Combined effects of stream hydrology and land use on basin-scale hyporheic zone denitrification in the Columbia River Basin

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Abstract

Denitrification in the hyporheic zone of river corridors is a crucial pathway to remove excess nitrogen (N) in rivers from anthropogenic activities. However, previous modeling studies of the effectiveness of river corridors in removing excess nitrogen via denitrification were often limited to the reach-scale and low-order stream watersheds. We developed a basin-scale river corridor model based on SWAT-MRMT-R to account for denitrification in the hyporheic zone (HZ) for the Columbia River Basin (CRB) with random forest models to identify what factors control the spatial variation of HZ denitrification in streams with different sizes and land uses. Our modeling results suggest that the combined effects of hydrologic variability in streams and substrate availability influenced by land-use control the spatial variability of HZ denitrification at the basin scale. Hyporheic exchange flux can explain the denitrification extent in different-sized streams, while among the streams affected by different land uses, the combination of hyporheic exchange flux and stream concentration of dissolved organic carbon (DOC) can explain the denitrification differences. Also, we can generalize that the most influential watershed and stream variables controlling denitrification variation are stream morphology parameters (D50, stream slope), climate (annual precipitation), and stream DOC-related parameters (percent of forest area). The modeling framework in our study can serve as a valuable tool to identify the limiting factors in removing excess N pollution in large river basins where direct measurement is often infeasible.

Keywords: hyporheic zone, denitrification modeling, random forest model, stream sizes, and land uses

Key Points

- Hyporheic exchange flux controls the spatial variation of denitrification across streams with different sizes and land uses.
- The combination of hyporheic exchange flux and stream DOC explains the differences in denitrification for different land-use streams.
- D50, stream slope, precipitation, and forest area are important variables explaining the spatial variability of denitrification.

1. **Introduction**

An increase in air pollution and an excess in fertilizer often result in stream N pollution, which increases the frequency of eutrophication, hypoxia, and harmful algal blooms in lakes and estuaries (Boyer et al., 2006). The removal of nitrates via the denitrification process in river corridors is the most effective way to transform inorganic forms of excess nitrogen to a gas form (N^2) emitted to the atmosphere. With the importance of denitrification, there are still considerable uncertainties in modeling denitrification in terrestrial and aquatic systems (Groffman, Butterbach-Bahl, et al., 2009) due to the high spatial/temporal heterogeneity of key controlling factors (oxygen, nitrate, carbon and pH, temperature, etc.).Therefore, quantifying denitrification in river corridors with varying spatial and temporal scales is challenging, especially for the hyporheic zone at large spatial scales.

Denitrification in the hyporheic zone (HZ) varies with local conditions including substrate availability (dissolved organic carbon (DOC), dissolved oxygen (DO) and nitrate), sediment properties (e.g., grain size), and hydrologic exchange flux/residence time within the hyporheic zone (Kreiling et al., 2019, Seitzinger et al., 2006, Fork and Heffernan 2014, Findlay et al., 2011, Boyer et al., 2006, Tank et al., 2008, Zarnetske et al., 2015). Large-scale drivers—including land use/cover, climate, and hydrologic conditions—can alter local conditions. For example, agricultural/urban watersheds tend to have higher potential denitrification than undisturbed watersheds (Mulholland et al., 2008). However, the key controlling factors may change with scale and land use. Kreiling et al. (2019) showed that stream nitrate availability is a key variable that controls the spatial variation of denitrification in the Fox River watershed, Wisconsin, with a mixed land use. Baker and Vervier (2004) showed that the first best predictor for explaining spatial/temporal denitrification variables is the concentration of low molecular weight organic acids. Even though we know that the combined effects of hydrologic variability and substrate concentration control denitrification, it is unclear which factor becomes more critical under which conditions. Bardini et al. (2012) used numerical modeling to demonstrate the streambed can transform from net nitrification to net denitrification by varying physical transport. Their numerical simulation study showed that hydrologic variability is more important than reaction substrate availability (DOC and NO_3^-). The relative importance of hydrologic and substrate variables may vary with land use and stream sizes; for example, denitrification in agricultural streams is limited by the hyporheic exchange flux, while in forest streams it is limited by substrate availability (Myers, 2008).

Previous denitrification studies are often limited to reach-scale to lower-order streams and have emphasized the importance of the role of lower-order streams in denitrification (Alexander et al., 2000, 2007; Gomez-Velez et al., 2015). Due to the higher ratio of benthic surface to water volume and nutrient loading in lower-order streams, it is known that the efficiency of denitrification in lower-order streams is higher than that of higher-order streams (W. M. Wollheim, 2016). This result may be relevant to the empirical studies' sample bias, as Tank et al. (2008) pointed out in their meta-analysis that most stream nutrient uptake studies for NH_4^+ and NO_3^- were conducted at streams with less than 200 (l/s). Tank et al. (2008) also demonstrated that larger streams in the Upper Snake River, Wyoming, USA (seventh order, and 12000 l/s), have higher inorganic N uptake (NH_4^+ and NO_3^-) using a pulse method than smaller streams. Ensign and Doyle (2006) analyzed the result of nutrient spiraling experiments spanning from first-order to fifth-order streams and found that cumulative uptake rate of NO_3^- increases with stream orders. Similarly, a recent modeling study showed the potentially important role in removing excess nitrogen in larger rivers (W. M. Wollheim, 2016). Therefore, it is vital to investigate further how stream size affects hyporheic exchange processes. Furthermore, many previous modeling studies did not separate the role of HZ denitrification from whole stream denitrification. Therefore, it is critical to study HZ denitrification along streams with varying hydrologic and biogeochemical conditions.

Previously, few basin-scale models have been developed to simulate the role of river corridor process in removing excess nitrogen from streams and rivers (Alexander et al., 2007, 2009; Curie et al., 2011; Fang et al., 2020; Gomez-Velez & Harvey, 2014). However, most of the basin-scale models are based on empirical reaction models, or the reaction parameters are estimated by fitting the empirical data (Alexander et al., 2000, 2009). For example, The Networks with Exchange and Subsurface Storage (NEXSS) model used an empirical hydrogeomorphic model and a suite of hydraulic/groundwater models to compute the exchange flux/residence time between stream/river waters and the hyporheic zone (Gomez-Velez et al., 2015; Gomez-Velez & Harvey, 2014). The NEXSS model computes potential denitrification based on the ratio of computed Damkohler number and river turnover length. However, this potential denitrification assumes constant and uniform biogeochemical time scale and does not consider the limitation of substrate availability in denitrification rate. The SPAtially Referenced Regressions on Watershed attributes (SPARROW) model was used to estimate in-stream removal of nitrogen (Alexander et al., 2000, 2007) in the Mississippi River Basin. In-stream removal of nitrogen was estimated by fitting the model parameters with the measured mean nitrogen fluxes without considering explicitly nitrogen processes in streams. Also, this model does not separate the N removal from water column and the hyporheic zone. On the other hand, Fang et al. (2020) developed SWAT-MRMT-R, a model that couples the watershed water quality model, Soil and Water Assessment Tool (SWAT), with the reaction module from a flow and reactive transport code (PFLOTRAN). It can compute aerobic respiration and denitrification in the hyporheic zone. The model was successfully tested in the upper Columbia–Priest Rapids watershed in the Columbia River Basin (CRB), and it shows the spatial variation of HZ denitrification depends on a combination of varying hyporheic exchange and source locations of nitrate.

In this study, we adopted the reaction network model from the SWAT-MRMT-R to study the role of the hyporheic zone in removing excess nitrogen at the basin scale. We expanded this modeling framework to the CRB with varying stream sizes/land uses and improved the model resolution by using the National

Hydrography Dataset PLUS (NHDPLUS v2). A detailed description follows in the methodology section. In this study, we used the CRB as a testbed to study the spatial variation of HZ denitrification at the basin scale. The CRB has been historically of particular interest due to its significant multipurpose river system benefits in ecology, environment, irrigation, navigation, recreation, flood control, and hydropower generation. However, even though significant research has been performed on the hydrology of the CRB (e.g., Hamlet et al., 2013), river corridor modeling studies are limited, except for river reach-scale modeling studies (Zarnetske et al., 2015).

This study developed a basin-scale HZ river corridor model (RCM) to quantify the spatial variation of HZ denitrification across the streams of the CRB and used a machine learning (ML) approach (i.e., random forest model) to identify what factors control the spatial variation of HZ denitrification at the basin scale (Figure 1). Specifically, we asked two scientific questions:

1. What are the important variables in explaining the spatial variation of HZ denitrification in the CRB? We hypothesized that the relative importance of hydrologic variability/substrate availability can control spatial variation of HZ denitrification, and their importance may change with stream sizes and dominant land use. We built random forest models with key model input variables and modeled denitrification and tested what variables can better explain the spatial variation of modeled denitrification across streams with different sizes and land uses.

2. Which watershed/stream characteristics can better explain the spatial variation of HZ denitrification in the CRB? We extended our efforts to develop another random forest model to capture the modeled denitrification in the CRB with publicly available watershed and stream characteristic data. This random forest model can generalize what watershed/stream characteristics can better explain the spatial variation of the HZ denitrification in the CRB.

1. Methodology

(a) Columbia River Basin

This study site is the CRB (Figure 2), and the modeling domain only covers the United States (US)-CRB regions due to different level of data availability. For example, the detailed stream network map (e.g., National Hydrography Dataset (NHD) PLUS v2 flowlines) are only available for the USA-CRB region, and the key input data for our river corridor model—which are hyporheic residence time and exchange flux—are only available for the USA-CRB region. The CRB is one of large river basins in the Continental United States (CONUS), and the total basin size is about 620,000 km^2, and US-CRB size is about 570,413km^2. Elevation ranges from 0 to 5230 m, and the CRB has nine sub-river basins: (1) Lower Columbia, (2) Middle Columbia, (3) Upper Columbia, (4) Lower Snake, (5) Middle Snake, (6) Upper Snake, (7) Kootenai-Pend Oreille-Spokane, (8) Willamette, and (9) Yakima River (Figure 1b). The climate over the USA-

CRB varies widely. For example, western Washington and Oregon have humid continental climate, and eastern Oregon and Washington and Idaho have a semi-arid steep climate, and the Cascade Range in Washington, Oregon and the Rocky Mountains in Idaho, Montana, and Wyoming have an alpine climate. With various climate conditions, the annual precipitation ranges from 158 mm to 5230 mm (based on 30 years of normalized PRISM data), and annual mean temperature ranges from -3 to 12 °C. The seasonal pattern of precipitation is very consistent; winter precipitation is dominant. At the mountain regions located in high elevations, the dominant precipitation phase is snow, but at the lower elevation regions, precipitation falls as rain. Major land use/cover (Figure 1c) is composed of 33.7% forest land (33% evergreen forest and about 0.3 and 0.4% deciduous forest and mixed forest), 33% of shrub lands, 12% agriculture lands (10% croplands and 2% hay and pasture), and 2.3 % urban lands.

