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Nitrate contamination in groundwater of the Yellow River Delta and its effect on the marine environment

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Abstract The current condition of nitrate (NO_3^-) contamination in groundwater and its effect on the marine environment were evaluated in the Yellow River Delta, northeastern China. In the groundwater recharge area, NO_3^- contamination is suggested to be more severe compared with that in the groundwater discharge area. Also a relatively large amount of nitrogen is estimated to have accumulated in the aquifer of the recharge area. However, distribution of nitrate-nitrogen (NO_3^--N) concentrations and $\delta^{15}N$ implied a denitrification process in the aquifer of the coastal area. In addition, a high rate of denitrification was indicated there by *in situ* experiments involving injected tracer water with high concentrations of NO_3^--N. Based on these results, it is suggested that a large amount of nitrate will be removed before it reaches the sea.

Key words Yellow River Delta; nitrate contamination; denitrification process; marine environment

INTRODUCTION

Nitrate (NO_3^-) contamination in surface water and groundwater is a worldwide environmental problem, especially in the intensive agricultural areas (Burt *et al*., 1993; Böhlke, 2002). In Asian countries, consumption of nitrogen fertilizer has increased more than 20 times from the 1960s to 2000 (FAO, 2004). Shindo *et al*. (2006) have pointed out that the nitrogen load was extremely large in the North China Plain, especially around the lower reaches of the Yellow River and Yangtze River basins, and the contamination of groundwater by nitrate is most serious in this region. Evaluation of the current condition of nitrate contamination in groundwater is important to maintain the water resources for the future.

It is also necessary to clarify the nitrate transport process from land to the sea through groundwater discharge and to predict its effect on the marine environment (Burnett *et al*., 2006). Howard (1985) and Slomp & Cappellen (2004) have reported nitrate attenuation in a coastal aquifer by denitrification processes, and it is therefore necessary to consider the effect of natural attenuation on the nitrate load delivered to the sea.

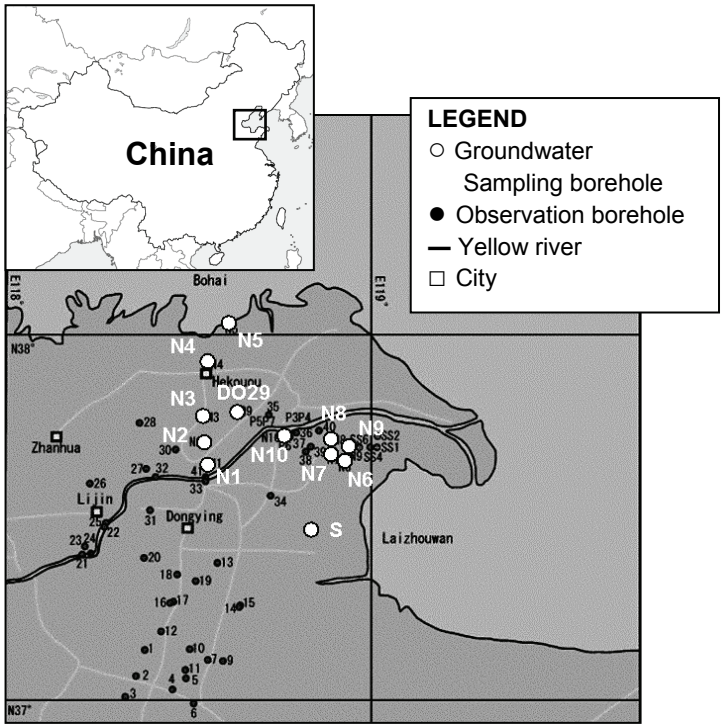

Fig. 1 Location of the study area.

The objectives of this study are to confirm the recent trend of nitrate contamination in groundwater of the Yellow River delta and to evaluate its effect on the marine environment for the future.

SITE DESCRIPTION

The Yellow River Basin is located between 96º–119ºE and 32º–42ºN, has a total area of 752 443 km^2 and a river length of 5464 km. The Yellow River supplies water to 12% of the population and 15% of the cultivated land in China. Since the 1990s, river water shortage has occurred frequently in the Yellow River basin because of the huge amount of water used for human activity, such as agricultural practices. This shortage is suggested to be a cause of decreases in groundwater levels and of nutrient transport to the Bohai Sea.

