



Integrated assessment on groundwater nitrate by unsaturated zone probing and aquifer sampling with environmental tracers

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ARTICLE INFO

Article history:

Received 7 March 2012
Received in revised form
11 July 2012
Accepted 20 July 2012

Keywords:

Soil water nitrate
Groundwater nitrate
Isotopes
Evaporation
Denitrification

ABSTRACT

By employing chemical and isotopic tracers (^{15}N and ^{18}O in NO_3^-), we investigated the main processes controlling nitrate distribution in the unsaturated zone and aquifer. Soil water was extracted from two soil cores drilled in a typical agricultural cropping area of the North China Plain (NCP), where groundwater was also sampled. The results indicate that evaporation and denitrification are the two major causes of the distribution of nitrate in soil water extracts in the unsaturated zone. Evaporation from unsaturated zone is evidenced by a positive correlation between chloride and nitrate, and denitrification by a strong linear relationship between $\delta^{18}\text{O}_{\text{NO}_3}$ and $\ln(\text{NO}_3^-/\text{Cl}^-)$. The latter is estimated to account for up to 50% of the nitrate loss from soil drainage. In the saturated zone, nitrate is reduced at varying extents (100 mg/L and 10 mg/L at two sites, respectively), largely by dilution of the aquifer water.

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1. Introduction

Nitrate is often one of the most abundant anions in contaminated groundwater (Riley and Zachara, 1992). However, the unsaturated zone, which is the passageway for all the water and contaminants transporting from the land surface to groundwater, has been a less concern to the hydrogeologists (Harter et al., 2005). Much of the scientific work related to the transformation and leaching of nitrogen focused on two subjects: documenting the extent of contamination in groundwater (e.g., Spalding and Exner, 1993; Wassenaar, 1995; Chen et al., 2005), and investigating the fate of these chemicals in the soil root zone (including the potential of groundwater leaching) as it relates to particular agricultural crops and management practices (e.g., Prasertsak et al., 2001; Merigout et al., 2008; Price et al., 2010).

Effects of unsaturated zone on groundwater pollution have not been studied until recent years. At present the nitrate appears most capricious in the unsaturated zone. There is a large body of literature based on studies at individual sites that indicates that unsaturated zone can be effective in attenuating nitrate before it enters the aquifer. Based on mass-balance, Pratt et al. (1972) estimated that denitrification accounts for up to 50% of nitrate loss in a thick unsaturated soil profile. Aulakh et al. (2000) gave direct evidence

on nitrate loss via denitrification in semiarid subtropical soil under laboratory conditions. Guo et al. (2006) also pointed out that denitrification may occur in the unsaturated zone with a shallow water table. However, all of these findings are generally questionable if the limitations of the mass-balance estimate and the laboratory experiment are considered. Firstly, mass-balance estimate in the field cannot give direct proof to show that the nitrate loss in the aquifer is attributed to denitrification. Secondly, a suitable environment is artificially created for the denitrification in the incubation experiments. This suitable environment is often unavailable in the field. Therefore, the results obtained from the experiments can only provide an indication of the upper limit of in-situ denitrification. A lot of recent studies from arid and semiarid areas suggest that nitrate attenuation in the unsaturated zone is probably unrealistic and nitrate is believed to move conservatively through the unsaturated zone (Walvoord et al., 2003; McMahan et al., 2006; Baran et al., 2007; Barkle et al., 2007; Green et al., 2008). As a result, nitrate is regarded as a conservative contaminant when its migration is numerically modeled. These models are used to predict the transport of nitrogen from land surface to the aquifer as a method to quantify the groundwater quality in areas threatened by the excessive application of nitrogen at the land surface (Chesnaux et al., 2007; Chesnaux and Allen, 2008). Therefore, considering the complex situation in its own, the role of unsaturated zone on the concentration of groundwater nitrate is not well understood. Furthermore, the two parts (unsaturated zone and aquifer) of

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a common hydrogeological system are usually studied separately, so it is impossible to achieve an integrated assessment of the coupled processes.

The complex cycling of nitrate in soil is responsive to variations not only in the inputs from precipitation and irrigation, but also to numerous co-occurring microbial processes. Cl^- combined with NO_3^- , nitrogen and oxygen isotopes are effective tools in disclosing these complications. Cl^- exhibits a similar transport behavior as NO_3^- so that Cl^- could be used to predict the mobility of NO_3^- in areas where NO_3^- is not susceptible to transformation (Gonzalez-Delgado and Shukla, 2011). While during the denitrification, microbe in soil trends to favor uptake of the lighter isotopes, ^{14}N and ^{16}O , leaving the residuum enriched in heavier isotopes (Holden and Fierer, 2005). For example, the process of denitrification (the microbially mediated reduction of nitrate to N_2) results in a trend of higher values of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ and, accordingly, has been of particular interest to groundwater and surface water research (Einsiedl et al., 2005; Wankel et al., 2009). Limited by the test technology, this isotopic method is proven to be effective in unsaturated zone lately (Singleton et al., 2005; Domagalski et al., 2008).

The objective of the present paper is to integrate the transport and transformation of nitrate in the unsaturated zone and saturated zone to provide the mechanisms of groundwater pollution. We will use both soil water and groundwater samples at the same sites with chemical and isotopic analyses and make a comparison of nitrate distribution in the unsaturated zone and the groundwater beneath it. We will then identify the nitrate sources and discuss processes responsible for the changes of nitrate in the soil water as well as in the groundwater of a selected study area-Tangshan City of the North China Plain.

