumberger method and RES2DINV version 3.50 (Geotomo Software) were used for the resistivity analyses. Tidal shift, current speed and direction were continuously monitored using a CTD sensor (HOBO U20-001-01) and an electromagnetic current meter (COMPACT-EM) at Stn D.

Nutrient profiles in sediment

The sediment samples for the analysis of nutrient profiles were collected in duplicate at the same four stations using an acrylic cylinder with silicon stoppers. After the recovery on the boat, the sediment core was sectioned into 1.0 to 2.0 cm intervals, transferred into plastic bags, and kept in an ice box. Within half a day after recovery, interstitial water in the sediment was extracted by centrifugation at 1200 G for 20 min. The extracted interstitial water was stored in capped acrylic tubes and kept frozen for later analysis. The sediment was characterized mostly as clay throughout the transect line.

Hydrogen and oxygen isotopes in water

The water samples for the stable isotope ratios in water, i.e. δD and $\delta^{18}O$, were kept at room temperature, and analysed by mass-spectrometry (Finnigan Mat252). As pretreatment for stable isotopes analysis, water samples were equilibrated with CO_2 gas for $\delta^{18}O$ and H_2 gas with a platinum catalyst for δD. The reproducibility of $\delta^{18}O$ and δD values was better than 0.1‰ and 1.0‰, respectively.

Nitrogen and oxygen isotopes in nitrate with/without nitrite

The water samples for the nutrients and their stable isotopes analyses were processed using 0.45 μM cellulose acetate filter in the field, and kept frozen until the analyses. Nutrient concentrations ($[NO_3^-]$, $[NO_2^-]$, $[NH_4^+]$, and $[PO_4^{3-}]$) in river water, seawater and porewater were measured colorimetrically with an autoanalyser (AACS III, BRAN+RUEBBE). The stable nitrogen and oxygen isotope ratios, i.e. $\delta^{15}N$ and $\delta^{18}O$, in nitrate + nitrite were determined with the "denitrifier" method of Sigman *et al.* (2001) and Casciotti *et al.* (2002). For the samples that included substantial amounts of nitrite (over 10% of nitrate), $\delta^{15}N$ and $\delta^{18}O$ were determined both for nitrate with and without nitrite, using the mass spectrometer (Finnigan Delta^{plus}XP). For the latter sample, nitrite was excluded in advance using ascorbic acid ($AscH_2$), following Granger *et al.* (2006). Isotope values were calibrated using internationally recognized nitrate standard USGS34 ($\delta^{15}N$ of –1.8‰ and $\delta^{18}O$ of –27.9‰), USGS35 ($\delta^{15}N$ of 3.6‰ and $\delta^{18}O$ of 51.5‰) and laboratory working standard ($\delta^{15}N$ of 1.6‰ and $\delta^{18}O$ of 23.6‰). Based on replicate measurements of standards and some samples, the analytical precision for $\delta^{15}N$ and $\delta^{18}O$ was generally better than ±0.2‰ and ±0.4‰, respectively.

RESULTS

Seepage meter and physical conditions

Specific flow rates obtained every minute at each station by automated seepage meters ranged widely from 1.0 to 110 cm/day (Fig. 2). Although the flow rate showed large variation at any given time, the average flow rate at each location during the monitoring period was 17.7 ± 5.3, 8.8 ± 4.8, 1.2 ± 0.2 and 21.4 ± 14.1 cm/d at Stns A,

