Interpreting the seasonal and long-term trend of nitrate in both groundwater and spring water in a typical headwater wetland with well-defined groundwater flow pathways

Yingjie Cao, Changyuan Tang, Zhiwei Han, Sako Yoko and Xing Li

ABSTRACT

Timescale problems of nitrate behavior (i.e. seasonal variation and long-term trend) in headwater are closely related to its hydrological process. In a typical agricultural headwater catchment in the Chiba prefecture, Japan, the groundwater nitrate concentration showed an increasing trend, while for spring water, a substantial decreasing trend was observed during our monitoring period. Two key issues, (1) identification of multiple flow pathways and (2) evaluation of the residence time for different pathways, were emphasized to reveal the factors controlling the different patterns of nitrate trend. Three major flow pathways including vertical soil water flow (VF), lateral groundwater flow (LG) and deep groundwater flow (DG) along the upland-slope-valley were differentiated. Different timescales of three flow pathways were identified. The residence time of VF was calculated as 9–10 years based on the soil water budget equation and the apparent age of LG was estimated as 41 years by chlorofluorocarbon (CFC) traces. The increasing trend of NO₃ in groundwater agreed well with the historical nitrate loading, and the decreasing trend of NO₃ in spring was mainly influenced by nitrate behavior of LF, which substantially decreased due to reduction of nitrogen fertilizer loadings since 2000.

Key words | CFCs, headwater, multiple flow pathways, nitrate trend, residence time

INTRODUCTION

In the hydrological system, headwater catchments are source areas for water, nutrients, sediment, and biota for larger streams (Feger et al. 1990; Wilson et al. 1991; Sidle et al. 2000; Tang et al. 2004). River drainage networks are hierarchically organized systems in which first and second-order streams, commonly referred to as headwater streams, make up at least 70% of total stream length (Leopold & Leopold 1955). In addition, most of the nitrogen flowing through the whole hydrological network is estimated to come from the headwater catchments (Alexander et al. 2007). Therefore, considerable research continues regarding the importance of various hydrologic pathways in headwater catchments as well as the interaction of these pathways with respect to peak runoff, solute transport, surface erosion, and mass wasting.

Hillslope, as the most important landscape feature of headwater catchments, is the fundamental hydrologic unit connecting the atmosphere and streams (Graham et al. 2010), and plays an important role in understanding runoff generation processes (Tromp Van Meerveld & McDonnell 2006) and corresponding processes relating to solute migrations and transformations (Fu et al. 2013). In this study, a typical headwater catchment hillslope was selected to conduct our investigation.

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Agricultural activities have impaired the quality of spring water and surface water by contributing large quantities of nutrients to groundwater recharge in many parts of the world (Katz et al. 2001). In Japan, under natural conditions, nitrate (NO$_3$-N) concentrations in headwater streams have low values ranging from 8.64 µmol/L (0.12 mg/L) to 105 µmol/L (1.47 mg/L) (Zhang et al. 2008). The concentrations will be enlarged by factors of 10 or 100 due to the introduction of nitrogen originated from fertilization (Oenema et al. 1998; Tang et al. 2004; Vitòria et al. 2005). According to the monitoring data of surface water quality from the Ministry of Land, Infrastructure, Transport and Tourism, Japan, it is found that Chiba Prefecture with the maximal yield of pears in Japan has suffered from surface water nitrate pollution due to pear-planting. Although the upstream pear plant has been identified as the major nitrate pollution source, the pollution path has not been well depicted.

Hillslope, as the physical passage connecting the upland cultivated into crop lands and the wetland valley, shows important functions of nutrient leaching (Katupitiya et al. 1997; Costa et al. 2002), and the leach pattern is mainly controlled by hydro-meteorology, soil texture and corresponding hydraulic properties and fertilization rate.

