# TRANSIENT STORAGE AND NITROGEN RETENTION IN HEADWATER STREAM OF A SUBURBAN WATERSHED IN BEIJING, CHINA

Almacenamiento transitorio y retención de nitrógeno en la corriente de agua de cabecera de una cuenca suburbana en Beijing, China

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Key words: Transient storage, nitrogen retention, headwater stream, OTIS model, ecological restoration

## ABSTRACT

Transient storage refers to a vital process affecting nutrient retention dynamics. To explore how streambed topography, discharge, and nutrient ambient concentration impact the transient storage and nitrogen retention of the headwater stream, tracer experiments were performed in five reaches of the Yanqi watershed. The one-dimensional transport with inflow and storage model (OTIS) was employed to simulate the solute injection. Transient storage potential was evaluated by transient storage metrics. Moreover, the material balance method was adopted to obtain the amount of nitrogen retention in the respective reach, and the nutrient spiraling metrics were determined to assess the nitrogen retention potential. As revealed from this study, improving transient storage under low flow conditions effectively facilitated nitrogen retention (except for the case of low-head weirs reach), while the erosion of high discharge destroyed the transient storage zone, thereby reducing the nitrogen retention potential. Ecological restoration in the Yanqi watershed could rescue nitrogen retention potential to a natural state under low flow, whereas limitations were identified in nitrogen retention potential under high flow and high ambient concentration.

Palabras clave: almacenamiento transitorio, retención denitrogeno, corriente de cabecera, modelo, restauración ecológica

## RESUMEN

El almacenamiento transitorio se refiere a un proceso vital que afecta la dinámica de retención de nutrientes. Para explorar cómo la topografía, la descarga y la concentración de nutrientes en el ambiente impactan el almacenamiento transitorio y la retención de nitrógeno de la corriente de salida, se realizaron experimentos con trazadores en cinco tramos de la cuenca del río Yanqi. El modelo de transporte unidimensional con entrada

y almacenamiento (OTIS) se empleó para simular la inyección de soluto. El potencial de almacenamiento transitorio se evaluó mediante métricas de almacenamiento transitorio. Además, se adoptó el método de balance de materiales para obtener la cantidad de retención de nitrógeno en los tramos respectivos y se determinaron las métricas de espirales de nutrientes para evaluar el potencial de retención de nitrógeno. Como se desprende de este estudio, la mejora del almacenamiento transitorio en condiciones de flujo bajo facilitó efectivamente la retención de nitrógeno (excepto en el caso de los vertederos de baja altura), mientras que la erosión de alta descarga destruyó la zona de almacenamiento transitorio, reduciendo así el potencial de retención de nitrógeno. La restauración ecológica en la cuenca del río Yanqi podría rescatar el potencial de retención de nitrógeno a un estado natural bajo un flujo bajo, mientras que se identificaron limitaciones en el potencial de retención de nitrógeno bajo un flujo alto y una alta concentración ambiental.

# **INTRODUCTION**

Headwater streams, as a vital component of the river systems, are of critical importance to the control of nitrogen export to downstream ecosystems. Most dissolved nitrogen from adjacent terrestrial will be retained and removed in streams and rivers. Headwater streams carrying larger loads show greater potential for nitrogen retention for their larger specific surface area and lower flow velocities (Craig et al. 2008). 37%~76% of nitrogen entering streams and rivers may reportedly be removed during transport, and half of them may be removed from 1 to 4 streams (Seitzinger et al. 2002). Therefore, it is of great significance to study the nitrogen retention in the headwater stream for understanding how to affect the downstream nutrient loads (Price et al. 2016).

Transient storage (TS) is currently one of the most important and most straightforward concepts adopted to explain nutrient retention in hydrology and stream ecology (D'Angelo et al. 1993, Valett et al. 1996). The retention of nitrogen in streams is a result of multiple processes. A series of tracer studies of nitrogen dynamics had described the mentioned processes and overall explained how they affect the transportation of nitrogen to the downstream ecosystem (Thomas et al. 2003, Marion et al. 2008, Baker et al. 2012, Johnson et al. 2015, Price et al. 2016). Physical and biological processes either permanently remove nitrogen through denitrification or temporarily store it through sediment sorption and biological metabolism (Craig et al. 2008). Such type of temporary stored procedure is termed transient storage. This hydrodynamic process is capable of increasing contact time with organic matter and denitrifying bacteria, thereby improving the biogeochemical reactivity of streams. It has also been proved as a vital process affecting the transport of nitrogen in stream

ecosystems (Kemp and Dodds 2002, Groffman et al. 2005, Briggs et al. 2010, Baker et al. 2012, Johnson et al. 2014). Transient storage of water and solutes takes place in different compartments. The main channel (MC) refers to most of the river cross-sectional area, exhibiting a higher velocity. Transient storage zones are compartments exhibiting long residence times and low velocities, which can be partitioned into surface transient storage (STS) (e.g., side pools and back eddies) and hyporheic transient storage (HTS) (Briggs et al. 2010, Stewart et al. 2011, Baker et al. 2012, Johnson et al. 2014). Distinguishing the mentioned HTS and STS of storage is difficult, especially when considering dynamic spatial and temporal scales (Bohrman and Strauss 2018). Recently, some researchers have studied the mentioned two different TS zones and their different hydraulic and biogeochemical conditions, which has promoted the development of nitrogen retention dynamics in river systems (Thomas et al. 2003, Groffman et al. 2005, Briggs et al. 2009, Briggs et al. 2010, Stewart et al. 2011, Baker et al. 2012, Johnson et al. 2014). Retention of solute through low permeability exchange can be the main method to control nutrient absorption in streams. However, this exchange is still difficult to accurately quantify at present (Boano et al. 2014). Thus, the mentioned process was not studied in depth in this study. In fact, STS and HTS were taken as a whole for analysis.