2. Site descriptions

Tangshan is a large city with some 7.6 M inhabitants and growing at around 3.9%. About 72.2% of its total water supplies, amounting to an estimated 1.99 billion m^3 , is obtained from groundwater. However, groundwater nitrate pollution is a serious problem. According to an investigation made by the Haihe River Water Conservancy Commission in 1996, more than 21.6% of the water samples collected in Tangshan had exceeded the nitrate

limit for drinking water of 90 mg/L at that time (now 45 mg/L). The Luanhe alluvial plain aquifer system is the primary source for groundwater in this area. It is deposited during the diversion of the Luanhe River in different eras, leaving three fans (from the west to the east, delta I, II and III, respectively (Fig. 1)). Tangshan is located at delta I, which was formed during the late Pleistocene.

Agriculture is the dominant land use in the Luanhe alluvial plain, accounting for 77.2% of the total area. The cropping system of winter-wheat/summer-maize has been employed in the study area for at least 35 years. Both of maize and wheat root are distributed in a depth shallower than 1.2 m in the vertical soil profile (Zhou et al., 2008). Application of nitrogen fertilizer, including urea ($\text{CO}(\text{NH}_2)_2$), diammonium ($(\text{NH}_4)_2\text{HPO}_4$) and ammonium bicarbonate (NH_4HCO_3), is about 320 kg N/ha yr during the last ten years. Mean annual precipitation is approximately 650 mm. Irrigation, another main source of recharge to soil water, is supported by groundwater, and the mean annual value is about 1350 mm.

Past work on the Tangshan has dealt largely with investigating the extent of groundwater contamination (Zhang et al., 1996; Domagalski, 2001). However, by employing multi-isotopic techniques, Pang et al. (in press) reported that fertilizer is the most common source of high nitrate levels in the shallow aquifer, and is flushed downward during groundwater recharge through the unsaturated zone. However, different area with equal amounts of applied fertilizer can show various levels of nitrate in groundwater. In the non-riparian zone, nitrate concentrations in shallow groundwater (less than 80 m) decrease with increasing distance from the apex. Groundwater nitrate at the apex and the edge of the alluvial fan are 258.0 mg/L and 43.2 mg/L, respectively, with the average value of 154.4 mg/L. This distribution is probably related to the sedimentary characteristic of the aquifer. At the apex of the alluvial fan, with the coarse sediment, groundwater has the relatively short residence time and shows a relatively high level of nitrate (Pang et al., in press). However, in the riparian zone, groundwater nitrate is extremely low (<12.4 mg/L) (Pang et al., in press). The unsaturated zone pathways dealing with nitrogen contaminants transport into groundwater remains poorly investigated in Tangshan. The causation of the low levels of groundwater nitrate is questionable.

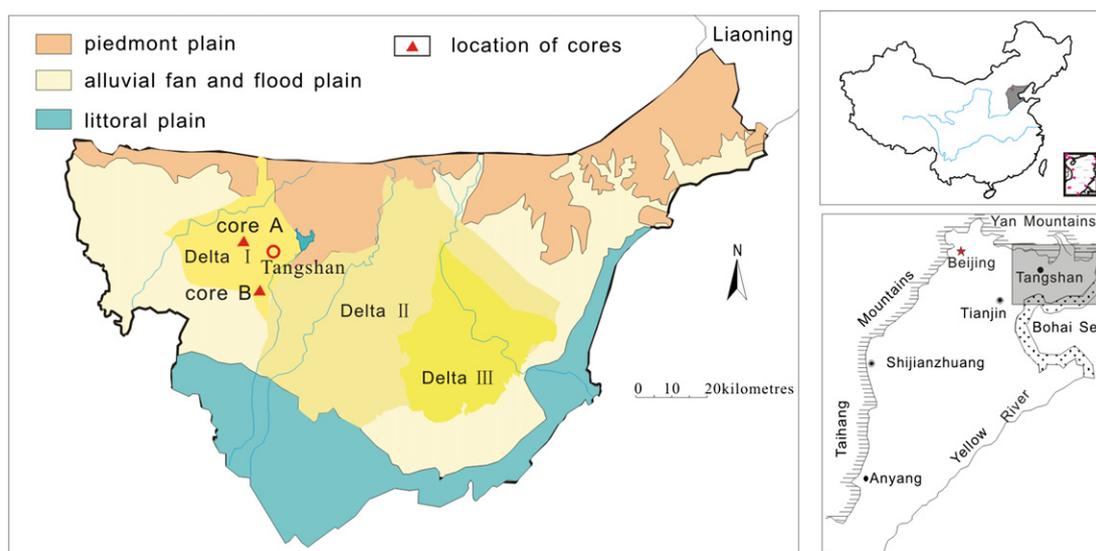


Fig. 1. Topography map of the location of study area.

3. Sampling and analyses

3.1. Sampling

To figure out the effect of migration and transformation of nitrate in the unsaturated zone on the distribution of nitrate in the aquifer, two sites (site A and site B, located at the non-riparian zone and riparian zone, respectively) were selected as target area. Fig. 1 shows their respective locations. Concentration of nitrate in groundwater at site A follows the spatial distribution rule of the alluvial fan, with the concentration of about 100 mg/L, while site B is noted for the low concentration of groundwater nitrate (<12.4 mg/L). Groundwater level at two sites is 25 m and 5 m, respectively.