With the broad application of groundwater age-dating such as chlorofluorocarbons (CFCs) tracing tools, nitrate timescale problem such as interpreting nitrate long-term trends (Katz et al. 2001) and reconstructing nitrate contamination history (Böhlke & Denver 1995) have also received intensive interest. A variety of different temporal variations of nitrate depend on both transient and steady state variables, including changes in nitrate loadings and hydrological and geophysical configurations of the catchment. Combination of these factors results in the delayed and sudden occurrence of nitrate to local groundwater, spring and surface water, which has been defined as a ‘chemical time bomb (CTB)’ by Stigliani (1991). It means for a baseflow-dominating headwater catchment, the soil water and groundwater can be treated as a pollutant reservoir to the spring and surface water.

Multi-traces such as conservation ions (no or little chemical reactions alter the concentration of ion during its transport process, C$^-$) and stable isotopes have been widely used to trace water flow pathways, identify pollutant sources and evaluate pollutant transport processes under different spatial scales. End-members mixing model based on chemical traces is a principal method to clarify stream water and groundwater hydrochemistry and its controlling mechanisms (Katsuyama et al. 2001), and has been widely used to evaluate the contribution of a particular component in catchments where the dominant hydrological flow paths are known (Mulholland 1993; Elsenbeer & Lack 1996; Burns et al. 2001).

To further evaluate the behavior and fate of nitrate in the water environment, nitrogen isotope such as δ$^{15}$N-NO$_3$ which was initiated in early 1970s by Kohl et al. (1971) has been widely applied to evaluate NO$_3$ sources and relevant processes which affect the nitrogen cycling, such as nitrification and denitrification. Because nitrate forms neither insoluble minerals that could precipitate, nor is it adsorbed significantly, the only way for nitrate removal from groundwater is microbial redox reactions, which can change δ$^{15}$N-NO$_3$ values significantly due to isotope fractionation. Therefore δ$^{15}$N-NO$_3$ is a useful index to evaluate the behavior of anthropogenic NO$_3$. Once the conservative property of NO$_3$ is established, it can also be treated as tracers to deduce the hydrological processes and pollution paths.

Groundwater age-dating has been applied as a tool for groundwater age estimation and analyzing trends of pollutants by relating the measured concentrations of pollutants to their recharge time (Böhlke & Denver 1995; MacDonald et al. 2005; Wassenaar et al. 2006; Burow et al. 2007). CFCs, recognized as one of the most powerful tools for groundwater age-dating, have been successfully used to determine groundwater ages and flow paths in many studies (Cook et al. 1995; Oster et al. 1996; Plummer et al. 2006; Liu et al. 2013). Since nitrate in groundwater records the changes of the land use or human activities at the recharge time, the age-dating allows for reconstruction of nitrate pollution history.

So in this study, how to evaluate the timescales of nitrate contaminations is the major problem to be dealt with, and two key related issues should be considered: (1) to identify the hydrological processes especially multiple flow pathways; and (2) to evaluate the residence time for different flow pathways. To emphasize these two principal points, an intensive study including soil physics investigation, long-term monitoring of the soil water and groundwater
hydrochemistry, and soil water-groundwater age-dating was conducted to: (1) describe the conceptual soil water-groundwater flow system and discriminate different soil water and groundwater flow pathways discharging into the wetland valley; (2) identify the origins of Cl\(^-\) and NO\(_3\)\(^-\) and analyze their behavior; (3) trace the soil water and groundwater flow pathways and evaluate their residence time; and (4) discuss and interpret the timescale of nitrate contamination including both seasonal variation and long-term trend.

**SITES DESCRIPTION AND METHODOLOGY**

**Site description**

The study area is a typical agricultural headwater catchment with Japan Pacific Ocean Side climate in Ichikawa City (35.76 N, 139.97 E), Chiba Prefecture, Japan. Chiba Prefecture has the largest pear-planting area in Japan and according to the monitoring data of surface water quality from the Ministry of Land, Infrastructure, Transport and Tourism, elevated NO\(_3\)-N concentration (4–8 mg/L) has been detected in the downstream Ookasiwa River of our study area. The annual average precipitation is about 1316 mm, and the annual average temperature is 15.6 °C with the highest temperature of 31.2 °C occurring in August. The topography for the study area is consisted of upland, slope and valley. The valley extends from north to south with a length of 1.25 km, and its drainage area is estimated at about 1.2 km\(^2\) based on the water budget analysis. A typical hillslope connecting the upland and valley is selected as the study object in our research. The elevation of upland and valley are about 25.0 m and 12.6 m, respectively. The hillslope is slightly protruding with an average slope of 28° (Figure 1). The upland is the recharge area covered by Kanto loam about 4 m in thickness. It is underlain in a sequence by Joso clay layer and Narita sand. In our study area, soil borehole shows that the Joso clay layer is partly mixed by Narida sand. The Narida sand layer is a thick fine sand layer constituting the major aquifer in the study area (Figure 1). In addition, as marine sediment, the Narida sand contributes high sea salt to the local groundwater.