Topography and physical characteristics of streambeds impact solute retention and transport by altering the exchange between subsurface water and hyporheic zone (Tonina and Buffington 2009). Geomorphic characteristics (slope, curvature, and crosssectional area) changed the size of TS areas by influencing hydrological transport processes (Bohrman and Strauss 2018). As suggested from a recent literature review, transient storage is significantly regulated by channel hydraulic conditions and morphologic gradients (Baker et al. 2012). The dynamics of TS are controlled by geological, hydrological, and hydraulic factors (Briggs et al. 2010). Biogeochemical processes have different effects on STS and HTS. Overall, TS in STS is directly proportional to stream discharge, and TS in HTS is controlled by the hydraulic gradient which is affected by streambed slope, local flow velocity, and groundwater dynamics (Johnson et al. 2014). The relationship between TK and stream size is not entirely clear. Results of 246 tracer experiments in 1st-6th streams found that both mean storage residence time and storage zone size decreased with greater stream size (Briggs et al. 2010). However, another study reported that the size of the storage area was not related to the size of flow (Johnson et al. 2015). The probable reason for these different results is that the transient storage areas applied in the mentioned literature do not distinguish between STS and HTS. Nutrient loading will also affect the exchange process of transient storage and recent studies have shown that high background concentration of nutrients will reduce the retention capacity of streams relative to low ambient concentrations (Weigelhofer et al. 2012, García et al. 2017).

Yangi Stream refers to a crucial mountain stream in the north of Beijing, China. It directly flows into the North Taishang reservoir (i.e., Lake Yanqi, an International Convention Center of Beijing), acting as one of the reserve water sources in Beijing. Yangi Stream plays an important role in ensuring the safety of the regional water supply. Over the past two decades, the tourism industry has been leaping forward, and anthropogenic disturbances were increasing in the Yanqi watershed. Under these backgrounds, some ecological environmental issues have arisen in the watershed, which has directly reduced the water quality of Lake Yanqi. This will have a profound impact on the evolution of the lake environment and the evolution of the ecosystem in the lower reaches of the reservoir. To ensure the safety of the regional water supply, currently, an Ecological Development Demonstration Area has been built in the watershed, and stream restoration has been carried out in several reaches. By increasing hydrological connectivity, stream restoration activities increase the transient storage time of the solute (Klocker et al. 2009) and increase the possibility of nutrient retention and removal. Improving transient storage effectively facilitated nitrogen retention is currently a concern of water quality management. To reduce the adverse impact on the water quality of the reservoir, we performed tracer experiments to investigate different discharge, different ambient

nitrogen concentrations, and different geomorphology in the Yanqi watershed, using the OTIS model which is a mathematical model for describing solute transport in small watersheds. At present, the research methods of nitrogen retention rate at home and abroad are relatively mature, but there are few studies on the impact of the above research methods on the aquatic ecological environment. The results of this study can be used to reveal the dynamics of nitrogen retention and transient storage in headwater streams and the influence of restoration activities on transient storage and nitrogen retention. This research is of great significance and is currently one of the important scientific issues in the field of river basin water environment management and governance. This research provides a scientific basis for reservoir governance and water quality management.

#### **MATERIALS AND METHODS**

#### Study area

This study was conducted in the mainstream of Yanqi Stream (YQ) and its tributary, Changyuan stream (CY), located in Yanqi Town in Huairou District, nearly 60 km north of Beijing city (**Fig. 1**). Land use in the Yanqi watershed consisted of forest, suburban, agriculture, and commercial. The 10-year average (2006-2016) mean annual discharge of the watershed is 0.24 m<sup>3</sup>/s (data from Baiyachang hydrological station, with the location illustrated in **Fig. 1**), which YQ is about 0.14 m<sup>3</sup>/s, and CY is about 0.10 m<sup>3</sup>/s. The sinuosity of YQ is 1.87 and the slope is 0.018. CY has a lower sinuosity (1.34) and a higher slope (0.029), relatively.

The main reasons for choosing Yanqi Stream as a study site were as follows. The development of tourism has led to the formation of many channelized rivers in the Yangi River Basin and the construction of many low weirs (Fig. 2). The multi-stage weirs delay the transport of nitrogen downstream through temporary interception. The backwater area formed by multistage weirs is also a typical transient storage area, which can promote nitrogen retention by increasing the hydraulic retention time of nitrogen in the backwater area. However, this transient storage area is strongly disturbed by hydrological conditions. High flow conditions will not only destroy the transient storage capacity of the backwater area, but also lead to the concentrated release of nitrogen in the backwater area. In order to solve this problem, some river sections of the basin are selected for river restoration, the water retaining weir is removed, and the



Fig. 1. Site map for the Yanqi stream and its tributary Changyuan stream, including locations of five study reaches and Baiyachang hydrological station. The site is in Yanqi Town in Huairou District, Beijing.

artificial wetland planting and bank slope restoration are carried out, which increases the hydrological connectivity of the river and enhances the biogeochemical effect in the river, so as to increase the retention of nitrogen and solve the problem of centralized release of nitrogen in the river section of the water retaining weir under the condition of high flow.

