Meter-scale lateral heterogeneity of nitrate concentrations of groundwater in aquitards

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Abstract

The long-term protection of the world's groundwater resources partially depends on the ability of aquitards to retard the movement of natural and anthropogenic solutes, and hence, it is important to understand the processes controlling the distribution, transport, and attenuation of dissolved materials. Moreover, the consequences of increasing amounts of anthropogenic N circulating in groundwater is of concern, and the attenuation and transport processes of NO_3^- present in the groundwater in aquitards must be examined. We have investigated the lateral distributions of NO_3^- concentrations in groundwater in an aquitard (4 m $\times$ 6 m area) at Tsukuba upland at a few meter-scales and attempted to identify the possible mechanisms for their heterogeneity; this, to our knowledge, is the first such study. High-resolution measurements were obtained using piezometers, and they revealed complex lateral NO_3^- heterogeneity. Large variations in the NO_3^- concentrations were found between groundwater samples from piezometers that were horizontally separated by a distance of as little as 2 m. Although the mechanism of lateral NO_3^- heterogeneity in the aquitard remained unclear, we believe that the occurrences of biochemical reactions such as denitrification and other factors such as the spatial variability of NO_3^- transport play a role in it. This first study of the meter-scale lateral heterogeneity of NO_3^- concentrations of groundwater in aquitards provides new insights into the mechanisms of natural attenuation of NO_3^- in aquitards; further, our study also discusses difficulties in some of the upscaling approaches of the NO_3^- natural attenuation zone in groundwater based on the data obtained from a small number of piezometers.

Key words: heterogeneity, nitrate, groundwater, aquitard

Introduction

Aquitards are low-permeability beds along aquifer systems, and they have significant influence on the groundwater quality of aquifer systems (Back, 1986; Van Stempvoort and van der Kamp, 2003). The long-term protection of the world's groundwater resources, especially their water quality, will depend in part on the ability of aquitards to attenuate and retard the migration of natural and anthropogenic solutes (e.g. Lei and Tase, 1986;

Ponzini *et al.*, 1989; Rudolph *et al.*, 1991; McMahon, 2001; Harrington and Hendry, 2005). Hence, it is important to understand the processes controlling the distribution, transport and attenuation of dissolved materials in aquitards worldwide.

In recent times, concerns regarding the consequences of increasing amounts of anthropogenic N circulating in the world's subsurface environments have been increasing (e.g., Otero *et al.*, 2009; Reddy *et al.*, 2009; Umezawa *et al.*, 2009). The distribution, transport and attenuation processes of NO_3^- in

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groundwater at the watershed scale have been reported previously (e.g. Böhlke and Denver, 1995; Tesoriero *et al.*, 2000; Böhlke *et al.*, 2002; Tesoriero *et al.*, 2007). In particular, several studies have attempted to examine the attenuation and transport processes of NO_3^- present in the groundwater in aquitards (Fujikawa and Hendry, 1991; Ernstsen, 1996; Robertson *et al.*, 1996; Ernstsen *et al.*, 1998; Eidem *et al.*, 1999; McMahon *et al.*, 1999; Rodvang and Simpkins, 2001; Jørgensen *et al.*, 2004; Ioka and Tase, 2004a; Hansen *et al.*, 2008). Further, a few studies have examined the heterogeneity of NO_3^- concentrations of groundwater in aquitards (Ernstsen, 1996; Robertson *et al.*, 1996) however, to our knowledge, the meter-scale lateral heterogeneity of NO_3^- concentrations in the groundwater in aquitards has not been investigated so far. Such an investigation is important because if no data is available on the local variations in the NO_3^- concentrations in aquitards, it is difficult to develop an upscaling methodology for NO_3^- cycle models and NO_3^- attenuation zones in aquitards.

Hence, in this study, we have aimed to investigate the lateral distributions of NO_3^- concentrations in the groundwater in an aquitard in Tsukuba upland at a few meter-scales and to identify the possible mechanisms for their heterogeneity.

