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Quantifying the Temperature Dependence of Nitrate Reduction in Woodchip Bioreactors: Experimental and Modeled Results with Applied Case-Study

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Abstract

Temperature significantly influences nitrate removal rates in woodchip bioreactors (WBRs), which are increasingly being adopted as engineered natural treatment systems for urban stormwater, agricultural drainage, and wastewater. In this study, three replicate columns with 15-month aged woodchips were operated under steady-state conditions with a synthetic stormwater matrix at three measured flow rates and in four temperature-controlled settings (4-30 °C). Dissolved oxygen (DO), nitrate, and dissolved organic carbon (DOC) concentrations were measured along the depth profiles of the columns. Temperature explained 45% of the variance in the measured nitrate removal rates and 40% of the variance in the measured DOC production rates. We used these data to adapt our previously-developed and validated WBR mechanistic model for different temperatures, flow rates, and influent nitrate concentrations. DO inhibition influenced nitrate removal rates at influent nitrate concentrations <2 mg-N L^{-1}; above that, nitrate removal could be effectively modeled as a zero-order reaction with temperature dependence using a simplified Arrhenius equation with a temperature coefficient (θ) of 1.16. The high temperature dependence suggests WBRs may be most cost / space efficient in applications with elevated water temperatures, such as wastewater effluent. We applied WBRs to a case study scenario site in Sonoma County, California. Temperature and variable flow led to a 3-6X higher annual nitrate removal rate in wastewater effluent than stormwater. Comparing nitrogen removal technologies, WBRs were the lowest cost per kg N removed using existing infrastructure to comply with future wastewater N restrictions to San Francisco Bay in a cost-efficient, environmentally-friendly manner.

Water Impact Statement:

Nitrate is a foremost ecological and human-health water quality concern. Woodchip bioreactors are being implemented to remove nitrate from water sources (e.g., stormwater, wastewater, and agriculture), but understanding and optimization these bioreactors is vastly underdeveloped. We quantify the temperature dependence of nitrate removal using robust experimental results and mechanistic modeling to increase predictive capacity and apply to a case study.

1. Introduction

Woodchip bioreactors (WBRs) are becoming an increasingly popular technology for controlling nitrate export from agriculture runoff,[1,2] urban stormwater,[3] aquaculture effluent,[4] and wastewater.[5] Several Midwestern states have recognized the potential of woodchips for managing nitrate and have adopted design guidelines for WBRs in their nutrient reduction strategies (*e.g.*, Iowa Nutrient Reduction Strategy). WBRs are also being integrated with bioretention for urban stormwater runoff.[3,6] Microbial denitrification for nitrate mass removal rather than mere stormwater capture and infiltration of nitrate is a goal of green infrastructure management,[7,8] and increasing mechanistic understanding of such bioreactors is desired to optimize removal of multiple pollutants.[9,10] WBRs work by facilitating microbial denitrification using the woodchips as a growth surface, carbon source, and electron donor under anaerobic conditions; woodchips are a popular medium due to their long lifespan.[2]

Effective design of WBRs requires understanding processes that govern nitrate removal rates. Several factors identified that affect nitrate removal performance include woodchip age,[11,12] wood volume,[13] residence time,[14] and temperature.[15] Of these factors, temperature is believed to have the largest effect on performance due to mainly to the fact that microbial denitrification is highly temperature sensitive.[16] A multivariate analysis of predictor variables determined that temperature alone explained 50% of the variance in nitrate reduction rates in laboratory columns filled with a mixture of sawdust and sand, with the other variables (*e.g.*, surface area, cellulose, etc.) accounting for only 1-2% each.[13] Additionally, a meta-analysis of 26 published studies and 57 separate bioreactor units reported temperature had a greater effect on nitrate removal rates than influent nitrate

concentration, wood type, and woodchip age.[11] Warneke et al.[1] reported that abundance of denitrifying genes in WBRs under cold conditions were consistent between experiments, whereas under warm conditions functional genes varied substantially, demonstrating the critical role of the microbial communities. Complex, dynamic microbial communities are likely to develop in the WBRs due to the different redox conditions;[1,2,17] for example, some portion of the reactor is aerobic to exhaust available oxygen and the majority is anaerobic to facilitate denitrification. Denitrification is likely to be the more temperature sensitive microbial process.[16]

Microbial denitrification reaction rate temperature dependence can be modeled with the Arrhenius equation,[16] which takes the simplified form:

$$R_2 = R_1\theta^{T_2 - T_1} \quad (1)$$

where R_2 is the reaction rate (mg L^{-1} h^{-1}) at temperature T_2 (°C), R_1 is the reaction rate (mg L^{-1} h^{-1}) at temperature T_1 (°C), and θ is the temperature coefficient (-). The reaction rate's dependence on temperature can be expressed in the form of a Q_{10} value, the factor by which the reaction rate changes for a 10 °C change in temperature. Q_{10} is expressed as $Q_{10} = (R_2/R_1)^{10/(T_2 - T_1)}$, where the Q_{10} value and the temperature coefficient, θ, are related by $Q_{10} = \theta^{10}$. A wide range of Q_{10} values have been reported in the literature for wood-based denitrification reactors; for example, reported Q_{10} values range from 1.7 for softwood chips aged over 10 months in experimental barrels,[18] 2.0 for a field-scale woodchip reactor treating effluent from a hydroponic greenhouse,[19] 4.7 for experimental mesocosms filled with sand/sawdust mixtures,[13,20] to 4.95 in 15 year-old sawdust columns.[20] A meta-analysis of 26 published studies calculated an overall Q_{10} of 2.15, albeit with large variation.[11]

A number of factors may explain the wide range of reported temperature effects. Most of the Q_{10} values reported in the literature were determined from field or pilot scale WBRs. Field scale reactors, especially in agricultural drainage applications, can experience rapidly changing flow conditions.[21] Fluctuating flow conditions can decrease the performance of WBRs compared to more steady-state reactors;[22] alternatively, nitrate removal rates can be overestimated when samples are collected during the overturn and flushing out of old water from the woodchips following dry periods.[23] Additionally, woodchips in field-scale reactors age unevenly, with woodchips at the bottom of the reactor experiencing much longer periods of saturation than woodchips at the top,[24] and the level of saturation in field reactors is rarely known.[21] Woodchips that have been saturated for less than one year have a significantly higher nitrate removal rate than woodchips one year or older,[11,12] making determination of the relative impact of different variables on nitrate removal rates difficult. Lastly, many field or pilot scale WBR studies suffer from sparse spatial and temporal data collection with measurements only taken at the influent and effluent,[18,23,25] or replicate measurements are unreliable due to the constantly changing conditions. Of the laboratory-scale studies that consider temperature, temperature is either not controlled or data collection is sparse. For example, Schmidt and Clark[13] measured the effects of temperature on nitrate removal in several sand/sawdust mixture columns, but relied on fluctuating groundwater temperature rather than explicitly controlling water temperature. Hoover et al.[15] performed the only temperature-controlled WBR study to date of which we are aware, but only measured influent and effluent nitrate concentrations. A more accurate measure of temperature dependence on the nitrate removal rate in WBRs is needed to improve performance predictability and mechanistic understanding.

Inconsistent field conditions and insufficient data when measuring nitrate removal rates have also led to disagreement regarding the most appropriate model to predict nitrate removal performance. Although many studies support a zero-order reaction rate in WBRs,[12,19,26] several other reaction models have been proposed, including the use of a first-order rate,[27] Michaelis-Menten kinetics,[15,28] and a dual porosity model with either first- or zero-order kinetics.[25] In recently published work,[29] we quantitatively compared five different mechanistic reactive transport models for laboratory-controlled aged woodchip columns at varying measured flow rates and influent nitrate concentrations (with training and cross-validating the models), and determined that at 21 °C nitrate removal can be effectively simplified to zero-order kinetics. Nevertheless, it is unclear whether such a zero-order reaction rate remains robust at all environmentally relevant temperatures, flow rates, and influent nitrate concentrations. For example, dissolved oxygen (DO) inhibition may become more influential at temperatures below 21 °C, both because DO has a higher saturation at lower temperatures and the aerobic respiration rate may slow. Additionally, at low influent nitrate concentrations, aerobic respiration may occur in a proportionally larger fraction of the reactor than denitrification. Under these conditions, DO inhibition may need to be included in the nitrate removal model. At temperatures above 21°C, dissolved organic carbon (DOC) production in the woodchips may increase and the reaction may shift from carbon-limited to nitrate-limited.

One promising yet relatively uninvestigated application for WBRs is removing nitrate from wastewater effluent. Wastewater effluent is likely to have higher temperature and more consistent flow patterns than stormwater runoff or agricultural tile drainage, factors known increase nitrate removal rates in WBRs.[13,20,22] Despite these advantages, few studies

have examined WBRs to treat wastewater effluent, and of those, none have investigated the use of WBRs to treat nitrified effluent from a medium-size wastewater treatment plant (WWTP). Meffe et al.[30] investigated the use of woodchips to treat synthetic wastewater in a lab-scale vegetated filter, but the data were not used to extrapolate how WBRs would perform on a larger scale. Likewise, Leverenz et al.[27] measured nitrate removal in an anoxic subsurface wetland filled with woodchips to treat septic wastewater, but also did not apply these findings to a larger scale.

