Nutrient dynamics with groundwater–seawater interactions in a beach slope of a steep island, western Japan

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Abstract To confirm the semi-diurnal and seasonal variation in nutrient flux with the dynamics in groundwater–seawater interaction, we conducted intensive observations at 25 piezometers in a tidal flat over a distance of 100 m across a steep-sloped island. Based on the chloride balance, groundwater was very well-mixed with seawater under the tidal flat. Nitrate-nitrogen (NO_3^--N) concentrations declined from >20 to near 0 mg L^{-1} along the groundwater flowpath from the hillslope to the tidal flat. In addition, nitrate concentrations in pore water of the tidal flat were lower (at 0.1 mg L^{-1}) than in seawater. These results suggest that the reduction process of NO_3^--N occurred in both contaminated groundwater and seawater. Discharge of inorganic nitrogen by groundwater was confirmed offshore. The suspected source was nitrogen mineralization of organic compounds and seawater recirculation. Phosphorus was produced offshore and transported from the land area. Seasonal variations in nutrient dynamics at the tidal flat were also confirmed.

Key words nutrient dynamics; groundwater; recirculated seawater; nitrate contamination

INTRODUCTION

Eutrophication and associated red tides in estuaries and inland seas are one of the critical environmental issues of this century. One of the controlling factors is the inflow of excess nutrients from the land. Recent research has shown that not only river water but also groundwater has a great effect on nutrient discharge from the land to the sea (Zektser & Loaiciga, 1993; Burnett *et al*., 2001; Slomp & Cappellen, 2004; etc.). Submarine groundwater discharge (SGD) has been reported by many researchers (Kim *et al*., 2005; Taniguchi *et al*., 2005; Burnett *et al*., 2006; etc.) and the dynamics of seawater–groundwater interactions are now better understood. In addition, the nutrient load and its propagation by SGD have been investigated (Slomp & Cappellen, 2004). However, the nutrient discharge has not been well identified in terms of the dynamics and mixing processes of groundwater and seawater.

In the case of nitrogen and phosphorous, inorganic components have very often been input in agricultural and urban lands (Tsurumaki, 1992; Burt *et al.*, 1993; Saito *et al*., 2005; etc.). However, the nitrate concentration was generally decreased with groundwater flow by denitrification and plant uptake (Howard, 1985; Ishizuka & Onodera, 1997; etc.), and the phosphorous concentration is also affected by the redox

condition. Nutrient dynamics are particularly complicated in the hyporheic zone, such as the riverside and seaside where oxic surface water is mixed temporarily with anoxic subsurface water under the ground during water-level changes (Böhlke *et al.*, 1995; Hinkle *et al.*, 2001; Ullman *et al.*, 2003; Phillipe & Hill, 2004; etc.). For the determination of the nutrient dynamics below the beach slope, it is especially necessary to understand the correlation of nutrient concentrations with temporal interactions between groundwater and seawater during tidal fluctuations.

The objective of this research has been to investigate the nutrient and water dynamics by tidal fluctuations and seasonal changes below a beach slope of an island in an inland sea. In addition, we tried to determine the sources of nutrients found on land or in marine sediment, using a hydrochemical approach.

STUDY AREA AND METHODS

The study area is located at Ikuchijima Island at the Seto Inland Sea, in Hiroshima prefecture of western Japan, which is a Japanese national park (Fig. 1). Environmental problems such as eutrophication and red tides were observed in the Sea. The study area is underlain by granites with a maximum altitude of about 450 m. The annual rainfall is about 1100 mm. The monthly rainfall is greatest from June to July, which is the Japanese rainy season. About 50% of the island is covered by orange groves and much fertilizer is applied during a whole year. The annual application amount is about 2400 kg ha^{-1} year^{-1}. Consequently, the surface water and groundwater of the island have been significantly contaminated by nitrates.

The observation site is located in the southern part of the island (Fig. 1(c)). This area is one of the steepest topography in the island, and there are no river channels. More than 50% of the slope around the observation site is covered by orange groves. The beach slope is mainly composed of very permeable coarse sands. The saturated hydraulic conductivity is 5×10^{-2} cm s^{-1}. Organic muddy and clayey sand is deposited on the flat area of the lower beach slope (Fig. 1(d)).