Two undisturbed sediment cores and groundwater beneath two sites were collected after the harvest of maize in 2010 and 2009, respectively. The unsaturated zone cores were accomplished by drilling and sampling with a 7.5 cm diameter hollow-stem hand auger. Two cores (Core A and Core B) from two locations (Site A and Site B) were taken continuously from the ground surface to a depth of 5 m. Core B reached groundwater level at 5 m. Bulk soil samples of ~400 g were collected at intervals of 0.25 m (40 samples in total). Samples were homogenized over the sampled interval and immediately sealed in polyethylene bags. Gravimetric moisture content was determined by drying a minimum of 80 g of soil sample at 110 °C for 12 h. For the unsaturated zone moisture extracts, 200 g of sediment was combined with 200 mL of deionized water, shaken for 30 min at room temperature, after which the mixture of deionized water and soil water was obtained using centrifuge at the rotational speed of 4000 rpm. Groundwater samples were obtained from irrigation wells located 500 m around the cores in the wheat-maize area. This distance is suggested by McLay et al. (2001) and is defined as a “buffer area” to avoid the impact of different land use on the level of nitrate in groundwater. All of the samples were kept at 4 °C prior to analyses.

3.2. Analysis

Once the soil water extracts was collected, a subsample of approximately 60 mL was transferred to a bottle and stored at a low temperature for major ions analyses with an ion chromatograph (Dionex-500) at the Beijing Research Institute of Uranium Geology. The ions concentration of the soil solution is then calculated based on gravimetric moisture content. The remainder was kept frozen for further analyses of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$. Preliminary screening of the

sample aliquots for NO_3^- concentration informed us if the sample would contain enough NO_3^- for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ analyses.

Isotope analyses of N and O in NO_3^- in soil water extracts were conducted at the Department of Applied Analytical and Physical Chemistry, Faculty of Bioscience Engineering, Ghent University, Belgium, by bacterial reduction of NO_3^- to N_2O using *Pseudomonas aureofaciens*, purging and trapping the N_2O , then releasing the N_2O through a Trace gas-preparation unit (ANCA TGII, PDZ Europa Ltd., Northwich, UK) coupled to an IRMS instrument (20–20, SerCon Ltd.) (Sigman et al., 2001; Casciotti et al., 2002). The data were calibrated by analyzing NO_3^- isotopic reference materials with the samples. ^{15}N in groundwater nitrate is measured at the laboratories of the Institute of Geology and Geophysics, Chinese Academy of Sciences. The groundwater sample preparation and analysis of N isotope ratios were performed in accordance with the method developed by Chang et al. (1999) and Silva et al. (2000). Dissolved NO_3^- was first enriched on anion-exchange-resin and then eluted from the anion exchange columns with HCl. The nitrate-bearing acid eluant is neutralized with Ag_2O , filtered to remove the AgCl precipitate, then freeze-dried to obtain solid AgNO_3 , which is then combusted to N_2 in sealed quartz tubes for $\delta^{15}\text{N}$ analysis through a gas chromatograph into a Thermo-Finnigan Delta Plus isotope-ratio mass spectrometer. However, nitrate content in eight groundwater samples collected around site B were under the minimum required quantity for nitrogen isotope ratios analysis, thereby the data is unavailable. The average standard deviation of normalized data was 1‰ for $\delta^{15}\text{N}$ and 2‰ for $\delta^{18}\text{O}$.

4. Results and discussion

The results of soil water content, chemistry in the soil water extracts, $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ are presented here for two cores (Figs. 2 and 3), as well as water chemical and nitrogen isotopic results of groundwater samples (Table 1).

4.1. Distribution of nitrate in soil water extracts and groundwater

4.1.1. Site A

Gravimetric water content ranges from 0.10 to 0.19, with a mean value of 0.14 (Fig. 2). There is a sharp increase below the depth of 0.25 m, which is probably due to the change of soil texture. Chloride content fluctuates slightly throughout the sample depth, with a range from 12 mg/L to 47 mg/L and a mean value of 30 mg/L (Fig. 2).

Nitrate in the shallow unsaturated zone ranges from 198 mg/L to 579 mg/L (Fig. 2). The variation in nitrate fluctuates greatly in the

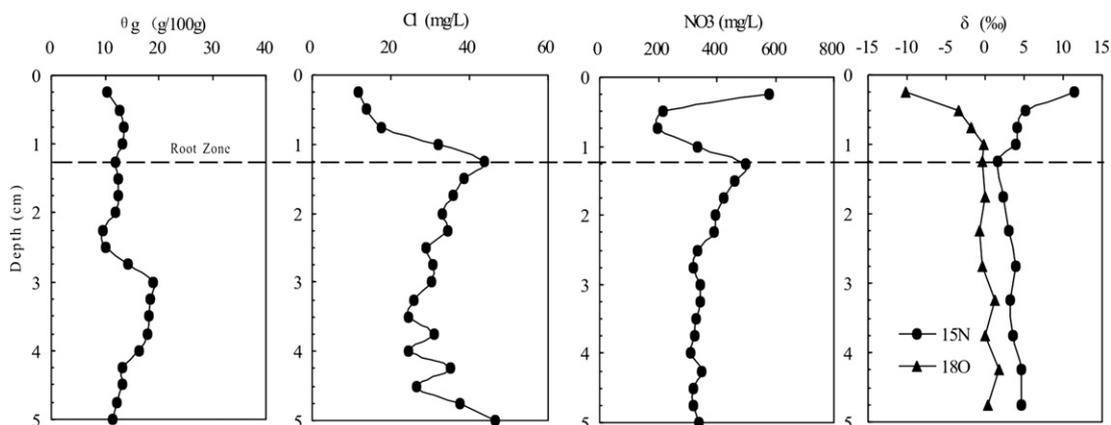


Fig. 2. Depth profiles of soil water content, concentrations of major anions containing NO_3^- and Cl^- , $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ isotopic composition in the unsaturated zone at site A.