1. Basin-scale HZ river corridor model

This study used a simplified, spatially fine resolution, basin-scale, coupled carbon and nitrogen, river corridor model (RCM), based on SWAT-MRMT-R (Fang, et al., 2020) to quantify spatial variations of HZ denitrification in the CRB. The SWAT-MRMT-R model coupled a watershed quality model (SWAT) with a PFLOTRAN-based, multi-rate hyporheic zone reaction model (X. Song et al., 2018). The exchange rate and residence time between stream and hyporheic zone were estimated using the NEXSS model (Gomez-Velez and Harvey 2014). The NEXSS model coupled empirical geomorphologic models with a suite of existing physical hyporheic exchange flux models; for example, NEXSS estimates the values of bankfull channel with discharge, median grain size (D50), channel slope, sinuosity, and regional head gradients along the NHDPLUS stream networks. In addition, physical hyporheic exchange modeling is used to predict the average hyporheic exchange flux, residence time distribution, median residence time in vertical direction, and lateral direction. Vertical hyporheic flux represents exchange between channel water and beneath bedforms, while lateral exchange flux represents exchange between channel water and river bars and meander banks. In the RCM, three microbially driven reactions including two-step denitrification and aerobic respiration are considered within the hyporheic zone (Table A1). In this study, we focus on denitrification processes (Figure A1). The detailed equations and descriptions are found in the appendix and the papers of Fang et al. (2020) and Gomez-Velez and Harvey (2014).

Our RCM replaced the in-stream module and nutrient loading of the SWAT model by the regression-based estimates. For example, we developed regression-based models or used other modeling results to estimate stream DOC, DO and NO_3^- concentrations (Figure 3). For the stream NO_3^- concentration, we used the results of 2012 SPARROW model(https://www.sciencebase.gov/catalog/item/5d407318e4b01d82ce8d9b3c). The SPARROW model is a statistical regression model and has been used to identify key pollutant sources and determine the role of in-stream process in removing nutrient process at the regional scale (Alexander et al., 2007). The SPARROW model outputs include annual mean streamflow, total nitrogen (TN) loading, total phosphorous (TP) loading, and suspended solid (SS) loading at the NHD-PLUS stream reaches. Since our RCM requires stream nitrate concentration, we calculated the annual mean TN concentration by dividing the total TN annual mean loading by the annual mean streamflow estimate. We assume that nitrate is a major component of the total nitrogen in the stream waters of the CRB. To test this assumption, the ratio of stream nitrate concentration to the total stream nitrogen concentration was calculated for the USGS stream gauging stations within the CRB; about 83% of stream nitrate accounts for the total nitrogen in the stream waters, which supports our assumption. Detailed analysis is included in the supplement materials. For stream DOC and DO concentrations, we developed multi-linear regression models based on the NHD stream database(Schwarz et al., 2018) and the measured stream DOC/DO concentrations at the USGS gauging stations in the CRB. The developed regression model for stream DOC concentration is a function of percent of forest area and baseflow index (BFI) (Wolock, 2003). The two variables were all negatively correlated with the modeled stream DOC concentration (stream DOC=-0.0239(percent of forest)-0.033(BFI)+5.71). The developed regression model for the stream DO concentration is a function of the percent of forest area, topographic wetness index (TWI), and catchment dam storage (stream DO=0.00899(percent of forest)-0.457(TWI)+0.209(storage)+15.539). The modeled stream DO concentration was positively correlated with the percent of forest area and NHD catchment dam storage and is negatively correlated with the TWI. The detailed procedure of building multiple regression models for spatial DOC/DO mean concentrations is included in the supplementary materials.

The RCM was simulated at the hourly time step and computed the cumulative annual NO_3^- removal amount (kgN) at the scale of the NHDPLUS stream reaches and scaled it by stream surface area (m^2). We calculated the stream surface area using two parameters (width and length). The stream length was from the NHDPLUS database (Schwarz et al., 2018), and the stream width was derived by the power relationship between measurement of instantaneous flow and bankfull width and NHD cumulative drainage area (Gomez-Velez et al., 2015). The model separately calculated the NO_3^- removal amounts via vertical hyporheic exchange and lateral hyporheic exchange. To test the variation of annual cumulative NO_3^- removal amounts between years, we ran the model over 10 years and found that after the 2$^{\text{nd}}$ year simulation, the annual removal amounts reached a steady state (Figure S1). For our modeling analysis, the second-year simulation results were used.

1. Key factors controlling spatial variability of cumulative NO_3^- removal amounts in the hyporheic zone at the basin scale.

To determine the key factors controlling the spatial variability of cumulative (annual) NO_3^- removal amount at the NHD stream reaches in the CRB, we explored the relationship between model key inputs and modeled cumulative

NO_3^- removal amounts. Key hydrologic variables include hyporheic exchange flux and residence time, and substrate variables are the estimated stream DOC, DO, and nitrate concentrations. We also tested how these variables changed with different-sized (order) streams and land use. This study classified the stream sizes in the three groups based on the Strahler's stream ordering system: (1) small-sized streams (1–3th), and (2) medium-sized streams (4–6th), and (3) large-sized streams/rivers (7th–12th). While the largest stream order in the CRB is 9th stream, the large-sized streams/rivers include the 7th to 9th order streams in our analysis. To determine the dominant land use for each stream reach, we calculated the percentage of each land use (forest, urban and agriculture) within the total upstream routed accumulated area. If the percentage of the drainage area for each land use type is larger than 80%, we assigned the land use type as a dominant land use type. National Land Cover Database (NLCD) 2001 land cover (https://www.mrlc.gov/) was used to calculate the percentage of each landcover. To simplify the landcover classification, forest land use includes mixed/deciduous/evergreen forest types, and urban land use includes developed open spaces and developed low/medium/high density area. Agriculture land use includes pasture/hay and cultivated crop areas. We quantified the difference in the cumulative HZ NO_3^- removal amounts in the streams with different sizes (small, medium, and large streams) and different land uses (forest, urban, and agriculture). The significance of the effect of land use/stream size on the cumulative NO_3^- removal amount was tested using Kruskal-Wallis test.

To evaluate the relative importance between hydrologic and substrate variables and modeled NO_3^- removal in the CRB, we used variable importance analysis implemented in a random forest model to identify what factors control the spatial variation of NO_3^- removal amounts (Figure 1). A random forest model was built with the R "randomforest" package using the key model input variables and modeled NO_3^- removal amounts (kgN/m^2). 80% of samples were used to train the random forest model, and 20% of samples were used to test the model prediction. We used the R^2 and mean squared error (MSE) to quantify the model prediction accuracy. The random forest model we developed was used to compute the partial dependence of each variable on the modeled NO_3^- removal amount and to measure importance ranks of key input variables we used. We tested whether the ranks of variable importance vary with stream sizes/land uses. To measure the importance of the key variables in the random forest model, we used Gini impurity measures. Gini impurity measures how well each tree is classified and measures the variance within each tree. Lower variance represents better classification of each variable. Also, to generalize which watershed and stream properties can better represent the spatial variation of HZ NO_3^- removal amount in the CRB, we developed a random forest model with public available watershed/stream variables (Figure 1 and Table 1). The detailed information for each variable used in the random forest model is found in the supplement materials (Table S4). The watershed properties information is based on the NHDPLUS database (Schwarz et al., 2018), and some stream properties, including median grain size of streambed sediment (D50) and stream width, are based on the NEXSS input data (Gomez-Velez and Harvey 2014).

1. **Results**

(a) Variation of hydrologic variability and substrate availability in the streams across different sizes and land uses

We computed the distribution of key model inputs of hydrologic/substrate variables in the stream across orders and dominant land uses (Figure 4). Hydrologic variables vary with stream orders (Figure 4a,4b, 4c, 4d and 4e). We note that we excluded the data for the 9th order stream since the total number of stream reaches with 9th order is only 5. For example, for hyporheic exchange flux, the median exchange flux increased from 1st to 5th order streams and decreased from 6th to 8th order stream. Median residence time increased from the 1st to the 8th. However, median stream NO_3^- concentrations did not change with stream orders. For stream DOC concentration, the median values of stream DOC concentration were very similar between the different order streams except for the 8th order streams, while lower-order streams had larger variation of DOC concentration. For stream DO concentration, lower-order streams tended to have higher median DO concentration with larger variations. Among the streams with different land uses, forest streams had the highest hyporheic exchange fluxes, while agricultural streams had the lowest values (Figure 5). For residence time, agricultural streams had the longest residence time, while forest streams had the shortest residence time. For substrate availability, forest streams had the lowest stream DOC and nitrate concentrations but had the highest stream DO concentrations. Agriculture and urban streams had similar level of stream DOC/DO concentration, but agricultural streams had higher stream nitrate than urban streams.

1. Spatial variation of the modeled denitrification across the streams with different sizes and land use/cover.

We computed the cumulative (annual) HZ NO_3^- removal amount (kgN/m^2) via vertical and lateral hyporheic exchange, respectively (Figure 6). The spatial variations of the lateral and vertical HZ NO_3^- removal amount were similar; the spatial correlation (as measured by the Spearman correlation coefficient) between the two estimates was 0.79. The vertical HZ NO_3^- removal was about one order of magnitude higher than the lateral HZ NO_3^- removal. The vertical HZ NO_3^- removal ranged from 0 to 76.0 kg N/m^2, and its mean value was 0.137 kg N/m^2, while the cumulative lateral HZ NO_3^- removal ranged from 0 to 1.87 kg N/m^2, and its mean value was 0.015 kg N/m^2. The ratio of vertical HZ NO_3^- removal to the total HZ NO_3^- removal ranged from 0.001 to 0.99, and the mean of the ratio was about 0.78. The ratio increased with the stream orders. For example, median ratios of the 1st order and 2nd order streams were about 0.6 and 0.83, respectively, and the median ratio of higher-order streams(>=5th) was close to 1. This result suggests that the HZ NO_3^- removal tends to be more dominated by the vertical exchange in higher-order streams. This result is similar to the modeling results of Gomez-Velez et al. (2015). Gomez-Velez et al. (2015) showed that the potential denitrification (measured by the reaction significant factor) was higher via vertical hyporheic exchange than via lateral hyporheic exchange in the Mississippi Rivers.