To confirm the nutrient and water dynamics below the beach slope, we installed 21 PVC pipes with diameters of 13 mm as piezometers for the manual measurement of water levels at seven points on an observation line over a distance of 100 m. For collecting water samples, 13 mm diameter pipes were installed at the same depths as the piezometers. The installation depths were from 50 cm to 400 cm (open circles in Fig. 1(d)). In addition, a large piezometer with a diameter of 10 cm was installed at a depth of 80 cm at site P1 (Fig. 1) for automatic measurement of water level and electrical conductivity. The altitude at P1 is approximately the mean sea level. At each observation time, we also collected: (1) samples of near-surface pore water at depths of 5 to 10 cm at five points along the beach using a penetration-type seabed pore water sampler, (2) seawater samples around the offshore sites, and (3) groundwater samples at two dug wells and a borehole behind the beach. The observations were carried out intensively from 2 to 5 times during two or three days in a spring tide in August and October in 2005, and in January, April and July in 2006. We purged the pipes for one hour before collecting the water samples.

The collected water samples were analysed for chemical components in the laboratory. The Cl$^-$ concentrations were analysed by ion chromatography after being
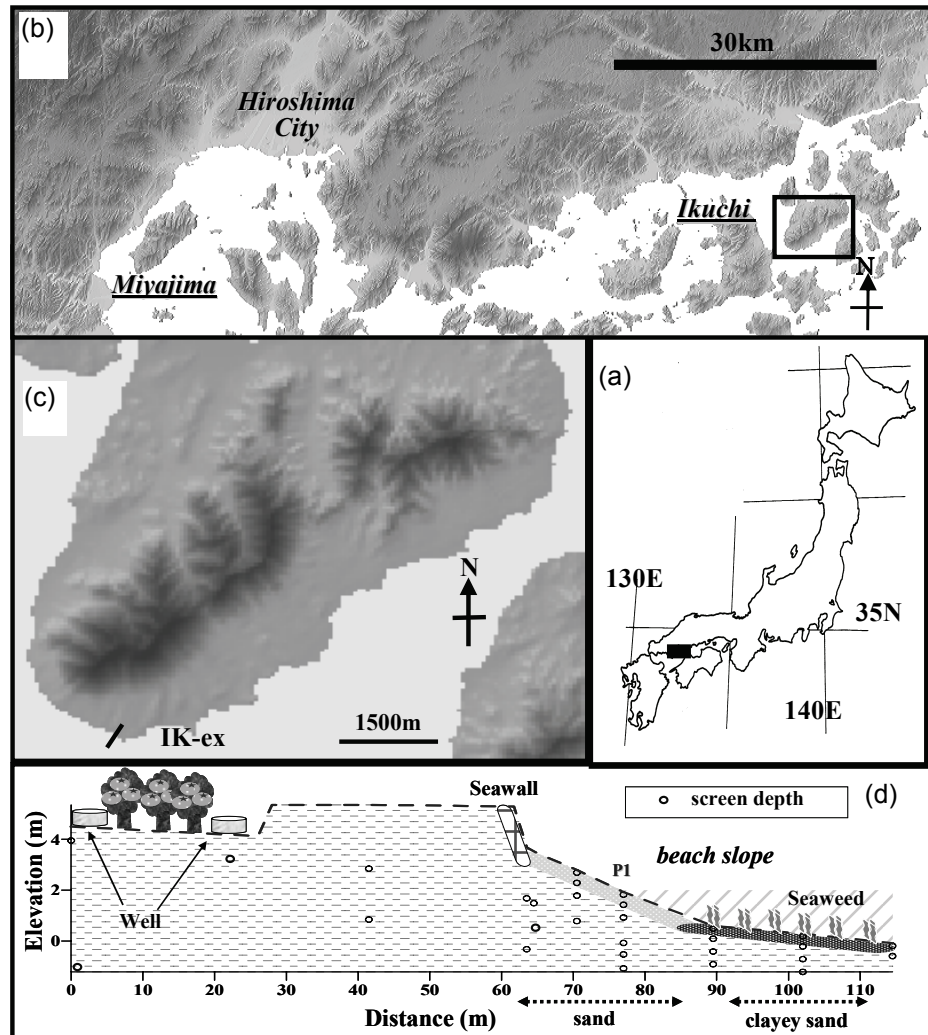
Fig. 1 Location of the observation site at Ikuchijima Island in Hiroshima Prefecture, western Japan; (d) shows the position of screen depth of piezometers and wells on the cross section of the observation beach slope.

filtered using a 0.20 μm cellulose ester filter. In addition, dissolved total nitrogen (DTN), dissolved total phosphorous (DTP), NO_3^--N, NO_2^--N, NH_4^+-N and dissolved silica (DSi) were analysed with a spectrophotometer. Dissolved organic carbon (DOC) was analyzed with a total carbon analyzer.