Table 1
Results for well depth, major ions, and nitrogen isotope in groundwater.

	Well depth (m)	$\delta^{18}\text{O}$ (‰)	$\delta^{15}\text{N}$ (‰)	NO_3^- (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)
Site A	40	-8.12	4.5	109.0	15.0	39.7
	80	-7.48	4.8	119.0	15.3	43.6
Average		-7.80	4.6	114.0	15.2	41.6
Site B	5	/	/	413.0	132.0	309.0
	20	-4.32	/	6.2	125.0	218.5
	30	-6.07	/	2.4	53.3	194.4
	40	-7.37	/	12.4	48.6	71.0
	40	-6.28	15.4	9.5	62.9	154.5
	60	-7.22	/	2.8	17.4	32.0
	60	-6.23	/	5.7	58.8	153.1
	60	-6.38	/	1.2	42.9	102.4
	65	-6.08	/	1.2	76.6	135.0
	70	-5.87	/	2.3	30.8	53.5
Average		-6.20	15.4	4.9	57.4	123.8

Note: Average at site B points to the average value of sample with well depth ranged from 20 m to 70 m.

root zone, which is probably due to the fertilizer application and plant uptake. Below the root zone, nitrate in soil water extracts shows a slight decrease and ranges from 311 mg/L to 459 mg/L with the mean value of 353 mg/L. Nitrate concentration is invariable below the depth of 2.5 m.

Nitrate concentrations of groundwater are distinctly lower than soil water extracts in the shallow unsaturated zone, as well as the chloride. The mean value of nitrate and chloride in soil water extracts are 353.0 mg/L and 30.0 mg/L, respectively. They reduce to 114.0 mg/L and 15.2 mg/L in groundwater, respectively.

4.1.2. Site B

Water content ranges from 0.07 to 0.30, with a mean value of 0.19 (Fig. 3), having a little higher and wider fluctuation than core A. Chloride concentration ranges from 31 mg/L to 149 mg/L, with a mean value of 95 mg/L. Chloride concentration is counterpoised to the equivalent changes in water content, indicating that chloride is concentrated by evaporation in the unsaturated zone (Fig. 3). Although the mean value of core B is almost 3 times as high as that of core A, the mean value of the SO_4/Cl ratio in core B is 5.1 between 1.25 m and 5.0 m in depth, almost identical to that found in core A (5.3). The similar ratio of two cores indicates that sulfate and chloride have the same source.

There is a concentration peak at a depth of 0.75 m, with nitrate of 2703 mg/L. Below the root zone, nitrate concentration varies from 179 mg/L to 549 mg/L, showing an apparently wider range compared with core A. The mean value is 368 mg/L (Fig. 3), and is

slightly higher than that of core A. However, unlike with SO_4/Cl , $\text{NO}_3^-/\text{Cl}^-$ ratios in two cores show large differences. $\text{NO}_3^-/\text{Cl}^-$ in core A ranges from 4.9 to 6.8, with a mean value of 6.2, while $\text{NO}_3^-/\text{Cl}^-$ in core B ranges from 1.5 to 2.6, with a mean value of 2.1. The narrow range of $\text{NO}_3^-/\text{Cl}^-$ ratio within one single core implies that the input of nitrate and chloride reach a steady state in each site. Nevertheless, different ratios of two cores probably indicate different input sources of two cores.

At site B, nitrate and chloride in groundwater collected at the water table are 413 mg/L and 132 mg/L, respectively. Both of them show a similar concentration to soil water extracts. However, groundwater collected below the water table decrease acutely, but chloride exhibits a mild decreasing trend. Nitrate in groundwater with well depths between 20 and 70 m, i.e., 15 m–65 m below the water table, ranges from 12.4 mg/L to 1.2 mg/L, with a mean value of 4.9 mg/L. The average value of chloride decreases from 132.0 mg/L at the water table to 57.4 mg/L in the shallow aquifer. The probable cause of the distinct decrease of nitrate will discuss in 4.4.

4.2. Sources of nitrate in soil water extracts

In the root zone, nitrogen and oxygen isotopes in both cores show large variations (Fig. 2). However, isotopes maintain a nearly stable value below the root zone in core A. Nitrogen and oxygen isotopes range from 2.4 to 4.6‰ and -0.8 to 1.7‰, respectively, with averages of 3.6‰ and 0.3‰. Both of nitrogen and oxygen isotope in core B show a wider range compared to core A. Additionally, core B is enriched in oxygen isotope. The range of nitrogen isotope is from 3.3‰ to 9.9‰ with a mean value of 5.4‰, and oxygen isotope varies from 1.2‰ to 8.3‰ with a mean value of 4.2‰ (Fig. 3).

Nitrogen and oxygen isotopes of nitrate in soil water extracts lie in a mixture area (Fig. 4). Three kinds of nitrogen sources are implicated: ammonium in fertilizer or precipitation; soil ammonium; manure and septic waste. No manure is applied in the summer-maize/winter-crop agriculture. Atmospheric N deposition and soil nitrogen on this primarily agricultural watershed cannot contribute significantly to the elevated nitrate concentration in soil water extracts because even the highest nitrate concentration (3.1 mg/L) in acid precipitation is much lower with comparison to the nitrate values of those two soil profiles (Fu and Wang, 2002; Zhang et al., 2008). Hence, ammonium in fertilizer is the most potential nitrogen source.