As impacted by an increase in anthropogenic disturbances, some reaches have been dammed and impounded in the upper portion, and the hydrology, channel morphology, nitrogen inputs, and nitrogen retention in the upper portion of the Yangi watershed were varied significantly (Fig. 2). Field experiments were primarily conducted in the lower portion, the reaches have implemented stream restoration techniques, and are few affected by anthropogenic disturbances. Restoration techniques consist of stream bank reshaping, pool and riffle zones establishing, and artificial wetland planting. Overall, five reaches are selected in two streams stream by complying with the different channel forms and hydraulic conditions. Of the three YQ reaches, YQN is considered a natural reach, and the hydrology and channel morphology have not been affected by human activities. YQR is located in the restored portion, consists of 51% artificial wetland, 42% pool zone, and 7% riffle zone, YQD is an anthropogenic disturbance reach, the streambed has been channelized and three

low-head weir sequences were constructed. The two study reaches of CY are a natural reach (CYN) and a restored reach (CYR). CYR consists of nearly 90% artificial wetland and 10% pool zone. Specific parameters are shown in **Table I**.

#### **Channel surveys**

The method in **Table II** of Baker (2012) was used to evaluate the reach geomorphology before the reach tracer experiment, including channel topography survey and channel size survey analysis. Based on the section data of the reach, five geomorphic indexes, including the channel slope ( $i = z_1 - z_n / L_s$ ), the sinuosity ( $s = L / L_s$ ) of the plane shape of the reach (the depth line), the longitudinal roughness ( $LR = (\sum_{i=1}^{n} |z_{obs,i} - z_{pred,i}|) / n$ ), the width change rate

**TABLE I.** PHYSICAL CHARACTERISTICS OF STUDY REACHES.

Reach	Discharge $Q (m^3/s)$	Average velocity <i>u</i> (m/s)	Stream length L (m)	Slope	Sinuosity
YQN	0.15~0.34	0.11~0.23	177	0.008	1.07
YQR	0.15~0.35	0.05~0.11	276	0.002	1.01
YQD	0.14~0.42	0.04~0.12	389	0.009	1.00
CYN	0.10~0.28	0.08~0.19	320	0.014	1.01
CYR	0.12~0.28	0.09~0.19	371	0.006	1.85



Fig. 2. Geomorphic morphology of study reaches.

Stream	Slope	Sinuosity	Longitudinal	Width	Section area	Geor

TABLE II. GEOMORPHIC COMPLEXITY CALCULATION RESULTS.

Stream segment	Slope <i>i</i>	Sinuosity s	Longitudinal roughness LR(m)	Width change rate $\varepsilon_w$	Section area change rate $\epsilon_A$	Geomorphic complexity $\chi(\times 10^{-4} \text{ m})$
YQN	0.014	1.321	0.320	1.539	0.044	2.60
YQR	0.014	1.539	0.436	1.113	0.030	2.82
YQD	0.029	1.165	0.270	0.003	0.004	0.36
CYN	0.024	1.456	0.511	1.264	0.015	2.68
CYR	0.021	1.636	0.456	0.072	0.016	2.51

 $(\varepsilon_w = (\sum_{i=1}^n |w_{avg} - w_i|) / n)$  and the section area change rate  $(\varepsilon_A = (\sum_{i=1}^n |A_{avg} - A_i|) / n)$ , were calculated, and the following equation was proposed as the measure of the geomorphic complexity  $(\chi)$ , which was directly related to the transient storage:  $\chi = i \cdot s \cdot LR \cdot \varepsilon_A$ . The calculation results of geomorphic complexity of each study reaches are shown in **Table II**.

The restored reach of the Yangi River (YOR) has significantly improved the geomorphic morphology of the river channel through large-area artificial wetland planting and different habitat shaping, so the geomorphic complexity is the highest. The natural reach of the Changyuan River (CYN) is in the deep valley of the river. The river shape is completely unaffected by human beings. There are many aquatic vegetation in the river, and the water flow is winding, so the landform is complex. The restored reach of The Changyuan River (CYR) is mainly reconstructed by bank slope, the wetland planting area is small, and many kinds of habitats such as deep pool shoal are not shaped, so the geomorphological complexity is the lowest. The mainstream of Yanqi River natural reach (YON) is the narrowest, so the change rate of cross-section area is not obvious, resulting in low geomorphic complexity. As the study object is a mountain river, the slope and longitudinal roughness are large, which will be conducive to the bottom-flow exchange driven by head gradient, so that the channel has large transient storage potential. Because the human disturbance reach (YQD) is affected by the weir, the water is deep, the elevation of the thalweg line is not different from the elevation of the surrounding terrain, and the river reach is affected by human interference (mainly channelization), the wet width and section area change is small, its geomorphic complexity is mainly affected by the longitudinal slope.

## **Conservative tracer experiment**

This experiment mainly compares the transient storage effect and nitrogen retention capacity of different types of river sections, and the adopted indicators (mainly  $F^{200}_{med}$ ) can be applied to the comparison between different river sections (The median value fmed of transient storage time is the most useful measure to evaluate the correlation between each transient storage process and the overall travel. This index includes the solute exchange coefficient ( $\alpha$ ). The relative area between the transient storage area and main flow area (As / a) and convective velocity (Q/A) are three important indexes, and the influence of river reach length (L) is also considered, which is usually used for the comparison of transient storage capacity of different river reaches).