RESULTS AND DISCUSSION

Variation in subsurface water flow in the beach slope

Figure 2 shows the distribution of water flow direction based on the piezometric potential and seawater contribution ratio at a low (Fig. 2(a)) and high (Fig. 2(b)) tide in August in 2005. The seawater contribution ratio (R_s) is calculated as:
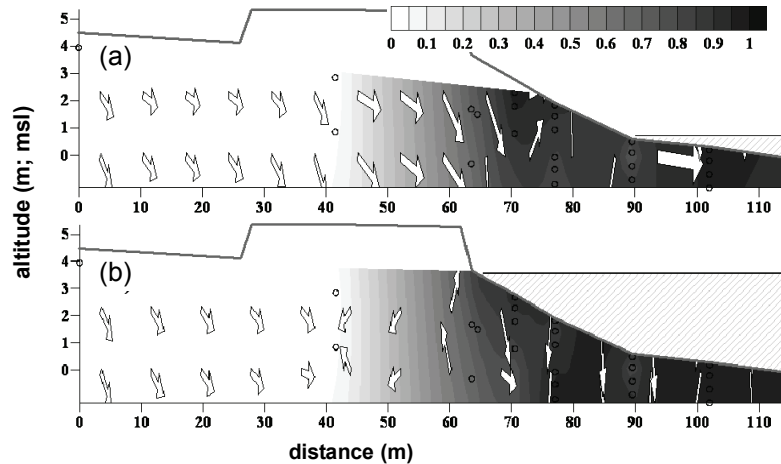
$$R_s = (C_i - C_g)/(C_s - C_g) \tag{1}$$

Fig. 2 Distribution of water flow direction and seawater contribution ratio (R_s) in a beach slope at: low (a) and high (b) tide in August 2005.

where C is a concentration and subscripts i, g and s denote a sample of water, groundwater and seawater, respectively. In this study, the Cl⁻ concentration was applied to calculate R_s, and the concentration in groundwater and seawater which were input to equation (1) were collected at the dug well at the mountain slope foot and offshore at high tide, respectively. In Fig. 2, as the horizontal scale is one fifth of the vertical scale, downward flow directions are emphasized. The flow direction is downward below the beach slope when covered by seawater at high tide (Fig. 2(b)). But, it changes to upward below the exposed beach slope and lateral from the slope to offshore below the seabed that is continuously covered by sea water at low tide (Fig. 2(a)). These results suggest there is infiltration of seawater at the upper beach slope during high tide and discharge of groundwater mixed with seawater at the lower beach slope during low tide. The seawater contribution ratio was more than 80% below the beach slope and 100% farther offshore. This means that the amount of seawater circulation is four times that of groundwater discharge in the beach slope and the discharge water is composed of recirculated seawater from the seabed offshore.

Figure 3 shows the relation between the water level from the bottom (80 cm) of the piezometer and electrical conductivity in the large piezometer at P1 for 15–16 July 2006. The variation pattern was characterized by three types. First, the water level varies by less than 80 cm during low tide with a constant electrical conductivity (EC) of around 47 mS cm⁻¹. The EC value indicates that 10% of terrestrial groundwater is mixed with 90% seawater of 51 mS cm⁻¹. Second, the EC varies between 47 and 51 mS cm⁻¹ during mid tide with a constant water level around 80 cm. This water level is closed to the ground surface level, as the ground surface has just been covered by seawater. Third, the water level increases to more than 80 cm during high tide with a constant EC of around 51 mS cm⁻¹. In this stage, the EC value almost equals the value of seawater. These results reveal the temporal fluctuation of the interface between the seawater and brackish groundwater as it relates to the tidal variation. This replacement of brackish groundwater to seawater lasted for 30 minutes according to the observation in the second stage (Fig. 3). If "fingering" of salty water in the high permeability (5 × 10⁻² cm sec⁻¹) sediment is assumed, the seawater transport time from the ground
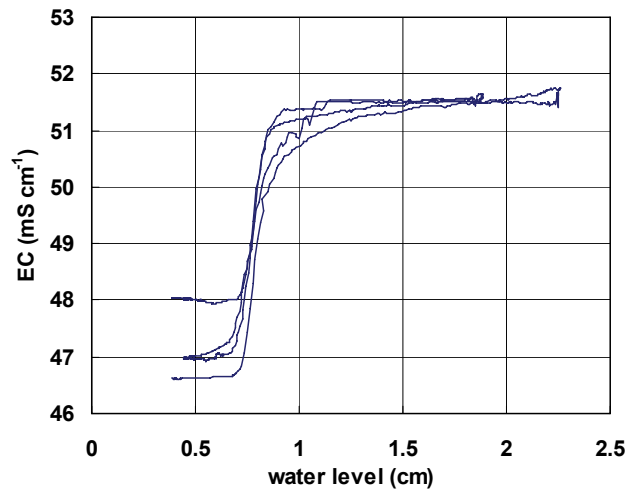
Fig. 3 Relation between water level and electrical conductivity in a large piezometer at the depth of 80 cm at site P1 for 15–16 June 2006.