Study plot description

The study area was located in Tsukuba upland, which is approximately 15 km northwest of Kasumigaura (Fig. 1a, b). At study area, according to information obtained from farmers, inorganic fertilizers (N: P: K: 15: 15: 15; 200 kg per 10 a) are applied for three times from April to October in the lawn grown land. The study plot consisted of fallow soil; its land elevation was 22.50–22.75 m, whereas its area was 4 m $\times$ 6 m (Fig. 2).

The alluvial aquifer-aquitard system in study

area is composed of unconsolidated sediments of Quaternary age. The system in the study plot consists of four layers. The top layer is Younger Loam Formation comprised of volcanic ash soil (Unozaawa, 1988). Beneath the Younger Loam Formation or Joso Clay was a sand and gravel layer. The hydraulic conductivity of the Joso Clay layer ranges from an order of 10^{-8} to 10^{-11} m/s (Yasuhashi *et al.*, 1991) and from an order of 10^{-6} to 10^{-11} m/s (Yuita *et al.*, 2002). This sand and gravel layer had an underlying by silt and clay layer (Fig. 3). The hydraulic conductivity of the silt and clay layer was investigated by using the slug test (Hvorslev, 1951) and found to be ranging from an order of 10^{-9} to 10^{-10} m/s. In this study, the silt and clay layer acting as an aquitard has been investigated. The water table at the study plot is approximately 0.5 to 1.0 m below the land surface (Ioka and Tase, 2004b).

Methodology

The groundwater samples for this study were collected using piezometer nests installed 2.0, 2.5, 3.0, and 3.5 m below the land surface using a polyvinyl chloride (PVC) tube (inner diameter (ID): 2 mm) and plastic syringes. The piezometer nests were constructed from commercially available PVC pipes having IDs of 40 mm and fitted with a drive point (Figs. 2 and 3). The sampling of groundwater was completed on August 28, 2003, October 24, 2003 and December 28, 2003. Unfiltered groundwater samples were taken for the field measurements of specific electrical conductivity (SEC) at 25 °C using an EC meter (Yokogawa Model SC82) and dissolved oxygen (DO) concentration using a DO meter (DKK-TOA, Model DO-24P) and for the laboratory measurement of alkalinity. Although DO concentration should always be measured either using an in situ probe or in a flow-through cell at the surface (Nielsen and Nielsen, 2006), in

Fig. 1 (a), (b) Topography and land use in the study area (modified after Ioka and Tase, 2004a).

Fig. 2 Locations of piezometer nests at the study plot. Contour lines reflect topography at 0.25m intervals.

Fig. 3 Geology and piezometer screen distributions along two transects (locations shown in Figure 2). ●: piezometers installed in the sand and gravel layer. ○: piezometers installed in the silt and clay layer.

this study, the DO concentrations were measured in an open container, where there is an air-water interface. Hence, the DO concentrations in this report are not true values but approximate values and these approximate values of DO concentrations will be higher than the true values. Other samples were passed through cellulose acetate membrane filters ($0.2\ \mu\text{m}$) and used for anion analysis. Water samples for the determination of alkalinity and NH_4^+ concentration were collected in 100-mL and 50-mL polyethylene bottles, respectively, and those for anion analysis were collected in 24-mL glass vials.

The NO_3^- , NO_2^- , Cl^- , and SO_4^{2-} concentrations were analyzed with a QIC analyzer (Dionex) equipped with a Dionex AS4A IonPac column and an anion micromembrane suppressor (Dionex, Model AMMS- II). NO_2^- was detected only in the groundwater sampled from a depth of 3.5 m in the

piezometer nest number 5 (Fig. 2) in October and December 2003. The NO_2^- concentrations were 0.11 and 0.10 mg/L, respectively. NO_2^- was not detected in any other groundwater samples. Thus, NO_2^- concentrations are not shown in a figure. The NH_4^+ concentrations were measured using an ion electrode (DKK, Multi-channel Ion Meter, Model IOL-40). Considering the linear relationship between the logarithms of NH_4^+ concentration and the difference in measured voltage, we set the quantification limit of the ion electrode as $50\ \mu\text{g/L}$. The 82 and $62\ \mu\text{g/L}$ concentrations of NH_4^+ were measured in groundwater samples obtained from a depth of 2.5 m in piezometer nest number 2 (Fig. 2) in August 2003 and a depth of 2.0 m in piezometer nest number 3 (Fig. 2) in December 2003, respectively. The NH_4^+ concentrations in other groundwater samples were below the quantification