We quantified the HZ NO_3^- removal amount (kgN/m^2) across the streams with stream orders and land uses (Figure 7, S2 and S3). Modeled NO_3^- removal had an unimodal function of stream orders (or stream sizes); medium-sized streams (4^{th}–6^{th} order streams) had the highest NO_3^- removal amounts (Figure 7a). Among the streams with different land uses, urban streams had the most NO_3^- removal amounts (Figure 7b), and agricultural streams had the least NO_3^- removal amounts. Their differences were all statistically significant when using Kruskal-Wallis test, and the p-value of the two tests are all less than 2.2e-16.

To identify what factor influences the spatial variation of the HZ NO_3^- removal, we developed a random forest model with the model key inputs and modeled NO_3^- removal amounts. The partial dependence plots (Figure S4) showed that stream DOC, residence time, and exchange flux had strong nonlinear relationships with the modeled NO_3^- removal across different-sized streams. Modeled NO_3^- removal increased with stream DOC/exchange flux, but it decreased with residence time. For streams with different dominant land uses, exchange flux and residence time had strong positive or negative relationships with the modeled NO_3^- removal, respectively. For forest and urban streams, stream DOC had a high positive nonlinear relationship with the modeled denitrification, respectively. The variable importance analysis using our random forest model showed that hydrologic variables were more important in explaining HZ NO_3^- removal amount's spatial variation than substrate variables (Figure 8). Among the hydrological variables, hyporheic exchange flux was the first important variable, and residence time was the second most important variable in all sizes of streams. Similarly, the hyporheic exchange flux and residence time were the first and second important variables for streams with different land uses, respectively. While residence time was always the second most important variable across the streams with different land uses, the level of importance in DOC concentration was similar to that of residence time in forest streams. DOC concentration was the most important variable among the substrate variables for forest streams.

We evaluated the impact of substrate availability on the HZ NO_3^- removal amount in streams across the different sizes and land uses (Figure 9). On average, removing substrate concentration limits tended to increase NO_3^- removal amounts. Among substrate availability, removing the DOC limitation most increased the modeled NO_3^- removal for all sized streams, and with different land uses. Among the streams with different land uses, forest stream showed most increase in NO_3^- removal by removing DOC limits. Agricultural streams showed the least increase in NO_3^- removal by removing the substrate limits. This result suggests that stream DOC is the most limiting substrate to NO_3^- removal, especially for small-sized and forest streams. Also, this result supports the variance importance analysis (Figure 8)

1. Relationship between watershed/stream characteristics and HZ NO_3^- re-

moval amount

With the publicly available watershed and stream properties data, we developed another random forest model to predict the HZ NO_3^- removal amount in the CRB to generalize what watershed/stream characteristics can better explain the spatial variation of the HZ denitrification in the CRB. We built random forest models using modeled NO_3^- removal via vertical, lateral, and total hyporheic exchange, respectively. Each model showed high predictive accuracy, and the R^2 values were greater than 0.96, and the MSE values were less than 0.06 (Figure 10a and Table 2). The variable importance plots showed that for the modeled lateral NO_3^- removal amount, D50, stream slope and annual precipitation were the most important variables (Figure 10b), while for modeled total NO_3^- /vertical NO_3^- removal amounts, D50, annual precipitation and the percent of forest area were the most important variables (Figure 10c, and 10d). The D50/stream slope variables were highly associated with the hyporheic exchange rate since the variables were used to calculate streambed hydraulic conductivity in the NEXSS model (Gomez-Velez et al., 2015). The percent of forest area was a key predictor variable in estimating stream DOC concentration (Figure 4, and S9). The results of variable importance supported that the HZ NO_3^- removal amount increased with hyporheic exchange flux, which positively correlated with streambed hydraulic conductivity (or D50), and the modeled NO_3^- removal was also sensitive to the available DOC concentrations, which was negatively correlated to the percent of forest area. To test how well our random forest model can be applied to the sub-basin in the CRB, we also built the random forest model with the same input data. Same as the CRB, the most important variable for each sub-basin was all D50 (Figure S6), and the second most influential variable was the percent of forest area or mean annual precipitation, depending on sub-basins.

1. **Discussion**

   (a) Key controls on spatial HZ denitrification variation in the streams across different sizes and different land uses

This study used the basin-scale river corridor model and random forest models to identify key factors controlling spatial variation of HZ denitrification in the CRB. Results showed that hydrologic variables were more important than substrate variables in explaining the spatial variation of HZ denitrification in streams across different sizes and land uses. Among the selected hydrologic variables, hyporheic exchange flux was the most important variables for all sizes of streams and different land use streams. Among the substrate variables, stream DOC was considered the most important variable, especially for the forest streams. Among the different-sized streams, medium-sized streams (4^{th}–6^{th} orders) had the highest denitrification due to the largest exchange flux. The literature shows mixed results in the effects of stream size on denitrification (Alexander et al., 2007, 2009; Tank et al., 2008; Wollheim et al., 2006). In our modeling, the highest exchange flux in the medium-sized streams was mainly due to the coarser grain size (or higher hydraulic conductivity) of the streambed sediment. Also, since the substrate concentrations did not vary much with the stream orders (or sizes) in the CRB (Figure 4), the spatial pattern of hyporheic exchange flux controlled the relationship between denitrification amounts and stream sizes. The potential difference of the effects of stream size on denitrification between studies may be due to the spatial variation of sediment hydraulic conductivity along the different stream size between the river basins if the substrate availability is not limiting factors. Also, our modeling study showed that hydrologic variables were more important in determining the spatial variation of denitrification in the stream networks than substrate variability. Thus, the hyporheic exchange attributed to the streambed hydraulic properties determined the effect of stream sizes.

Among the three dominant land use types' streams, urban streams had the highest HZ denitrification due to relatively high substrate availability and hyporheic exchange flux (Figure 5b). Agricultural streams' denitrification was transport-limited by having the lowest hyporheic exchange rate, while forest stream's one was source-limited by having the lowest substrate availability (e.g., DOC). This limiting factor was similar to the result of Myers (2008). Myers (2008) showed that among nine streams in Western Wyoming, agriculture and forest streams had the lowest and highest exchange flux, respectively, while agricultural streams had higher organic/nitrogen concentrations than forest streams. However, the agricultural streams showed the highest denitrification due to highest substrate availability (e.g., organic matters) in the hyporheic sediments, even though the modeled exchange flux was lowest in the agricultural streams. Our modeling study showed that agricultural streams had the lowest denitrification due to the lowest hyporheic exchange. Interestingly, the two studies showed opposite results, even though the two studies shared same limiting factor on denitrification in agricultural and forest streams. The difference may be because our mode results may represent the long-term averaged conditions, while the experimental study of Myers (2008) may represent the short-term conditions. On the other hand, a study of Mulholland et al. (2008) using data from nitrogen stable isotope tracer experiments across 72 streams and 8 regions showed similar result to ours, i.e., urban streams had the highest denitrification rate, while agricultural streams had the second largest denitrification rate, and forest streams had the lowest denitrification rate.

1. Generalization of important watershed/stream variables in controlling the basin-scale HZ denitrification.

This study used a machine learning (ML) approach (i.e., random forest model) to improve our understanding of which watershed/stream variables can better explain the spatial variation of HZ denitrification in the CRB. This ML approach is a powerful tool to predict complex systems, but due to low interpretability, ML is considered as a box model. However, our modeling study demonstrated that our random forest models successfully captured the sub-basin/basin-scale modeled denitrification, and the selected important variables all represented the dominant processes that controlled denitrification across streams with different sizes and land uses. Our random forest model showed very high prediction accuracies; R^2 values are greater than 0.96, and MSE values are less than 0.06. This result suggests that the random forest model with the publicly available watershed and stream properties data can capture key variables controlling basin-scale spatial denitrification variation, even though there are complex interactions between many processes/variables determining the spatial variation of HZ denitrification. Also, the variable importance analysis showed that the stream morphological parameters (D50 and stream slope), climate (annual precipitation), and stream DOC (percent of forest area) can explain most HZ denitrification variability. D50 and stream slope were highly correlated with the modeled exchange flux used in this study. The percent of forest area was one of two predictor variables in stream DOC concentration, which was a major limiting substrate concentration in the modeled denitrification. Therefore, our study demonstrates that our random forest model and the small numbers of key watershed/stream variables (D5O, stream slope, precipitation, and land cover), which are fairly easy to measure or characterize, can be used to determine the spatial variation of HZ denitrification at the basin scale, without explicit and complex numerical modeling. Therefore, the identified important variables and the random forest model we developed can be used as a hypothesis testing tool for spatial variation of HZ denitrification at the basin scale and as a sampling design tool for large-scale hyporheic zone experimental studies.

1. Implication of the future climate and land use in river corridor processes

In the CRB, future climate change expects to increase winter/spring flow, decrease summer flow (Hamlet et al., 2013), and increase stream water temperature(Ficklin et al., 2014). Also, the sensitivity of hydrologic changes to future climate change varies between subbasins in the CRB. This change obviously alters the effectiveness of the hyporheic zone. Based on our modeling results, denitrification increased with the hyporheic exchange, which was a function of grain sizes of streambed, annual precipitation, and stream slope, while stream DOC availability may limit denitrification. Compared with the other river basins in the USA, the streams of the CRB had lower DOC concentrations (Yang et al., 2017), and watershed DOC processes were characterized as transport-limited rather than source-limited (Zarnetske et al., 2018). Therefore, we expect that increasing runoff can generate higher DOC flux (or concentration) in streams, which may promote denitrification in the hyporheic zone. Also, more frequent and intense fires are expected due to future climate conditions. Fire can alter the conditions of terrestrial and aquatic systems. For example, fire removes vegetation and delivers more nutrient/sediments via higher peak flow. Higher exchange/more substrate availability in the hyporheic zone may increase denitrification, while lower sediment hydraulic conductivity values due to finer particle sediment transport by fire can reduce denitrification.