The central objectives of this laboratory and modeling study were expand our previously developed and validated mechanistic WBR models to: (1) quantify the temperatures, flow rates, and influent nitrate concentrations where a parsimonious model can be effectively applied, (2) determine the temperature coefficient for the denitrification reaction under laboratory-controlled conditions, (3) apply the temperature-inclusive model to a case study. To answer these central questions, three replicate woodchip columns were each fed an artificial stormwater matrix at different flow rates and operated sequentially in four temperature-controlled rooms. DO, nitrate, and DOC concentration profile data were analyzed to determine the influence of DOC and DO concentrations on nitrate removal rates. The data were used to develop two denitrification models to further quantify the effects of DO inhibition on nitrate removal rates and determine a temperature coefficient, θ, for denitrification within the experimental columns. We then applied the laboratory and model results to a case study (Sonoma, CA) to compare reactor size and cost effectiveness of WBRs for nitrate removal from wastewater effluent and stormwater runoff. The case study demonstrates promise of WBRs for nitrate removal from wastewater and justify the

need for more research of WBRs as a viable technology for removing nitrate from the nitrified effluent of medium-sized WWTPs.

2 Materials and methods

2.1 Experimental design

The general experimental set-up for the columns used in this study was described in our previously published work.[29] Briefly, woodchips were collected from an arborist waste pile in Portola Valley, CA, and dried at 50 °C for 48 hours in a drying oven then sieved to a diameter between 2 mm and 10 mm. The woodchips comprised a mix of species including California redwood, coastal live oak, valley oak, and Douglas fir. Woodchip type and particle size have been shown in other researchers' work to have no significant effect on nitrate removal rates;[12,15] thus, additional woodchip composition analysis was not performed. Other researchers have examined the impacts of alternative carbon substates;[1] this study is limited to woodchips. Three PVC columns (50 cm x 10 cm ID) were mounted on a vertical rack and evenly packed with the dried and sieved woodchips (Figures S1). Each column was packed with 700 g of dried woodchips, corresponding to a packing density of 0.18 g cm^{-3}. After experiments were complete, drainable porosity of the columns was determined by draining the columns from the bottom for 1 h, quantifying the drained water gravimetrically, and then subtracting the volume of the bottom cap from the total volume drained. Woodchips were removed from the column and specific retention was determined by measuring the difference between the wet and dry media following 48 h in a 50 ° C drying oven. Total porosity the sum of drainable porosity and specific retention. Drainable porosity and specific retention of the columns (mean±SD) was 0.54 ± 0.05 and

0.33 ± 0.02, respectively (Table S2). Sample ports (Figure S2) were installed every 5 cm along the length of the columns, starting at the inlet and ending at the outlet at 50 cm for a total of 11 sample ports per column.

The three columns were operated in a temperature-controlled room at 21 °C, followed by 15 °C, 4 °C, and finally 30 °C. In each temperature-controlled room, the columns were run for one week to equilibrate the stormwater matrix with ambient temperature conditions and achieve steady-state operation.[29] The columns were operated in up-flow mode with three variable speed digital peristaltic pumps (Masterflex). The columns were fed an artificial stormwater matrix composed of 0.75 mM $CaCl_2$, 0.075 mM $MgCl_2$, 0.33 mM Na_2SO_4, 1.0 mM $NaHCO_3$, representing the average concentration of major ions in urban stormwater.[31] $NaNO_3$ was added to the stormwater matrix to achieve an influent nitrate concentration of 5 mg-N L^{-1}. Each column was operated at a different flow rate (Table S2). The relationship between flow rate, porewater velocity, and dispersion coefficient of each column was determined previously[29] by bromide tracer tests (Figure S3, 99% Br mass recovery; Table S1, Table S2). Actual hydraulic residence time (HRT) ($\bar{t}$) was calculated as $\bar{t} = L/\upsilon$ where L is reactor length (cm) and ν is porewater velocity (cm h^{-1}). Prior to this experiment, the woodchip columns remained fully saturated and in continuous operation for over 15 months to condition the systems.

2.2 Sampling and analysis

The columns were sampled at each port for DO, nitrate, and DOC four times over the course of one week to obtain steady-state replicate measurements, as presented in the sampling approach and procedure presented in Halaburka et al.[29] Thus, four replicates were collected from the reactors at three different flow rates and four different ambient

temperatures for a total of 12 different data sets. For each sampling event, samples were collected from all sample ports as well as the artificial stormwater matrix tank to verify the stability of the solution. DOC and nitrate samples were collected starting at the top-most sample port (at outlet) and moving downward (toward inlet) such that each sample was representative of the porewater at or just above the sample port. Fifteen milliliters of sample were collected in a 25 mL plastic syringe and filtered using a sterile 0.45 μm PVDF filter into a 24 mL glass vial baked at 450 °C for four hours in a muffle furnace. All samples were analyzed within four hours of sample collection and in random order using a random number generator. Nitrate was measured using a WestCo SmartChem 200 Discrete Analyzer (detection limit: 0.05 mg-N L^{-1}). DOC was measured using a Shimadzu TOC-L Autoanalyzer. DO was measured *in situ* using a Unisense dissolved oxygen needle probe (model DO-NP) and the Unisense SensorTrace Software.

2.3 Experimental data analysis

Data distributions were tested using both the Shapiro-Wilk normality test and the D'Agostino & Pearson omnibus normality test (α=0.05 for each test) to determine if the data distribution differed significantly from a normal distribution. Data were not significantly different from a normal distribution using either test ($p>0.05$). One-way analysis of variance (ANOVA) or the Student's t-test was conducted to assess systematic differences between multiple groups or between two groups, respectively (α=0.05). A Tukey−Kramer post-test (sample-size adjusted total α=0.05) was used to perform comparisons if ANOVA revealed significant differences ($p<0.05$). Linear departure from the null slope of DOC or nitrate concentrations over the column length was used to determine if DOC export or denitrification rates were significant from zero (α=0.05). Two-

way ANOVA (α=0.05) was employed to determine how measured results were affected by two different factors (*e.g.*, the fraction of variance in nitrate concentrations explained by porewater velocity and temperature). The Spearman Rank correlation coefficients (Rho) were calculated between nitrate, DO, and DOC concentrations. Principal component analysis (PCA) was conducted to visualize relationships between the variables projected onto the 2-dimensional space defined by the two greatest-magnitude Eigenvectors. All statistical analysis / data post-processing was conducted in GraphPad Prism version 7 (La Jolla, CA) and Statistica 13.1 (Dell, Inc. Tulsa, OK).

2.4 DO inhibition model

We created a parameterized denitrification model that included DO inhibition to calculate the relative importance of DO inhibition on the overall nitrate removal rate at different temperatures, flow rates, and influent nitrate concentrations. This WBR denitrification model with DO inhibition was adapted from our prior model[29] (described in the ESI) to include temperature dependence using the Arrhenius equation (Equation 1). Our prior model was trained using specific experimental data sets and cross-validating with other data sets, then error and sensitivity analysis was quantified, allowing us to determine key parameters.[29] The objective of this prior model, and concomitantly this model, was to create the most parsimonious model,[32] i.e., fewest parameters that accurately described the phenomena observed to avoid over-constraining. The model described herein therefore builds upon our prior validated mechanistic model and incorporates a temperature dependence term through the well-established Arrhenius equation. DOC is not included in the model because including a DOC term in our previous research using this reactor setup

did not significantly reduce model error.[29] The modified WBR denitrification model with DO inhibition takes the form below:

Dissolved Oxygen: *(DO Inhibition Model)*

$$0 = D\frac{\partial^2 O}{\partial x^2} - \nu\frac{\partial O}{\partial x} - V_{O,21°C}\theta_O{}^{T-21}\left(\frac{O}{Ko + O}\right) \quad (2)$$

Nitrate:

$$0 = D\frac{\partial^2 N}{\partial x^2} - \nu\frac{\partial N}{\partial x} - V_{N,21°C}\theta_N{}^{T-21}\left(\frac{N}{K_N + N}\right)\left(\frac{K_I}{K_I + O}\right) \quad (3)$$

where O is DO concentration (mg-O_2 L^{-1}), N is nitrate concentration (mg-N L^{-1}), ν is linear pore water velocity (cm hr^{-1}), D is the dispersion coefficient (cm^2 hr^{-1}), x is linear distance (cm), K_O is the DO half-saturation constant (mg-O_2 L^{-1}), K_N is the nitrate half-saturation constant (mg-N L^{-1}), K_I is the DO inhibition constant (mg-O_2 L^{-1}), $V_{O,21°C}$ is the maximum uptake rate of DO for aerobic respiration at 21 °C (mg-O_2 L^{-1} h^{-1}), $V_{N,21°C}$ is the maximum uptake rate of nitrate for denitrification at 21 °C (mg-N L^{-1} h^{-1}), θ_O is the temperature coefficient for aerobic respiration (-), θ_N is the temperature coefficient for denitrification (-), and T is water temperature (°C). This temperature value was applied here to be consistent with at least one of the column experimental conditions and our prior model[29] while being environmentally relevant; however, using the theta, one could adjust the system to be inclusive of different conditions.