surface to the depth of 80 cm is estimated to be 30 minutes. This suggests that most of the replaced seawater around the depth of 80 cm at P1 is new water which was input during the recent high tide. On the other hand, the brackish groundwater underlain by the new water (composed of 90% seawater) is relatively old.

Distribution in nutrient content in the beach slope

Figure 4 shows the distribution of nutrients (DSi, NO_3^--N, NH_4^+-N and DTP) below the beach slope at low tide in January 2006. The DSi, NO_3^--N and DTP concentrations decline along the groundwater flowpath from the mountain-foot slope to the beach area. Only the DTP increases below the beach slope. The NO_3^--N concentration in groundwater at the mountain-foot slope is greater than 20 mg L^{-1}. In the agricultural area of this island, nitrate contamination of groundwater is severe. Nevertheless, the concentration in the subsurface water on the beach slope became negligible along the groundwater flowpath. Both the DSi and NO_3^--N concentrations in groundwater at the mountain-foot slope are more than 100 times of those in seawater. One of the expected major decline factors of the concentrations is the dilution by the seawater in the beach slope. However, it is not enough to quantify the nitrate decline process as the average seawater contribution ratio is approximately 90% in the beach slope.

In contrast, the NH_4^+-N and DTP concentrations increase slightly below the beach slope. In the case of NH_4^+-N, the concentration in the groundwater at the mountain-foot slope is close to 0 mg L^{-1} and less than that in seawater. If the nitrate decline is caused by NO_3^--N reduction to NH_4^+-N, the increasing concentration of NH_4^+-N becomes similar to the decline of NO_3^--N. But the increase of NO_3^--N was 100 times that of the NH_4^+-N. This suggests that NO_3^--N reduction to NH_4^+-N is not the major process in the NO_3^--N decline. In the case of the DTP, the concentration in the groundwater is higher than that both in seawater and pore water below the beach slope. It suggests the possibility that the DTP declines along the groundwater flowpath by mineralization of organic matter, and/or deep groundwater mixing.
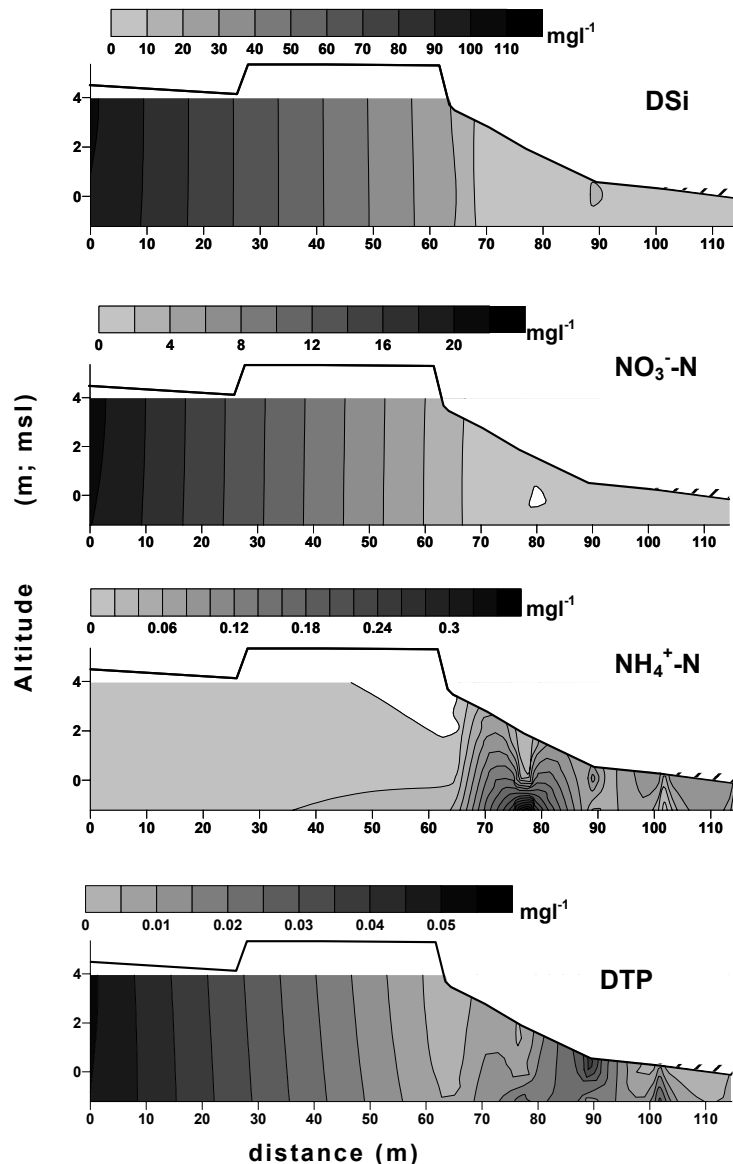
Fig. 4 Distribution of nutrients below the beach slope during a low tide in January 2006.