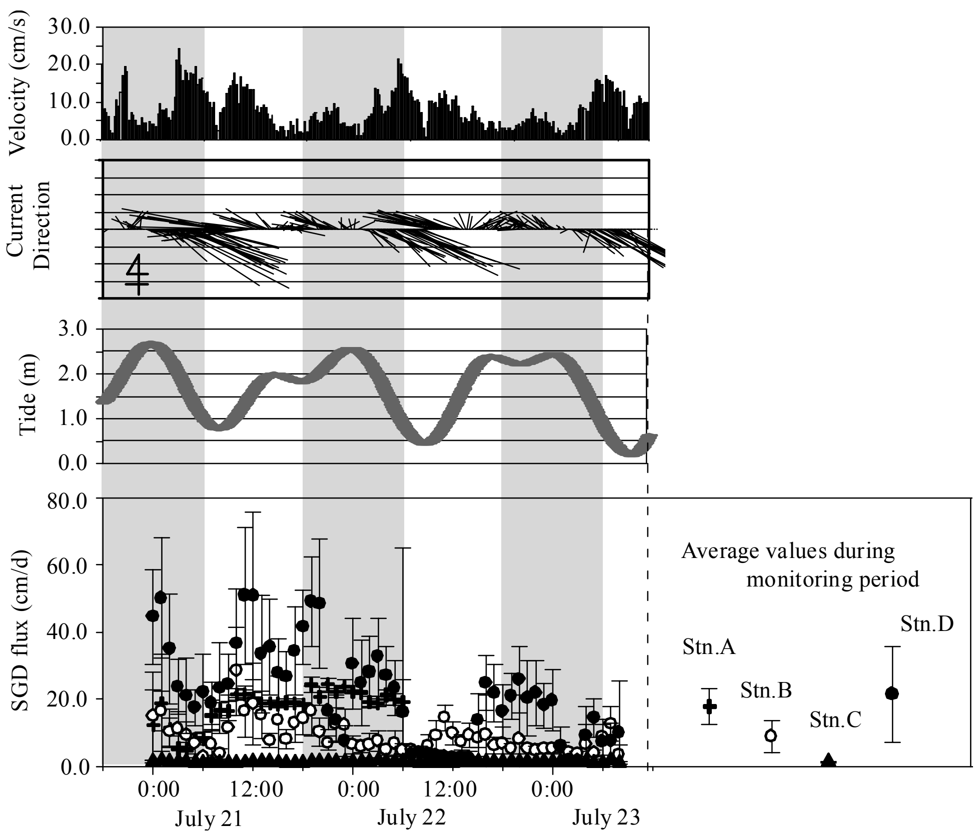

Fig. 2 Time-series data of current velocity and direction at Stn D, and SGD fluxes monitored at Stns A, B, C and D. The SGD data collected every 1 min was compiled into 1-hour average data with S.D. The small flux speed was converted to the daily flux. Average data throughout the monitoring period were separately plotted. Shaded areas mean night time.

B, C and D, respectively. The magnitude of the flux at Stn B was high at low tide, while at Stn D a higher flux was observed randomly at flood and ebb tide.

Higher current velocities, 15 to 20 cm/s, were recorded at flood and ebb tide, while the velocities at low and high tide were a fifth or sixth of the maximum ones.

Resistivity monitoring

Resistivity usually reflects the degree of conductivity and difference of sedimentation and geological characteristics. When the resistivity is continuously monitored at same location, therefore, the change of resistivity could show the change of conductivity (Taniguchi *et al.*, 2006). The distribution of resistivity below 10.0 m depth and onshore areas looked steady condition, while it fluctuated in surface layers according to the tidal shift (Fig. 3).

Hydrogen and oxygen isotopes in water

The δD and δ^{18}O concentrations showed large variation, but specific values were observed for each water source (Fig. 4). For instance, δD (–7.8‰) and δ^{18}O (–1.0‰),

