Real-Time Control of Exogenous Carbon Dosing in a Denitrifying Woodchip Bioreactor Treating Agricultural Drainage

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ABSTRACT: Nature-based treatment technologies such as denitrifying woodchip bioreactors (WBRs) are employed to manage nitrogen (N) pollution from agricultural nonpoint sources. Due to variability in environmental conditions like temperature and discharge, it is challenging to achieve consistent treatment effectiveness with these passive systems. To improve nitrate (NO_3^-) load reductions in a field-scale WBR in New York State during cool spring weather, we designed a system for controlled exogenous carbon (C) dosing, allowing rates of C dosing to respond in real time to changing discharge and NO_3^- concentrations. Treatment efficiencies for NO_3^-, acetate mass balances, and other bioreactor properties were monitored from April 5 to June 10, 2023. Biostimulation with 7.5 mg C/L acetate (assuming complete mixing of injected acetate with bioreactor pore water) increased NO_3^- removal rates up to 5-fold compared to a model-based scenario of baseline bioreactor performance, and were as high as 0.4 mg NO_3^-−N L^{-1} h^{-1} while water temperatures were <12 °C. Increasing acetate concentrations beyond 7.5 mg C/L did not confer a clear improvement in NO_3^- removal rates. Cumulative N load reductions increased from 11.3% under the baseline scenario without C dosing to 24.1% with C dosing. The mass ratio of metabolized C to additional N removal was 2.5:1, although the total dosed C/N mass ratio was 5.1:1 due to incomplete acetate utilization in the reactor. We found evidence that C dosing could enhance the future release of dissolved organic N (DON) and dissolved organic C related to biofilm sloughing. The expense of acetate, with a cost efficiency of 86 USD/kg N, was the main cost driver of the real-time control approach. Our results demonstrate the potential of real-time control of C dosing to meaningfully improve nonpoint source N removal during cool spring conditions but also highlight opportunities for methods to improve acetate utilization efficiencies in order to improve the overall cost-effectiveness of the approach.

KEYWORDS: real-time control, denitrifying bioreactor, biostimulation, nitrate, acetate
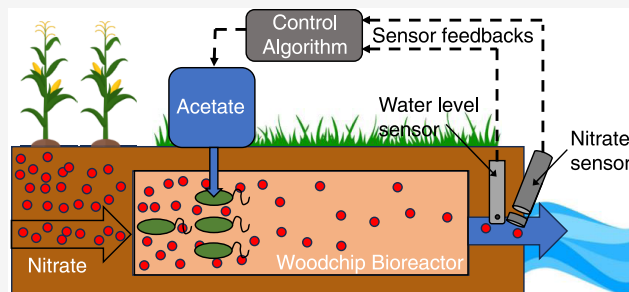
INTRODUCTION

Nonpoint source nitrate (NO_3^-) release from agricultural activities is a major contributor to water quality impairments around the world.[1,2] Under-field tile drainage systems are common in agricultural croplands and can exacerbate NO_3^- exports in agricultural drainage and leachate.[3] There are growing efforts to treat NO_3^- in agricultural tile drainage through the use of passive, edge-of-field systems including constructed wetlands,[4] saturated buffers,[5] and woodchip bioreactors (WBRs).[6−12] Woodchip bioreactors, a leading best management practice for treating agricultural NO_3^-, utilize woodchips as biofilm support structures and as a slow-release source of organic carbon (C) for denitrifying biofilms. Denitrification is the heterotrophic reduction of NO_3^- to dinitrogen gas (N_2) through a series of obligate intermediates. Because agricultural tile drainage has a low C/N mass ratio (on average 0.17 at the site examined in this study), a key challenge for passive denitrifying systems is the sustainable supply of labile C for denitrifying biofilms.[13]