The Yellow River Delta covers approximately 5200 km^2 in the lower reaches of the Yellow River. Moreover, the total area of the modern delta has increased by approximately 20–25 km^2 per year because of the extremely high sedimentation rate. As a result, agricultural areas have been developing in the modern part of the delta, and nitrogen inputs have also increased in recent years.

METHODS

Collection of groundwater samples were carried out at the 10 boreholes (N1–N10) and two dug wells (DO29 and S) at depths of 15 to 50 m (Fig. 1) in September 2003, May

2004, and September 2005 and 2006. Boreholes were constructed of 5 cm inside-diameter PVC pipe with a slotted screen at more than three different depths. Water samples were collected at the depths of screen inside the boreholes using a plastic tube and vacuum pump. At the dug wells, we collected samples from more than three different depths including the surface, middle and bottom of the wells. Electric conductivity (EC), pH and dissolved oxygen (DO) concentrations were measured using a portable meter in the field.

To evaluate the denitrification capacity in the groundwater of the coastal area, the authors conducted a simple *in situ* injection experiment (Trudell *et al*., 1986; Pauwels *et al*., 1998) in September 2006. The experiment was carried out at borehole N6 located near the coast. Because the groundwater in the delta area has extremely high salinity, the groundwater collected from site N8 was used as the injected solution to prevent the formation of density flow. The solution, which had dissolved nitrogen (DN) and Cl^- concentrations of 43 mg L^{-1} and 5100 mg L^{-1}, respectively, was injected near to the bottom of borehole which had DN and Cl^- concentrations of 3.0 and 23 000 mg L^{-1}, respectively. A groundwater sample was collected from the bottom of the borehole three hours after the injection.

Water samples were analysed for the concentrations of major anions (NO_3^-, Cl^-, SO_4^{2-}) using ion-chromatography (HPLC, SHIMADZU) and major cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) by ICP-AES (Optima3000, Parkin Elmer). HCO_3^- concentrations were determined by H_2SO_4 (0.01N) titration (pH 4.8 alkalinity). DN concentrations were measured with a total nitrogen analyser (TNM-1, SHIMADZU). The stable isotope ^{15}N was measured in aqueous NO_3^- of water samples using a mass spectrometer (Delta-S, Finnigan MAT).

RESULTS AND DISCUSSION

Groundwater flow and chemical profiles in the recharge and the discharge area

In the Yellow River Delta, groundwater typically flows from the Yellow River to the Bohai Sea (Miyaoka *et al*., 2006). The areas around the Yellow River are characterized as groundwater recharge zones, while the coastal area is a groundwater discharge area. Figure 2 shows the vertical profiles of Cl^- and DN concentrations in the groundwater of borehole N10 located near the Yellow River and N6 in the coastal area.

In the recharge area, Cl^- concentration was 66 meq L^{-1} near the water table (Fig. 2(a)). Because the groundwater in this area is recharged by the Yellow River water with relatively low concentrations of Cl^- (~5 meq L^{-1}), the upper groundwater is suggested to be diluted by the river water. However, in the deeper groundwater at more than 8 m depth, the Cl^- concentration was more than five times that in the surface. Chunting *et al*. (1995) have pointed out that there is a marine deposit making up a sedimentary layer at more than 10 m depth and high Cl^- concentrations in the deeper groundwater are likely influenced by the dissolution of Cl^- from this deposit.

In the discharge area, little changes were detected in vertical profiles of both Cl^- and DN (Fig. 2(b)). In general, the direction of groundwater flow is upward in the discharge area (Tóth, 1963). Based on this concept, it is suggested that mixing between the shallower groundwater with low dissolved concentrations and the deeper ground-

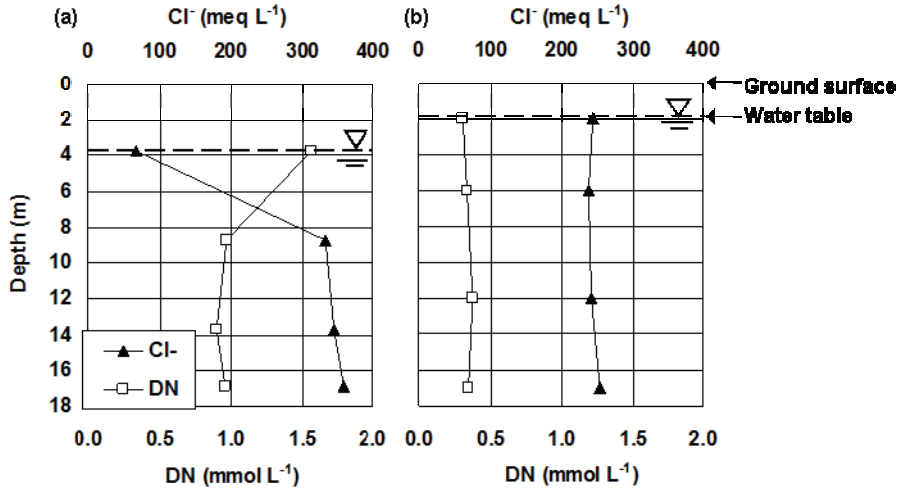

Fig. 2 Vertical profiles of Cl^- and DN concentrations in the groundwater of borehole N10 (a) and N6 (b).