From autumn 2017 to spring 2018, conservative tracer experiments were conducted to measure transient storage of reaches with the TS zone of study reaches (**Fig. 1**). The seasonal difference of water volume in the basin is very large, the flow in summer is very high, and the daily variation is large. We have roughly estimated the nitrogen retention in summer by using the material balance method. Under the condition of high flow, the nitrogen retention in Yanqi River Basin is very small, so the experiment is not carried out in summer.

In this experiment, NaCl was selected as tracer agents (Johnson 2014). According to the method described by Thomas (2003), the amount of tracer was about 7 kg~14 kg based on the flow rate during the experiment, and the water was dissolved and diluted by the stream for instantaneous release.

The repeated conservative tracer injections were performed in the respective reach. Before the respective experiment, the stream discharge and ambient concentration of chloride were measured to determine the reasonable amount of tracer injection. A known mass of tracer was injected as an instantaneous slug a mixing length (nearly 10~20 m) upstream of the first transect to allow for complete mixing. In addition, the duration of the tracer injection was nearly 3~10 min. Changes in chloride concentration with time during the injections were taken using an electrical conductivity meter at a spot near the thalweg (MC) and adjacent TS zone upstream and downstream of the reach at set intervals (1~2 min). The measurement results were referenced to plot breakthrough curves (BTCs) of chloride concentration and parameterize the TS model.

Limited by the experimental conditions, the biochemical process in the river was not studied in detail in this experiment. Therefore, the effects of temperature, light, and do were not considered. The impact of flow change was mainly considered. We will further study the impact of the biochemical process in subsequent research.

## Model

The transport model incorporating one-dimensional transport with inflow and storage (OTIS) (Runkel, 1998) was adopted to analyze the obtained data. And OTIS was suggested to explain the solute retention in numerous scenarios and infer the contribution of exchange with transient storage zone (TS) (Briggs et al. 2009). Tracer tests are used only to reflect simple exchange processes without considering biochemical reactions (Femeena et al. 2019). The model equations are expressed as follow:

$$\frac{\partial C}{\partial t} = -\frac{Q}{A} \frac{\partial C}{\partial x} + \frac{1}{A} \frac{\partial}{\partial x} \left( AD \frac{\partial C}{\partial x} \right) + q_L \left( C - C \right) + q(C - C)$$
(1)

$$\frac{\partial C_s}{\partial C_s} = \frac{A}{A} \left( C_s - C \right)$$

$$\frac{\partial C_S}{\partial t} = \alpha \frac{A}{A_S} \left( C - C_S \right) \tag{2}$$

where *t* denotes time[T]; *x* represents distance downstream[L]; *C*, *C*<sub>S</sub>, and *C*<sub>L</sub> refer to solute concentrations in the MC, TS, and lateral inflow, respectively [M/L<sup>3</sup>-]; *Q* is the in-stream volumetric flow rate [L<sup>3</sup>/T]; *q*<sub>L</sub> denotes the lateral inflow rate [L<sup>3</sup>/T/L]; *D* is the MC longitudinal dispersion coefficient [L<sup>2</sup>/T]; *A*, *A*<sub>S</sub> represent the cross-sectional areas of the MC and TS, respectively [L<sup>2</sup>];  $\alpha$  is the exchange coefficients between MC and TS [/T].

Parameter estimation was an important step in the model calculation, aiming to quantify the hydrologic parameters that characterize physical transport and mixing  $(Q, A, A_{\rm S}, \alpha, D)$ . In addition, the Nonlinear least square method was adopted to determine a set of optimal parameter estimates (OTIS User's Guide). The mentioned hydrological parameters of OTIS, which can characterize the relative size (As/A) of transient storage and its exchange rate with free-flowing water ( $\alpha$ ), have been widely adopted to study the effect of transient storage on stream nutrient retention. It is noteworthy that lateral inflow was not considered in the experiments here  $(q_{\rm L}=0)$ , since base-flow in Yangi Stream was constant, and the flow of each experimental reach is basically the same.

#### Parameters calculation Transient storage metrics

To ensure the reliability of hydrological parameters, model sensitivity of TS process was evaluated, and judge whether the length of experimental reaches can be used for the estimation of TS, the Damkohler (DAI) values (Wagner and Harvey, 1997) were determined by:

$$DAI = \frac{(\alpha \ a + \frac{A}{A_S})L}{u}$$
(3)

When DAI range of 0.1~10, the parameter value is considered acceptable, indicating that there is sufficiently solute exchange between MC and TS, which can be used to estimate the TS process(Wagner and Harvey, 1997).