On account of a nitrification pathway, the composition of groundwater $\delta^{18}\text{O}_{\text{NO}_3^-}$ in core A and core B from nitrification of fertilizer-derived NH_4^+ should be about +2.2‰ and +2.9‰, respectively (Anderson and Hooper, 1983; Hollocher, 1984). This

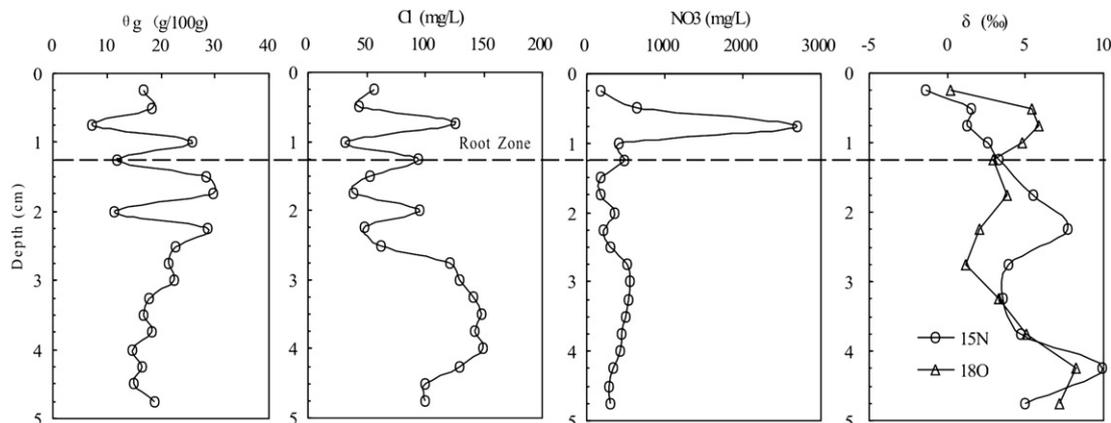


Fig. 3. Depth profiles of soil water content, concentrations of major anions containing NO_3^- and Cl^- , $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ isotopic composition in the unsaturated zone at site B.

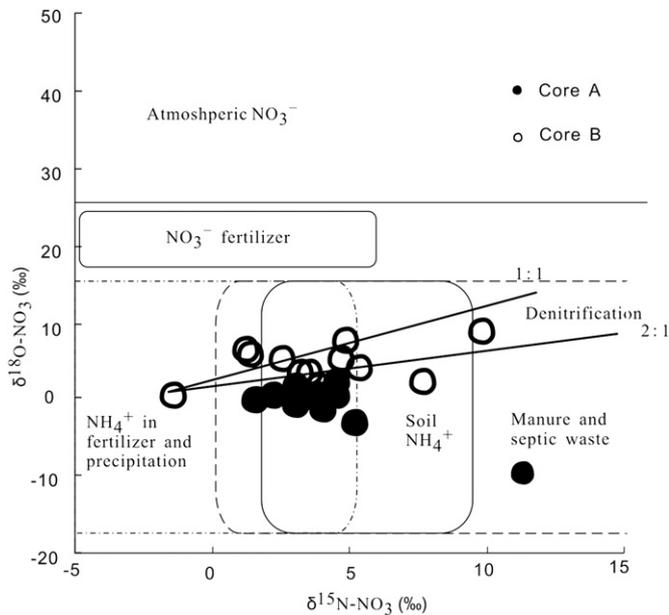


Fig. 4. Relationship between $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ in the extracted soil water at two cores (A and B).

nitrification pathway suggests that one-third of the oxygen used in nitrification is from atmospheric oxygen ($\delta^{18}\text{O} = +22\text{‰}$) while two-thirds is from the water, which are calculated at -7.7‰ and -6.6‰ (the weight average of rainwater and irrigated water) for core A and core B, respectively. Rainfall from the region is represented by Tianjin station some 100 km SW of Tangshan. Weighted mean composition of $\delta^{18}\text{O}$ of rainfall is -7.5‰ , and the data can be taken from the IAEA network (<http://isohis.iaea.org>). The average value of irrigated water can be found in Table 1. The $\delta^{18}\text{O}_{\text{NO}_3}$ data show that core A is deficient in ^{18}O but core B is enriched. This inconsistency can be expected under field conditions due to changes in the proportion of the oxygen source (water vs. atmospheric oxygen) during nitrification (Aravena et al., 1993). Otherwise, oxygen isotopic fractionation during the transformations of nitrate is another possible explanation of the variation in oxygen isotope. The larger degree of the denitrification process, the more enrichment of the oxygen isotope in residual nitrate. Denitrification caused the variety of oxygen isotope is discussed in 4.3.

4.3. Processes affecting nitrate in the unsaturated zone

4.3.1. Evaporation

Nitrate concentration of soil water extracts in core A below the root zone ranges from 311 mg/L to 459 mg/L with the mean value of 353 mg/L, while soil water nitrate of core B ranges from 179 mg/L to 549 mg/L, with a mean value of 368 mg/L. Nitrate increases proportionally with chloride in both cores, as would be expected if evaporation occurred (Figs. 2 and 3).