4.4 Current research limitation and future study

This study demonstrated that the combination of the reaction network model and empirical methods can quantify the spatial variation of HZ denitrification at the basin scale. However, due to the simplified model structure and assumptions used, this model had several limitations. The first limitation of this study was that hydrological/substrate variables were assumed to be constant over time, and the variables are empirically estimated or dependent on the other model outputs (e.g., SPARROW flow and TN fluxes). This assumption may create a bias in a different way depending on the hydrologic and substrate conditions. For example, in the streams where hydrologic conditions are unsynchronized or synchronized with substrate variables, modeled cumulative denitrification may be overestimated or underestimated with the current model assumption. Future studies should implement the dynamic hydrologic/substrate concentration in-stream and in the HZ; for example, the SWAT-MRMT-R model (Fang et al., 2020) can be used, and to account for the dynamic hydrologic exchange flux/residence time in the hyporheic zone, the SWAT-MODFLOW (Bailey et al., 2016) or other integrated hydrologic–biogeochemistry models (Chen et al., 2020) may be considered in future studies. As well, the current model was heavily dependent on the NEXSS-based hyporheic exchange flux and residence time. Even though the NEXSS used the physical hydraulic/groundwater models, the exchange flux and residence time were highly correlated with the estimated hydraulic conductivity of the streambed. The NEXSS model used an empirical relationship between D50 and sediment hydraulic conductivity to derive the hydraulic conductivity of the streambed at the NHDPLUS stream reach (Gomez-Velez et al., 2015). High spatial heterogeneity of grain size distribution within reach-scale stream sediment (Ren et al., 2020) and its change due to disturbance make it challenging to estimate the representative hydraulic conductivity at the reach-scale (Stewardson et al., 2016). Hydrologic condition also alters the vertical distribution of hydraulic conductivity in streambeds; for example, gaining streams have higher conductivity with depth, but losing streams have lower conductivity with depth (X. Chen et al., 2013). Therefore, future study should focus on introducing advanced methods (i.e., machine learning approaches) and also should find better predictor variables for streambed hydraulic conductivity (Abimbola et al., 2020) to reduce the uncertainty in the RCM.

The second limitation is that this model does not explicitly simulate nitrification processes in the hyporheic zone. The current model only implements aerobic respiration and denitrification in the hyporheic zone. When oxygen is abundant and residence time is short, nitrification can be dominant (Zarnetske et al., 2012). This model assumes that nitrification is not dominant. Based on the Dakomber number, lower-order streams tend to have lower residence time so that nitrification may be important process. Interestingly, most of streams with a low residence time in the CRB tend to have the drainage area with forest lands. Our modeling study suggest that denitrification in the forest streams was mainly limited by the available DOC, but not stream nitrate concentration. Even if nitrate can be more abundant via nitrification because of shorter residence time in the hyporheic zone, denitrification of forest streams may not increase because nitrate is not a major limiting factor.

The last limitation is that the current model estimates of HZ denitrification are not validated with field measurements, even though the RCM computed the HZ denitrification using the reaction network model with reasonable estimates of hydrologic and substrate variables. This deficiency may reflect the limitation of currently available denitrification measurements for the hyporheic zone, especially for large river basins. Many experimental studies focus on total in-stream processes of nutrient uptake rather than exclusively denitrification measurements in the hyporheic zone (Tank et al., 2008, Findlay et al., 2011). As well, since our model estimates represent spatially varied denitrification and temporally averaged conditions, the comparison of our model estimates with short-term snap measurements that are usually available in the experimental studies is a big challenge. Recent study in the HJ. Andrew watershed in the Oregon state, USA has done the detailed mapping of stream geomorphology, hydrology, biology, and chemistry along the 5^{th} order streams of the forested watershed (Ward et al., 2019). This data may be a good starting data set to validate the model inputs (e.g., concentrations of

DOC/DO/nitrate in the HZ and streambed hydraulic conductivity) and the modeled denitrification along with the stream orders in the future study.

1. **Summary and conclusion**

   The important role of hyporheic zone denitrification is well recognized in hydrologic and biogeochemistry communities (Groffman et al., 2009; Harvey & Gooseff, 2015). However, modeling studies quantifying basin-scale hyporheic zone denitrification are still limited in current literature. To fill the knowledge gaps, this study used a simplified, spatially fine resolution, basin-scale, coupled carbon and nitrogen hyporheic zone model and random forest models to identify key controls on the spatial variation of HZ denitrification in the CRB. The variable importance analysis demonstrated that hydrologic variables (hyporheic exchange flux and residence time) were more important in explaining the spatial variation of HZ denitrification than substrate variables (stream DOC, nitrate, and DO) across streams with different sizes and land uses. Among the hydrologic variables, hyporheic exchange flux can explain most spatial variation of the modeled denitrification amounts. Among the substrate variables, the denitrification amount was limited most by the available DOC. Among the different-sized streams, medium-sized streams (4^{th}–6^{th} orders) with highest exchange fluxes had the largest denitrification amounts. Among the streams affected by different land use, urban streams exhibit the most denitrification due to relatively high exchange flux and substrate concentrations. Denitrification in agricultural streams was transport-limited with the lowest hyporheic exchange rate, while forest streams were source-limited with the lowest DOC availability.

We expanded our efforts to develop a general random forest model to identify key factors controlling the spatial variation of HZ denitrification in the CRB with publicly available watershed/stream properties data. Our random forest model showed a high performance (R^2>0.96 and MSE<0.06), and stream morphology parameters (D50 and stream slope), climate (annual precipitation), and land use (percent of forest) were the most important variables for explaining spatial variation of the modeled HZ denitrification. These results support the relative importance analysis with the model's input variables; hyporheic exchange flux and available DOC concentration were key limiting factors in HZ denitrification variation in the CRB, based on our findings. In this study, hyporheic exchange flux was estimated based on the NEXSS simulation (Gomez-Velez et al., 2015), and its flux was highly dependent on the streambed sediment grain size/hydraulic conductivity estimates. To reduce the uncertainty of our RCM, future studies should focus on collecting detailed measurements of hydraulic conductivities (Ren et al., 2020; Stewardson et al., 2016) and developing advanced methods characterizing the spatial variation of hydraulic conductivities (Abimbola et al., 2020). In addition, the current model only represented the spatial averaged conditions of HZ denitrification in the CRB, and key model input variables were temporally constant. Therefore, temporal components should be incorporated by using the SWAT-MRMT-R or other integrated hydrologic–biogeochemistry models to accurately represent basin-scale denitrification in the CRB.

Overall, this study indicates that the combination of the reaction network modeling and empirical substrate concentration models can quantify the spatial variation of HZ denitrification at the basin scale. This modeling framework can be easily applied to the regional and continental scales and can help to understand the role of the hyporheic zone across stream networks in large river basins with different hydrologic/geochemical conditions.

Appendix

Descriptions of the basin-scale river corridor model

Our river corridor model (RCM) computes the aerobic respiration and two-step denitrification in the hyporheic zone at the scale of the NHDPLUS stream reaches in the Columbia River Basin. Figure A1 shows the conceptual diagram of the RCM. Table A1 and A2 include the three reactions and their associated model parameter values. The model computes at hourly time steps, but the model key input data—including exchange flux, residence time, and stream solute (DOC, DO, and NO_3^-) concentrations—are constant over time. In addition, each reaction in the hyporheic zone and the exchange between hyporheic zone and stream are vertically and laterally computed independently. This model computes the solute exchange between stream and hyporheic zone (expressed in the equation A1 and A2). In equation A2, the exchange volume (V) is computed by multiplying exchange flux (q) by the residence time (τ) and stream surface area (width (w)×length (l)). The three reactions are computed by solving the R_1, R_2 and R_3 with the approach proposed by Song *et al.,* (2017), and the associated parameters are obtained from the Table 2 in Song *et al.* (2018).

The following equation is used to calculate the concentration change in the hyporheic zone due to the mass exchange between the stream and the hyporheic zone as well as microbial reactions in the hyporheic zone:

$$\frac{d[C_{i,t}]}{\mathrm{dt}} = \frac{1}{\tau}\left([C_{s,i} - [C_{i,t}]\right) + \sum_{j=1}^{3} \mu_j R_j \text{ (A1)}$$

Where τ is the hyporheic zone residence time, $C_{s,i}$ is the stream 'i' solute concentration (DOC, NO_3^-, and DO), $C_{i,t}$ is the hyporheic 'i' solute concentration at the 't' time step. μ_i is the stoichiometric coefficient of solute i in reaction j. R_j is the reaction rate the j-th reaction.

$$\frac{d[C_{i,t}]}{\mathrm{dt}} V = V \times \frac{1}{\tau}\left([C_{s,i} - [C_{i,t}]\right) + V \times \sum_{i}^{3} \mu_j R_j \text{ (A2)}$$

Where V is the hyporheic exchange volume ($q \times w \times l \times \tau$). Using equation A2 can compute the mass exchange between stream and hyporheic zone.

$$R_i = e_i r_i^{\mathrm{kin}}, \text{ i=1,2,3. (A3)}$$

$$r_i^{\mathrm{kin}} = k_i \frac{a_i}{K_{a_i} + a_i} \times \frac{d_i}{K_{d_i + d_i}} (BM) \text{ (A4)}$$

$$e_i = \frac{r_i^{\mathrm{kin}}}{\sum_i^3 r_i^{\mathrm{kin}}} \text{ (A5)}$$

Where k_i, $K_{a_i}$and K_d denote the maximum specific uptake rate of organic carbon, half-saturation constants of the electron acceptors, and half-saturation constants for the electron donors. $a_i$is the concentration of electron acceptor (mol/L), $d_i$is the concentration of electron donor (mol/L), and biomass (BM)is the concentration of biomass (mol/L). Reaction rate Ri is computed using unregulated effect (a Monod-type kinetics coefficient (r_i^{kin}) in Equation A4, and regulated effects (e_i) in Equation A5.