In the upland, pear orchard is the dominant land use type. The fertilizers used for pear-tree planting, mainly horse manure, urea and ammonium sulfate, are recognized as sources of pollutants to soil water and groundwater. The slope is covered by broadleaf woods, conifers and bamboos with a few understories to prevent soil erosion from the upland.

**Sampling and analytical procedures**

**Sampling procedure and field work**

In order to understand the water flow system and nitrate transport processes along the upland-slope-valley continuum, 4 years of field work including soil property investigation, soil water and groundwater chemistry monitoring was performed from June 2010 to May 2014. Undisturbed soil was sampled by hand auger with cutting ring from surface to 4.5 m depth with an interval of 20 cm in the upland (B1) and used to determine the soil physical properties such as porosity (\(n\)) and saturated hydraulic conductivity (\(K_s\)). Two sets of ceramic cup soil water samplers for soil water sampling were installed at B1 in the upland and B2 in the slope, respectively. At S4, two boreholes with depth of 1 m and 2 m were drilled with hand auger, and PVC pipes with water entering from the bottom were inserted into the boreholes as piezometers. The piezometers were designed for groundwater levels and hydrochemistry.
monitoring. Groundwater level monitoring and sampling were conducted nearly every month from June 2010 to May 2011 to examine the seasonal variation of water levels and groundwater quality, then the sampling frequency decreased for the long-term monitoring since May 2011. Spring water at S4 was also sampled with groundwater sampling synchronously. In addition, a 20 m-deep well located in the headwater valley was sampled to give the background values of groundwater quality. Water samples were filtered through a 0.22 μm filter and preserved in 100 ml precleaned bottles. CFCs samples of groundwater were taken twice in 2011 and the samples was preserved in 400 °C baked dark class bottle by using a continuous flow sampling device which can prevent the water from contacting with atmosphere during the sampling. Nitrogen isotope (NO₃-δ¹⁵N) samples of groundwater were taken by 500 mL bottles. All the water and soil samples had been stored at 4 °C until laboratory analysis. The double-ring infiltration test was performed on the upland to obtain the stable infiltration rate.

Laboratory analysis

Major anions including Cl⁻ and NO₃⁻ were analyzed by Ion Chromatography (SHIMADZU LC-10AD) in Chiba University. The limit of detection (LOD) for ion analysis is 0.05 mg/L. Groundwater CFCs (CFC-11, CFC-12 and CFC-113) were analyzed by closed system purge and trap gas chromatography with electron capture detector (GC-ECD) in Chiba University, Japan, and the details of the method and its detection limit were summarized by Busenberg & Plummer (1992). The LOD for CFCs analysis is 0.01 pmol/L. The pretreatment and analytical approach of δ¹⁵N-NO₃ samples was conducted according to the method developed by Silva et al. (2000).

RESULTS

Soil physics and groundwater potential fluctuation

Soil texture is one of the most important factors affecting the physical characteristics of a soil (Radcliffe & Šimůnek 2010). In the upland, based on our result of borehole survey, it is found that there are Kando loam (0–3.5 m), Joso sandy clay (3.5–4.5 m) and Narida sand (>4.5 m) in sequence (Figure 1). Due to soil erosion, the contact relationship changed along the slope. Sandy clay layer disappears along the slope towards the valley and the colluvial loam mixing with clay directly covers the Narida sand layer. A humus soil with high organic carbon content is deposited above the loam. Soil physics features porosity (n) and saturated hydrologic conductivity (Ks) for different layers are listed in Table 1. Average porosity for loam, sandy clay and sand layer were 0.77, 0.76 and 0.40, respectively.