The above system of partial differential equations was solved at steady-state using the central finite-difference method in Matlab (The Mathworks, R2014b, 8.4.0.150421) with a grid spacing of 1 cm. A fixed concentration (Dirichlet-type) boundary condition was used

at the inlet (*i.e.*, C(0) = C0), and an advection transport (Neumann-type) boundary condition was used at the effluent (i.e., dC/dx = 0). Parameter values for D, K_O, K_N, K_I, $V_{O,21°C}$, and $V_{N,21°C}$, were determined previously for the same experimental setup[29] (Table S2, Table S3). θ_O and θ_N were determined using the fminsearch() function in Matlab. The fminsearch algorithm uses the Nelder-Mead simplex algorithm as described in Lagarias et al.[33] The objective function for the algorithm was the root-mean-squared error (RMSE) between the model and experimental nitrate and DO profile concentrations; RMSE is more robust for non-linear models.[34–36] We previously trained and cross-validated the DO inhibition model[29] ("model 3'). The 12 datasets collected in this work were used to determine the temperature parameters θ_O and θ_N (Table S3) in the modified temperature dependent DO inhibition model.

The DO inhibition model was used to calculate the required reactor length to consume DO to less than 0.1 mg L^{-1} and the length required to consume nitrate to less than 0.1 mg-N L^{-1} for a given temperature and porewater velocity. The model was run at temperatures of 4 °C, 15 °C, 21 °C, and 30 °C and porewater velocities of 1.4 cm h^{-1}, 3.4 cm h^{-1}, and 8.2 cm h^{-1}, with an influent nitrate concentration of 5 mg-N L^{-1} to correspond with the experimental columns. The reactor length required to consume DO was divided by the length required to consume nitrate to determine the fraction of the column attributed to DO depletion for each scenario. The model was run again at four different influent nitrate concentrations of 0.5 mg-N L^{-1}, 2.0 mg-N L^{-1}, 5.0 mg-N L^{-1}, and 11.0 mg-N L^{-1} and porewater velocities of 1.4 cm h^{-1}, 3.4 cm h^{-1}, and 8.2 cm h^{-1}, at a temperature of 21 °C. The fraction of the column required to consume DO to less than 0.1 mg L^{-1} was similarly calculated for each of these scenarios.

2.5 Zero Order Model

Davidson and Janssens[37] reported substrate concentration must be in abundance for the Arrhenius equation and Q_{10} to be valid. Our previously reported results[29] demonstrated no significant difference (quantified by root mean square error residuals; p=0.886) for these column woodchip reactors between a zero-order model and more parameterized models using Michaelis-Menten kinetics for predicting nitrate concentrations under the tested conditions, and the zero-order model was more parsimonious. Thus, nitrate concentrations are not likely a confounding variable when calculating Q_{10}.

Nitrate removal in the experimental woodchip columns was therefore also modeled using a zero-order rate with temperature dependence using Equation 1. The model takes the form

(Zero-Order Model)

$$N = N_0 - k_{21°C}\theta^{T-21}\bar{t} \quad (4)$$

where N is nitrate concentration (mg-N L^{-1}), N_0 is influent nitrate concentration (mg-N L^{-1}), $k_{21°C}$ is the zero-order nitrate removal rate constant at 21 °C (mg-N L^{-1} h^{-1}), θ is the temperature coefficient (-), T is water temperature in the reactor (°C), and $\bar{t}$ is the actual HRT (h). $\bar{t}$ was calculated as $\bar{t} = (x/v)$, where x is linear distance along column (cm), and v is linear porewater velocity (cm h^{-1}). N was constrained such that $N \geq 0$. The value of $k_{21°C}$ was determined in prior research.[29] To estimate θ, a non-temperature dependent zero-order model was fit to each of the 12 different data sets using least-squares regression, providing three estimated zero-order reaction rates for each temperature. A least-squares regression was used to calculate the optimal temperature coefficient, θ, by fitting the zero-order temperature-dependent model to the estimated reaction rates.

2.6 Application of Model to Case Study: WBRs for Controlling Nitrate Export in Stormwater vs. Nitrified Wastewater in Sonoma, California.

We applied the temperature-responsive model developed to a case study was to identify the potential advantages of using woodchip reactors to remove nitrate from wastewater effluent versus runoff, determine whether WBRs are a viable and competitive option for removing nitrate from the nitrified effluent of a medium-size wastewater treatment plant in terms of reactor size and cost effectiveness, and identify some potential negative side-affects that should be considered in the design of a such a WBR system. Flow, temperature, and nitrate concentration data were obtained from Sonoma County Water Agency (SCWA) for Santa Rosa Creek and the Sonoma Valley County Sanitation District (SCVSD) wastewater treatment plant (WWTP) and used as a case study. Our model calculated the variability in nitrate removal rates for wastewater effluent and creek water, the relationship between reactor size and reactor performance for treating wastewater effluent, and the theoretical reduction in nitrate concentrations from wastewater effluent over the course of a year.

2.6.1 Site Descriptions

Sonoma County is a primarily agricultural region with some urban zones in Northern California located approximately 70 km north of San Francisco. The SVCSD serves an area of approximately 1,800 ha in southern Sonoma County (Figure 1), which includes the City of Sonoma and nearby unincorporated areas.[38] The WWTP treats an average dry-weather flow of 0.12 m^3 s^{-1} (2.7 MGD) using primary and secondary treatment, filtration, and disinfection.[38] The effluent from the plant is then either used for agricultural irrigation (May 1 – October 31) or is discharged to Schell or Hudeman Slough (November 1 – April

30) and eventually enters the San Francisco Bay.[38] Santa Rosa Creek passes through the City of Santa Rosa, located approximately 30 km northwest of the SVCSD WWTP. Just west of the city of Santa Rosa, Santa Rosa Creek empties into Laguna de Santa Rosa, a tributary of the Russian River, then the Pacific Ocean. Data analyzed for the creek were at Willowside Rd., upstream of the confluence with Laguna de Santa Rosa. Due to the region's Mediterranean climate, the creek is can be reasonably presumed to be primarily composed of stormwater (combination of precipitation and irrigation flows).

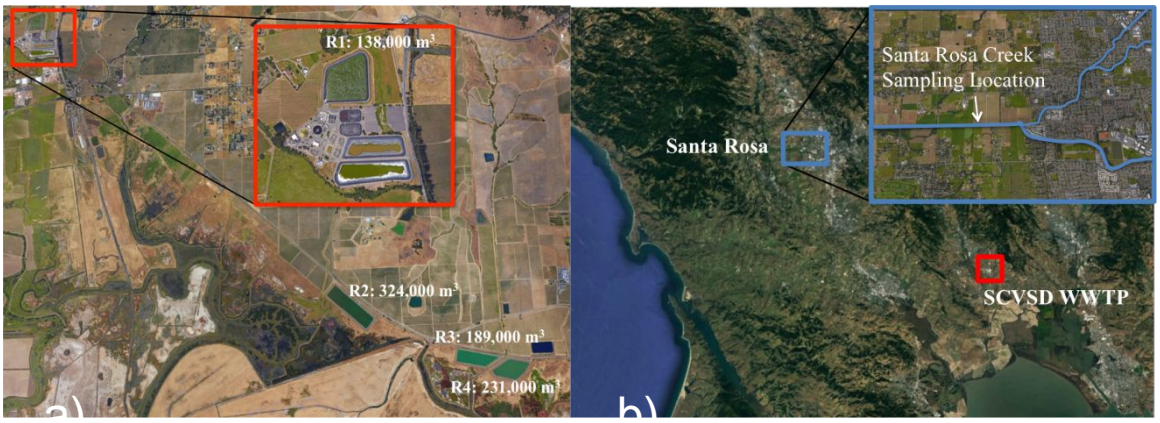

Fig. 1: (left) Sonoma Valley County Sanitation District (SCVSD) wastewater treatment plant. R1 through R4 are effluent storage basins that could be converted into woodchip bioreactors for nitrate removal. (right) Sonoma County with a magnification of Santa Rosa Creek (blue box) near the confluence with Laguna de Santa Rosa where data were collected.

2.6.2 Data Sources

Temperature, flow, and effluent nitrate concentration data for the WWTP were obtained from SCWA. Daily measurements for effluent temperature and flow were provided from January 1, 2015 to December 31, 2015. Dates missing either temperature or flow data were linearly interpolated. Weekly effluent nitrate data were provided from June 2, 2015 to May

26, 2016. Due to limited data availability, we estimated nitrate concentrations from January to June 2015 using nitrate concentrations from the same day and month in 2016, providing weekly nitrate concentration estimates from January to December 2015. To obtain daily nitrate concentrations, we assumed weekly measurements represented effluent nitrate concentrations for the whole week in which the measurement was taken. Monthly temperature and nitrate concentrations for Santa Rosa Creek were obtained from SCWA for the period from January 2011 to December 2013. Average daily streamflow data from January 1, 2011 to December 31, 2013 were obtained from the USGS National Water Information System,[39] site number 11466320.

2.6.3 Nitrogen discharge limits

New nitrate discharge limits are being set for wastewater discharges to the San Francisco Bay.[40] The new limits specify a maximum ammonia concentration of 2 mg-N L^{-1} and a maximum total nitrogen concentration of 6 mg-N L^{-1}.[40] Additionally, the new discharge limits may allow dischargers who exceed the treatment goal to sell the extra nitrogen removed in the form of nitrate credits to other dischargers who are unable to meet their goal (M. Falk, personal communication). Three scenarios investigated the potential for WBRs to meet the treatment goals of the SVCSD WWTP: (1) ammonia is completely nitrified to nitrate by optimizing plant operations and all nitrogen is in the form of nitrate; (2) the WWTP meets the 2 mg-N L^{-1} ammonia limit and all remaining nitrogen is in the form of nitrate; (3) the WWTP lowers nitrogen concentrations further in an effort to sell potential nitrogen credits to other SF Bay wastewater dischargers who are unable to meet their nitrogen limits. Under these scenarios, the SVCSD WWTP would need to lower nitrate concentrations below 6, 4, and 2 mg-N L^{-1}, respectively. The impact of reactor size

on meeting these treatment limits was calculated using daily temperature, flow, and nitrate concentration from the WWTP.