Two key problems for the effective field-scale performance of denitrifying WBRs are (1) cool water temperatures can decrease microbial reaction rates,[14] which is especially problematic in the Upper Midwest and Northeast U.S., where water temperatures can be low for much of the year, and (2) high-flow periods, including spring snowmelt and storm events, lead to short hydraulic retention times (HRTs) that limit NO_3^- removal efficiencies.[15] A large fraction of NO_3^- loads exported from tile drains to agricultural watersheds is driven by storm events,[16] so improving N removal during high-flow (and short HRT) periods is a priority for agricultural nutrient management. Dosing bioreactors with exogenous labile organic C[17−19] has been proposed as a method to
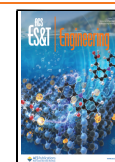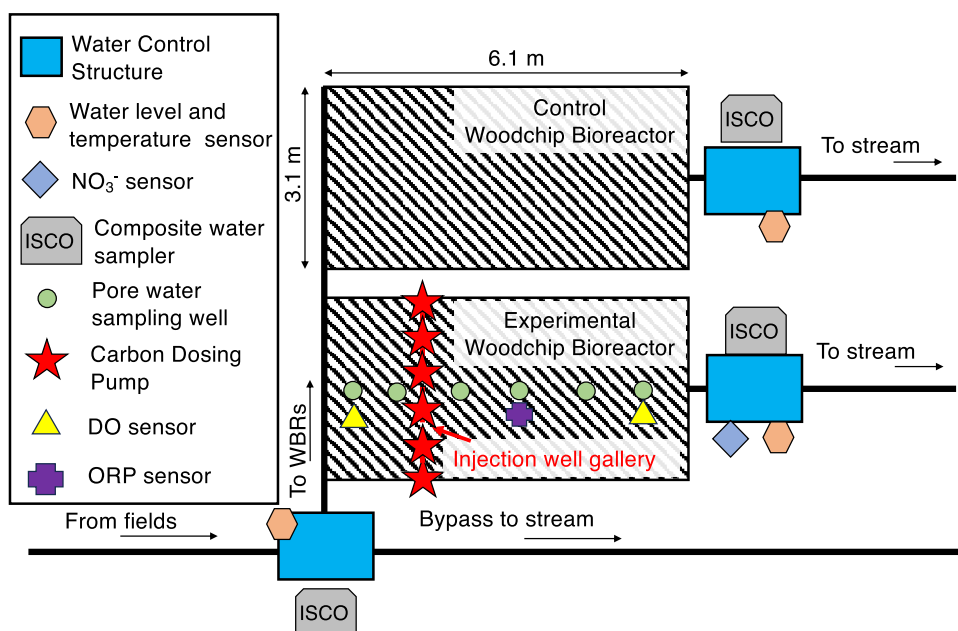
Figure 1. Schematic of the experimental and control woodchip bioreactors in central New York State.

overcome these challenges by stimulating denitrifier activity, and the potential for C dosing to respond to storm events or other high-flow periods in real time is a major advantage.

Laboratory-based studies have demonstrated that dosing with acetate is effective at increasing NO_3^- removal rates during low-temperature and high-flow conditions.[18,20] Exogenous C dosing has also been implemented and evaluated in field-scale WBRs.[19,21,22] These studies employed constant dosing rates of methanol or acetate and confirmed that C dosing effectively increased the NO_3^- removal rates under real-world conditions. However, they also showed that C dosing can lead to biofouling of woodchip media and decreases in hydraulic efficiency[19,21] and the release of unmetabolized labile C in bioreactor effluent, contributing to biochemical oxygen demand (BOD) in receiving waters.[17] Other potential adverse impacts of exogenous C dosing include dissimilatory NO_3^- reduction to ammonium (NH_4^+) (DNRA)[23] and microbial sulfate reduction, which can lead to odors and may stimulate mercury methylation.[24,25] These risks have not been systematically addressed in field-based C dosing studies.

Here, we use real-time sensing of discharge and effluent NO_3^- concentrations in a field-scale bioreactor to perform feedback control of acetate dosing to stimulate denitrification rates. Real-time control allows dosing rates to automatically adapt to dynamic environmental conditions such as high-flow periods that require increased C dosing to treat greater NO_3^- loads. It also allows dosing rates to decrease when the "natural" performance of bioreactors is strong (e.g., longer HRTs in warm weather) and thereby decrease risks of overdosing acetate. Real-time control of "smart" stormwater systems is a rapidly growing topic in water quality engineering and research,[26−28] with most applications focused on the control of HRT in stormwater detention basins to promote sedimentation of suspended solids.[29,30] To our knowledge, this is the first use of real-time control to enable discharge-dependent C dosing to stimulate removal of nonpoint source N. The objectives of this study were 2-fold: first, to quantify the effects of real-time control of acetate dosing on cumulative NO_3^- load reductions achieved in a field-scale bioreactor over

a 2-month period, including an assessment of cost-effectiveness, and second, to systematically evaluate environmental risks of adverse water quality impacts of exogenous C dosing.

MATERIALS AND METHODS

Study Site and Instrumentation of Woodchip Bioreactor. We retrofitted two field-scale woodchip bioreactors in Tompkins County, NY, originally built in October 2012, with sensors and actuating pumps to test the real-time control of labile C dosing under real-world conditions (Figure 1). One reactor was designated the Experimental Reactor and was used to test acetate dosing, and the second reactor was designated as the Control Reactor and was operated without acetate dosing except from May 14 to 15, when acetate was injected into the inlet control structure to ensure complete mixing of the injected acetate. Both bioreactors are 6.1 m long × 3.1 m wide and treat tile drainage with a NO_3^-−N concentration between 8 and 9 mg N/L.[15] The experimental reactor woodchip bed was 0.69 m thick, while the control reactor's woodchip bed was 0.74 m thick. In an earlier study, we used bromide tracer tests to determine the effective porosity of the bioreactors to be 0.8.[15] The bioreactors were filled primarily with ash woodchips (genus *Fraxinus*)[9] and enclosed with an impermeable polyethylene sheet. The woodchip matrix in the control reactor was originally amended with 10% biochar by weight by researchers originally interested in effects of biochar on pesticide removal in tile drainage.[31] Agricultural tile drainage from 4 ha of croplands at the Homer C. Thompson Vegetable Farm was diverted into the reactors in parallel using an AgriDrain inlet water control structure with a bypass for extreme flow events. Water levels within the reactors were maintained using V-notch weirs in AgriDrain water control structures at the outlet of each reactor. Additional details on the field site are available in previous research reports.[9,10,15]