In a NO_3^- vs. Cl^- plot, a theoretical evaporation line (TEL) can be constructed by using the sample with the lowest contents of chloride as the initial input from the land surface (Fig. 5a). Then the initial concentrations of nitrate loaded to core A and core B are 311 mg/L and 179 mg/L, respectively. With the same rate of nitrogen fertilizer applied in agriculture in these two sites, this large difference of the initial nitrate input between these two sites (311 mg/L and 179 mg/L, respectively) is probably attributed to the various degrees accumulation of groundwater with different levels of nitrate at two sites (with the average value of 114 mg/L and 4.9 mg/L, respectively) since that groundwater that supports the irrigation

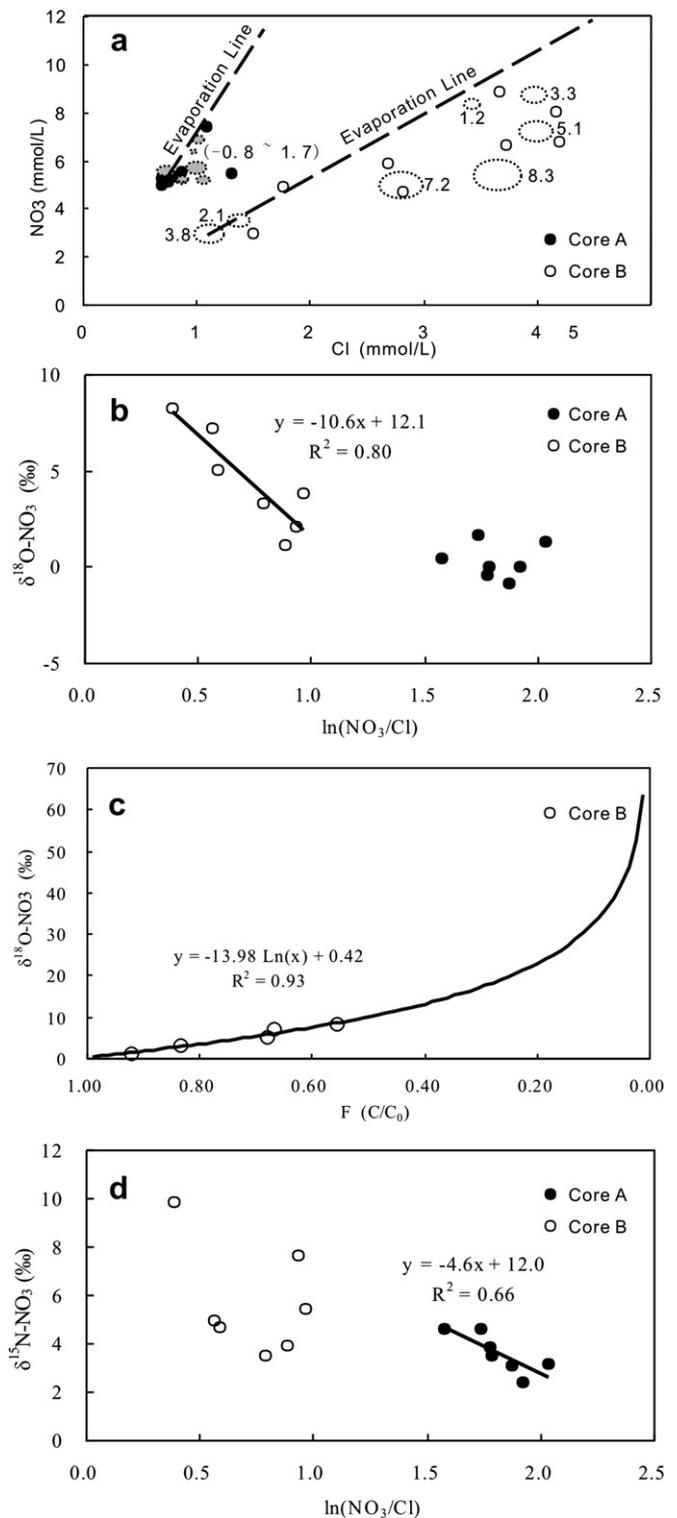


Fig. 5. (a) Cl^- vs. NO_3^- in the extracted soil water at the two cores below the root zone. The "evaporation line" indicates the enrichment of nitrate and chloride in soil water extracts using the lowest chloride as the initial input. The composition of oxygen isotope is marked, and proportional to their diameters. (b) $\delta^{18}\text{O}_{\text{NO}_3}$ versus $\ln(\text{NO}_3^-/\text{Cl}^-)$ in the extracted soil water at the two cores under the root zone. (c) Rayleigh process of $\delta^{18}\text{O}_{\text{NO}_3}$ during denitrification. (d) $\delta^{15}\text{N}_{\text{NO}_3}$ versus $\ln(\text{NO}_3^-/\text{Cl}^-)$ in the extracted soil water at the two cores under the root zone.

is the other principal source for replenishment of moisture in the soil water. Initial level of nitrate in the vadose zone depends primarily on: (1) the availability of water at the land surface, and (2) the availability of nitrate at the land surface. These two factors control the initial input of soil water nitrate. Within the study region, the amount of the water is a certain value, which is a sum of the precipitation and irrigation. Nitrate is available in nitrogen fertilizer, precipitation and groundwater sourced irrigation. Nitrate in the former two is similar in the region, but nitrate in the latter is various in the study area. Elevated groundwater nitrate at site A leads to the relatively high initial input (311 mg/L) of NO_3^- in the unsaturated zone.