2.6.4 Calculations

Nitrate removal rates in WBRs with aged woodchips (saturated for over one year) were modeled as a zero-order reaction rate with temperature effects included in the model (Eqn. 4) using the simplified Arhennius equation.[29] Temperature, flow, and nitrate concentration data were used to estimate nitrate removal rates, reduction in nitrate concentrations, and total nitrogen removed in WBRs using the zero-order model with temperature dependence as presented in Halaburka et al.[29] The nitrate removal rate was calculated as $k = 0.13 \times 1.16^{T-21}$, where k is the nitrate removal rate (mg-N L^{-1} h^{-1}), and T is temperature (°C). The decrease in nitrate concentration was then calculated as $N_{rem} = k(n_e V_r/Q)$, where N_{rem} is the decrease in nitrate concentration (mg-N L^{-1}), n_e is the effective porosity of the reactor, Vr is the volume of the reactor (m^3), and Q is the flow rate (m^3 h^{-1}). We assumed an effective porosity of 0.75 from the average measured effective porosity from previous WBR studies;[17,29,41] we chose to use literature values rather than our measured column value to attempt to make the model more representative of likely field conditions in this case. Effluent nitrate concentration was calculated as $N_{eff} = N_0 - N_{rem}$, where N_{eff} is the effluent nitrate concentration and N_0 is the influent nitrate concentration. The total mass of nitrate removed over the course of a year was then be calculated as

$$N_{tot} = \sum_{d=1}^{365} N_{0,d} - N_{rem,d} \quad (5)$$

where N_{tot} is the mass of nitrate removed per year (kg-N yr^{-1}), d is day of the year where 1 representing January 1 and 365 representing December 31, $N_{0,d}$ is the influent nitrate

concentration at day d (mg-N L^{-1}), and $N_{rem,d}$ is the reduction in nitrate concentration at day d (mg-N L^{-1}).

3 Results and Discussion

3.1 Laboratory and Modeling Experimental Column Results.

Temperature had a substantial impact on the nitrate removal and DOC production rates measured in the experimental woodchip bioreactor columns (Table 1). Indeed, both nitrate removal rates and DOC production rates significantly increased as a function of temperature ($p=0.0228$, $p=0.0233$, respectively). Temperature explained 45% of the variance in the measured nitrate removal rates ($p<0.0001$) and 40% of the variance in the measured DOC production rates ($p<0.0001$). Nitrate and DOC rates did not significantly change with porewater velocity over the measured range ($p=0.1466$ and $p=0.2338$, respectively). Porewater velocity explained 24% of the variance in the nitrate rates ($p<0.0001$) and 16% in the DOC rates ($p<0.0001$); however, significant interaction effects between temperature and porewater velocity occurred ($p<0.0001$), suggesting that these parameters are interrelated. Interactive effects account for approximately 21% of the total variance (Table 1). We conducted principal component analysis (PCA) of the measured column data (Figure 2) to provide visual context for the data analysis in relating variables; however, PCA should be seen as a data visualization approach rather than fully-quantitative outcome (see explanation in ESI and Tables S4, S5). The first and second principal components explain 46% and 18% of the system variance, respectively. In the PCA, nitrate concentration and DO concentration appear nearly opposite to DOC concentration and temperature. Indeed, correlation analysis of continuous variables indicates that nitrate and

DOC concentrations are significantly negatively correlated (Spearman's Rho= -0.806, p<0.0001); DO and DOC concentrations are significantly negatively correlated (Spearman's Rho= -0.766, p<0.0001); whereas nitrate and DO concentrations are significantly positively correlated (Spearman's Rho=0.750, p<0.0001). In context, this means that the lower measured nitrate concentrations (and thus higher denitrification rates) are related to the presence of lower DO and higher DOC concentrations, which is consistent with basic denitrification principles.[16]

Table 1. Estimated nitrate-nitrogen ($\boldsymbol{NO_3^- - N}$) removal rate and dissolved organic carbon (DOC) production rate based on measurement for each experimental condition (temperature; effective porewater velocity, ν).

CONDITION		**NITRATE**		**DOC**	
Temp (°C)	**PWV** (cm h^{-1})	**Rate ± SE** (mg-N L^{-1} h^{-1})	Rate significant? (p-value) †	**Rate ± SE** (mg-N L^{-1} h^{-1})	Rate significant? (p-value)
4	1.4	-0.00340 ± 0.0009966	0.0015	0.00462 ± 0.00154	0.0046
4	3.4	-9.09 x 10^{-6} ± 0.000685	0.9895 **NO**	0.00422 ± 0.000767	<0.0001
4	8.2	-0.000391 ± 0.000898	0.6657 **NO**	0.00504 ± 0.00152	0.0019
15	1.4	-0.0806 ± 0.00338	<0.0001	0.0162 ± 0.00124	<0.0001
15	3.4	-0.0183 ± 0.00187	<0.0001	0.00594 ± 0.000421	<0.0001
15	8.2	-0.00652 ± 0.00209	0.0033	0.00806 ± 0.00121	<0.0001
21	1.4	-0.108 ± 0.00377	<0.0001	0.0251 ± 0.00197	<0.0001
21	3.4	-0.0415 ± 0.00165	<0.0001	0.00996 ± 0.000573	<0.0001
21	8.2	-0.0151 ± 0.00152	<0.0001	0.00958 ± 0.00133	<0.0001
30	1.4	-0.360 ± 0.0192	<0.0001	0.0898 ± 0.00924	<0.0001
30	3.4	-0.136 ± 0.0101	<0.0001	0.0371 ± 0.00482	<0.0001
30	8.2	-0.0581 ± 0.00284	<0.0001	0.0176 ± 0.000804	<0.0001
Effect* of Temperature:		45% of variance (p<0.0001)		43% of variance (p<0.0001)	
Effect of Porewater Velocity:		24% of variance (p<0.0001)		16% of variance (p<0.0001)	
Interaction Effects?		21%; **YES** (p<0.0001)		0.63%; **YES** (p<0.0001)	

†The p-value indicates significant departure from a null slope of the rate regression.

*The effect quantifies the fraction (and significance) of the total variance observed in the data explained by the given factor. Rates are calculated including data where DOC >1 mg/L

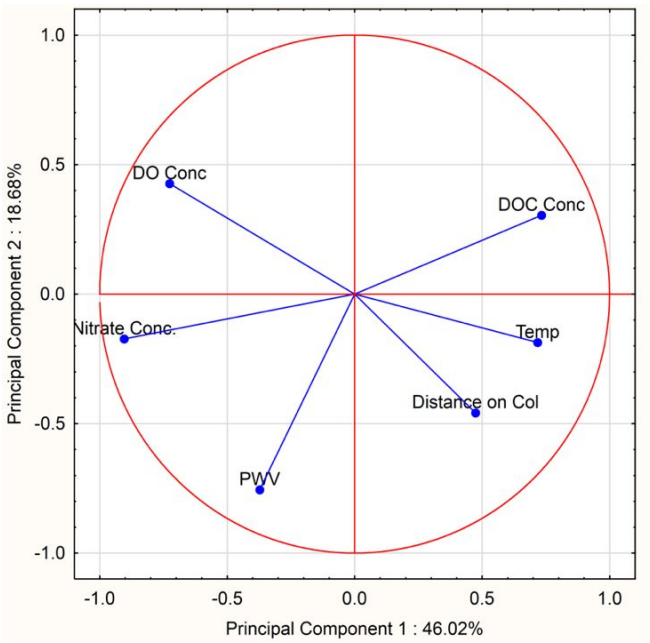

Figure 2: Principal component analysis (PCA) of the measured column data from all experiments. The first and second principal components explained 65% of the total variance in the data. The unit circle shown surrounding the vectors provides a visual scale of the variable vector magnitude; values closer to the unit circle edge are more strongly represented in the given projection. (Table S4 details the individual and cumulative Eigenvalues; Table S5 details the variable factor analysis correlation matrix. These values numerically comprise full numerical data for the above 2-dimensional PCA projection.)

Nitrate concentrations were <0.5 mg/L when DOC was >2 mg/L for all conditions tested (Figure 3), while DOC concentrations became elevated when nitrate concentrations dropped below 0.5 mg-N L^{-1}. Both Robertson[12] and our previous work[29] report similar behavior in separate experimental woodchip columns operated at 21-23.5 °C. DOC production rates remained below 0.04 mg-C L^{-1} h^{-1} for all conditions tested except where T = 30 °C and v = 1.4 cm h^{-1}, where the DOC production rate increased to 0.225 mg-C L^{-1} h^{-1} (Table 1, Figure S4). Under these latter conditions (*i.e.*, T = 30 °C and v = 1.4 cm h^{-1}), nitrate concentrations dropped below 0.5 mg-N L^{-1} at 15 cm along the column (Figure 5), creating nitrate-limiting conditions.