Three ISCO automated water samplers (one ISCO 3700 and two ISCO 6712) were used to collect daily composite water samples from the inlet and both outlet water control structures. 100 mL water samples were collected every 4 h, and

microbial activity in samples was inhibited by adding 5 mL of 2 M HCl to each sample bottle. Water levels and temperatures in the inlet and outlet control structures were monitored using pressure transducers (Campbell Scientific CS451). Water levels in the experimental reactor were converted to discharge (L/s) using the rating curve (Figure S1)[32]

$$Q = 0.0065(H + 1.02)^{2.5} \tag{1}$$

where H represents the water height (cm) above the v-notch. Due to a sensor malfunction, we did not collect continuous water level data in the control reactor during the experimental period. Sensor measurements of water levels in both experimental and control reactor outlet structures obtained in December 2023 showed that the water level in the control reactor was always 5 cm higher than the level in the experimental reactor (Figure S2). Because the height of the v-notch weir above the base of the control structure was also 5 cm higher than the height in the experimental reactor, the discharge in both reactors was assumed to be the same. Periodic manual discharge measurements confirmed that the discharges in both reactors were identical (Figure S1).

An ultraviolet (UV) absorbance-based NO_3^- sensor (OTT HydroMet ecoN, 5 mm path length) was installed in the outlet control structure of the experimental reactor, with the antifouling wiper programmed to clean the windows every 24 h. The NO_3^- sensor was calibrated using a 5-point calibration curve prepared with a certified NO_3^- standard. Two dissolved oxygen sensors (Campbell Scientific CS511-L) and one ORP sensor (Campbell Scientific CSIM11-ORP-L) were also installed in PVC access pipes in the woodchip matrix at a depth 35 cm below the surface of the woodchip matrix (Figure 1).

Six injection wells constructed from PVC pipe were installed perpendicular to the direction of flow in the experimental reactor, 1.8 m from the upstream end of the reactor, for exogenous acetate dosing (Figure 1). The bottom 20 cm of the pipes were perforated so that the C dosing solution was injected at a depth 25−45 cm below the bioreactor surface in three of the wells and 45−65 cm below the bioreactor surface in the other three wells. We performed a pilot set of acetate dosing experiments in the summer and fall of 2022 to test the dosing infrastructure and establish the feasibility of the approach. A total of 1.08 kg of acetate-C was injected into the experimental reactor in 2022.

During the 2023 dosing campaign described here, the carbon dosing solution consisted of food-grade sodium acetate (12,000 mg C/L) and sodium bromide (8000 mg Br⁻/L), used as a conservative tracer, adjusted to pH 7. One exception was the first 2-day dosing period, when the solution consisted of 40,000 mg Br⁻ instead of 8000 mg Br⁻/L. Tap water was injected for 20 s after each injection of acetate solution as a "chaser" to ensure the acetate was fully injected into the woodchip matrix. The C dosing solution was injected directly into the woodchip matrix of the experimental reactor through the injection wells, allowing the control reactor to be used to study the bioreactor performance without exogenous C dosing. One exception was a 2-day period from May 14 to 15, when acetate was dosed into the inlet control structure instead of the injection wells, in order to ensure complete mixing of dosed acetate in the water entering the reactors. The C dosing solution was injected using peristaltic pumps, controlled from a measurement and control datalogger (Campbell Scientific

CX1000). The system was powered by a solar panel and a 12 V battery.

Control Logic. We designed the acetate dosing regime to overcome kinetic limitations to denitrification kinetics rather than target a specific C/N ratio as has been done in prior studies of C dosing in WBRs. Based on dual-substrate Michaelis−Menten biokinetic models for heterotrophic denitrification and a half-saturation constant (K_C) for bioavailable carbon of 1.0 mg C/L,[12] we chose a target acetate level of 7.5 mg C/L (assuming instantaneous mixing of the injected acetate with the bioreactor pore water around the injection wells) for most of the experimental campaign in order to achieve roughly 90% of the maximum NO_3^- removal rate, assuming NO_3^- was not limiting. This relatively low level of C dosing, equivalent to a C/N mass ratio of ∼0.9 based on influent NO_3^- concentrations typically observed at our site,[15] was also chosen to minimize the risk of acetate release from bioreactor effluent which could occur if excess acetate was dosed. From May 7 to 11, a target acetate concentration of 15 mg C/L instead of 7.5 mg C/L was used to assess whether a higher acetate concentration could lead to improved NO_3^- removal rates.