Although a similar positive correlation of nitrate and chloride can be found in these two cores, which would be expected if evaporation was effecting nitrate concentration in soil water extracts after nitrogen fertilizers dissolved and transformed to nitrate, there are still two major differences. Firstly, ranges of nitrate and chloride in core B are wider than those of core A (Fig. 5a). A probable explanation to this wider range is that a greater degree of evaporation occurs in the core B, leading to the large enrichment of nitrate and chloride. Secondly, most of the samples in core B lie below the TEL, but samples collected from core A can be divided into two groups. One group lies on the TEL, and the other appears below the line. The former is sampled just below the root zone, and the latter is located in the deep part of the core. The sampling depth of two groups is of 1.5–2.25 m, 4.25–5 m, respectively. The probable explanation to the samples below the TEL is that there exist processes reducing nitrate concentration in soil water extracts, including dilution (mixed with uncontaminated water) and denitrification. Additionally, nitrate attenuation processes seem to be ubiquitous in the whole unsaturated zone at site B, whereas it occurs particularly in the deep part of site A.

4.3.2. Denitrification

Soil water samples lie below the TEL have enriched nitrogen and oxygen isotopic composition. In core A, two samples lie below the TEL have the most enriched isotopic composition for nitrogen and oxygen in the whole core. Five samples below the TEL in core B are enriched in heavy isotopes compared with core A (Fig. 5a), and there exist a similar trend with nitrogen and oxygen isotopes against the depth in core B (Fig. 3). This distribution give a probable

explanation that denitrification, rather than dilution, is the major process reducing nitrate concentration in soil water extracts, as the mixture-process do not change the composition of nitrogen isotope in nitrate.

The $\delta^{18}\text{O}_{\text{NO}_3}$ data give further evidence to the occurrence of denitrification. In core B, there is a negative linear relationship between $\ln(\text{NO}_3^-/\text{Cl}^-)$ and $\delta^{18}\text{O}_{\text{NO}_3}$ ($n = 8$, $R^2 = 0.67$) (Fig. 5b). This relationship indicates the existent of a denitrification-dominated system, which have been implied by previous investigations in the groundwater systems (Otero et al., 2009). Furthermore, an individual enrichment factor in the unsaturated zone for oxygen isotope of nitrate can be estimated using a simplified Rayleigh equation (Mariotti et al., 1988; Boettcher et al., 1990):

$$\delta \cong \delta_0 - \epsilon \cdot \ln(f) \quad (1)$$

Where: δ = delta values in the substrate; δ_0 = initial delta value in the substrate; ϵ = enrichment factor; f = substrate concentration divided by the initial substrate concentration.

In groundwater system, it is often difficult to determine the initial substrate concentration due to variations of the nitrogen input during different seasons (Boettcher et al., 1990). In this study, the complex situation arises in that the NO_3^- concentrations is related to the occurrence of evaporation. Nevertheless, assuming that soil water samples lying on the TEL did not undergo denitrification process, a rough estimate of the initial NO_3^- concentration can be obtained by the concentration of chloride and the TEL as shown in Fig. 5a. The denitrification loss can be assumed to be the vertical difference between the sample and the TEL. The initial oxygen isotopic ratio of nitrate and the oxygen isotopic enrichment factor ϵ are 0.42‰ and 14‰, respectively, which are revealed by the equation of the regression curve shown in Fig. 5c. Denitrification loss varies at different depths in core B, which can reach up to 50% at a certain depth of 4.25 m.

Various field studies have demonstrated that the heavy isotopes, ^{15}N and ^{18}O , were concurrently enriched in the residual NO_3^- pool during the denitrification (Boettcher et al., 1990; Aravena and Robertson, 1998; Mengis et al., 1999). Thus, if denitrification is the main process for NO_3^- removal, ^{15}N and ^{18}O should become progressively more enriched as NO_3^- depleted. However, a presumed negative correlation between $\delta^{15}\text{N}_{\text{NO}_3}$ and $\ln(\text{NO}_3^-/\text{Cl}^-)$ cannot be