limit. Thus, NH_4^+ concentrations are not shown in a figure. Alkalinity was measured by titration using 0.02-N H_2SO_4 with methyl red and bromocresol green (MR-BCG) as the colorimetric indicator. The HCO_3^- concentrations were calculated from the values of alkalinity values.

Results and discussion

The contour lines of the hydraulic head (m), SEC ($\mu\text{S}/\text{cm}$), and the Cl^- concentration (mg/L) in piezometer nests (ID of 40 mm) observed on August 28, 2003, October 24, 2003, and December 28, 2003 are presented in Figs. 4-6. The piezometer nests are divided into transects A and B (Fig. 2). The contour lines of hydraulic head revealed that the dominant direction of groundwater flow in both transects is horizontal in the sand and gravel layer and downward in the silt and clay layer; this implies that the aquitard is supplied with water from the sand and gravel layer in the upper layer. The downward groundwater flow was observed from a depth of 2.5 m to 3.5 m in transect A and from a depth of 3.0 m to 3.5 m in transect B. The contour lines of the SEC and Cl^- concentration in both transects indicated that the values ranged from approximately 250 to 310 $\mu\text{S}/\text{cm}$ and from 22 to 28 mg/L, respectively. The SEC and Cl^- concentrations did not clearly exhibit a large vertical gradient of concentration. These results indicate that the SEC and Cl^- concentrations in all the layers had high homogeneity. In particular, Cl^- is a conservative ion, and the homogeneous distribution of Cl^- concentrations in all the layers will facilitate the supply of groundwater from the sand and gravel layer to the aquitard; this hypothesis was confirmed by the contour lines of hydraulic head.

The contour lines of NO_3^- concentrations observed on August 28, 2003, October 24, 2003, and December 28, 2003 are presented in Fig. 7. The

chemical heterogeneity of NO_3^- in the aquitard has been clearly demonstrated. It is very interesting that the heterogeneity of NO_3^- in the aquitard was larger than that of NO_3^- in the sand and gravel layer. In the aquitard of transect A, at a depth of 3.0 m and horizontal range of 6.0 m, NO_3^- varied from 27.8 to 2.9 mg/L. On the other hand, at a depth of 3.5 m, the NO_3^- concentrations were low and constant. Similarly, in the case of the aquitard of transect B, at a depth 3.5 m and horizontal range of 6.0 m, NO_3^- varied from 28.6 to 1.8 mg/L. Furthermore, the NO_3^- distributions at a depth of 3.5 m in transects A and B revealed complex lateral heterogeneity at the 4 m $\times$ 6 m scale in the aquitard. It is evident that the chemical conditions can change significantly in these piezometers within lateral intervals in the aquitards that are as narrow as 2 m. This result shows that it is difficult to identify the heterogeneity of NO_3^- concentrations of groundwater in an aquitard using a small number of piezometers. Hence, upscaling methodologies for the NO_3^- cycle models in an aquitard must be developed carefully. Piezometers were installed in the aquitard of transect A at a depth of 2.5 m. However, the contour lines of hydraulic head indicate that the groundwater quality in these piezometers was more affected by the horizontal groundwater flow than that in case of the other piezometers installed in the aquitard. Hence, the piezometers were not considered for discussing the possible mechanisms for the heterogeneity of the NO_3^- distribution in aquitards at a few meter-scales.

In this study, the meter-scale lateral heterogeneity of the NO_3^- concentrations in the groundwater in the aquitard has been obtained, as described previously. The NO_3^- concentrations in the groundwater in the shallower regions of the aquitard, i.e., in the higher elevations of transect A, was particularly high. This result agrees with the groundwater flow deduced from the contour lines of hydraulic head

Fig. 4 Contour lines of hydraulic head (m) observed on August 28, 2003, October 24, 2003 and December 28, 2003 in piezometer nests along two transects. ●: piezometers installed in the sand and gravel layer. ○: piezometers installed in the silt and clay layer.