Dosing pumps were actuated every 10 min, with the volume of C dosing solution injected during every 10 min interval controlled by the duration that the pumps were actuated. The volume of acetate injected was determined as a function of real-time bioreactor discharge and effluent NO_3^- concentrations (Table 1). When bioreactor discharge was low ($Q <$

Table 1. Summary of Control Logic[a]

condition	dosing regime
I. $Q <$ 0.05 L/s or $NO_3^- <$ 0.45 mg N/L	no dosing
II. 0.05 L/s $< Q <$ 3 L/s and $NO_3^- >$ 0.45 mg N/L	targets 7.5 mg C/L (or 15 mg C/L during 5-day trial in early May)
III. $Q >$ 3 L/s and $NO_3^- >$ 0.45 mg N/L	acetate dosing rate set to level at $Q =$ 3 L/s

[a]Q is the bioreactor discharge (L/s) and NO_3^- is the effluent NO_3^-−N concentration (mg N/L) measured with real-time sensing.

0.05 L/s) or effluent $NO_3^- <$ 0.45 mg N/L (Condition I), no dosing occurred since supplemental carbon was not needed under these conditions. If 0.05 L/s $< Q <$ 3 L/s and effluent $NO_3^- >$ 0.45 mg N/L (Condition II), dosing volumes were designed to target an acetate concentration of 7.5 mg C/L (or 15 mg C/L for a dosing period in early May), assuming complete mixing of the injected volume with the volume of bioreactor discharge over the 10 min interval. Finally, because the rating curve was uncertain above $Q =$ 3.0 L/s, the dosing rate was capped at the level corresponding to $Q =$ 3.0 L/s even if the true discharge Q was higher than that level (Condition III). The volume of dosing solution injected ranged from 0 to 110 mL in each 10 min interval.

Water Quality Parameters. Water chemistry was monitored in daily composite samples collected from the inlet and outlet control structures. Pore water samples from the woodchip matrix were also periodically collected from six monitoring wells in the experimental reactor. All water samples were filtered through 0.22 μm membrane filters and stored at 4 °C until analysis. Anions (NO_3^-, NO_2^-, SO_4^{2-}, Br^-, acetate) and cations (NH_4^+) were measured using ion chromatography (Thermo Dionex ICS-2100). Dissolved organic carbon (DOC) and total N (TN) were analyzed using a Shimadzu

TOC analyzer (nonpurgeable organic carbon (NPOC) method) with TN module. Dissolved organic nitrogen (DON) (mg N/L) was determined using

$$\text{DON} = \text{TN} - (\text{NH}_4^+\text{–N} + \text{NO}_3^-\text{–N} + \text{NO}_2^-\text{–N}) \tag{2}$$

Nonacetate DOC released from woodchips and/or degradation of microbial biomass within the reactor was determined as the difference between NPOC and the acetate-C concentration.

Br$^-$ and acetate concentrations were used to determine the acetate utilization efficiency (%) and quantify the fraction of the dosed acetate that was metabolized in the reactor

$$\text{acetate utilization effficiency} = \left(1 - \frac{\left(\frac{C}{C_0}\right)_{\text{acetate}}}{\left(\frac{C}{C_0}\right)_{\text{bromide}}}\right) \times 100\% \tag{3}$$

where C refers to the concentration of either acetate (mg C/L) or bromide (mg Br$^-$/L) in the composite or pore water sample, and C_0 refers to the initial concentration of either acetate or bromide in the C dosing solution. This approach assumes that retardation of Br$^-$ inside the reactor is negligible.

Cumulative NO$_3^-$–N load reductions (kg) were calculated using

$$\text{cumulative load reduction} = \sum_i^n Q_i N_{\text{influent},i} - Q_i N_{\text{effluent},i} \tag{4}$$

where n is the number of days in the time window being examined, Q_i is the mean discharge on the ith day, and $N_{\text{effluent},i}$ and $N_{\text{influent},i}$ are, respectively, daily averaged effluent and influent NO$_3^-$–N concentrations on the ith day determined from daily composite water samples.

Daily nitrate removal efficiencies on the ith day (NRE$_i$) (%) were determined using

$$\text{NRE}_i = \frac{N_{\text{influent},i} - N_{\text{effluent},i}}{N_{\text{influent},i}} \times 100\% \tag{5}$$

Nitrate removal rates on the ith day (NRR$_i$) (mg NO$_3^-$–N L^{-1} h^{-1}) were determined using

$$\text{NRR}_i = \frac{N_{\text{influent}} - N_{\text{effluent}}}{\overline{\text{HRT}}_i} \tag{6}$$

$\overline{\text{HRT}}_i$ is the mean HRT (h) on the ith day, and was determined using

$$\overline{\text{HRT}}_i = \frac{\theta d_i w l}{Q_i} \tag{7}$$

where θ is the effective porosity of the woodchip bioreactor, d_i is the mean saturated depth of the woodchip matrix on the ith day, w is the bioreactor width, and l is the reactor length.