Nitrate concentrations in the columns decreased only after DO concentrations dropped below approximately 1 mg L^{-1} (Figure 3), indicating that DO inhibited denitrification at all temperatures tested. Nevertheless, DO concentrations >0.1 mg L^{-1} were only present in the first 10 cm of the columns for T > 15 °C (Figure 5). For T = 4 °C, DO was present at concentrations >0.1 mg L^{-1} throughout all the columns (Figure S5). This may be due both to higher saturation of DO and lower microbial activity, i.e., microbial denitrification kinetics are particularly temperature sensitive.[16] We previously reported[29] that a zero-order model resulted in similar predictive error as an advection-dispersion model where both DO inhibition and nitrate concentrations were considered for aged woodchip columns operated at 21 °C and the zero-order more was more parsimonious. Thus, although DO inhibition limited denitrification for all conditions tested, it may represent a relatively unimportant fraction of the overall reaction at warmer temperatures.

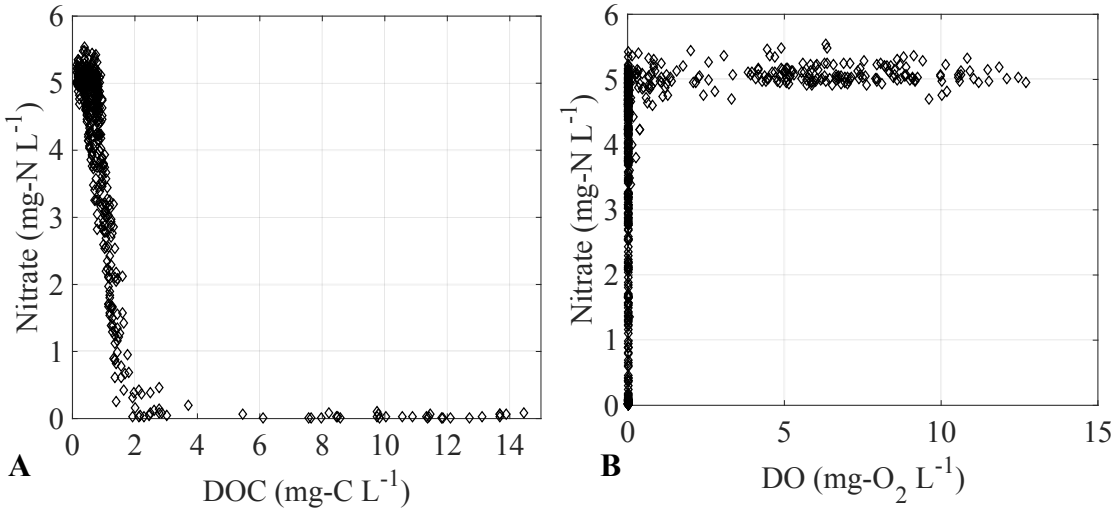

Figure 3. A) Measured (not modeled) aggregated nitrate (initial concentration= 5 mg-N L^{-1}) and corresponding dissolved organic carbon (DOC) concentration data for each temperature, porewater velocity, and sample port. **B)** Measured (not modeled) aggregated nitrate (initial concentration= 5 mg-N L^{-1}) and dissolved oxygen (DO) concentration data for each temperature, porewater velocity, and sample port. Figures represent all data points; thus, the DO=0 mg L^{-1} point contains a spread of nitrate concentrations from all points where denitrification occurred throughout the reactor.

3.2 DO inhibition model

The parameters used for the DO inhibition model are shown in Table S3. Optimal values for θ_O and θ_N were 1.20, and 1.15, respectively. These parameters are lumped values that reflect the experimental biokinetic conditions and result from the complex processes of the microbial communities; however, as stated previously for this work, we did not quantity direct changes in the microbial community on the molecular level (e.g. metagenomic sequencing or functional gene enumeration). All the experimental data were used to train the model, resulting in a model RMSE of 0.91.

The linear fraction of a reactor required to consume DO represented only 5-7% of the total WBR at different temperatures in the model (Figure 4a) at a given initial influent nitrate concentration. Temperature (over the range tested) did not significantly influence how far DO traveled into the reactor ($p = 0.345$), but porewater velocity did ($p<0.004$). Both temperature and porewater velocity were significant sources of variance ($p=0.017$ and $p=0.0006$, respectively) in the depth of DO travel, with the temperature and porewater velocity parameters accounting for 24.6% and 69% of the total variance in the data, respectively. These calculations indicate that temperature does not change the relative impact of DO inhibition on nitrate removal in WBRs, despite DO solubility increases at lower temperatures and aerobic respiration and denitrification reactions rates may not necessarily have similar temperature dependencies. Because only a relatively small fraction of the reactor is required to consume DO and facilitate subsequent operational denitrification, bulk DO inhibition on denitrification in WBRs is unlikely to substantially impact reactor operation under normal flow and loading conditions. Nevertheless, mass

transfer of DO, nutrients, and dissolved substrates through biofilms can be complex[16] and thus transport through biofilms can occur even when bulk porewater DO levels are low.

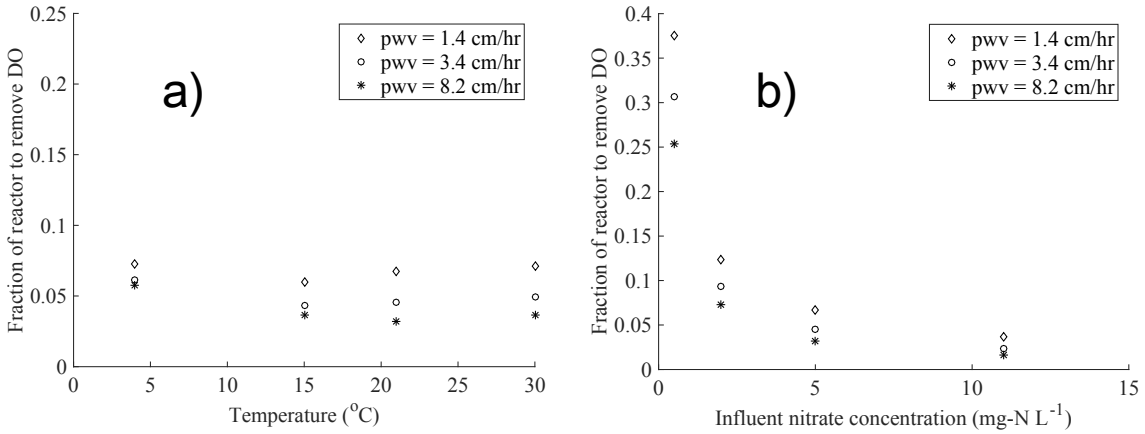

Figure 4. (a) Modeled fraction of the woodchip bioreactor required to consume dissolved oxygen (DO) at four different temperatures and three flow rates. The model assumes influent nitrate 5 mg-N L^{-1} and a reactor length where nitrate is fully consumed. (b) Modeled fraction of the woodchip bioreactor required for consuming dissolved oxygen (DO) at four different influent nitrate concentrations and three flow rates. Note that the modeled fraction to remove DO assumes full exhaustion of DO and then nitrate; thus, this fractional approach incorporates different length modeled reactors for normalization and dispersion effects cause the porewater velocity results pictured.

Model results demonstrate the linear fraction of reactor required to consume DO increased as influent nitrate concentration decreased (Figure 4). At an influent nitrate concentration of 2 mg-N L^{-1}, for example, the linear fraction of the reactor dedicated to aerobic respiration represented 8-12% of the reactor length. Influent nitrate concentration had a significant impact on the linear fraction of reactor required to consume DO ($p < 0.001$). Although both porewater velocity and influent nitrate concentration were significant sources of variance ($p=0.031$ and $p<0.001$, respectively), initial nitrate concentration accounted for 94% of the variance whereas porewater velocity accounted for

only 4% of variance. Thus, the higher fraction of the reactor required to consume DO (Figure 4b) at influent nitrate concentrations below 2 mg-N L^{-1} suggests DO inhibition should be included as a model parameter to increase model accuracy under low initial nitrate conditions but is not necessary at under most conditions. It should be noted that the modeled fraction to remove DO (y-axis of Figure 4) assumes full exhaustion of DO and then nitrate; this fractional approach incorporates different length modeled reactors for normalized comparison purposes. Dispersion effects cause the differential porewater velocity impacts as shown in Figure 4, which have greater impacts at lower velocities.

Under low influent nitrate concentrations ($N_0 < 2$ mg-N L^{-1}), DO consumption by aerobic bacteria requires a substantial fraction of the carbon released from woodchips. For example, the model indicates up to 37% of the carbon in a reactor would be consumed by aerobic respiration at an influent nitrate concentration of 0.5 mg-N L^{-1} (Figure 4). Thus, WBRs may achieve higher removal rates where nitrate concentrations are consistently above 2 mg-N L^{-1}. Applications that meet this requirement include agricultural drainage (*i.e.,* dairy effluent, greenhouse effluent, and field tile drainage), where nitrate concentrations[2,12,42] can range from 5 up to 250 mg-N L^{-1}; wastewater effluent with nitrate concentrations[43] from 15 to 20 mg-N L^{-1}; and aquaculture effluent[4,44] with nitrate concentrations ranging from 5 to 150 mg-N L^{-1}. Urban stormwater, in contrast, may not be an ideal application for WBRs. Urban stormwater runoff[3,45–48] has lower nitrate concentrations (typical values: 0.1 to 4.8 mg-N L^{-1}, median = 0.6 mg-N L^{-1}), thus a substantial proportion of carbon will be consumed through aerobic respiration (approximately 3-35%; Figure 4b). Additionally, woodchips exposed to aerobic conditions degrade much faster than woodchips in anaerobic conditions,[24] requiring more frequent

replenishment. Treating low-concentration nitrate pollution sources, such urban runoff, is nevertheless important for protecting ecosystem health, as total nitrogen levels above 0.5-1.0 can result in eutrophication in coastal waters.[49] Nevertheless, alternative engineered natural treatment systems may be better suited for these applications.