Table 1 | Average porosity (n) for different soil layers

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>Average porosity (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loam</td>
<td>0–3.0</td>
</tr>
<tr>
<td>Sandy clay</td>
<td>3.0–4.5</td>
</tr>
<tr>
<td>Sand</td>
<td>&gt;4.5</td>
</tr>
</tbody>
</table>

Fluctuations of groundwater potential at piezometers S4-1/2, located just downslope of the valley perimeter, are indicative of variations in shallow groundwater inputs to our study wetland from the uplands during the study period. Average groundwater potentials for S4-1/2 were 12.55 m and 12.72 m, respectively, showing a vertical upward flow component occurring during the monitoring period. In addition, the perennial spring at S4 shows that the input of groundwater to the valley is permanent and proves the study headwater wetland is a typical baseflow dominating wetland.

NO₃⁻ and associated Cl⁻ in soil water, groundwater and spring

To clarify the spatial distribution and behavior of NO₃⁻, the concentration of NO₃⁻ and associated Cl⁻ were measured from two soil boreholes B1 and B2 along the slope (Figure 1). B1 located at the pear orchard in the upland showed high Cl⁻ and NO₃⁻ due to fertilization. Volumetric weighted average concentrations Cᵥ which is defined by $Cᵥ = \sum Cₖ \Delta hₖ / \sum \Delta hₖ$ of NO₃⁻ and Cl⁻ for B1 were 356.28 and 31.72 mg/L, respectively. A substantial increasing trend of NO₃⁻ with the depth in soil water was observed at B1 (Figure 2). In addition, seasonal variations of Cl⁻ and NO₃⁻ in soil water
at depth near groundwater surface were slight due to buffer function of the thick unsaturated zone. Therefore, the vertical flow component of soil water infiltration can be treated as stable N inputs to the local groundwater. B2 located along the slope, in contrast, had relatively low Cl/C0 and NO3/C0 concentrations, and the Cv of NO3 and Cl− for B2 were 19.32 and 4.96 mg/L, respectively, implying the lateral transport of NO3 is weak along the slope.

Concentrations of Cl− and NO3 for spring and groundwater in the valley are summarized in Figure 3. Elevated NO3 concentrations in both spring and groundwater were measured. The NO3 concentration of the spring had the highest values with an average of 308.6 mg/L. Relative low NO3 concentrations were 133.9 mg/L and 153.5 mg/L on average for 1.0 m and 2.0 m groundwater, respectively. A slight decreasing trend was observed for groundwater from 2.0 m to 1.0 m. Both spring water and groundwater have exceeded the World Health Organization (WHO) standards for drinking water quality to human (50 mg/L in NO3) (WHO 2008), indicating severe nitrate pollution in local groundwater. The average value for Cl− concentration was 36.37 mg/L during the monitoring period. No significant vertical variations of Cl− were detected in comparison with NO3.

Temporal variations for NO3 and Cl− in spring and groundwater during the monitoring period from 2010 to 2014 are shown in Figure 4. Two typical temporal trends, seasonal trend and long-term trend (4 years) were observed. Both the spring (S4) and groundwater (S4-1/2) showed seasonal variations with high concentrations during the rainy season from April to October, and low concentrations during the dry season from November to March 2011. Opposite long-term (4 years) trend of NO3 was detected for spring and groundwater. For spring water, NO3 concentration generally decreased during the monitoring period, while for the groundwater at S4-1/2, NO3 concentrations showed an increasing trend from about 150 mg/L to almost 200 mg/L. The long-term trends for Cl− in both spring and groundwater were similar to the trend of NO3.

**CFCs and nitrogen isotope result**

CFCs (CFC-12, CFC-11 and CFC-113) at S4-1/2 were analyzed to estimate the groundwater residence time in the study area (Table 2). It is found that the measured CFC-113 concentrations were higher than its possible maximum equilibrium concentration and cannot be used as age-dating traces. A possible reason was that CFC-113 suffered from pollution due to the PVC pipes in the study area. The measured CFC-12 and CFC-11 have reasonable concentrations for age-dating. Nitrogen isotope (δ15N-NO3) were about +5.31‰ for S4-1 and +5.58‰ for S4-2, respectively.
The δ15N-NO3 value for local groundwater was about +4.65‰. Similar δ15N-NO3 values showed no significant denitrification processes during the groundwater flow into the wetland valley, and NO₃⁻ could be treated as a conservative ion to be used as trace.