Process Modeling of NO$_3^-$ Removal Rates. A zero-order biokinetic model developed by Israel et al.[15] was used to estimate effluent NO$_3^-$ concentrations in the experimental bioreactor in a "baseline scenario" without exogenous C dosing. Zero-order models have been shown to adequately describe WBR NO$_3^-$ removal rates when NO$_3^-$ concentrations are >2 mg N/L, which was true for almost all of the investigation period.[12] Effluent NO$_3^-$ concentrations (mg N/L) were modeled using

$$N_{\text{effluent},i,\text{model}} = N_{\text{influent},i} - k_0(T)\overline{\text{HRT}}_i \tag{8}$$

where $k_0(T)$ is the temperature-sensitive zero-order rate constant [mg NO$_3^-$–N L^{-1} h^{-1}]. Details on the estimation of $k_0(T)$ are available in Israel et al.[15] This model-based N_{effluent} was then used to determine model-based NRE and NRR by using eqs 5 and 6.

Woodchip Characterization. Woodchips were collected from an access port in the experimental reactor every 3−4 weeks during the measurement campaign and analyzed for surface protein as a measure of microbial biomass. Acetate sorption to woodchips was also assessed as a potential abiotic sink for acetate in the woodchip matrix by using sorption experiments with woodchips collected from the experimental bioreactor. The linear distribution coefficient K_d was determined as $K_d = q_e/C_e$, where q_e is the adsorbed concentration at equilibrium and C_e is the dissolved concentration at equilibrium. All protein and sorption experiments were performed in triplicate, and further details are available in SI.

**Techno-Economic Assessment.** We determined the annualized cost of the real-time acetate dosing approach using[33]

$$\text{annualized cost} = \left[\frac{r(1 + r)^L}{(1 + r)^L - 1}\right] \cdot C_{\text{CAP}} + C_{\text{O\&M}} \tag{9}$$

where C_{CAP} and $C_{\text{O\&M}}$ are the capital and operating costs, respectively, and the term inside the brackets is the capital recovery factor. The investment lifetime (L) was 10 years, and the discount rate (r) was 2.5%. C_{CAP} values are summarized in Tables S1 and S2. $C_{\text{O\&M}}$ was determined as the cost of food-grade acetate and was expressed as U.S. dollars (USD) per kg N removed using acetate dosing.

■ RESULTS

Bioreactor Physical−Chemical Conditions. The experimental dosing campaign lasted from April 5 until June 10, 2023. During this time, water temperatures increased from 6 to 12 °C (Figure 2A). There was a large storm event which flooded the experimental site on May 1, and because the entire site was underwater, it was not possible to accurately determine the flow rate on that date. As a result, data from May 1 have been excluded from further analysis. The floodwaters subsided quickly, and the bioreactor discharge on May 2 was again within our rating curve; we were able to retain data from that date. Outside of this large storm, average daily discharge ranged from 0 (no flow) to 0.4 L/s. Our monitoring period ended when a prolonged no-flow period began after June 10. Dissolved oxygen (DO) concentrations were between 2 and 8 mg/L at the upstream end of the reactor, with higher DO concentrations driven by high bioreactor flows (Figure S4). DO concentrations at the downstream end were always near or below the limit of detection, indicating the activity of aerobic microbial activity within the bioreactor even in early April when water temperatures were only ~6 °C. The redox potential (ORP) also covaried with flow and declined sharply in June when discharge fell below 0.05 L/s (Figure S5).