water with high concentrations occurred in the discharge area. In contrast, DN concentrations were lower in the discharge area (~0.3 mmol L^{-1}) than in the recharge area (~0.9 mmol L^{-1}).

Nitrate contamination and attenuation in the groundwater

Figure 3 shows the relation between the nitrate-nitrogen (NO_3^--N) concentrations and the stable nitrogen isotope ratio ($\delta^{15}N$) in the groundwater of the northern area and southern area of the Yellow River. Natural ^{15}N abundance is expressed as:

$$\delta^{15}N\ (‰) = 1000\ \{(R_{sample} - R_{standard}) / R_{standard}\} \quad (1)$$

where $\delta^{15}N$ (‰) is the isotope ratio of the sample relative to the atmospheric air standard and R_{sample} and $R_{standard}$ are the molar ratios of ^{15}N–^{14}N (Mariotti *et al.*, 1988).

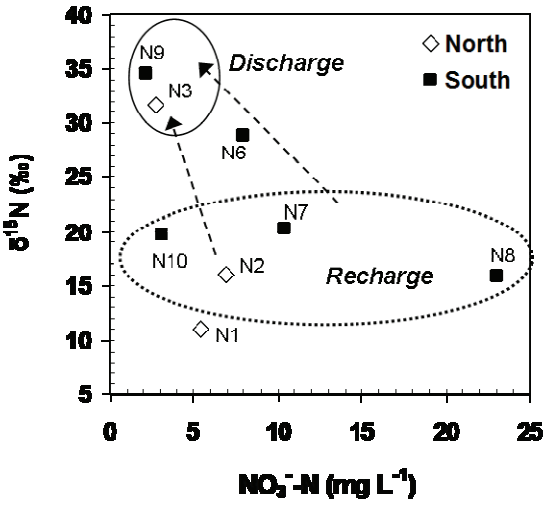

Fig. 3 Relationship between $\delta^{15}N$ and NO_3^--N concentrations in the groundwater.

In both of the northern and the southern area, the groundwater in the recharge area is characterized by relatively high concentrations of NO_3^--N and relatively low $\delta^{15}N$ (Fig. 3), while the groundwater of the discharge area is characterized by relatively low concentrations of NO_3^--N and relatively high $\delta^{15}N$. Some previous studies have shown that a decrease of NO_3^--N concentrations in groundwater can be attributed to biochemical denitrification process (Howard, 1985; Böhlke *et al*., 2002). The reaction involved is presented as follows (Böhlke, 2002):

$$4NO_3^- + 5C + 3H_2O = 2N_2 + 5HCO_3^- + H^+ \quad (2)$$

Denitrification is the biochemical reduction of NO_3^- occurring under anaerobic conditions. In the denitrification process, a decrease in NO_3^- concentrations and a high ^{15}N enrichment of the NO_3^- occurs (Mariotti *et al*., 1988). The results of the present study therefore suggest that a decrease of NO_3^--N concentrations in the discharge area is caused by the denitrification process.

The results of injection experiment are shown in Fig. 4. The variations of Cl^- and DN concentrations are expressed as the residual ratio (%) assuming that the concentration immediately after injection was 100%. The Cl^- is used as the conservative tracer. It is assumed that the variation of Cl^- concentration is caused by the advection–dispersion process both in the bottom water inside the borehole and in porewater in the adjacent aquifer. Three hours after the injection, 93% of Cl^- and 99.4% of DN concentrations were eliminated from the borehole (Fig. 4). The variation of Cl^- implies that 7% of the tracer water remained inside the borehole while that for DN suggests that only 0.6% remained. Based on these results, it is estimated that approximately 90% of NO_3^- remaining within the borehole was removed by denitrification during a three hour period. This rate is relatively high, compared with that reported in previous research (Trudell *et al*., 1986; Pauwels *et al*., 1998; Khan & Spalding, 2004).