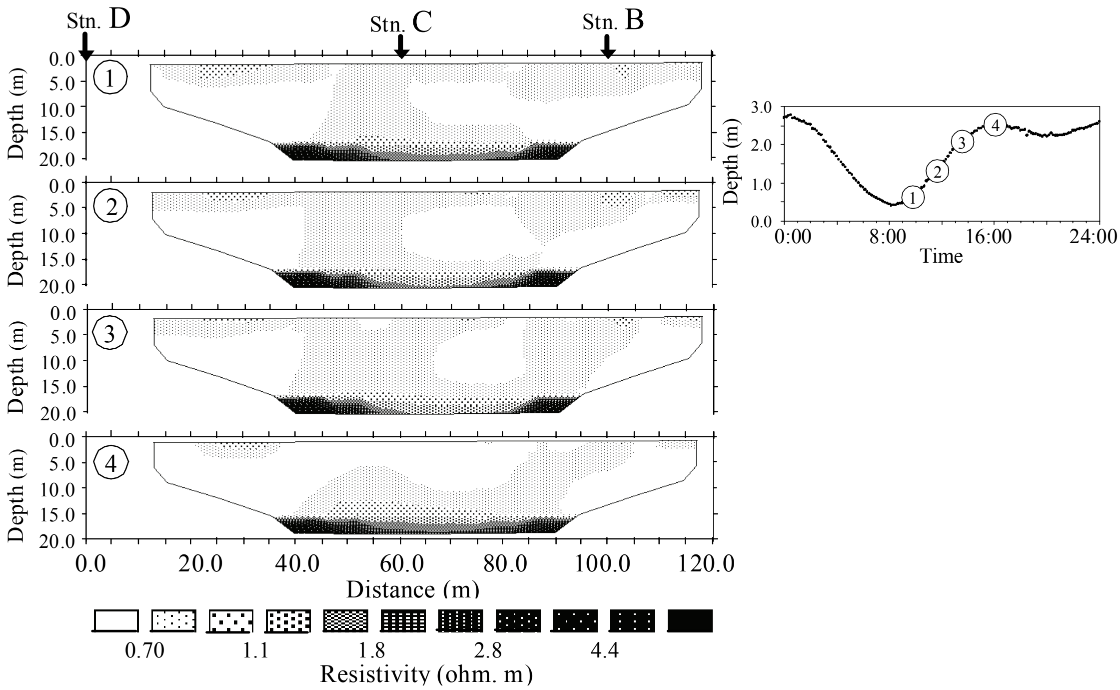

Fig. 3 Resistivity cross-section in a 140 m long transect. The sections 1 to 4 show the situation from low tide to high tide. The *y*-axis shows the depth of the sea bottom.

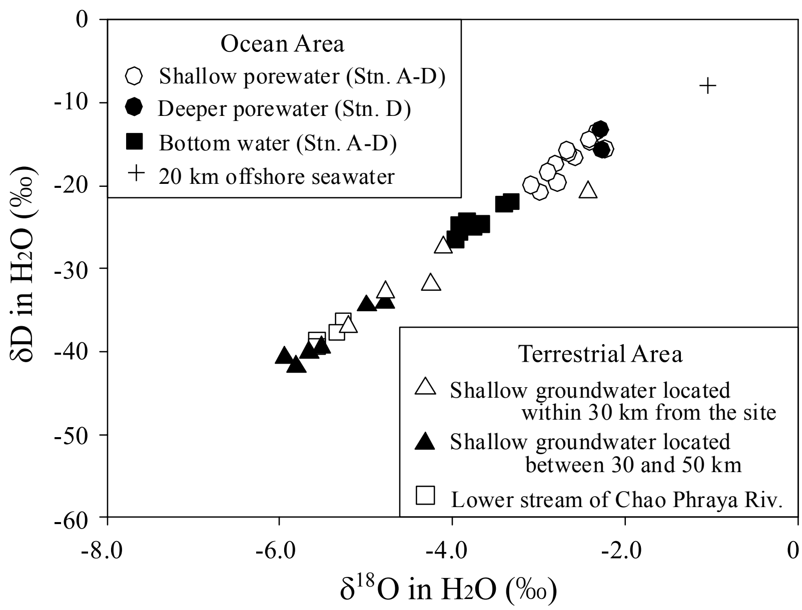

Fig. 4 Variation of δD and $\delta^{18}O$ values in H_2O collected from different water sources around the monitoring station. The data for fresh groundwater in the wells located within 30 or 50 km of the study site were provided by T. Yamanaka (unpubl. data).

for offshore water salinity which was 8.2 psu, were significantly heavier than the others. Values in both fresh groundwater and river water were relatively low. But it was still hard to differentiate groundwater and river water from these signatures alone, because the values in the well groundwater showed variation depending on the locations.