We did not directly measure microbial populations or quantify markers of denitrification genes[8] in this study, which would add another perspective on understanding the systems, but was beyond the scope of this work. Some denitrifying organisms are facultative aerobes and thus can use either oxygen or nitrate as their terminal electron acceptor,[16] allowing flexibility within the microbial community for varied redox conditions. This would be particularly applicable to the need to consume DO and respire nitrate in the same reactor. Some previous research has demonstrated that temperature in a WBR has a greater impact on increased denitrification genes than does woodchip type or alternative carbon sources;[1] however, the complex and essential role of the microbial communities in WBRs cannot be ignored in the context of explaining temperature-dependent denitrification.

3.3 Zero-order model

A zero-order model was calibrated for each test condition for a total of 12 different zero-order reaction rates. The calibrated models described nitrate concentrations in the experimental columns at all temperatures and flow rates tested with a mean RMSE = 0.21 (Figure 5). The temperature-dependent zero-order model was fit to the experimentally-measured estimated nitrate removal rates, resulting in a temperature coefficient, θ, of 1.16 and a $k_{21^{\circ}C}$ of 0.13 mg-N L^{-1} h^{-1} (Figure 6). A temperature coefficient of 1.16 corresponds to a Q_{10} of 4.41, comparable to what other researcher have determined under similarly

controlled temperature and flow conditions. Schmidt and Clark[13] reported a Q_{10} of 4.7 for a temperature range of 7.9-24.1 °C in up-flow laboratory scale reactors filled with a mixture of sand and sawdust. Robertson et al.[20] reported an exponential relationship between reaction rate and temperature in laboratory columns filled with 15 year-old sawdust following the equation $R = 0.17e^{0.16T}$, where R is nitrate removal rate (mg-N L^{-1} h^{-1}) and T is temperature (°C). This equation corresponds to a Q_{10} of 4.95. Lower Q_{10} values have also been reported in field- or pilot-scale studies on WBRs. For example, Cameron and Schipper[18] reported an average Q_{10} of 1.7 for soft woodchips and 1.4 for hard woodchips aged over 10 months in experimental barrels. Nevertheless, some approaches employed to calculate nitrate removal rates may underestimate the true Q_{10}; indeed, measuring HRT using drainable porosity can underestimate actual HRT. Several woodchip reactors studies have reported that HRT measured using tracer tests was 33-112% greater than HRT calculated using drainable porosity.[12,18,29] Using the same experimental setup, Warneke et al.[1] reported a Q_{10} as low as 1.2 in reactors filled with maize cobs, wheat straw, green waste, sawdust, and woodchips operated at temperatures of 16.8 and 27.1 °C. The lower reported Q_{10} was also likely a result of the method used to calculate HRT. Lower temperature dependence reported for field reactors may also be a result of inaccurately measured HRT. The residence time in field- and pilot-scale reactors is commonly measured using Darcy's Law, which can be inaccurate in WBRs because field-scale reactors are prone to fluctuations in flow and saturation depth.[50,51] Additionally, inaccuracies in measuring flow and hydraulic residence time can make measuring the true nitrate removal rate of a reactor difficult.[23]

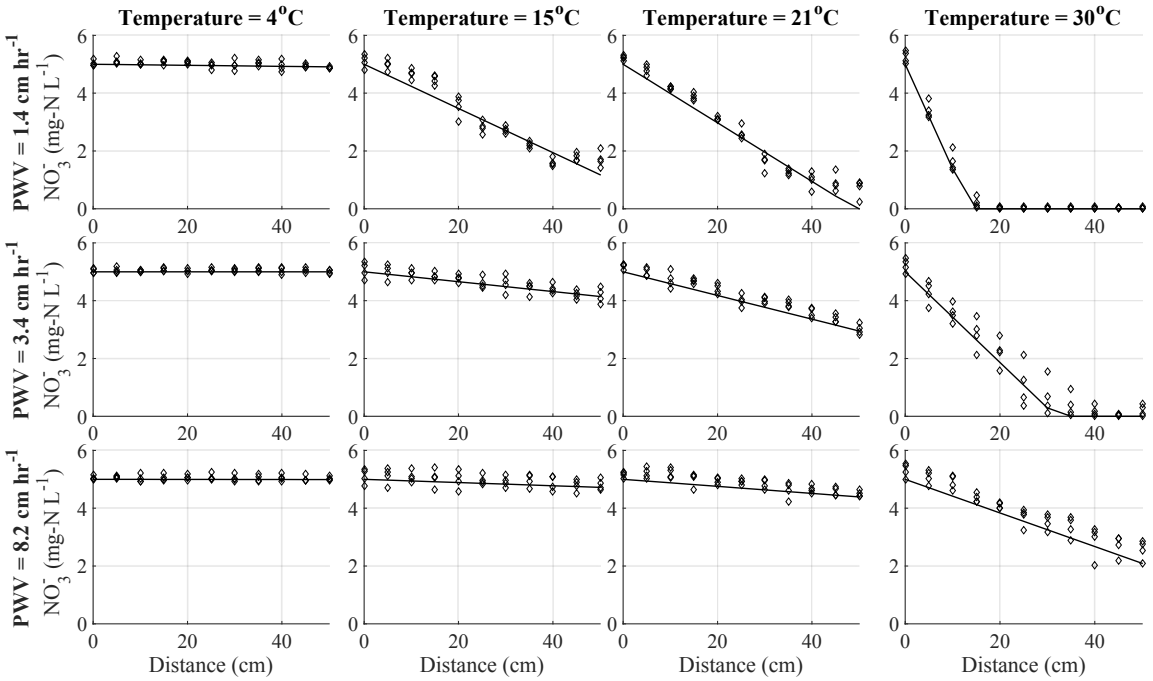

Figure 5. Nitrate-N concentration profile data (diamonds), and calibrated zero-order model results (solid line) for porewater velocities of 1.4 cm h^{-1} (row 1), 3.4 cm h^{-1} (row 2), and 8.2 cm h^{-1} (row 3) and temperatures of 4 °C (column 1), 15 °C (column 2), 21 °C (column 3), and 30 °C (column 4).

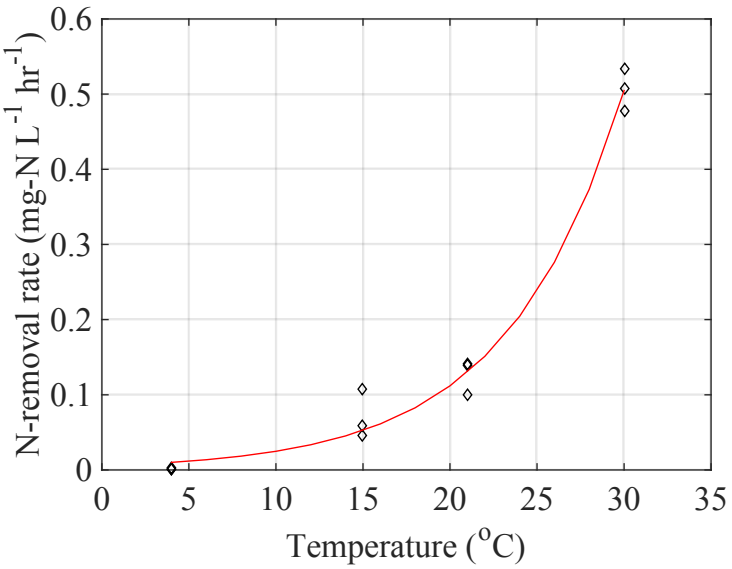

Figure 6. Nitrate removal rates plotted against temperature (diamonds) and a zero-order reaction rate model with a temperature coefficient of 1.16 (solid line).

When choosing appropriate applications for WBRs, the large dependence on temperature is critical. The experimental data indicated that every 10 °C change in temperature changes the nitrate removal rate by a factor of 4.41 (Figure 6). In comparison, typical microbial reactions[16,52] have a Q_{10} from 2-3, although some Q_{10} values reported are higher[53] (*e.g.*, ex-situ anammox rates). Schmidt and Clark[13] hypothesized that the unusually high Q_{10} value of woodchip reactors may be a result of synergistic effects between numerous biological reactions, including DOC release, nitrate uptake, and DO uptake, that occur in WBRs. Nevertheless, additional research is needed to determine the mechanisms responsible for the large temperature dependence of nitrate removal in WBRs, including specifics of the microbial communities. According to the zero-order model used in this study, removing 10 mg-N L^{-1} in a WBR at 20 °C would require a hydraulic residence time of 4 days. At 10 °C, an HRT of almost 18 days would be required. Thus, WBRs would have substantially higher nitrate removal rates in warmer climates or for applications with elevated water temperatures. One such application that appears promising for WBRs is polishing nitrified wastewater effluent, which is typically higher in temperature than the receiving waters;[54] these results thus provide further motivation for applying this model to the case study herein.