**DISCUSSION**

**Multiple flow pathways identified by soil physics and hydrochemistry**

Three major flow pathways would be discriminated along the upland-slope-valley continuum in this study. They are vertical soil water flow (VF), lateral groundwater flow (LG) and deep groundwater flow (DG) (Figure 1). The vertical soil water flow is defined as the water infiltrating through the sandy clay layer, carrying large amount of nitrate downward to local groundwater. The major characteristic of this component, VF, is the high NO₃⁻ and Cl⁻ concentrations. The DG is recognized as flow pathway coming from deep aquifer free of nitrate contaminations, and its hydrochemistry is characterized by a 20 m deep well with low concentrations of NO₃⁻ and Cl⁻. The LG is discriminated from VF and DG according to Cl⁻ origins. In our study area, there was no doubt that the elevated NO₃⁻ of soil water, groundwater and spring mainly came from the chemical and organic fertilizers used in the pear orchard on the upland. Different from the single source of NO₃⁻, both natural and anthropogenic origins existed for Cl⁻. The anthropogenic origin of Cl⁻ was recognized as organic fertilizers such as manure, the same as NO₃⁻. The same origin for NO₃⁻ and Cl⁻ implies that the ratio of NO₃⁻/Cl⁻ will remain stable during their transport process under the assumption that no significant denitrification processes occur. For the spring samples, nearly all the points lie close to the line with an average slope (ratio) of 10 and this ratio was similar to the ratio of soil water in the upland (Figure 5). However, for the groundwater samples at S4-1/2, the points are located around the line with an average slope of 3.64, deviating from the soil water lines, implying that additional sources (natural origins) of Cl⁻ existed in the groundwater (Figure 5). The natural origins of Cl⁻ include precipitation input and geologic origin. The average Cl⁻ concentration of precipitation in the study area was measured as 1.45 mg/L (Okuda et al. 2005). Thus the contribution of precipitation inputs could be neglected. It is concluded that the

<table>
<thead>
<tr>
<th>ID</th>
<th>CFC-12 pmol/kg</th>
<th>CFC-11 pmol/kg</th>
<th>CFC-113 pmol/kg</th>
<th>δ¹⁵N‰</th>
</tr>
</thead>
<tbody>
<tr>
<td>S4-1</td>
<td>0.48</td>
<td>0.95</td>
<td>0.20</td>
<td>+5.31</td>
</tr>
<tr>
<td>S4-2</td>
<td>0.54</td>
<td>1.44</td>
<td>0.36</td>
<td>+5.58</td>
</tr>
</tbody>
</table>

The δ¹⁵N-NO₃ value for local groundwater was about +4.65‰. Similar δ¹⁵N-NO₃ values showed no significant denitrification processes during the groundwater flow into
elevated Cl\(^{-}\) coming from the marine deposit Narida sand resulted in the decreasing of NO\(_{3}\)/Cl\(^{-}\) ratio in the groundwater, and hereafter the groundwater flowing through the Narida sand layer was defined as the LF component. This component was characterized by relatively low NO\(_{3}\) and relatively high Cl\(^{-}\) compared with VF. The component I, which was generated on the sandy clay with low permeability (Table 1) shown in Figure 1 was neglected in the study, because low NO\(_{3}\) concentrations detected at B2 indicated insignificant lateral nitrate transport along the slope to the wetland.

In summary, based on the soil hydraulic properties and NO\(_{3}\) and Cl\(^{-}\) origins, three major soil water and groundwater flow pathways have been identified: (1) VF characterized by high NO\(_{3}\) and moderate Cl\(^{-}\); (2) LG characterized by moderate NO\(_{3}\) and high Cl\(^{-}\); and (3) DG characterized by low NO\(_{3}\) and low Cl\(^{-}\).