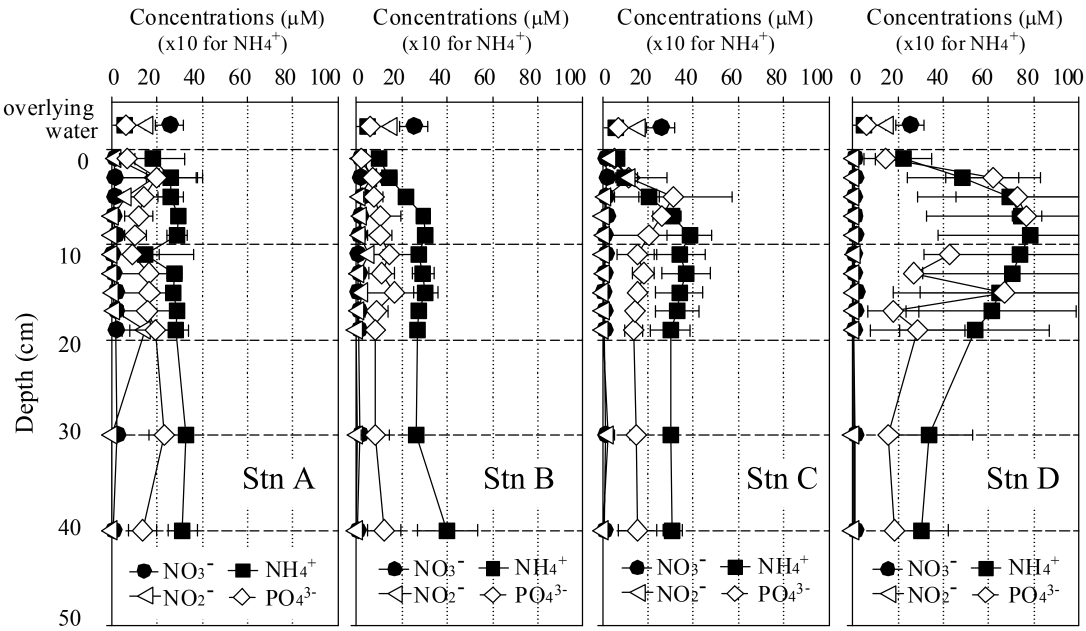

Fig. 5 Vertical profiles of porewater nutrient contents at stations A, B, C and D (from the left). Those in overlying water are also plotted at the top of the profiles using the same symbols.

The values in porewater and overlying bottom water were intermediate between the fresh water and offshore water. However, the characteristics of the offshore water were more similar to that of deeper porewater than the bottom water and shallower porewater. Because these values lined up tightly on the straight line ($y = 7.37x + 2.06$, $r^2 = 0.98$), it was assumed that the porewater and overlying bottom water were formed by simple mixing of fresh ground/river water and offshore water. Some outliers of the groundwater collected from the well might have shown the effect of evaporation or connate water.