The fraction of median transport time due to storage ( $F_{med}$ ) refers to the most reliable metric of transient storage to reflect the effect of transient storage on solute transport (Runkel, 2002). The assessment of  $F_{\text{med}}$  in different reaches is usually compared at a standard distance of 200 m. The mean storage zone residence time ( $T_{\text{S}}$ ) indicates the average travel time that solute remains in TS before reentering MC. Moreover, the hydraulic turnover length ( $L_{\text{S}}$ ) acts as the average travel distance of solute in MC before entering TS.

$$F_{med}^{200} = \left(1 - e^{-200} \frac{a}{(Q/A)}\right) \frac{A_S}{(A + A_s)}$$
(4)

$$T_S = \frac{A_S}{\alpha A} \tag{5}$$

$$L_S = \frac{Q}{\alpha A} \tag{6}$$

#### Nutrient spiraling metrics

The nutrient retention potential is characterized by the nutrient spiraling metrics. Nutrient uptake length ( $S_w$ ) expresses the transport distance of the solute with the flow. Nutrient uptake velocity ( $V_f$ ) was adopted to quantify the transport rate of solute, a scale-free parameter, and related to the  $S_w$  through the relationship of Eq. (8) (Marcé and Armengol, 2009). Areal uptake rate (U) is linearly dependent on nutrient concentration, was adopted to characterize the uptake capacity of streams.

$$S_w = \frac{u}{k} \tag{7}$$

$$V_f = \frac{uh}{S_w} \tag{8}$$

$$\mathbf{U} = V_f \cdot C \tag{9}$$

where k denotes first-order absorption coefficient  $(m^{-1})$ ; u represents flow velocity (m/s); h is the depth of stream water (m); C refers to the ambient concentration of nutrients (mg/L).

#### **Data collection**

The reservoir downstream of the study watershed is a drinking water source protection area, the study streams have been protected from nutrient tracer experiments. Accordingly, the mass balance method was employed in this study to quantify N retention in the streams. Mass balance calculation complied with N concentration and water discharge measurements at an upstream and downstream location (Seitzinger et al. 2002). Data sets of N concentration and water discharge were collected upstream and downstream of the experiment reach before and after each experiment. In addition, the data sets of the N concentration of several characteristic sections of YQ and CY were collected, as well as runoff data sets of the mentioned two rivers in 2017.

### RESULTS

The OTIS was adopted to assess the solute injection at five reaches of Yanqi Stream and its tributary Changyuan Stream. More than 5 conservative tracer experiments were performed in each experimental reach, and two or three effective experiment results were selected to analyze. A total of 14 concentrationtime breakthrough curves were collected in the mentioned five experimental reaches. The estimated results of the model parameters are shown in **Table III**, except for YQD (one normal discharge scenario and one high discharge scenario), the remaining reaches include two normal discharge scenarios and one high discharge scenario.

 $A_{\rm S}/A$  acts as a direct parameter to characterize transient storage, greater  $A_{\rm S}/A$  value means a longer residence time of solute. Moreover,  $F^{200}_{\rm med}$  was a more reliable metric to reflect the influence of TS on solute transport, greater  $F^{200}_{\rm med}$  value means stronger transient storage. Therefore, we collected these data to estimate the TS. From **Table III** and **Table IV**, under the three discharge conditions, the mean values of  $A_{\rm S}/A$  and  $F^{200}_{\rm med}$  of YQR were 0.770 and 16.29 respectively, while the mean values of  $A_{\rm S}/A$  and  $F^{200}_{\rm med}$ 

TABLE IV.	CALCULATION	RESULTS	OF	TRANSIENT
	STORAGE METR	RICS.		

Reach	$T_{S}$ (min)	$L_{S}(m)$	DAI	$F^{200}_{med}$
	84	358	1.94	18.56
YQR	74	276	2.06	25.73
	97	$\begin{array}{c} L_{\rm S}({\rm m}) \\ 358 \\ 276 \\ 1449 \\ 177 \\ 2031 \\ 429 \\ 170 \\ 2717 \\ 381 \\ 565 \\ 732 \\ 415 \\ 642 \\ 829 \end{array}$	0.67	4.57
VOD	62	177	4.43	27.81
YQD	162	2031	0.47	2.73
	33	429	1.47	18.35
YQN	12	170	4.28	31.50
	79	$\begin{array}{c c} & L_{S}(m) \\ \hline & 358 \\ 276 \\ 1449 \\ \hline & 177 \\ 2031 \\ \hline & 429 \\ 170 \\ 2717 \\ \hline & 381 \\ 565 \\ 732 \\ \hline & 415 \\ 642 \\ 829 \\ \hline \end{array}$	0.27	2.77
	16	381	7.35	17.58
CYR	27	565	5.27	15.31
	16	732	3.58	10.41
	36	415	3.55	18.25
CYN	34	642	2.51	11.43
	32	829	1.62	9.66

of YQN were 0.816 and 17.54 respectively. So, the transient storage of the restored reach of Yanqi Stream (YQR) showed lower transient storage, but significantly close to the natural reach (YQN). Moreover, under the condition of high discharge, the  $F^{200}_{med}$  of YQR is larger, while the *As/A* of YQN is larger. Therefore, it can be shown that YQR has a better transient storage effect, while YQN has a longer solute residence time. Therefore, it can be inferred that whether at low discharge or high discharge anthropogenic disturbance reach (YQD) has the lowest

TABLE III. ESTIMATION RESULTS OF MODEL PARAMETERS.