**Residence time estimation for different flow pathways**

The timescale of nitrate contamination for soil water, groundwater and spring is closely related to its residence time (Katz et al. 2003). For our study hillslope, where the soil water and groundwater flow system have been characterized by discriminating three flow pathways of VF, LG and DG, residence time for each flow pathway and the related mixing processes determine the final nitrate behaviors. Here, different methods were employed for residence time estimation based on flow properties. The VF was assumed as one-dimensional soil water vertical infiltration. Its residence time (\(R_{VF}\)) was estimated by soil water budget equation. The residence time of LG was estimated by CFCs traces. The flow component DG was assumed as ‘old’ groundwater.

**Residence time for VF**

The VF was assumed as one-dimensional soil water vertical infiltration, and its residence time (\(R_{VF}\)) was estimated by soil water budget equation (Equation (1)) under the assumption of piston-flow.

\[
R_{VF} = \frac{H \times \theta}{f}
\]  

where \(R_{VF}\) (year) is the residence time of VF, \(H\) (m) is the thickness of unsaturated zone (about 8.5 m), \(\theta\) is the average porosity (about 0.59), and \(f\) (mm/year) is the average annual soil water infiltration rate. Due to the high stable infiltration rate (3.9 mm/min), runoff generation above the surface was neglected, and \(f\) was calculated by Equation (2).

\[
f = P - ET_c
\]  

where \(P\) (mm/year) is the average annual precipitation and \(ET_c\) (mm/year) is the evapotranspiration determined by the FAO-56 Penman-Monteith (Allen et al. 1998) and Thornthwaite equation (Thornthwaite 1948). Meteorological data such as precipitation, relative humidity, air temperature and wind speed were obtained from an adjacent Japan Meteorological Agency meteorological station named Funa-bashi station. Net radiation was estimated according to the sunshine duration. The calculated \(f\) was about 617 mm/y, and the soil water residence time was therefore estimated at about 8–9 years.

**Residence time for LG**

The LG was estimated by CFCs traces. Because the groundwater was sampled from the piezometer wells with narrow depth intervals of less than 10 cm, the
piston flow age-dating model without mixing consideration was applied to groundwater apparent ages estimation. Based on the groundwater age dating method reported by Plummer et al. (2006), the CFCs input functions, groundwater recharge temperature and recharge elevation were necessary to estimate the groundwater apparent ages. In this study, the historical concentrations of CFCs in the North American atmosphere (Plummer et al. 2006) were used as the CFCs input functions. The excesses of CFC concentrations in East Asia urban air are relatively small (Qin et al. 2011), so the CFC input functions derived from the CFC partial pressures in the North American atmosphere are usually used without modification (Han et al. 2012; Han et al. 2014; Liu et al. 2015). The average annual air temperature of 14.8°C was assumed as the recharge temperature, and the recharge elevation was equal to the upland elevation of 26.0 m. The CFC-12 and CFC-11 apparent ages for S4-1 and S4-2 agreed well (Table 3) for about 41 years. However the CFC-113 result showed younger groundwater ages (about 20 years) and a possible reason was that the groundwater was slightly contaminated by CFC-113.

Interpretation of nitrate temporal trend in groundwater and spring

This section focuses on the trend interpretation based on the historical nitrate loading changes, the well-defined flow system along the slope and the residence time estimation, and emphasizes the important role of mixing of flow pathways with different residence time when interpreting nitrate temporal trend.

| Groundwater apparent ages estimated by CFCs, the recharge time is calculated by the difference between groundwater residence time and sampling time |
|---|---|---|---|---|---|---|
| Apparent age (year) | Recharge time |
| CFC-12 | CFC-11 | CFC-113 | CFC-12 | CFC-11 | CFC-113 |
| S4-1 | 42 | 41 | 27 | 1969 | 1970 | 1984 |
| S4-2 | 41 | 38 | 21 | 1970 | 1973 | 1990 |

Sensitivity analysis shows that the recharge temperature does not have significant influence on CFCs ages, when the recharge temperature varied around 16.8 ± 3.0°C, the variation of apparent ages for CFC-12, CFC-11 and CFC-113 are less than ±0.8, ±0.5 and ±1.0 years, respectively.