Nutrient in sediment and overlying water

Low concentrations of nitrate and nitrite (i.e. 0.8 to 1.5 μM for NO_3^-, 0.8 to 3.5 μM for NO_2^-, Fig. 5) and high concentrations of ammonium and phosphate (i.e., 62.5 to 230 μM for NH_4^+, 2.5 to 15.0 μM for PO_4^{3-}, Fig. 5) were observed in interstitial water of surface sediments at each station, suggesting that suboxic conditions were maintained throughout the shallow subtidal areas. Especially at Stn D, extremely high ammonium and phosphate concentrations were detected at around 5 to 15 cm depth. On the other hand, overlying bottom water, which was collected several times at each location, had relatively steady values independent of location and tidal shift (i.e. 27.5 ± 2.6, 12.0 ± 0.6, 49.2 ± 6.9 and 5.6 ± 0.6 μM or NO_3^-, NO_2^-, NH_4^+ and PO_4^{3+}, respectively; $n = 9$).

Nitrogen and oxygen isotopes in nitrate

$\delta^{15}N$ and $\delta^{18}O$ in nitrate with/without nitrite were analysed for the samples from river water, bottom water, offshore water and porewater, which had enough amounts of

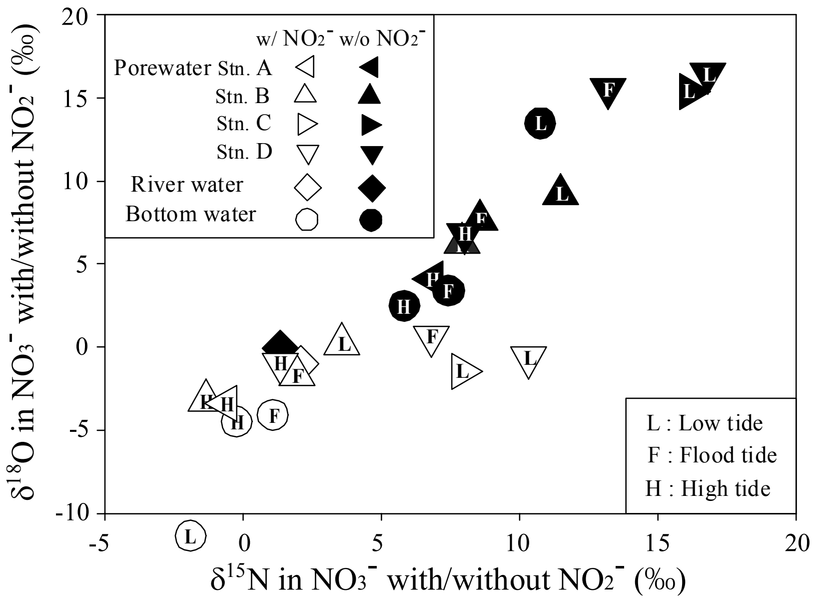

Fig. 6 $\delta^{15}N$ and $\delta^{18}O$ values of nitrate + nitrite (open) and nitrate alone (solid) from river water, bottom water and porewater collected in specific tidal situation at Stn A, B, C and D. The samples for nitrate + nitrite and nitrate analyses were divided from the same sampling bottle.

nitrate for the analyses (i.e. over about 2 μM). The amounts of nitrite in these samples were comparable to nitrate contents, and accounted for 40 to 120% of them.

$\delta^{15}N$ and $\delta^{18}O$ in river water nitrate were around 1.5‰ and –0.5‰, respectively, irrespective of whether it included nitrite or not (Fig. 6). However, those values in nitrate from the other sources became heavier when they were analysed after removing nitrite. In other words, $\delta^{15}N$ and $\delta^{18}O$ in nitrite were significantly lighter than those in nitrate. For example, $\delta^{15}N$ and $\delta^{18}O$ in a bottom water sample shifted to 5.9‰ and 2.5‰ from –0.3‰ and –4.5‰, respectively. As for the samples from piezometers, $\delta^{15}N$ in nitrate + nitrite at C and D were about 5‰ heavier than those at A and B. Furthermore, after the manipulation to remove nitrite, the increase in the ratio of $\delta^{18}O$ to $\delta^{15}N$ (i.e. $\Delta\delta^{18}O : \Delta\delta^{15}N$) was over 2.0 for the samples at C and D, and about 1.0 at A and B.