Acknowledgments

This research was supported by the U.S. Department of Energy (DOE), Office of Science (SC) Biological and Environmental Research (BER) program, as part of BER's Environmental System Science (ESS) program. This contribution originates from the River Corridor Scientific Focus Area (SFA) at Pacific Northwest National Laboratory (PNNL). This research used resources from the National

Energy Research Scientific Computing Center, a DOE-SC User Facility. PNNL is operated for DOE by Battelle Memorial Institute under contract DE-AC05-76RL01830. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

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Tables

Table 1. Lists of key watershed/stream characteristics and properties

Properties	**Variables**
Climate	Precipitation and air temperature
Topography	Elevation, slope, wetness index, and drainage area
Hydrology	Annual flow, baseflow index, potential evapotranspiration, and actual evapotranspiration
Land	% of land use/cover types (forest, wetland, agriculture, urban and shrubland), vegetation index
Soil	Hydraulic conductivity of soil and permeability of surface geology, % of soil texture and organi
Stream	Sinuosity, D50, contact time, stream slope

Table 2. Summary of model performance in the developed random forest model

Model	Train		Test	
	R^2	MSE	R^2	MSE
Lateral denitrification	0.96	0.06	0.96	0.05
Vertical denitrification	0.97	0.04	0.97	0.04
Total denitrification	0.97	0.03	0.97	0.03

Table A1. Aerobic respiration and two-steps of denitrification reactions

Reaction process	Reaction equations	
Aerobic respiration	R_1	$\mathrm{CH_2}O + f_1O_2 + \frac{1}{5}(1-f_1)\,\mathrm{NH_4^+} \rightarrow f_1\mathrm{CO_2} + \frac{1}{5}(1-f_1)\,C_5H_7O_2N$ -
Denitrification	R_2	$\mathrm{CH_2}O + 2f_2\mathrm{NO_3^-} + \frac{1}{5}(1-f_2)\,\mathrm{NH_4^+} \rightarrow f_2\mathrm{NO_2^-} + f_2\mathrm{CO_2} + \frac{1}{5}(1-f_2$
	R_3	$\mathrm{CH_2}O + \frac{4}{3}f_3\mathrm{NO_2^-} + \frac{1}{5}(1-f_3)\,\mathrm{NH_4^+} \rightarrow \frac{2}{3}f_3N_2 + f_3\mathrm{CO_2} + \frac{1}{5}(1-f_3$

Table A2. Reaction parameter values and initial substrate concentrations

Reaction rates	Parameter	R_1	R_2	R_3
	f_i	1/3×0.65	0.65	0.99
	k_i	3×28.26	28.26	23.28
	$K_{d,i}$	0.25	0.25	0.25
	$K_{a,i}$	0.001	0.001	0.004
Hyporheic zone	DOC	NO_3^-	DO	
Initial concentrations (mole/l)	6.37e-5	7.92e-5	2.87e-4	

Figures

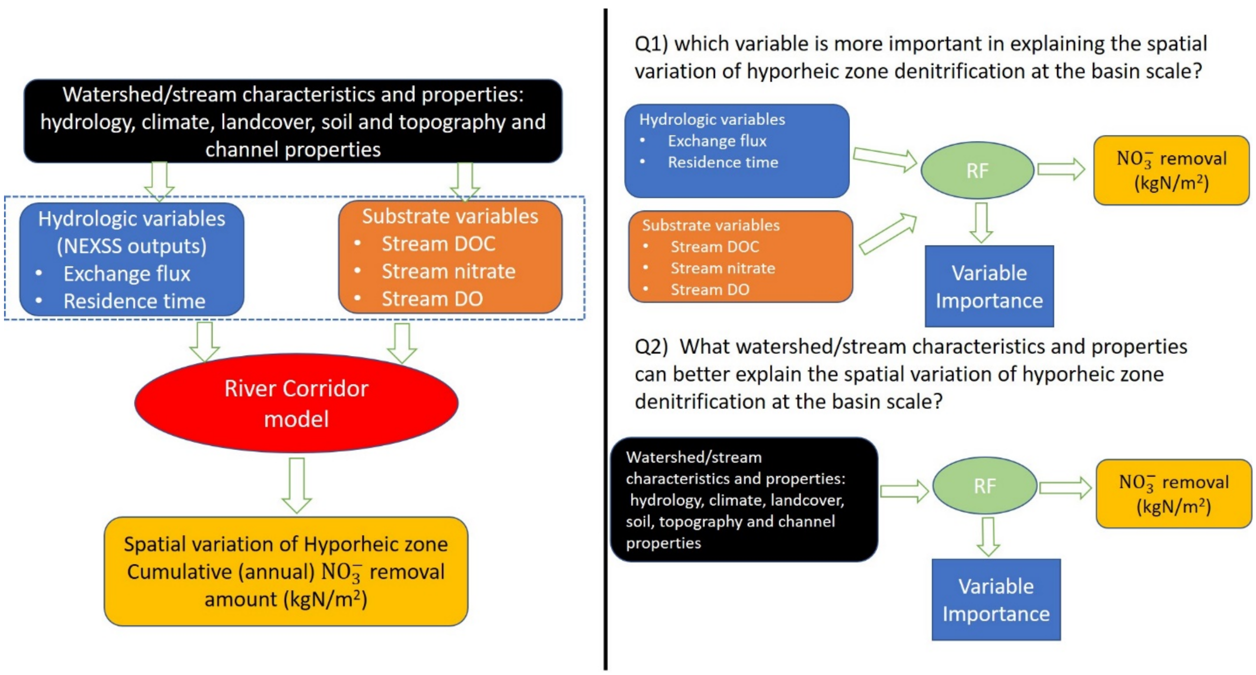

Figure 1. The framework for studying the key factors controlling the spatial variation of hyporheic zone denitrification in streams across different sizes and land uses in the Columbia River Basin.

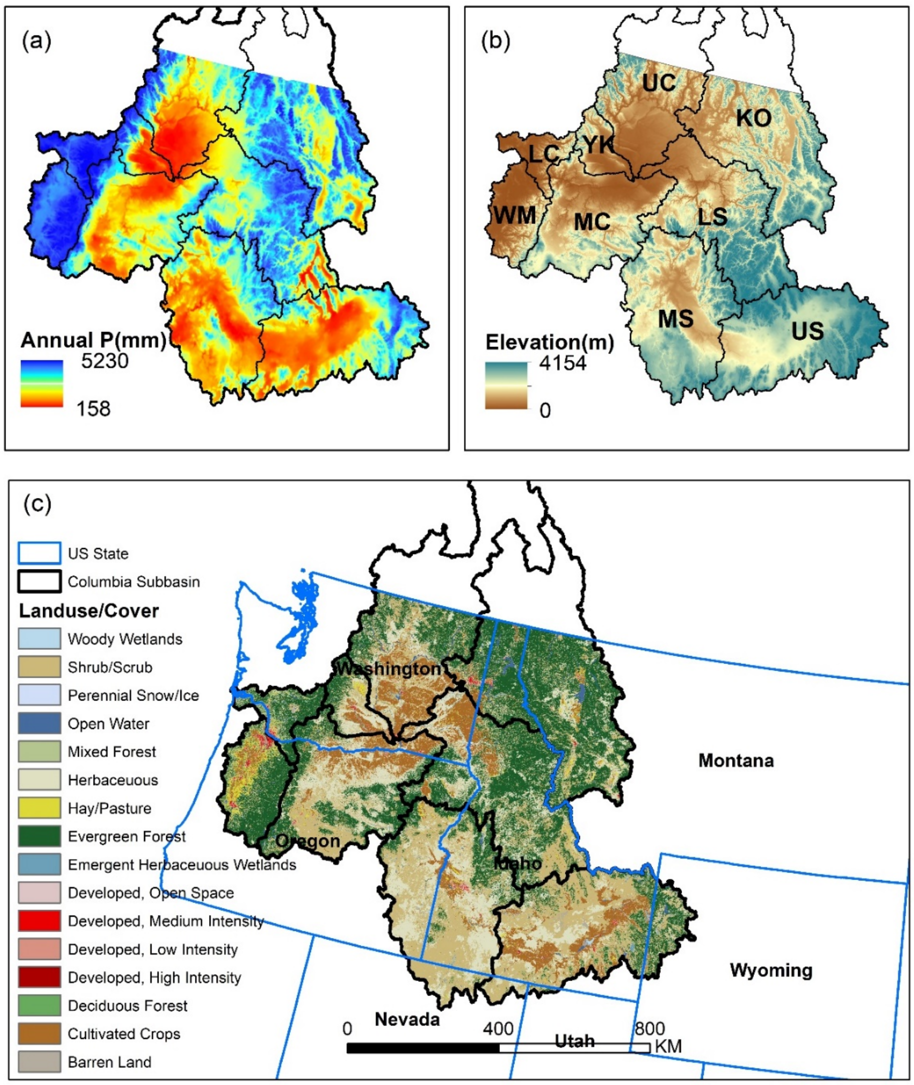

Figure 2. Columbia River Basin maps: (a) Mean annual precipitation (mm); (b) Elevation and 9 major sub-river basins: (1) Lower Columbia (LC), (2) Middle Columbia (MC), (3) Upper Columbia (UC), (4) Lower Snake (LS), (5) Middle Snake (MS), (6) Upper Snake (US), (7) Kootenai-Pend Oreille-Spokane (KO), (8) Willamette(WM), and (9) Yakima (YK); and (c) Land use and cover map (NLCD 2016 data).