Reach	Q (m <sup>3</sup> /s)	u (m/s)	α	$A(m^2)$	$A_{S}(m^{2})$	D	A <sub>S</sub> /A
	0.15	0.05	$1.52 \times 10^{-4}$	2.76	2.11	0.314	0.764
YQR	0.17	0.06	$2.24 \times 10^{-4}$	2.75	2.74	0.411	0.996
	0.35	0.11	9.40×10 <sup>-5</sup>	2.57	1.41	0.512	0.549
VOD	0.14	0.04	$1.87 \times 10^{-4}$	4.24	2.95	0.118	0.696
YQD	0.42	0.12	$4.22 \times 10^{-5}$	4.90	2.01	0.182	0.410
	0.15	0.12	4.92×10 <sup>-4</sup>	0.71	0.69	0.392	0.972
YQN	0.15	0.11	$1.21 \times 10^{-3}$	0.73	0.61	0.244	0.836
	0.34	0.23	$1.36 \times 10^{-4}$	0.92	0.59	0.116	0.641
	0.12	0.09	7.68×10 <sup>-4</sup>	0.41	0.31	0.199	0.756
CYR	0.13	0.09	$6.57 \times 10^{-4}$	0.35	0.37	0.100	1.057
	0.28	0.19	$7.97 \times 10^{-4}$	0.48	0.37	0.136	0.771
	0.10	0.08	4.23×10 <sup>-4</sup>	0.57	0.52	0.175	0.912
CYN	0.13	0.11	3.68×10 <sup>-4</sup>	0.55	0.41	0.183	0.745
	0.28	0.19	4.33×10 <sup>-4</sup>	0.78	0.64	0.017	0.821

transient storage (showing the smallest mean values for  $F^{200}_{med}$  and  $A_S/A$ ) in comparison with YQR and YQN. Besides, under the three discharge conditions, the mean values of  $A_S/A$  and  $F^{200}_{med}$  of CYR are 0.861 and 14.43 respectively, while the mean values of  $A_S/A$ and  $F^{200}_{med}$  of CYN are 0.826 and 13.11 respectively. Therefore, the restored reach of Changyuan Stream (CYR) demonstrated slightly greater transient storage when compared with the natural reach (CYN).

Exchange coefficient  $\alpha$  refers to an important hydrologic parameter to assess TS (Li, 2019). It was reported that the values of  $\alpha$  almost remained in an equal order of magnitude  $(10^{-4})$ . As illustrated in Table III, compare with YQR and YQN, the anthropogenic disturbance reach (YQD) showed a relatively small  $\alpha$  value. The DAI values for each reach of Yanqi Stream ranged from 0.27 to 4.43 with an average of 1.95, while that of Changyuan Stream ranged between 1.62 and 7.35, with an average of 3.98. Because DAI values were all between 0.1 and 10, the model exhibits a high fitting effect that there is sufficient solute exchange between MC and TS. For different reaches, no significant regularity was identified in  $T_{\rm S}$  value and  $L_{\rm S}$  value. For Yangi Stream, YQD showed the highest mean values for  $T_{\rm S}$  (41.33 min), while the mean Ts of YQR and YQN were 85 min and 112 min, respectively. This means that YQD has the longest residence time of solutes in TS zones. YQR showed the lowest mean values for  $L_{\rm S}$  (649.33 m), while the mean  $L_{\rm S}$  of YQD and YQN were 1104.00 m and 1105.33 m, respectively. So, the solutes in YQR were easier to enter TS zones. And for Changyuan Stream, CYN has the longest residence time of solutes in TS zones and solutes in CYR are easier to enter TS zones. Discharge is an important factor affecting transient storage.

The transient storage of solutes in small-scale rivers is mainly affected by physical conditions, including hydrological conditions (flow), channel topographic and geomorphic characteristics etc. The impact of different channel topographic characteristics on transient storage is mainly reflected in the value of As / A. Because the flow also has a certain impact on the channel topography, it will also affect the value of As / A. It can be seen that flow is the most important factor affecting the transient storage process of river solute. According to the previous research literature, F<sup>200</sup><sub>med</sub> is inversely proportional to Q (Stofleth, 2008, Johnson, 2014), research by Ruzhong Li et al. (Li, 2019) in a headwater stream showed that  $L_{\rm s}$  presented an exponential function relationship with Q. In order to study the effect of hydrological conditions on transient storage

capacity, we analyze the correlation between several key indicators reflecting the role of river transient storage and flow. According to the correlation analysis results, it is found that there is a significant negative correlation between  $F_{med}^{200}$ ,  $A_s/A$ ,  $L_s$ , and  $\ln Q$ , there is no significant correlation between  $\alpha$  and  $\ln Q$ , and there is no correlation between  $T_s$  and flow (P > 0.05) (**Table V**).

TABLE V. PARAMETER REGRESSION ANALYSIS.

Parameter	Regression equation	R <sup>2</sup>	Р
$F^{200}_{med}$ $A_{S}/A$ $T_{S}$	$F^{200}_{med} = -12.52 lnQ - 4.93$ $A_{s}/A = -0.26 lnQ + 0.35$ $T_{s} = 18.49 e^{3.92Q}$ $L_{s} = 152.25^{-5.87Q}$	0.454 0.461 0.278	0.008 0.008 0.052

lnQ has a significant negative correlation with  $A_{\rm s}/A$ , indicating that high flow will destroy the transient storage area of the river, resulting in the reduction of the area of transient storage area and the decrease of  $A_s/A$ . lnQ is positively correlated with  $\alpha$ , indicating that high flow will promote the solute exchange between the mainstream area and the transient storage area to some extent, leading to the increase of  $\alpha$ . F<sup>200</sup><sub>med</sub> and L<sub>s</sub> indicators reflect the comprehensive impact of  $A_s/A$  and  $\alpha$  on transient storage capacity. According to the correlation analysis results, the flow affects the transient storage capacity of the river by affecting the area of the main flow area and the transient storage area, and the solute exchange coefficient. lnQ has a significant negative correlation with  $A_{s}/A$ , and  $\ln Q$  has a positive correlation with  $\alpha$ . Obviously,  $A_s/A$  has a great impact on each index, resulting in a significant negative correlation between  $F_{med}^{200} L_s$ ,  $R_h$  and  $\ln Q$ . It can be seen that hydrological conditions mainly affect the transient storage capacity of the river by affecting the area of the mainstream area and the transient storage area, and have relatively little impact on the solute exchange between the two areas.