Effects of Carbon Dosing on Nitrate Removal. Dates with acetate dosing are indicated in Figure 2 with gray shaded
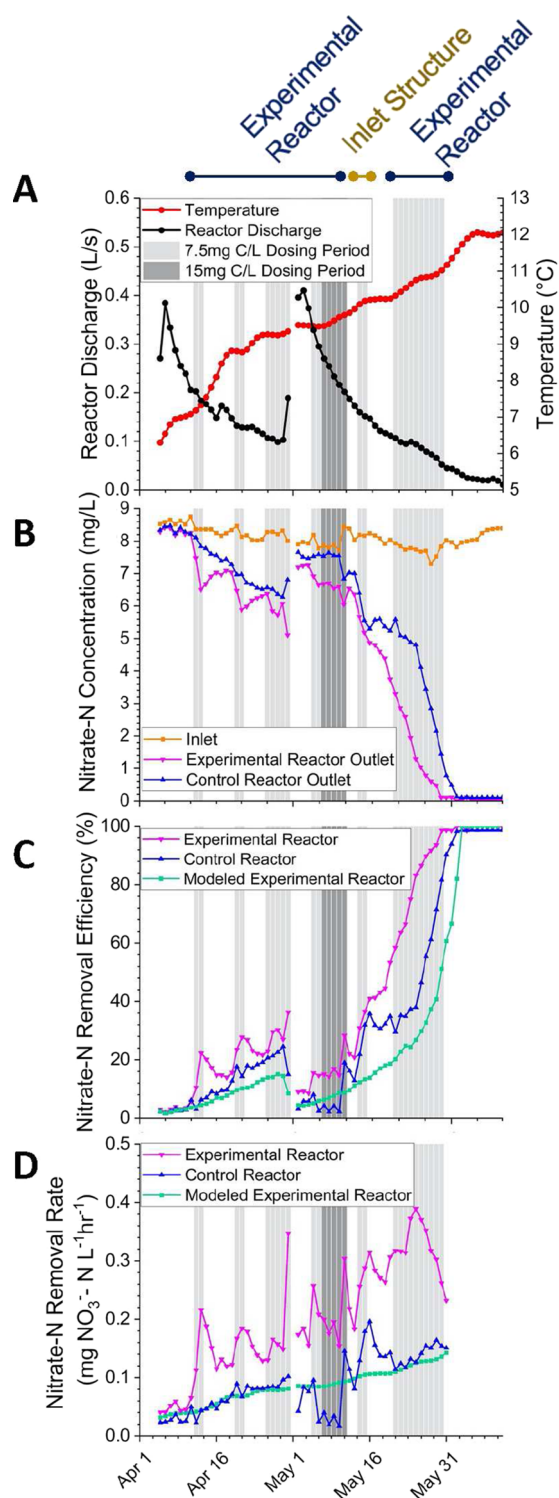
Figure 2. (A) Daily average discharge and water temperature in the experimental reactor. Gray bars show days on which acetate dosing occurred, and blue and gold lines at the top of the figure indicate dosing into the experimental reactor only or into both reactors through the inlet structure. (B) Daily average influent and effluent NO_3^-–N in experimental and control reactors. (C) Observed NO_3^-–N removal efficiency (NRE) in experimental and control reactors, and model predictions from "baseline" model. (D) Observed and model-predicted NO_3^- removal rates (NRRs).

areas. In April, discharge-based acetate dosing into the woodchip matrix was performed for two 2-day periods and

one 5-day period. The onset of acetate dosing corresponded with sharp decreases in effluent NO_3^- concentrations in the experimental reactor compared to the (undosed) control reactor (Figure 2B). After acetate dosing ended, the effluent NO_3^- in the experimental reactor increased and slowly converged to the effluent concentrations in the control reactor. There was generally good agreement between daily composite measurements of effluent NO_3^- and daily averaged sensor data when NO_3^- concentrations were >4 mg N/L, though the sensor data overestimated the daily composite samples when NO_3^-–N < 4 mg/L (Figure S3). The NRE was greater in the experimental reactor than in the control reactor and the model-based "baseline" scenario during C dosing periods (Figure 2C). The sharp increases in NRE in the experimental reactor from C dosing were clearly distinguished from the more gradual temperature-driven increase in NRE observed in the control reactor and the "baseline" scenario model.

Nitrate removal rates (NRRs) followed a similar pattern, increasing by a factor of 2−5 in the experimental reactor relative to the "baseline" model in April (Figures 2D and S6). NRRs remained elevated in the experimental reactor compared to the control reactor and "baseline" model after the dosing period stopped and acetate and bromide had largely been flushed out of the reactor. This may be due to greater biomass concentrations on the surface of experimental reactor wood-chips compared to woodchips from the control reactor (Figure S7). Because the surface protein concentrations were already higher in the first experimental reactor samples collected in early April, it is likely that this was a longer-term impact of the pilot C dosing performed in 2022 and suggests there may be long-term impacts of C dosing beyond the specific period of active C dosing.

From May 7 to 11, the dosing regime was modified to test the effects of 15 mg C/L (C/N mass ratio of ∼1.9) on NO_3^- removal performance. The higher acetate concentration did not significantly increase the NRR ratio between the experimental reactor and baseline model compared to the lower acetate concentration used in earlier C dosing (Figure S6), suggesting that 7.5 mg of C/L may be sufficient to overcome kinetic limitations on denitrification, as expected based on a half-saturation constant of 1 mg of C/L.

Pore water measurements from the woodchip matrix showed that Br^- tracer co-injected with acetate was poorly mixed (Figure S9), suggesting that the effects of injected acetate might be limited by incomplete mixing and/or preferential flow paths which would lead to acetate concentrations different from the target concentrations in different portions of the reactor. To address potential problems related to incomplete mixing, acetate was dosed into the inlet control structure instead of the injection well gallery from May 14 to 15. While both the experimental and control reactor NRR responded to the inlet C dosing (Figure 2D), the stimulation of the experimental reactor NRR was not systematically greater than it was when acetate was dosed into the injection well gallery before and after the dosing into the inlet (Figure S6).