**Nitrate loading history**

The nitrate loading data used in the study were compiled according to the statistical information of local cultivation area of pear trees and fertilization rate published by the Ministry of Agriculture, Forestry and Fisheries, Japan. To make the N loading comparable with the measured NO$_3^-$ concentrations, nitrate loading was transformed into nominal NO$_3^-$ concentration by Equation (3).

$$\text{nominal } \text{NO}_3^{-} = \frac{\text{NO}_3^{\text{max}}}{\text{N loading}_{\text{max}}} \times \text{N loading}$$

where N loading (kg/year) is calculated by the product of cultivated area of pear trees and N-bearing fertilization rate, NO$_3^{\text{max}}$ is the maximum concentration observed in the soil water and groundwater, N loading$_{\text{max}}$ is the maximum historical N loading and N loading is the N loading for each year. Reconstructed nominal NO$_3^-$ history is shown by hollow circle points in Figure 8. Before the 1960s, nitrate loading varied slightly due to relative stable cultivated areas of pear trees. During the period from 1960s to 1990s, sudden increase of cultivated areas had resulted in large amounts of nitrate leaching into the local groundwater. After around the year 2000, due to organic agriculture development, reduction of N-bearing fertilizer used caused the decreasing of nitrate loadings.

**Mixing of flow pathways and seasonal variation of spring at S4**

Hydrological processes (mixing of different flow pathways) were considered the most important factors controlling the seasonal variations for the anthropogenic NO$_3^-$ observed for the spring at S4. Here, end-member mixing model which has been widely used to examine the partitioning of water among various pathways (Kinner & Stallard 2004) was employed to calculate the mixing ratios for different flow components. As discussed in the section ‘Multiple flow pathways identified by soil physics and hydrochemistry’, three end-members (VF, LF and DG) were identified as the contribution to spring water, and the hydrochemical characteristics for each end-member and the mixing lines are shown in Table 4 and Figure 6. The hydrochemical
Table 4 | Hydrochemical characteristics for three end-members (flow pathways) vertical soil flow (VF), lateral groundwater flow (LG) and deep groundwater flow (DG)

<table>
<thead>
<tr>
<th></th>
<th>Cl(^{-}) (mg/L)</th>
<th>NO(_3) (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>S.D.</td>
</tr>
<tr>
<td>VF</td>
<td>40.0</td>
<td>5.0</td>
</tr>
<tr>
<td>LG</td>
<td>50.0</td>
<td>5.0</td>
</tr>
<tr>
<td>DG</td>
<td>15.0</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Different mixing ratios resulted in the seasonal variation of NO\(_3\)\(^{-}\) in the spring (Figure 7). During the wet season, the flow component VF driven by precipitation had high ratios with the maximum value greater than 75%. In dry season, contribution of VF became lower and decreased to about 60%.

Long term (4-year) trend for both groundwater and spring

Opposite trends of nitrate concentrations for the groundwater (increasing trend) and spring (decreasing trend) were the most important temporal trends to be discussed in this study. As discussed during the residence time analysis, groundwater at S4-1 and S4-2 was treated as piston flow without mixing, and the groundwater apparent age (CFC-12 age) was estimated at about 40 years. Under the assumption that nitrate transports together with water, the corresponding nitrate transport time is the sum of the time taken by soil water infiltration from ground surface to groundwater table and the residence time of lateral groundwater. Therefore, the nitrate transport time from recharge point to S4-1/2 was estimated at 49–50 years, and the corresponding recharge time of nitrate at S4-1/2 during the monitoring period was from 1960 to 1964. The relation between yearly averaged NO\(_3\)\(^{-}\) concentration for S4-1/2 and the respective recharge time is shown in Figure 8. It was found that the observed NO\(_3\)\(^{-}\) trend of S4-1/2 agreed on the whole with the reconstructed historical fertilizer