DISCUSSION

Dynamics of SGD at the subtidal area adjacent to metro-Bangkok

As shown in the resistivity data (Fig. 3), it was unlikely that dynamic mixing between intruded seawater and fresh groundwater occur in the inter- and sub-tidal areas adjacent to the Bangkok metropolitan area. Because the overlying water consists of discharged river water and seawater, depending on the tidal cycles, small change of resistivity in the surface sediment seems to directly reflect the characteristics of the overlying water.

Curious δD and $\delta^{18}O$ signatures of the porewater, which were intermediate between the offshore water and the overlying bottom water, may correspond to such an inactive mixing in the salinity transition zone. Around the shallow areas at Chao

Phraya River mouth, salinity drastically changes between the rainy season and dry season (Burnett *et al*., 2007). So we assume that the overlying water with high salinity during the dry season still remained in the deeper sea bed, and only the porewater in the surface layer was replaced by the current overlying water with low salinity during our study period, i.e. at the beginning of the rainy season. From the behaviour of radon concentrations around Chao Phraya River, Dulaiova *et al*. (2006) proposed that fresh groundwater flow would be directed down gradient along topographic contours and thus would tend to be concentrated toward the central axis of the river valley or just beyond its mouth. Other than intensive pumping of groundwater, this may be another explanation of the small flux of fresh groundwater at inter- and sub-tidal areas close to metro-Bangkok city.

Consequently, the upward water flow observed by seepage meters can be mostly attributed to the recirculation of the overlying water. Although a major mechanism of seawater intrusion is tidal oscillation in the coastal area (Prieto & Destouni, 2005; Burnett *et al*., 2007), the correlation between SGD flux and tidal shift was not clear in our transect (Fig. 2). Intensive study is required to investigate the agents enhancing the SGD flux, focusing on other potential sources like surge currents with higher velocity.

Nutrient behaviour around Chao Phraya River mouth

Burnett *et al*. (2007) concluded that DIN supplied by SGD amounted to 40–50% of that delivered by the Chao Phraya River, despite the small flux of freshwater via SGD. As for the interaction between the sediment and water column, however, only a uni-directional flux from the sediment through the dynamic SGD was taken into account in the estimation in their paper. Here, therefore, the potential of nutrient transportation via bidirectional diffusion fluxes was compared with that via advective flux (Table 1). The vertical fluxes of DIN/P by diffusion between sediments and overlying water were calculated using the nutrient concentration in both (Fig. 5) based on the Fick's First Law of diffusion (detail in Table 1). The advective flux was roughly calculated by multiplying seepage flow rate (cm/d) and nutrient concentrations in the surface porewater (0–2 cm depth). Due to the high concentrations of nitrate and nitrite in the overlying water, delivered by river water, these components showed a downward flux into the sediment by diffusion. In contrast, ammonium and phosphate showed upward fluxes into the overlying water, but the total fluxes were considerably smaller compared to the fluxes via advective flow (Table 1).

$\delta^{15}N$ and $\delta^{18}O$ in nitrate became heavier with a ratio increase of 1.0 or 2.0 for $\delta^{18}O$ to $\delta^{15}N$, after removing nitrite. Denitrification in the ocean water preferentially consumes isotopically lighter nitrate, so its occurrence leads to a marked increase in $\delta^{15}N$ and $\delta^{18}O$ of nitrate by 20–30‰ for the isotopic effect at suboxic areas (e.g. Sigman *et al*., 2003). However, sedimentary denitrification in a variety of environments causes very little net isotope enrichment of oceanic nitrate, probably due to the limited rate of nitrate supply to denitrifying bacteria (e.g. Brandes & Devol, 1997). This apparent difference of isotopic fractionation factors between sediments and open waters could be a potential tool for estimating the locations and condition where denitrification is occurring in this estuary. Because tidal oscillation-derived water flow

Table 1 Estimated nutrient fluxes (mmol m^{-2} d^{-1}) between sediments and overlying waters. Positive values mean the flux is from sediment into the overlying water.