In the final acetate dosing period in late May, acetate was unintentionally overdosed at a level of 19 mg C/L (C/N mass ratio of ∼2.4). This was attributed to an overestimation of the bioreactor discharge by the rating curve at low Q (Figure S1). NRR was stimulated at a comparable level as previous C dosing period with lower acetate concentrations, further indicating that acetate concentrations >7.5 mg C/L did not lead to superior NO_3^- removal rates.

Comparison of Observations and Model Predictions. The model-based NRE in the experimental reactor "baseline" scenario was lower than that in the control reactor because the control reactor has a larger saturated volume and thus a longer HRT (Figure 2C). The model-based NRR was in mostly good agreement with the control reactor NRR because, unlike NRE, NRR depends only on temperature which was assumed to be the same in both reactors. There were two distinct periods where the model-predicted and the observed NRR in the control reactor were in poor agreement. In the May 7−11 dosing period, following the large storm event on May 1, the observed NRR was significantly lower than the modeled NRR, potentially due to biofilm sloughing or some other perturbation related to the storm event. In the May 14−15 dosing period, the observed NRR was greater than the modeled NRR. This was due to carbon dosing into the inlet control structure, causing the control reactor to be influenced by acetate and having NRRs greater than what would occur under "baseline" conditions. Since the biokinetic model was found to be a good predictor of NRR and therefore effluent NO_3^- concentrations, carbon dosing decisions were simulated using model-based effluent NO_3^- estimates rather than sensor-based measurements (Figure S8). The dosing decisions were identical, indicating that model-based predictions of effluent NO_3^- concentrations can be used in place of NO_3^- sensing, thereby avoiding the need for expensive NO_3^- sensors in future implementations.

Acetate Utilization Efficiency. Acetate and Br^- in the control reactor effluent were always below the limit of quantification (0.5 mg/L) except during the inlet control structure dosing period (data not shown). In April and early May, when the reactor discharge was high, injected acetate and Br^- were flushed out of the experimental reactor within a few days after the dosing stopped (Figure 3A). In late May and June, when reactor discharge was lower, Br^- and sometimes acetate were detected in the reactor effluent for more than a week after dosing ended, the result of storage of the dosing solution in dead zones since the mean HRT in the experimental reactor never exceeded 35 h in April and May. Due to low effluent NO_3^- concentrations, the control logic discontinued acetate dosing on May 31.

The daily average acetate utilization efficiency varied from 20 to 100% (Figure 3B). The utilization efficiency was generally lower during acetate dosing periods and then increased after dosing stopped when concentrations in the effluent reflected the effects of longer residence times in the reactor. The acetate utilization efficiency tended to increase with temperature (Figure S10), suggesting that greater microbial activity led to more efficient acetate utilization. Acetate utilization also increased with lower Q and approached 100% when the discharge was less than 0.05 L/s (Figure S10), indicating that longer HRT also enabled greater acetate utilization. Notably, the acetate utilization efficiency was at its lowest when acetate was dosed at 15 mg C/L instead of 7.5 mg C/L (dark gray bars in Figure 3B), highlighting that higher acetate load can increase the risk of unmetabolized acetate release.

Cumulative NO_3^- Load Reductions and Fate of Dosed Acetate in Reactor. Cumulative NO_3^- loads entering and leaving the experimental and control reactors were determined using daily composite ISCO samples, with the exception of May 14 to 20 when the model-based NRR was used to estimate control reactor NO_3^- load reductions. This was done
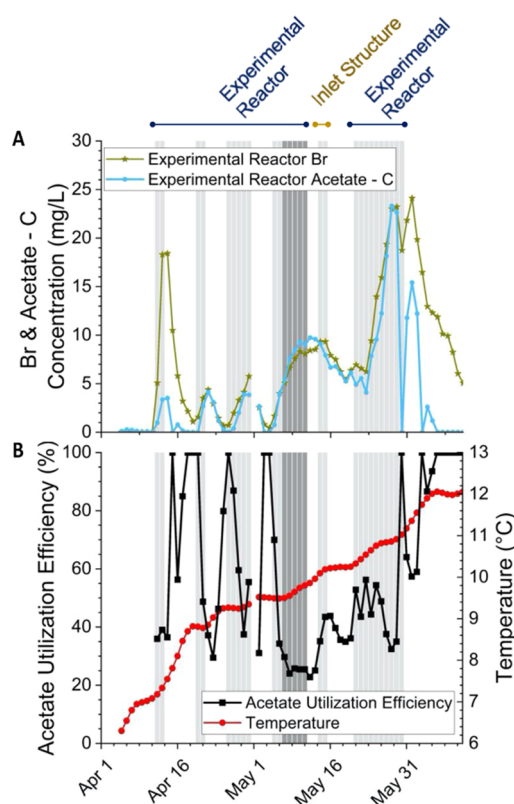
Figure 3. (A) Daily average acetate-C and bromide in experimental reactor effluent. (B) Daily acetate utilization efficiency in the experimental reactor, as determined with eq 3, and water temperature. The dosed Br^-/C mass ratio was set at 0.7 during all dosing periods, except the first dosing period where the Br^-/C ratio was 3.3, leading to higher effluent Br^- concentrations in the first dosing period. Gray bars show days on which acetate dosing occurred, and blue and gold lines at the top of the figure indicate dosing into the experimental reactor only or into both reactors through the inlet structure.