3.4 WBRs for Stormwater vs. Nitrified Wastewater: Case Study Analysis

We applied the temperature-sensitive model to a specific case study to evaluate optimal nitrate removal feasibility and costs. Flowrate, temperature, and nitrate conditions in the Sonoma County case study contrasted substantially between the stormwater runoff and wastewater effluent under ambient conditions (Figure S6). Average daily streamflow in

Santa Rosa Creek was highly variable, with flows ranging from 0.3-26.6 $m^3 s^{-1}$. In contrast, the effluent flow from the WWTP was more consistent at 0.1-0.2 $m^3 s^{-1}$, with occasional periods of low flow down to 0.02 $m^3 s^{-1}$. Water temperature in the stream ranged from 10-20 ˚C, while wastewater effluent temperature ranged from around 17-27 ˚C, with higher temperatures in the summer months and lower temperatures in the winter. The smallest temperature difference between creek water and wastewater effluent was around 5 °C in June, and the largest difference was approximately 13 °C between October and December. Nitrate concentrations in the wastewater effluent were highly variable, ranging between 5 – 30 mg-N L^{-1}, whereas the creek had very low but stable nitrate concentrations of 0.2 – 0.5 mg-N L^{-1}.

As a result of annual temperature variation, modeled nitrate removal rates in the wastewater effluent varied from 0.06-0.31 mg-N L^{-1} hr^{-1}, whereas nitrate removal rates in the creek were 0.01-0.11 mg-N L^{-1} hr^{-1} (Figure 7). These results represent a six-fold difference in the nitrate removal rate between wastewater and stormwater in winter and a three-fold difference in the summer. Temporal flow, water temperature, and nitrate concentration data for the wastewater effluent and stormwater (creek) are in Figure S6.

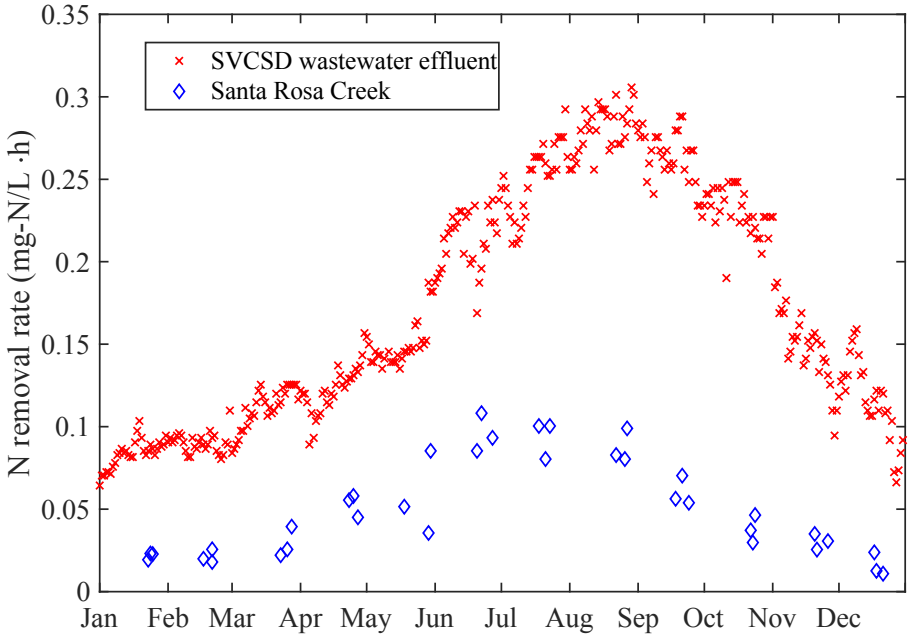

Figure 7. Calculated nitrate removal rates using the temperature-dependent zero order model developed over the course of a year for a WBR treating SVCSD wastewater effluent (red x) and Santa Rosa Creek water (blue diamond) in Sonoma County, CA.

The 5-13 ˚C temperature difference between the wastewater effluent and the creek resulted in dramatically different modeled nitrate removal rates. Additionally, initial nitrate concentrations in the runoff water were much lower. WBRs become less efficient[29] at nitrate concentrations less than 2 mg-N L^{-1} as a substantial fraction of the woodchip reactor volume is consumed by aerobic respiration, leaving a smaller portion of the reactor for denitrification. Lastly, WBRs greater nitrate mass removal with more consistent flow,[22] and runoff flow was much more variable than the wastewater effluent. The use of WBRs for reducing nitrate may be more promising when treating wastewater effluent compared with runoff water due to wastewater effluent having higher nitrate concentration and temperature.

To achieve nitrogen limits of 6, 4, and 2 mg-N L^{-1} with a WBR at the SVCSD WWTP, a reactor pore volume size of 100,000 m^3 would be required (Figure 8a). We assumed passive operation of the WBR where flow through the reactor is the same as flow from the WWTP. Alternatively, a 20,000 m^3 reactor would be required to meet the 6 mg-N L^{-1} limit approximately 50% of the year, or a 40,000 m^3 reactor would be required to meet the 6 mg-N L^{-1} 80% of the year. The benefit of increasing reactor size to meet the 6 and 4 mg-N L^{-1} discharge goals begins to decrease beyond a reactor size of 40,000 m^3 (as determined by the number of days the limit is met). In contrast, at the 2 mg-N L^{-1} limit the benefit of increasing reactor size decreases beyond a reactor size of 55,000 m^3. SVCSD has four detention basins (R1-R4, Figure 1) to store wastewater effluent before it is either used for agricultural irrigation or discharged to Schell or Hudeman Slough. These basins have a capacity of 231,000 m^3, 324,000 m^3, 138,000 m^3, and 189,000 m^3, respectively, for a total capacity of 882,000 m^3 (R. Kirchner, personal communication). Thus, the reactor size required to achieve these treatment goals using a WBR is well within SCCSD's total storage capacity. The diminishing returns for larger reactors in terms of fraction of days meeting the treatment goal (Figure 8a) and mass of nitrate removed (Figure 8b) occur because under conditions where full nitrate removal occurs, having a larger reactor does not provide any additional benefit. The non-linear curves in Figure 8 are due to this complete removal and diminishing return phenomenon, despite using a zero-order model. The fraction of days when the treatment goal is achieved is a less smooth line because of the variable input nitrate concentrations. The results in Figure 8 are for the Sonoma County case study.

Over the course of a year, the relative benefit of lowering total nitrate exports begins to decrease beyond a reactor size of 20,000 m^3 with passive operation (Figure 8b). Assuming woodchips cost[2] \$26.50 m^{-3} and the cost of transportation[55] is \$200 per semi-truck load (approximately 10 m^3), a 20,000 m^3 reactor would require \$530,000 of woodchips plus \$400,000 in transportation costs for a total cost of \$930,000. Furthermore, assuming a 15-year life span,[20] a 20,000 m^3 reactor would result in a nitrate removal efficiency of \$2.38 per kg-N removed. For a 100,000 m^3 reactor this number would increase to \$6.53 per kg-N removed due to decreased removal efficiency. Cost would be lessened substantially if woodchips were obtained as a free waste product. Regardless, even when purchasing the woodchips, the removal efficiency of WBRs is competitive with other nitrate removal technologies available (Table 2).

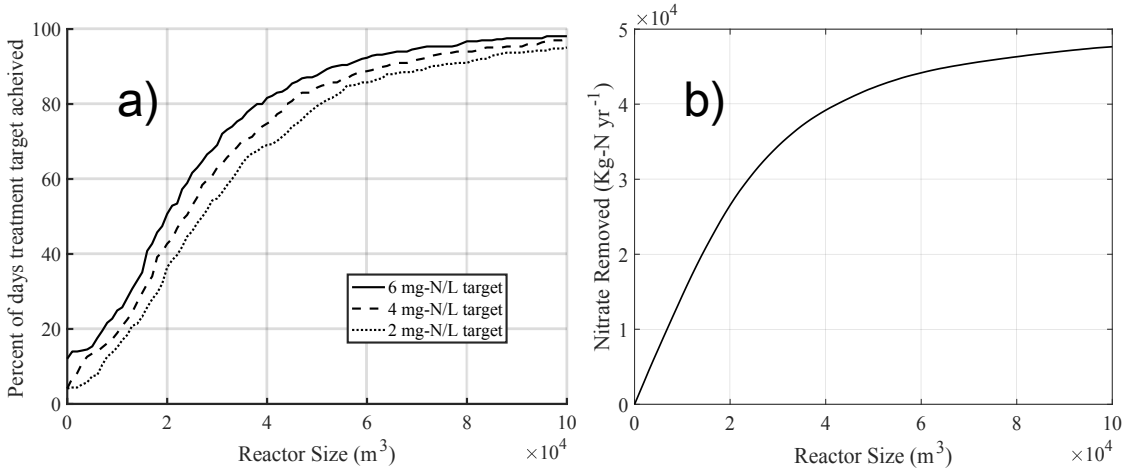

Figure 8. (a) The percent of days over the course of a year that the WWTP can achieve nitrate discharge target limits of 6, 4, and 2 mg-N L^{-1} for a given WBR size. (b) Mass of nitrate removed per year as a function of woodchip bioreactor pore volume size for the Sonoma Valley Wastewater Treatment Plant.