\[
\begin{align*}
C_{\text{NO}_3,\text{VF}} &+ C_{\text{NO}_3,\text{LG}}\alpha_{\text{LG}} + C_{\text{NO}_3,\text{DG}}\alpha_{\text{DG}} = C_{\text{NO}_3} \\
C_{\text{Cl}^-,\text{VF}}\alpha_{\text{VF}} + C_{\text{Cl}^-,\text{LG}}\alpha_{\text{LG}} + C_{\text{Cl}^-,\text{DG}}\alpha_{\text{DG}} = C_{\text{Cl}^-} \\
\alpha_{\text{VF}} + \alpha_{\text{LG}} + \alpha_{\text{DG}} &= 1
\end{align*}
\]

where \(C_{ij}\) is the concentration for end member \(j\) and \(C_k\) is the measured concentration for the spring S4. On average, the spring discharge to the valley consisted of waters from VF (65%), LG (23%) and DG (12%), showing that the spring was mainly maintained by the young vertical infiltration of soil water.
loadings data, and proved that the historical fertilizer loading change was the main factor controlling the long-term trend of NO\textsubscript{3} in the groundwater. For the decreasing trend of NO\textsubscript{3} in the spring at S4, based on the mixing ratio calculation, about 60–75% of spring water was contributed by VF with a residence time of less than 10 years. Therefore, the residence time of VF was used to estimate the residence time of the nitrate transport time in spring water. The relation between the recharge year of spring water and measured yearly averaged NO\textsubscript{3} concentration in the spring as S4 shown in Figure 8 had more rapid decreasing rate than the historical nitrate loading change rate. This time lag and deviation between the observed NO\textsubscript{3} concentration and reconstructed loadings was attributed to the dilution effect of mixed LG and DG components in the spring water.

**CONCLUSIONS**

An intensive analysis was conducted along an upland-slope-valley continuum in a baseflow dominating agricultural headwater wetland to discuss the timescale problems of nitrate contamination. In the study area, the temporal variations of NO\textsubscript{3} have different patterns for groundwater and spring water. Slight seasonal change and decreasing long-term trend of NO\textsubscript{3} concentration were observed for the groundwater, while for the spring, significant seasonal change and increasing long-term trend were detected. Two key issues, identification of the flow pathways and evaluation of the residence time for different flow pathways, were emphasized in this study to give a reasonable explanation of the different trends observed.

Three major flow pathways were discriminated as VF, LG and DG contributing to the baseflow, which is recognized as the most important water input to maintain the wetland. Each flow pathway bears different flow properties and residence time. The VF represented the soil water vertical infiltration in the upland pear orchard. This component was recognized as the major nitrogen input to the wetland, and had a residence time of 9 years based on the water budget calculation. The LG flowing through the Narita sand layer carried relative high Cl\textsuperscript{−} and moderate NO\textsubscript{3} concentrations and its apparent age was about 41 years. The DG was characterized as having low NO\textsubscript{3} and Cl\textsuperscript{−} and this ‘old’ groundwater flow was recognized as the dilution factor for the NO\textsubscript{3} contamination.

Based on the result of δ\textsuperscript{15}N-NO\textsubscript{3}, no significant denitrification process was identified when groundwater flowed into the wetland valley. Therefore, NO\textsubscript{3} combined with Cl\textsuperscript{−} was treated as traces to deduce the mixing processes occurring in the spring at S4. End-member mixing calculation showed that VF took up about 65% of the total spring water and was recognized as the major factor controlling the spring NO\textsubscript{3} behavior. The seasonal variation of infiltration rate resulted in the significant seasonal variation of NO\textsubscript{3} in the spring.

The opposite long-term trends of NO\textsubscript{3} concentration in groundwater (increasing trend) and in spring water (decreasing trend) were explained by the flow properties, nitrate transport time and nitrate historical loading changes. The estimated NO\textsubscript{3} transport time in groundwater was about 60 years, and the relation between the groundwater recharge year and measured NO\textsubscript{3} concentration showed that the increasing trend of NO\textsubscript{3} in groundwater was concordant with the nitrogen loading trend between the year of 1955 and 1965, when the nitrogen loading underwent rapid increase. The spring water was mixed by different flow
pathways and its residence time was estimated by VF which contributes about 65% of the spring water. The decreasing trend of NO$_3$ concentration in spring agreed with the N loading decrease after the year 2000.

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