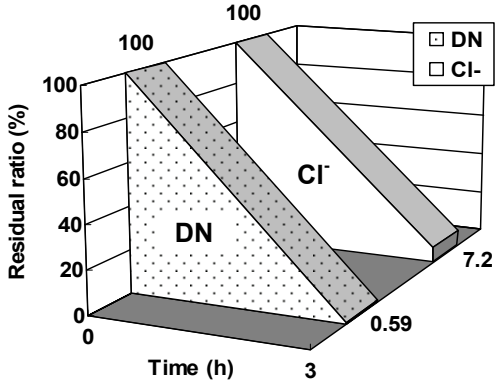

Fig. 4 Variation of the residual ratio of DN and Cl^- *versus* time in the injection experiment.

Future prospects for nitrogen discharge from the Yellow River Delta to the sea

Figure 5 shows the amounts of DN accumulated in the aquifer estimated using data from 10 boreholes (N1–N10). These were calculated under the assumption that the

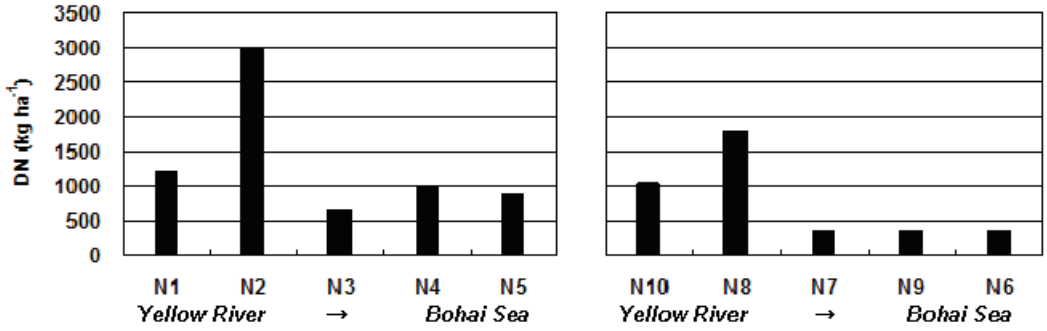

Fig. 5 Estimated amount of DN accumulated in the aquifer of the Yellow River Delta.

aquifer depth is 20 m, porosity in the aquifer is 40%, and the area of well bottom is 1 m^2. The maximum amount of accumulation (~3000 kg ha^{-1}) was calculated for borehole N2, and a minimum value (~300 kg ha^{-1}) for boreholes N6, N7 and N9. In the recharge area, i.e. boreholes N1, N2, N10 and N8, the accumulation of DN is relatively large compared with that in the discharge area (boreholes N4, N5, N6 and N9). This implies that nitrogen that has accumulated in the recharge area will be transported gradually to the sea with groundwater discharge in the future.

In the Yellow River Delta, NO_3^- contamination in groundwater is predicted to accelerate with an increasing use of nitrogenous fertilizer in the future (Shindo *et al*., 2006). Nonetheless, this study has confirmed the high potential for NO_3^- removal in the coastal groundwater, and it is suggested that the potential for removal exceeds the NO_3^- flux in groundwater flow even under conditions of severe NO_3^- contamination. However, we need to note the high potential for NO_3^- discharge to the sea via the river in the case where the groundwater is discharged to the river relatively quickly. In consequence, it is suggested that NO_3^- discharge through the groundwater to the sea is negligible in the Yellow River Delta.

CONCLUSIONS

In order to demonstrate the current conditions of NO_3^- contamination in groundwater of the Yellow River Delta and its effect on the marine environment, the profiles of chemical components and $\delta^{15}N$ in the groundwater were confirmed, and the capacity of natural denitrification in the aquifer of the coastal area was evaluated by an *in situ* injection experiment.

We confirmed that NO_3^- concentrations in groundwater of the recharge area were higher than those in the discharge area. It was also estimated that the amount of DN accumulated in the aquifer of the recharge area was approximately, at a maximum, 10 times larger than that in the discharge area. However, the distribution of NO_3^--N concentrations and $\delta^{15}N$ imply denitrification is occurring in the aquifer of the coastal area. Moreover, the results of the *in situ* experiment quantified the extent of this process and suggested that the capacity to remove NO_3^- from groundwater in the coastal area exceeds the NO_3^- load delivered by groundwater discharge, except for the case where the groundwater is discharged to the river relatively quickly.

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