Dynamics of nutrient in an interaction zone of groundwater and seawater

Figure 5 shows the relations between Cl⁻ and: (a) NO_3^--N, (b) NH_4^+-N, (c) DSi, and (d) DTP concentrations in January 2006. The broken line in this figure represents the mixing process of groundwater and seawater without chemical reactions. The values used as the end members are the shallow groundwater at the mountain-foot slope as groundwater (GW in Fig. 5), and seawater at high tide offshore as seawater. The area below and above the line in Fig. 5 indicates the disappearance and production process of nutrients, respectively. In the case of DSi, most of the values indicate a mixing process of seawater and groundwater with less dissolution (Fig. 5(c)). In the case of NO_3^--N and NH_4^+-N, the values in the pore water of the beach slope plot below the line (Fig. 5(a), (b)). These show the trends of the nitrogen disappearance in the beach slope.
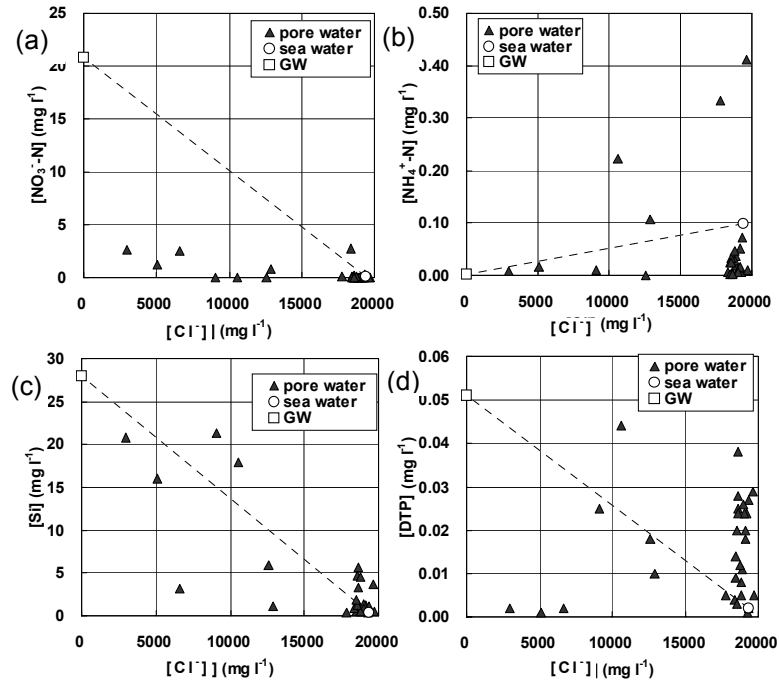
Fig. 5 Relations between Cl⁻ and (a) NO_3^--N, (b) NH_4^+-N, (c) DSi and (d) DTP concentrations in January 2006.

On the other hand, most of plots between Cl⁻ and DTP indicate the trend of the production of DTP.