Station	Nitrate		Nitrite		Ammonium		Phosphate	
	Diffn*	Advn	Diffn*	Advn	Diffn*	Advn	Diffn*	Advn
A	–0.2	0.3	–0.1	0.35	1.3	32.0	0.01	2.74
B	–0.2	0.1	–0.1	0.15	0.5	8.6	–0.02	0.44
C	–0.2	0.0	–0.1	0.04	0.1	0.8	0.00	0.13
D	–0.2	0.2	–0.1	0.16	1.8	48.3	0.05	6.98

* Fick's 1st law of diffusion; $J = -\Phi D'(\Delta C/\Delta Z)_{Z=0}$ — (1) where J is the diffusive flux of the nutrient species (μg cm^{-2} s^{-1}), Φ is the porosity of that species and D' is the diffusion coefficient in pore water (cm^{-2} s^{-1}). The porosity (Φ) was estimated following to equation (2): $\Phi = \rho / (\rho + (1 - \omega)/\omega)$ — (2) where ρ is density of the sediments, and ω is water content ratio. $(\Delta C/\Delta Z)_{Z=0}$ is the gradient of dissolved nutrient concentrations across the sediment–water interface, and represented by equation (3) (Rutgers *et al.*, 1984): $(\Delta C/\Delta Z)_{Z=0} = (C - C_0)/0.5\ L$ — (3) where C is the nutrient concentration in the top of the sedimental segment with thickness L and C_0 is the usual concentrations in the overlying water at each area. L was substituted by 2.0, and the spatially averaged values in overlying water was used as C_0 (i.e. 27.5 μM for NO_3^-, 12.0 μM for NO_2^-, 49.2 μM for NH_4^+ and 5.6 μM for PO_4^{3-}) uniformly at all locations. The molecular diffusion coefficient (*Ds*) was represented approximately by equation (4) for muddy sediments (Yamamoto *et al.*, 1998): $D' = D^0(1 + \alpha t)\Phi^2$ — (4) where D^0 is D' at 0°C and the value for each species are cited in Yamamoto *et al.* (1998) (i.e. 0.978×10^{-5} cm^2 s^{-1} for NO_3^-, 0.922×10^{-5} cm^2 s^{-1} for NO_2^-, 0.98×10^{-5} cm^2 s^{-1} for NH_4^+ and 0.61×10^{-5} cm^2 s^{-1} for PO_4^{3-}), α is invariable depending on species (i.e. 0.048 for cation and and 0.040 for anion; Lerman, 1979). Temperature was uniformly substituted by 28.0°C.

and wind-derived shear stress actively disturb the surface layer of the sediment, the nitrate supply rate into the surface sediment could be high. Therefore, continuously diffused nitrate into the suboxic sediment or overlying water may be rapidly reduced with significant isotopic discrimination. On the other hand, further investigation is needed to identify the source of nitrate with heavier $\delta^{15}N$, which was distinctly different from the river-borne nitrate (Fig. 6). Determination of $\delta^{15}N$ values in organic nitrogen and/or ammonium in the sediment may demonstrate the potential for nitrification in local areas.

As also suggested in Burnett *et al.* (2007), re-circulated seawater can be directly important to nutrient dynamics in the Upper Gulf of Thailand, even in circumstances where fresh groundwater discharge is not quantitatively important. However, high concentrations of ammonium and phosphate in surface suboxic sediment can depend on the supply of allochthonous and autochthonous organic matter. The discharges of nitrogen (N) and phosphorus (P) into the Chao Phraya River from the Bangkok city area are estimated to account for 97% and 41% of the total loss, respectively (Færge *et al.*, 2001). Therefore, river water-derived nutrient could still be important as original N and P sources, even if high amounts of SGD with nutrients is observed at these areas.

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