According to the data set of nitrogen concentration collected, the amount of nitrogen retention in each reach was determined by the material balance method (**Figure 3**). By calculating the nutritional spiral metrics (**Table VI**), we assessed the nitrogen retention in the Yanqi watershed.

As you can see from **figure 3** the results manifested no significant difference was identified in nitrogen retention between YQR and YQN. Under



Fig. 3 Nitrogen retention of each study reaches at different discharge.

 
 TABLE VI. CALCULATION RESULTS OF NUTRITIONAL SPIRALING METRICS.

Reach	$S_{\mathrm{w}}\left(\mathrm{m} ight)$	$V_{\mathrm{f}}$	U
YQR	$\begin{array}{c} 3.6340{\times}10^{3} \\ 3.4600{\times}10^{3} \\ 2.2151{\times}10^{4} \end{array}$	$\begin{array}{c} 4.40{\times}10^{-6} \\ 5.90{\times}10^{-6} \\ 1.84{\times}10^{-6} \end{array}$	$\begin{array}{c} 8.89{\times}10^{-3} \\ 8.67{\times}10^{-3} \\ 4.17{\times}10^{-3} \end{array}$
YQD	$7.330{\times}10^{3} \\ -3.8942{\times}10^{4}$	$\begin{array}{c} 2.84{\times}10^{-6} \\ -1.60{\times}10^{-6} \end{array}$	$7.86{\times}10^{-3} \\ -3.41{\times}10^{-3}$
YQN	$\begin{array}{c} 3.2680{\times}10^3 \\ 0.9310{\times}10^3 \\ 3.9831{\times}10^4 \end{array}$	$\begin{array}{c} 1.32{\times}10^{-5} \\ 4.61{\times}10^{-5} \\ 2.43{\times}10^{-6} \end{array}$	$\begin{array}{c} 3.27{\times}10^{-2} \\ 6.41{\times}10^{-2} \\ 4.95{\times}10^{-3} \end{array}$
CYR	$\begin{array}{c} 2.4990{\times}10^{3}\\ 2.4860{\times}10^{3}\\ 1.4947{\times}10^{4}\end{array}$	1.15×10 <sup>-5</sup> 1.19×10 <sup>-5</sup> 4.58×10 <sup>-6</sup>	$\begin{array}{c} 3.94{\times}10^{-2} \\ 7.42{\times}10^{-2} \\ 1.90{\times}10^{-2} \end{array}$
CYN	$\begin{array}{c} 5.2560{\times}10^{3} \\ 6.0270{\times}10^{3} \\ 1.8126{\times}10^{4} \end{array}$	$\begin{array}{c} 4.87{\times}10^{-6} \\ 5.84{\times}10^{-6} \\ 4.19{\times}10^{-6} \end{array}$	$\begin{array}{c} 1.59{\times}10^{-2}\\ 3.46{\times}10^{-2}\\ 2.09{\times}10^{-2} \end{array}$

low discharge, YQR had a slightly higher  $S_w$  value, lower  $V_f$  and U values (both one order of magnitude smaller) compared with those of YQN (**Table VI**), indicating nitrogen uptake capacity of YQN is slightly higher than that of YQR under low discharge. While under higher discharge, YQR had a slightly lower  $S_w$  value than YQN (**Table VI**), indicating the higher nitrogen uptake capacity of YQR. In general, nitrogen retention in CYR and CYN was much the same (**Fig. 3**), but the nitrogen uptake capacity of CYR is slightly higher than that of CYN because CYR exhibits a lower  $S_w$  value and a higher  $V_f$ (one order of magnitude higher) and U values (in the same order of magnitude) under both discharge conditions (**Table VI**). As suggested from the negative values of nitrogen retention and nutritional spiral metrics in YQD, there was no nitrogen retention but nitrogen release in YQD under higher flow.

# DISCUSSIONS

## Effect of streambed topography on nitrogen retention

The geomorphic variables and streambed conditions impact the TS and nutrient retention dynamics (Bohrman and Strauss 2018). In comparison with natural reaches, the anthropogenic disturbance reaches and the restored reach have different transient storage characteristics. As impacted the channelization of the streambed and the construction of low-head weir sequences, the original flow regime and streambed roughness of the anthropogenic disturbance reach of Yanqi Stream has changed, resulting in the decreased flow velocity, the increased hydraulic retention time, and the lessened resistance coefficient. The construction of artificial wetland altered the stream geomorphic complexity and the abundance of macrophytes and increased the thickness and porosity of the hyporheic transient storage zone. Aquatic vegetation beds provided more space for microorganism attachment, thereby significantly contributing to metabolically active transient storage in streams under low flow conditions (Kurz et al. 2017) and effectively promoting nitrogen retention.

Overall, the ecological restoration technology of the study stream could positively improve the transient storage potential and the retention of pollutants of the headwater stream and effectively reduce the adverse impact on the downstream water ecosystem. Thus, ecological restoration technology should be popularized and applied.