Fig. 5 Contour lines of SEC ($\mu\text{S/cm}$) observed on August 28, 2003, October 24, 2003 and December 28, 2003 in piezometer nests along two transects. ●: piezometers installed in the sand and gravel layer. ○: piezometers installed in the silt and clay layer.

Fig. 6 Contour lines of Cl^- concentrations (mg/L) observed on August 28, 2003, October 24, 2003 and December 28, 2003 in piezometer nests along two transects. ●: piezometers installed in the sand and gravel layer. ○: piezometers installed in the silt and clay layer.

Fig. 7 Contour lines of NO_3^- concentrations (mg/L) observed on August 28, 2003, October 24, 2003 and December 28, 2003 in piezometer nests along two transects. ●: piezometers installed in the sand and gravel layer. ○: piezometers installed in the silt and clay layer.

and Cl^- concentrations. Hence, it can be deduced that NO_3^- in the groundwater in the aquitard was supplied by the groundwater in the sand and gravel layer. Further, the low NO_3^- concentrations observed in the groundwater in the aquitard at certain depths may be because of biochemical reaction processes such as in-situ denitrification or spatial variability of NO_3^- transport from the sand and gravel layer to the aquitard.

Figs. 8-10 shows the contour lines of DO, SO_4^{2-} , and HCO_3^- concentration observed on August 28, 2003, October 24, 2003, and December 28, 2003 at the study plot. The DO concentrations ranged from 1 to 8mg/L in all the layers of both transects. Low DO concentrations ranging from 1 to 3 mg/L were observed in the piezometers with low NO_3^- concentrations at the depth of 3.5 m in the aquitard in both transects. Denitrification will probably occur at concentrations below 1 mg/L and may even occur at concentrations below 2 mg/L (Buss *et al.*, 2005). Considering the fact that the DO concentrations were measured in an open container, where there is an air-water interface, that value of the in situ DO concentrations must be lower than that of the measured DO concentrations. Thus, denitrification may occur in an aquitard with low DO concentrations. The SO_4^{2-} concentrations ranged from 40 to 60 mg/L in transect A and from 40 to 55 mg/L in transect B. The highest SO_4^{2-} concentrations were obtained at a 3.5m depth in the aquitard of transect A. The distribution of SO_4^{2-} concentrations in groundwater was inversely proportional to that of NO_3^- concentrations —an approximate increase of 5 mg/L (0.052 mM) of SO_4^{2-} was accompanied by a decrease of 30 mg/L (0.484 mM) of NO_3^- . The HCO_3^- concentrations ranged from approximately 10 to 40 mg/L in both transects. High HCO_3^- concentrations ranging from 25 to 40 mg/L were observed in the piezometers with low NO_3^- concentrations. This indicates an

approximate increase of 15 mg/L (0.246 mM) of HCO_3^- with a decrease of 30 mg/L (0.484 mM) of NO_3^- . The increase in SO_4^{2-} and HCO_3^- concentrations along with the decrease in NO_3^- concentrations in the aquitard can be considered as evidence of NO_3^- reduction, or in other words, denitrification coupled with pyrite and organic carbon oxidation in groundwater (e.g. Postma *et al.*, 1991; Aravena and Robertson, 1998; Ioka and Tase, 2004a). The corresponding reactions are as follows:

Considering the chemical mass balance associated with reactions 1 and 2 and examining the inversely proportional relationships between the increase of SO_4^{2-} and HCO_3^- concentrations and the decrease of NO_3^- concentrations described above, the simple mass balances indicate that approximately 67% of NO_3^- lost was due to denitrification. Therefore, the lateral heterogeneity of the NO_3^- concentrations in the groundwater in the aquitard at the study plot probably indicates that denitrification and other processes, e.g., spatial variability of NO_3^- transport, occur in aquitards. This study indicates that it is necessary to conduct further researches on the denitrification processes in the aquitard to clarify this completely. In particular, the occurrence and rate of denitrification must be investigated; further, the compositions and bioavailability of organic carbon electron donors must be examined, and the nature of biotic and abiotic autotrophic denitrification reactions involving sulfur electron donors must be studied. In addition, mechanism of spatial variability of NO_3^- transport processes in the aquitard must be investigated.