The production concentration (*Pr*) is calculated by the difference of the measured (C_i) and calculated (C_c) concentration:

$$Pr = C_i - C_c \tag{2}$$

The calculated concentration (C_c) is calculated as follows:

$$C_c = C_g (1 - R_s) + C_s R_s \tag{3}$$

Figure 6 shows the distribution of the production concentration of NO_3^--N in the cross section of the beach slope at low tide in January 2006. In equation (2), the negative value denotes the disappearance of a nutrient. The NO_3^--N disappearance is dominant in the groundwater from the mountain-foot slope to behind the beach slope. The concentration of disappearance is 12 mg L⁻¹ maximum just behind the beach slope at a point 60 m from the mountain-foot slope. The NO_3^--N disappearance process is typical of denitrification and reduction. Based on the NH_4^+-N concentration, NO_3^--N reduction to NH_4^+-N is negligible. Consequently, denitrification is suggested as the disappearance process. On the other hand, the NO_3^--N production process is dominant in the beach slope. The maximum concentration is 3 mg L⁻¹ in the lower beach slope.

Seasonal variation in nutrient dynamics is shown in Fig. 7 as the relation between Cl⁻ and NO_3^--N in January and July 2006. The NO_3^--N concentration is relatively high in July compared with January. The nitrate production is suggested to be increasing with temperature.
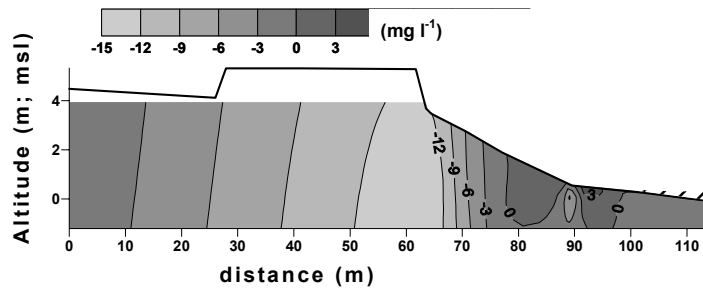
Fig. 6 Distribution of the production concentration of nitrate-nitrogen in the cross section of the beach slope at low tide in January 2006.
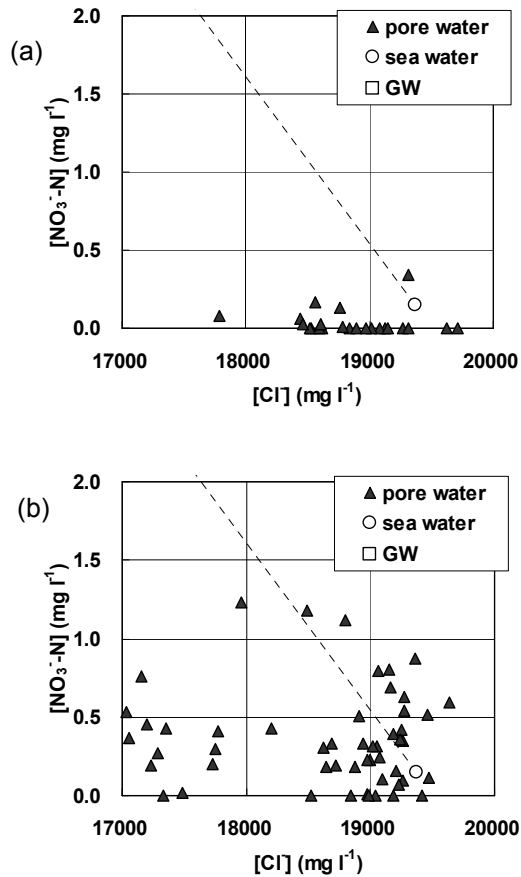
Fig. 7 Relation between Cl⁻ and NO_3^--N in January (a) and July (b) 2006.

CONCLUDING REMARKS

In this research, water and nutrient dynamics in a tidal flat caused by tidal fluctuation and seasonal changes were confirmed, using intensive observations in a network of piezometers.

1. Based on the chloride balance and piezometric head, groundwater was very well-mixed with seawater under the tidal flat, both temporally and spatially.

2. NO_3^--N concentrations declined from more than 20 mg L^{-1} to nearly 0 mg L^{-1} along the groundwater flowpath from the hillslope to the tidal flat. It is suggested that the nitrate reduction process originated in both the seawater and contaminated groundwater.

3.   Based on the nitrogen balance, inorganic nitrogen discharge was confirmed offshore, with the suggested process being nitrogen mineralization of organic compounds and seawater recirculation.

4.   The phosphorus was produced offshore as well as transported from the land area.

5.   A seasonal variation in nutrient dynamics was corroborated by changes in temperature.

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