Table 2. Nitrogen removal cost-effectiveness for wastewater technologies

Wastewater Technology	Cost Effectiveness (US$/Kg-N)
CaRRB[1]	13.2-17.0[3]
ANAMMOX[2]	14.1-22.7[3]
Ammonia Stripping	29.5-32.8[3]
Electrodialysis	118.2-302.5[3]
Nitrification/Denitrification	3.3-4.6[4]
Woodchip Bioreactor	2.38-6.53

1. Centrate and Recycle Activated Sludge Re-aeration Basin
2. Anaerobic Ammonium Oxidation
3. Ref[56]
4. Ref[40]

3.5 Advantages of WBRs for sustainable operations

An advantage of WBRs compared to other nitrate removal technologies is the low operations and maintenance costs. WBRs require no chemical addition, only occasional maintenance, and no additional pumping. In an effort to mitigate climate change, SCWA (the agency overseeing WWTP operations) committed itself to the goal of operating a carbon free water system[57] by 2015. SCWA has achieved that goal by obtaining 100% of their power needs from renewable energy sources such as solar, hydro, and geothermal power.[57] The use of WBRs is consistent with this goal, as the carbon from the wood is renewable and other than transportation, little to no energy and chemicals must be added.

Over-sized woodchip reactors can lead to excess dissolved organic carbon (DOC) leaching, H_2S formation, and methyl mercury production.[12,58,59] To avoid these negative side-affects, nitrate concentrations should not drop below 0.1 mg-N L^{-1} in the reactor.[59] Fluctuating temperature, nitrate concentrations, and flow rate in the wastewater effluent contribute to the large variability in WBR performance, and days with low flow and high

temperature resulted in large theoretical reductions in nitrate concentration that exceeded actual nitrate concentrations (Figure 9). For the 40,000 and 60,000 m^3 reactors, the theoretical reduction in nitrate concentration more often than not exceeded the actual nitrate concentration, resulting in nitrate concentrations below 0.1 mg-N L^{-1}. The 20,000 m^3 reactor only had few instances where nitrate concentrations were expected to drop below 0.1 mg-N L^{-1}.

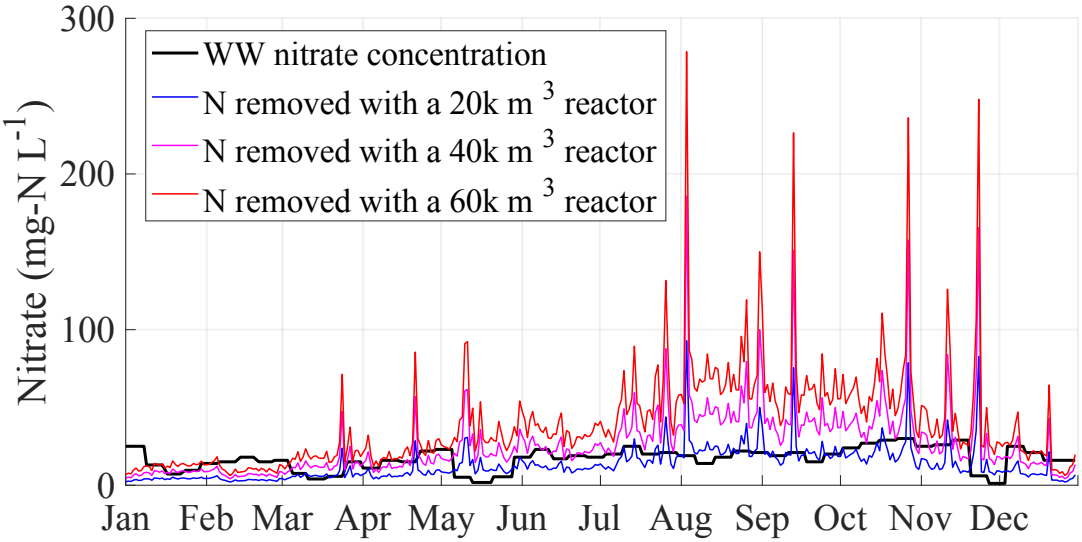

Figure 9. Wastewater effluent nitrate concentrations over the course of a year (black line) and modeled nitrate concentration removal with reactor sizes of 20,000 m^3 (blue line), 40,000 m^3 (magenta line), and 60,000 m^3 (red line).

In this case study, a 20,000 m^3 reactor would result in an annual average nitrate level of 7.7 mg-N L^{-1}. Similarly, a 40,000 m^3 and 60,000 m^3 reactor could achieve an annual average nitrate level of 3.43 and 1.73 mg-N L^{-1}, respectively. Nevertheless, by using only passive control, the effluent nitrate concentrations would be highly variable (Figure 10). To lessen variability and improve performance, the reactors could be actively managed by controlling retention time based on temperature and estimated nitrate concentrations. In

addition, a WBRs could be arranged in different hydraulic configurations[10] (i.e., in series or parallel) to allow for site-specific flow needs, such system redundancy or reactor by-pass options under specific flow conditions. Active flow control would not only improve treatment performance, but also it would likely improve the cost-effectiveness of this technology.

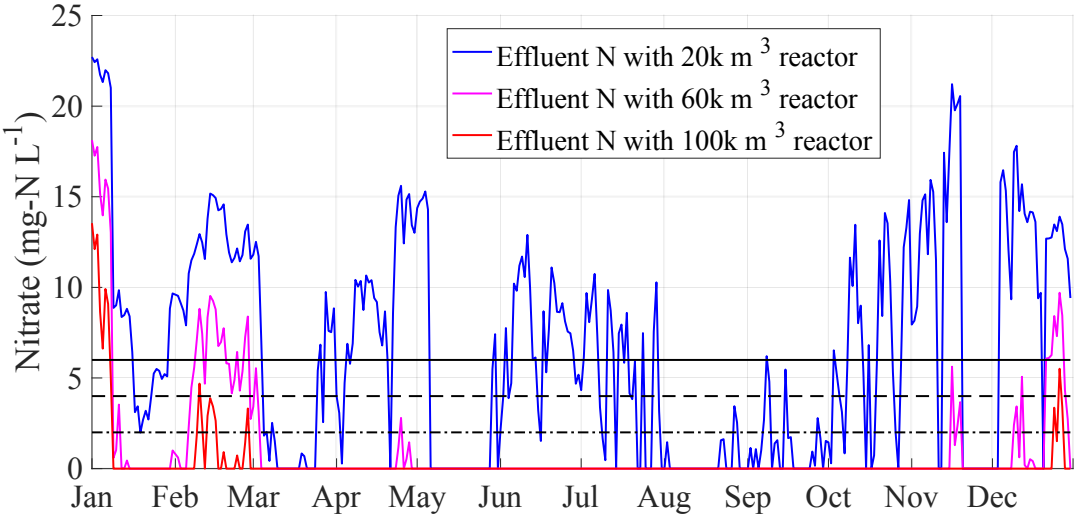

Figure 10. Daily effluent nitrate concentrations at SVCSD WWTP assuming woodchip reactor sizes of 20,000 m^3 (blue line), 40,000 m^3 (magenta line), and 60,000 m^3 (red line).

4 Conclusions

Denitrification in WBRs followed zero-order kinetics over a range of environmentally relevant temperatures (4 to 30 ºC). DOC concentrations did not alter reactor performance at the temperatures or porewater velocities tested. Our modeling results indicated that DO inhibition effects on nitrate removal rates were not significant for influent nitrate concentrations above 2 mg-N L^{-1}. Below 2 mg-N L^{-1}, aerobic respiration would consume a substantial fraction (>10%) of the carbon in the woodchips, thereby lowering the effective nitrate removal rate. Nitrate removal in WBRs was very sensitive to temperature, with a

Q_{10} value of 4.41. The strong high temperature dependence suggests WBRs may be more cost and space efficient in warmer climates or applications with elevated water temperatures, such as wastewater effluent. The case study presented suggests nitrified wastewater effluent is a promising application for WBRs and should be investigated further. When designing reactors for applications with varying temperature, flow, and nitrate concentrations, it is important limit the amount of DOC and H_2S exported from the reactor by proper sizing or more active flow control. The methodology described here may be used in other settings to investigate the use of WBRs to remove nitrate from effluent streams. Future research should investigate the dynamics of the microbial communities inhabiting WBRs under changing conditions to establisher a fuller picture of system performance and further cross-validate the temperature coefficients reported here to broaden application to alternative conditions.

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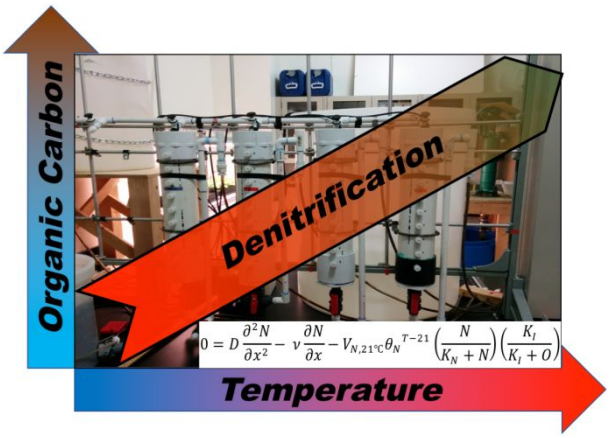
Table of Contents Entry:



The temperature dependence of denitrification in woodchip bioreactors was quantified using experimental and modeled results to enhance predictive power and applied to a case study.