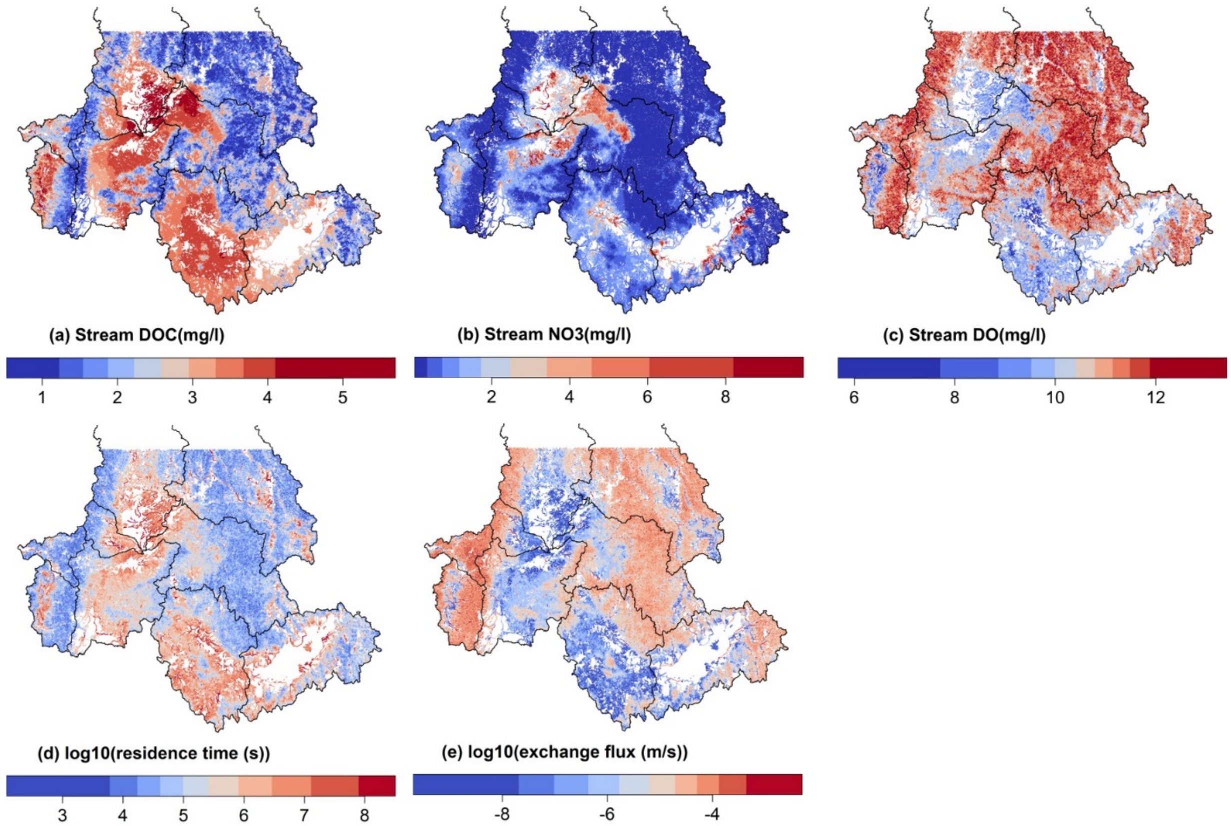

Figure 3. Key input data for the River Corridor Model: (a) Stream DOC (mg/l), (b) stream NO_3^- (mg/l), (c) stream DO (mg/l), (d) total (lateral and vertical) residence time (log10, second) and (e) total (lateral and vertical) hyporheic exchange flux (log10, m/s).

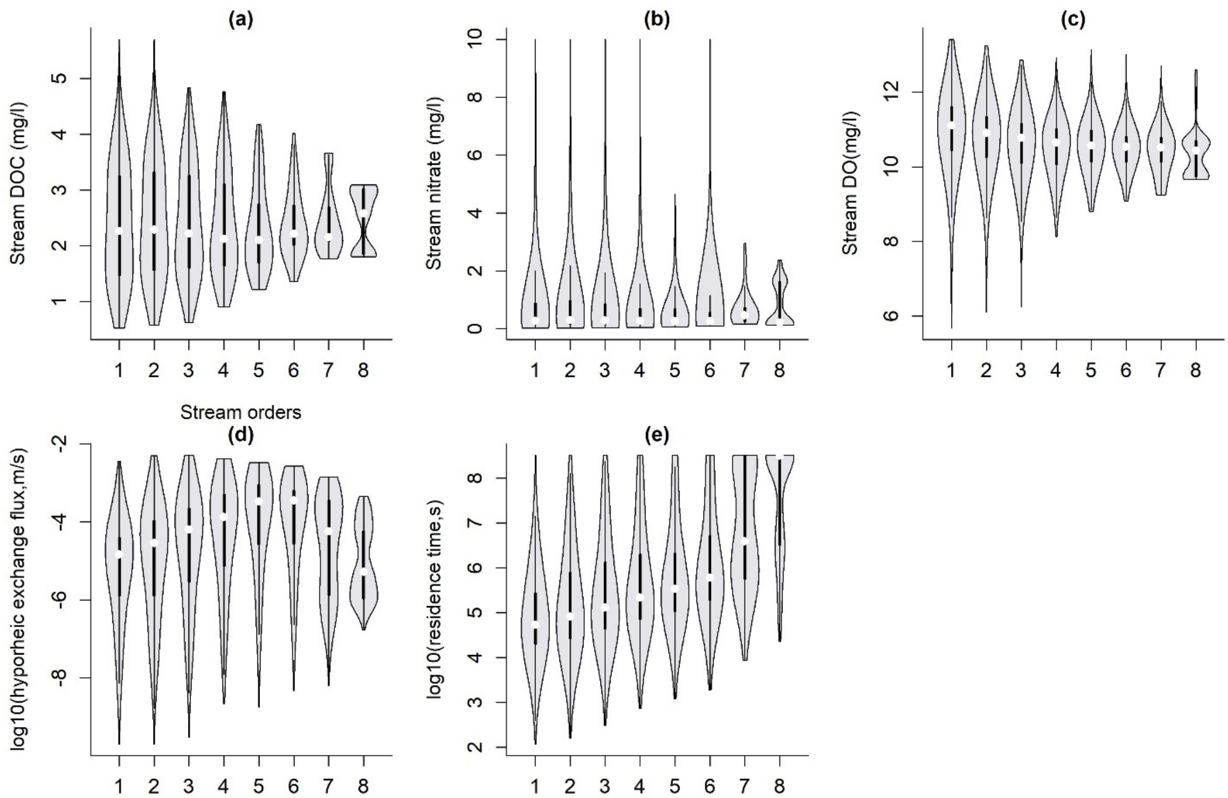

Figure 4. Distribution of key hydrologic and substrate variables in streams with stream orders. In the violine plot, the white point represents the median value, and the thick black line represents the interquartile range (Q1 and Q3), and the thin black lines represent the 1.5×interquantile range.

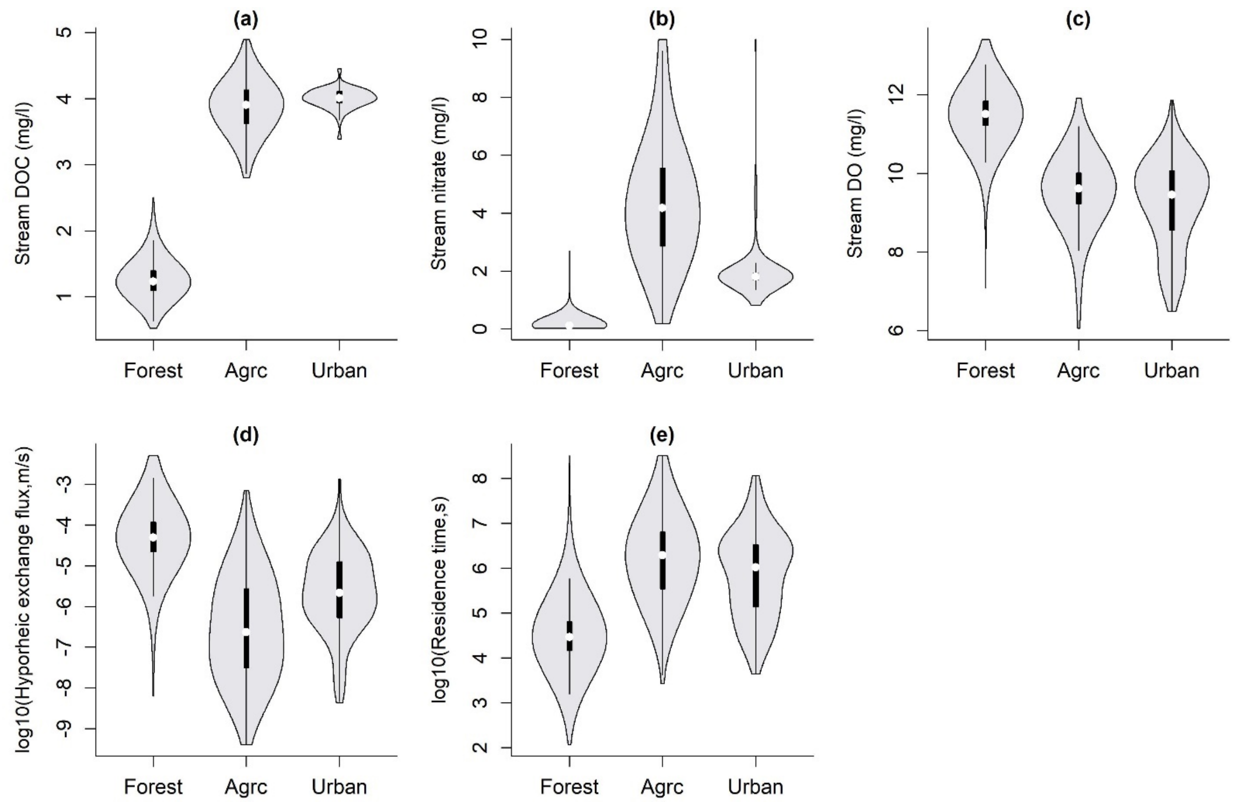

Figure 5. Distribution of key hydrologic and substrate variables in streams with different land uses. In the violine plot, the white point represents the median value, the thick black line represents the interquartile range (Q1 and Q3), and the thin black lines represent the 1.5×interquantile range.