Fig. 8 Contour lines of DO concentrations (mg/L) observed on August 28, 2003, October 24, 2003 and December 28, 2003 in piezometer nests along two transects. ●: piezometers installed in the sand and gravel layer. ○: piezometers installed in the silt and clay layer.

Fig. 9 Contour lines of SO_4^{2-} concentrations (mg/L) observed on August 28, 2003, October 24, 2003 and December 28, 2003 in piezometer nests along two transects. ●: piezometers installed in the sand and gravel layer. ○: piezometers installed in the silt and clay layer.

Fig. 10 Contour lines of HCO_3^- concentrations (mg/L) observed on August 28, 2003, October 24, 2003 and December 28, 2003 in piezometer nests along two transects. ●: piezometers installed in the sand and gravel layer. ○: piezometers installed in the silt and clay layer.

Conclusion

The lateral heterogeneity of NO_3^- concentrations of groundwater in an aquitard at Tsukuba upland was investigated using 11 piezometers over an area of $4 \text{ m} \times 6 \text{ m}$ and to a maximum depth of $\sim 3.5 \text{ m}$ below the ground surface. NO_3^- in the aquitard was supplied from NO_3^- in the sand and gravel layer by groundwater flow. This study demonstrated that relatively large changes in NO_3^- concentrations—from approximately 30 to 1 mg/L —occur on a lateral axis in an aquitard as narrow as 2 m . We have suggested mechanisms responsible for the heterogeneity of NO_3^- concentrations in aquitards; denitrification processes and other processes such as spatial variability of the NO_3^- transport process; the mechanism is related to natural NO_3^- attenuation processes. However, presently, we do not have any field data to test these hypotheses and consider the accumulation of such data as important information for future research. In addition, the heterogeneity of NO_3^- concentrations indicated that the difficulties in developing an upscaling methodology for the NO_3^- cycle models in groundwater.

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- この論文に対する「討論」を2012年5月30日まで受け付けます。

難透水層中地下水における NO_3^- 濃度の メートルスケールの不均質性

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要 旨

世界中において地下水の長期的な保全是、部分的に難透水層に依存している。なぜなら、難透水層は、自然・人為起源物質の移行に影響を与えるからである。そのため、難透水層中の溶存物質の分布、輸送、そして挙動を制御している過程を理解することが重要である。さらに、近年では地下水中における人為的な窒素循環量が増大し、関心を集めている。そのため、難透水層中における地下水の NO_3^- の挙動が検証されなければならない。私たちは、筑波台地において、数メートルスケールで難透水層中 ($4\text{m} \times 6\text{m}$) の NO_3^- 濃度の水平的な分布を調査し、その不均質性をもたらす機構を明らかにすることを試みた。なお、このような研究は私たちが知っている限り最初の研究である。高密度の観測は、ピエゾメータを用いて実施し、複雑な水平的な NO_3^- の不均質性を明らかにした。ピエゾメータから採取された地下水の大きな NO_3^- 濃度の差異は、わずか 2m の範囲内において認められた。本観測で明らかになった NO_3^- 濃度の不均質性をもたらす要因は、確定することはできなかったがおそらく脱窒や NO_3^- 輸送過程の不均一性によるものであると推察される。本研究は、難透水層中地下水の NO_3^- 濃度の不均質性を数メートルスケールで示した初めての研究であり、難透水層中における NO_3^- の自然減衰に対して新たな視点を与えるものである。また同時に、少ない本数のピエゾメータの観測から得られた結果を用いて、 NO_3^- の自然減衰帯の広域評価を実施するのは困難であることが示唆された。

キーワード：不均質性, NO_3^- , 地下水, 難透水層