# Normal discharge transient storage and nitrogen retention

Our results are consistent with the existing evidence that low flow conditions are beneficial to increase hydraulic retention time, which would promote TS in headwater streams (Wondzell, 2006), and be some benefits of solute retention (Macrae et al. 2003). In our present work, each reach had a certain nitrogen retention potential under low flow conditions, consisting of the anthropogenic disturbance reach. The nitrogen retention rate at low flow conditions was significantly higher than that at higher discharge, demonstrating that low flow conditions might be more conducive to nitrogen retention.

In this study, it is predicted that the transient storage metrics of the anthropogenic disturbance reach would be smaller than that of the restored reach and the natural reach under low flow. In fact, anthropogenic disturbance reach exhibits a larger mean value for  $F^{200}_{med}$ . We speculated the possible reason is, in YQD, the low-head weirs would increase water depth and the hydraulic retention time, probably expanding the area of the TS zone and increasing the TS potential of the reach. However, YQD was showed a relatively small exchange coefficient  $\alpha$ , indicating the weak exchange potential between the MC zone and TS zone. The reason might be under low flow, the kinetic energy of water was difficult to facilitate the movement of the whole deep poo. Besides, as impacted by the channelization of the reach, there were few macrophytes in YQD, nitrogen uptake driven by macrophytes was weak, causing a significant poor effect of nitrogen retention.

The restored reaches (YQR and CYR) and natural reaches (YQN and CYN) are significantly affected by the obstacles (e.g., vegetation, stones, and woods), thereby facilitating the exchange between the overlying water and the hyporheic zone and laying favorable conditions for the solute entering TS zone, with a larger  $\alpha$  value. Stream ecological restoration could expedite transient storage and nitrogen retention in the stream (Hester and Gooseff 2010, Ward et al. 2018, Li et al. 2019). According to the results achieved in this study, the nitrogen retention of the restored reaches was significantly close to natural reaches, especially in CYR. The effect of restoration techniques is determined by the type and extent of restoration implemented (Price et al. 2016), which is achieved primarily by improving transient storage potential (Becker et al.

2013, Lammers and Bledsoe, 2017, Li et al. 2019). For topography composition, the main component of CYR is an artificial wetland, capable of imitating the natural stream to create a more similar transient storage zone, similar macrophyte beds, and a similar microbial attachment environment. Thus, artificial wetland exhibits a more significant ecological restoration effect than other topography like pools and riffles.

#### Effect of higher discharge on nitrogen retention

In headwater streams, hydrological factors are commonly considered the major contributors to nutrient retention mechanisms. Discharge is the major hydrological control variable of nutrient uptake and removal. With the increase in discharge, the contact probability of sediment and the attached microbial community with nutrients in the stream decreases, reducing the adsorption of sediment and the uptake of microorganisms. Moreover, the erosion of high discharge will significantly destroy the transient storage zone in a stream, and the nutrients deposited at the bottom of the river will also be washed downstream, which will significantly decrease the nitrogen retention potential.

In the experiment of YQD, it was reported that the fine sand deposited on the stream bed moved due to the increase in discharge and the acceleration of flow velocity, and it was re-deposited at the place with relatively low velocity, resulting in negative nitrogen retention. Thus, we considered that the nitrogen retention potential of YQD is reduced under higher discharge, which is affected by the destruction of transient storage zone and erosion of sediment.

The length of *Sw* also decreased significantly in the restored reaches and natural reaches under higher discharge, demonstrating that the nitrogen retention in the headwater streams was to a certain extent adversely affected by the high discharge.

## Effect of ambient concentration on nitrogen retention

According to Güker and Pusch et al. (2006), high nutrient concentration streams exhibit long nutrient uptake lengths, and the in-stream nutrient retention potential is limited (Weigelhofer et al. 2012), i.e., nutrient retention decreased with increased nutrient concentration (Li et al. 2019). In our present work, the ambient N concentration in Changyuan Stream is higher than Yanqi Stream as impacted by coldwater fish culture, suggesting that the natural reach of Changyuan Stream has a longer uptake length under low flow conditions, whereas no similar conclusion was drawn in restored reaches. As it is difficult to consider how stream processes affect nutrient dynamics, this study inferred that CYR has a better restoration effect in contrast to YQR.

In general, under the complexity of the nutrition dynamic mechanism, some limitations remain in nitrogen retention potential in the restored reach under high flow and high ambient concentration. Though numerous studies suggested that low-head weirs can effectively elevate the transient storage potential and nutrient retention potential of streams (Rana et al. 2017, Cunha et al. 2018), this study considers that the risk of pollutant transport downstream will increase under high discharge conditions. Accordingly, the anthropogenic disturbance reach should be repaired as soon as possible; otherwise, the downstream water ecological environment will be affected.

## CONCLUSIONS

In order to investigate the effects of streambed topography, discharge, and nutrient ambient concentration on transient storage and nitrogen retention in the Yanqi watershed, tracer experiments were performed in five reaches of the Yanqi watershed. Based on the OTIS model and the material balance method, the transient storage metrics and the nutrient spiraling metrics were obtained respectively, and the transient storage and nitrogen retention capacity were quantitatively evaluated. The results show that the capacity of transient storage and nitrogen retention is better under low flow conditions. However, the retention potential of nitrogen is still limited under high flow conditions and high nutrient ambient concentrations. The application of ecological restoration technology can effectively improve the transient storage and nitrogen retention capacity of the watershed, thus reducing the adverse impact on the downstream ecosystem.

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