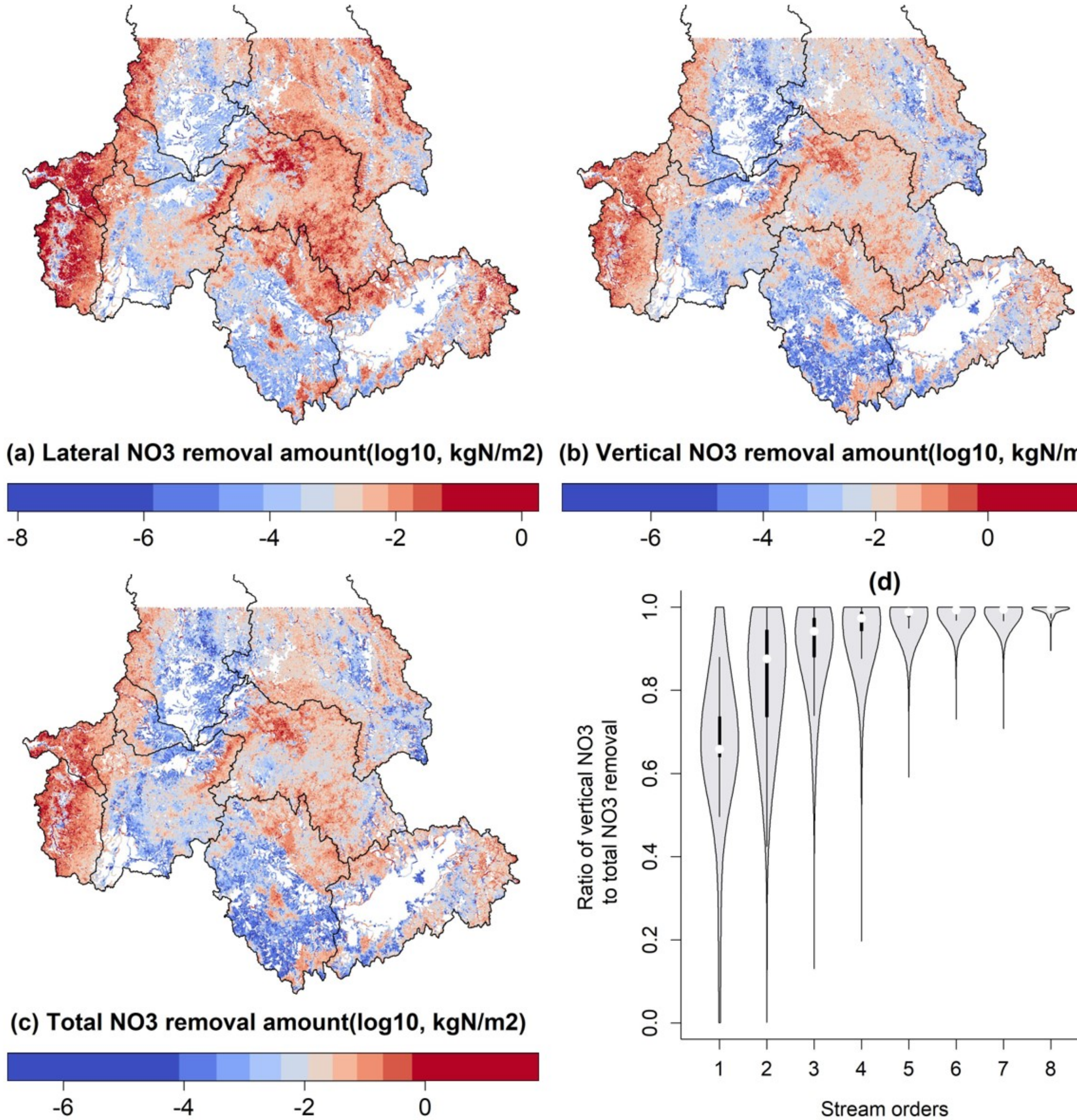

Figure 6. Spatial variation of modeled cumulative NO_3^- removal amount ($\log10(kgN/m^2)$): (a) cumulative NO_3^- removal amount via lateral hyporheic exchange, (b) cumulative NO_3^- removal amount via vertical hyporheic exchange, (c) cumulative NO_3^- removal amount via total hyporheic exchange, (d) ratio of the vertical NO_3^- removal amount to the total (vertical and lateral) NO_3^-

removal amount with the stream orders.

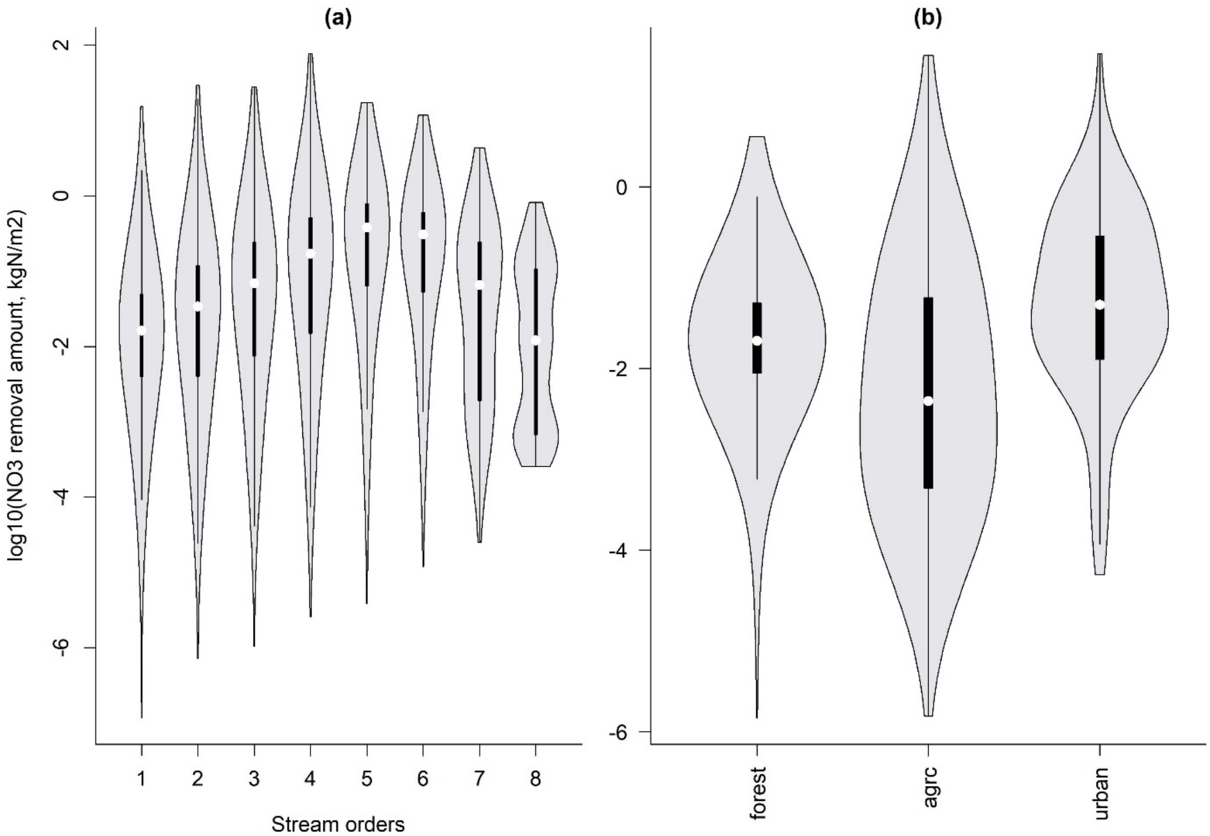

Figure 7. Variation of modeled cumulative NO_3^- removal amount with different stream orders and land uses: (a) effects of stream sizes and (b) effects of land use.

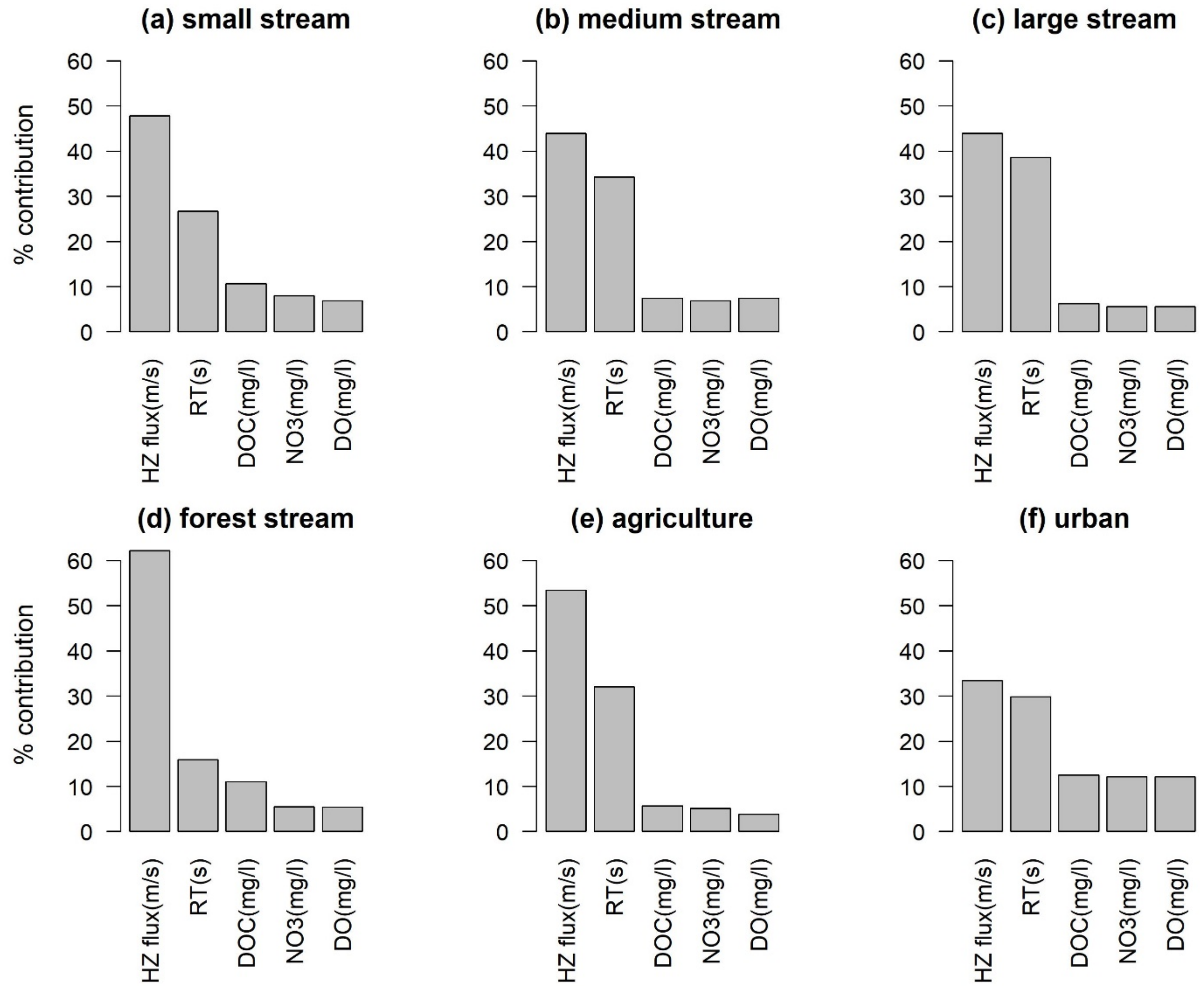

Figure 8. Relative importance of hydrologic variability and substrate availability in controlling the spatial variation of the HZ NO_3^- removal amount along different stream sizes and dominant land uses. The variable importance (measured by Ginni value) is normalized to calculate the relative importance value (% contribution) that ranges from 0 to 100.