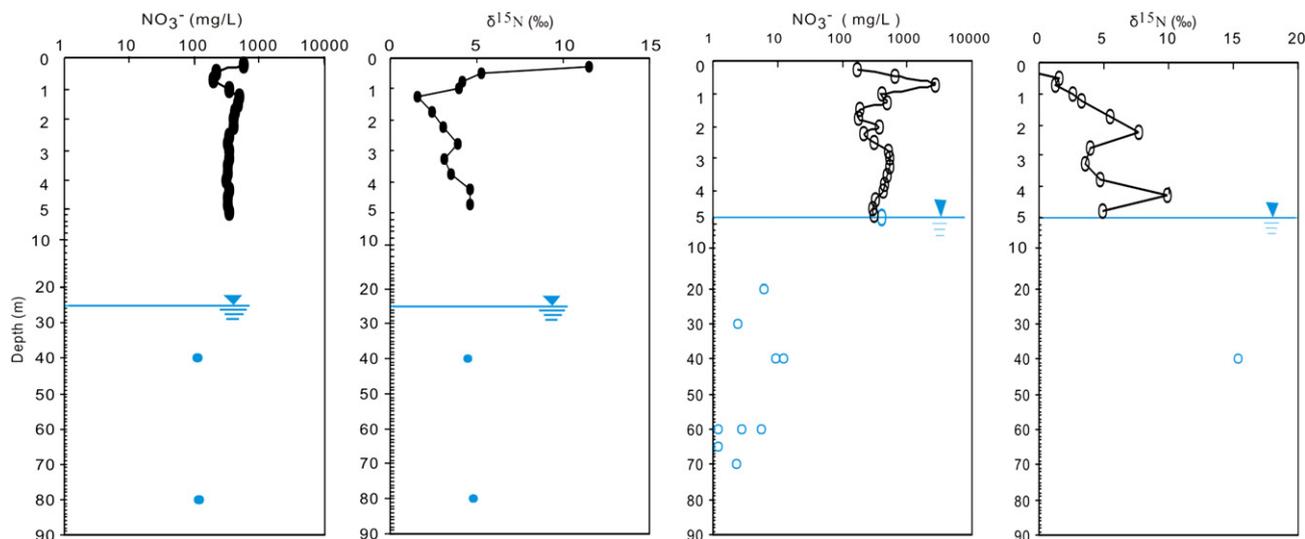


Fig. 6. Nitrate and nitrogen isotopic composition depth profiles at the two cores. The filled and unfilled symbols represent samples core A and core B, respectively. Black and blue symbols represent samples located at the unsaturated zone and saturated zone. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

found in core B (Fig. 5d). Hence, we speculated that denitrification is not the only process determining the composition of nitrogen isotope in nitrate. Other transformation processes that involved in nitrogen isotope fractionation, including urea volatilization and nitrification, probably occur. Nevertheless, the diversification of $\delta^{18}\text{O}_{\text{NO}_3}$ value is entirely attributed to the denitrification after the nitrification.

In core A, a negative correlation between $\delta^{15}\text{N}_{\text{NO}_3}$ and $\text{NO}_3^-/\text{Cl}^-$ can be found, however, such a relationship between $\delta^{18}\text{O}_{\text{NO}_3}$ and $\text{NO}_3^-/\text{Cl}^-$ does not exist (Fig. 5d). The most probable explanation seems to be that other processes, e.g. volatilization of ammonia, are the leading causes in core A resulting the variety of isotopes. Both of processes (e.g., volatilization) can lead to the decrease of NO_3^- combined with the increase of $\delta^{15}\text{N}_{\text{NO}_3}$, but have limited impact on the composition of oxygen isotope in nitrate (McMahon and Bohlke, 2006).

4.4. Denitrification in groundwater

Evidenced by the consistent decreases of chloride and a slight change of $\delta^{15}\text{N}$ in the vertical profile at site A from the unsaturated zone to saturated zone (Fig. 6), the decreases of nitrate in groundwater is probably dilute by natural groundwater with low concentrations.

However, the sharp drop of groundwater nitrate in the shallow aquifer combined with the inconsistent decreases of chloride, indicates that nitrate is entirely consumed within the exact depth of 15 m below water table (Fig. 6). Enriched ^{15}N indicates that denitrification may be responsible to the nitrate consume. With a shallow unsaturated zone, the upper several meters of water table is favorable for the occurrence of denitrification (Pabich et al., 2001).

According to the Rayleigh equation, denitrification loss can be calculated. It has been reported that ^{15}N fractionates by a factor of 2–1 compared to ^{18}O for denitrifying system (Gates et al., 2008). Therefore, the enrichment factor of nitrogen isotope in the aquifer ranges from 14‰ to 28‰. The enrichment factor of nitrogen during the denitrification is comparable to those factors that have been reported (10‰–33‰) (Mengis et al., 1999). The average value of $\delta^{15}\text{N}$ (5.4‰) in soil water sample collected in core B is assumed to be the initial composition before nitrate into the aquifer. Assuming that the enriched nitrogen isotope of groundwater nitrate collected at site B is entirely caused by denitrification, nitrate loss could be calculated ranging between from 51% to 30% by Eq. (1). At site B, the remainder of nitrate is known as 9.5 mg/L, and the initial nitrate should range from 19 mg/L to 14 mg/L. Nonetheless, nitrate is much higher at the water table (413 mg/L) than its theoretical value (19–14 mg/L). This denitrification consumed nitrate hypothesis is not supported by the inconsistency, and the dilution probably dominates to the extremely low level of nitrate in groundwater at site B.

5. Conclusions

$\text{NO}_3^-/\text{Cl}^-$ value plus dual isotopic composition of nitrate (nitrogen and oxygen) in soil water extracts and groundwater give some implications for the sources of nitrate in soil water extracts and processes affecting the nitrate concentration in the unsaturated zone and aquifer. Results show that nitrogen fertilizer applied at the surface is the major source of elevated nitrate in soil water extracts.

In agricultural areas where groundwater shows high nitrate levels, conservative transport of nitrate in the unsaturated zone is evidenced by correlation between Cl^- and NO_3^- , and that between nitrogen and oxygen isotopes. Evaporation and denitrification play a relatively minor role in the distribution of soil water nitrate.

While in the agricultural area with low levels of groundwater nitrate, evaporation leads to the increasing of nitrate in soil water extracts, and denitrification cannot be ignored in the whole unsaturated zone, and the denitrification loss can reach up to 50% of the nitrate input though it varies with depth.

Elevated nitrate appears in aquifer beneath the unsaturated zone where conservative transport dominates. Low levels of nitrate in groundwater below the shallow unsaturated zone is controlled by dilution process that cause the groundwater nitrate to decrease, though denitrification loss from the vertical input can be as high as 31%–50%.

It is clear therefore that the distribution of groundwater nitrate is controlled by a dilution-dominated system. Changes, e.g. significant decrease of fertilizers amount, a sound distribution of land use considering dilution capacity of the aquifer, are urgently needed in water protection.

Acknowledgments

The work is supported by the National Natural Science Foundation of China (Grant 40872162, 41202183) and the International Atomic Energy Agency (RC15397). The authors are grateful to C.T. Berridge for editing the English.

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