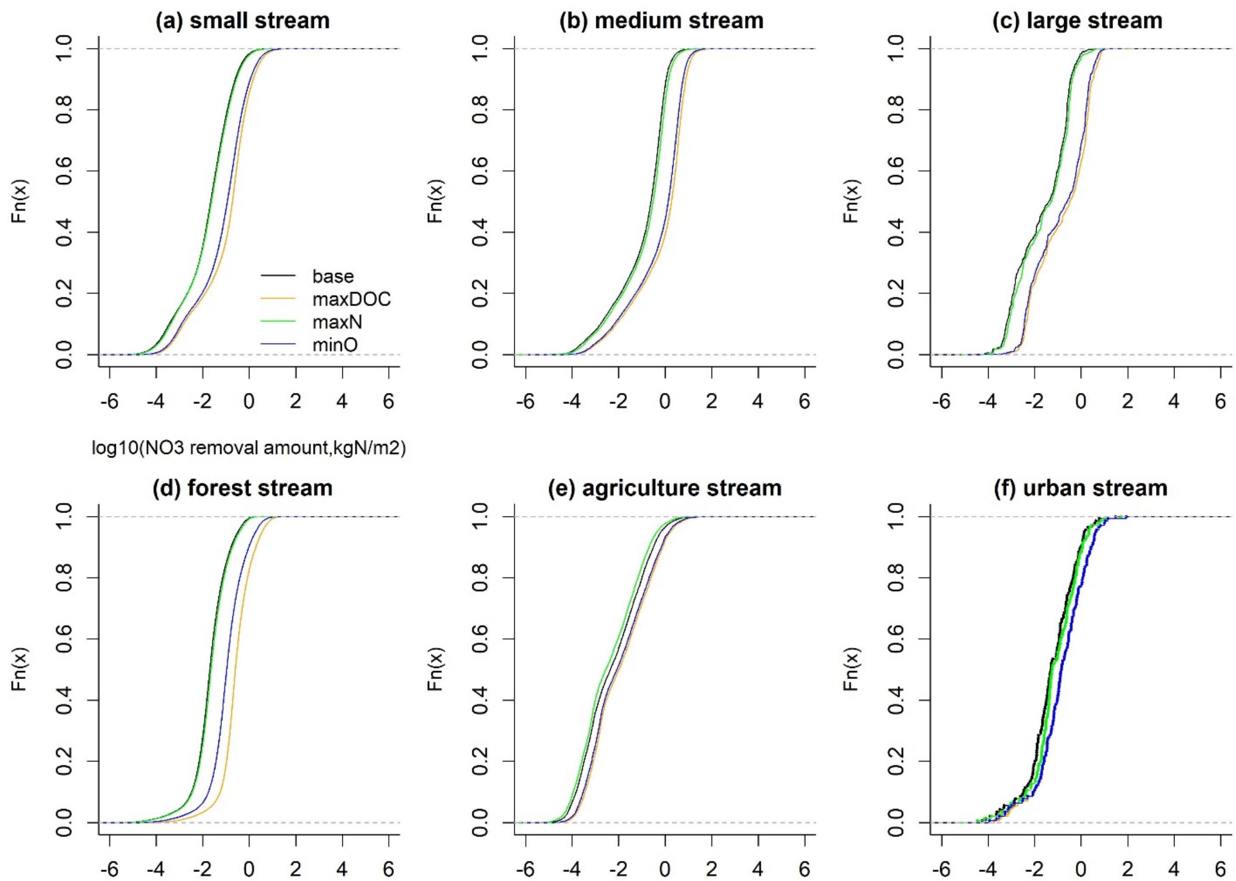

Figure 9. The sensitivity of modeled NO_3^- removal amount (log10(kgN/m^2) to the available substrate concentrations across streams with different sizes and land uses: (a) small-sized streams, (b) medium-sized streams, (c) large-sized streams, (d) forest streams, (e) agricultural streams, and (f) urban streams. The base scenarios used the modeled substrate concentration data (figure3abc). The maxDOC scenarios applied a maximum concentration of modeled DOC (figure3a) to all streams, and the maxN scenario applied a maximum concentration of modeled NO_3^- (figure 3b) to all streams, and the minO scenarios applied a minimum concentration of modeled DO (figure 3c) to all streams.

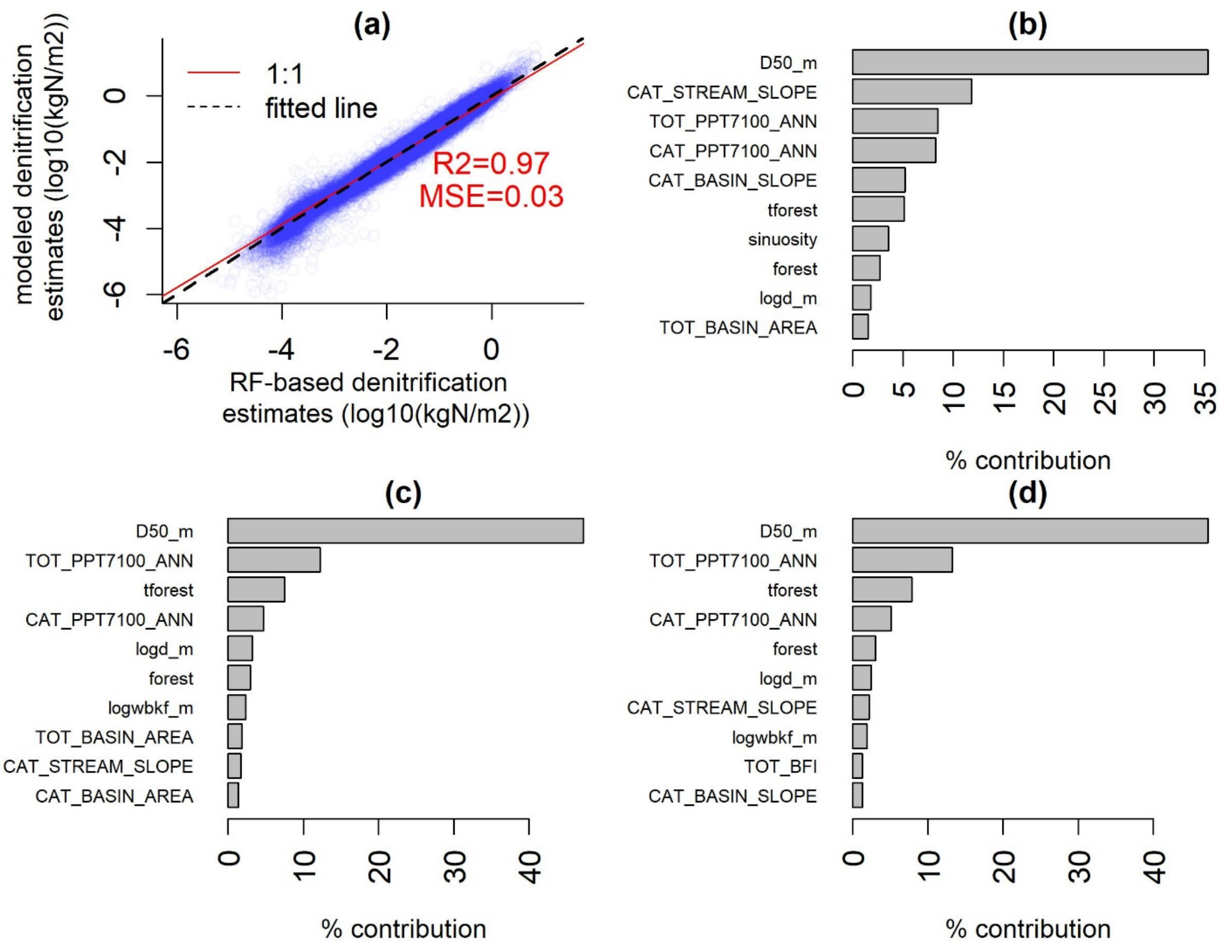

Figure 10. The predictions of the random forest model in the testing period and variable importance analysis results: (a) test results for the total NO_3^- removal amount, (b) top-ten importance variables for lateral NO_3^- removal amount (kgN/m^2), (c) top-ten important variables for modeled vertical NO_3^- removal amount (kgN/m^2), and (d) top-ten important variables for modeled total NO_3^- removal amount (kgN/m^2). The top-ten variables are D50_m (median grain size), TOT_PPT100_ANN (30-year mean annual precipitation at the NHD cumulated drainage area), tforest (percent of forest area at the NHD cumulated drainage area), CAT_PPT (30-year mean annual precipitation at the NHD catchment drainage area), forest (percent of forest area at the NHD catchment area, logd_m (log10(stream depth.,m)), logwbkf_m (log10(bankfull depth, m)), sinuosity (stream sinuosity), TOT_BASIN_AREA (NHD cumulated drainage area,) CAT_BASIN_AREA (NHD catchment drainage area), and CAT_STREAM_SLOPE (NHD catchment stream slope).

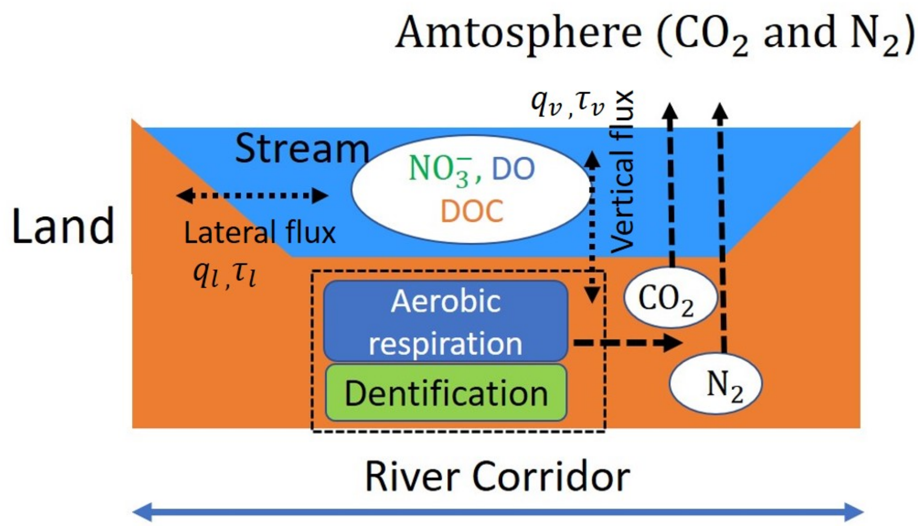

Figure A1. The simplified conceptual diagram of River Corridor model (RCM): stream dissolved organic carbon (DOC), dissolved oxygen (DO) and NO_3^- concentrations were estimated by the two regression models, and the SPARROW 2012 model, and the vertical and lateral exchange fluxes (q_v, q_l) and their median residence times(τ_v, τ_l) between the streams and hyporheic zone were estimated from the NEXSS modeling(Gomez-Velez et al., 2015).