because the control reactor was influenced by acetate dosing into the inlet structure during that period, leading to greater NRRs that did not reflect nondosed control conditions. Cumulative NO_3^- loads entering the reactor were primarily driven by storm events, with large increases in influent NO_3^- loads occurring in the aftermath of storms on April 6 and May 1 (Figure 4). Cumulative NO_3^-−N load reductions over the 2-month experimental period were 14.8% in the control reactor and 24.1% in the experimental reactor, reflecting the impact of exogenous C dosing. The control reactor may not provide an ideal comparison for the experimental reactor due to differences between the reactors (e.g., differences in saturated volumes; presence of biochar in the control reactor), so we also used the model-based NRE to estimate NO_3^- load reductions in the experimental reactor under a "baseline" scenario to be 11.3%. The relatively low N load reduction without C dosing of either 11.3 or 14.8% is due to low water temperatures in April and May, leading to slow microbial kinetics. The improvement of the N load reduction to 24.1%, or more than double the model-based "baseline" scenario for the experimental reactor, demonstrates the potential for exogenous C dosing to meaningfully improve NO_3^- load reductions in WBRs during low-temperature spring conditions. These numbers overestimate the actual cumulative load reductions to some extent since data from the large storm event on May 1 were excluded, and influent NO_3^- loads were
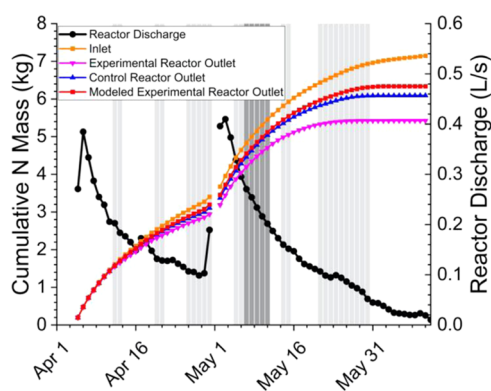
Figure 4. Cumulative NO_3^- N loads entering and leaving the WBRs during the investigation period. Gray bars show days on which acetate dosing occurred. The difference between the orange line and the red line shows the cumulative N load reduction under the model-based "baseline" scenario, while the difference between the orange line and the magenta line shows the cumulative N load reduction achieved with acetate dosing. The data gap on May 1 is due to a lack of reliable discharge data during the large storm event on that date.

high and treatment efficiencies were most likely low on this date due to very short HRTs and bypass flows.

The cumulative mass of acetate-C dosed into the reactor was 4.7 kg of C (Figure S11). Based on measured daily acetate utilization efficiencies (Figure 3B), 2.3 kg of C was metabolized or otherwise retained in the reactor. The ratio of utilized C to additional NO_3^-−N removal achieved by acetate dosing compared to control reactor and "baseline" model estimates were 3.3 kg C/kg N and 2.5 kg C/kg N, respectively. This compares to a theoretical C/N mass ratio of approximately 1.5 for denitrification with acetate as an electron donor and accounting for both energy/maintenance and biomass assimilation[34] (see the SI for details). This analysis indicates that between one-third and two-thirds of the utilized acetate was consumed by processes other than denitrification. We tested whether acetate sorption to woodchips could represent an abiotic sink for acetate in the reactor by using sorption batch experiments. The K_d was determined to be 0.88 L/kg (Figure S12). This K_d is small, roughly 2 orders of magnitude lower than the K_d for pesticide sorption to woodchips,[35] so it was concluded that sorption represented a negligible sink for acetate. Acetate was therefore most likely biologically consumed, including by aerobic metabolism facilitated by the presence of dissolved oxygen in the upstream portions of the reactor (Figure S4). The ratio of total C dosed to additional NO_3^-−N removed was either 6.7 kg C/kg N or 5.1 kg C/kg N, depending on whether the control reactor or the "baseline" model was used to estimate the additional N removed. These high ratios were due to the fact that large fractions of the dosed acetate were unmetabolized in the reactor. Note that this analysis assumes that denitrification based on wood-derived carbon would not be affected by the presence of acetate.

Adverse Water Quality Impacts of Carbon Dosing. In addition to release of acetate in reactor effluent, potential adverse environmental impacts of exogenous carbon dosing include release of DON or other organic matter related to biofouling and/or biofilm sloughing as well as stimulation of microbial sulfate reduction and/or DNRA. A significant release of DON was observed in early April, corresponding to a storm event on April 6 (Figure 5A). This was also associated with a
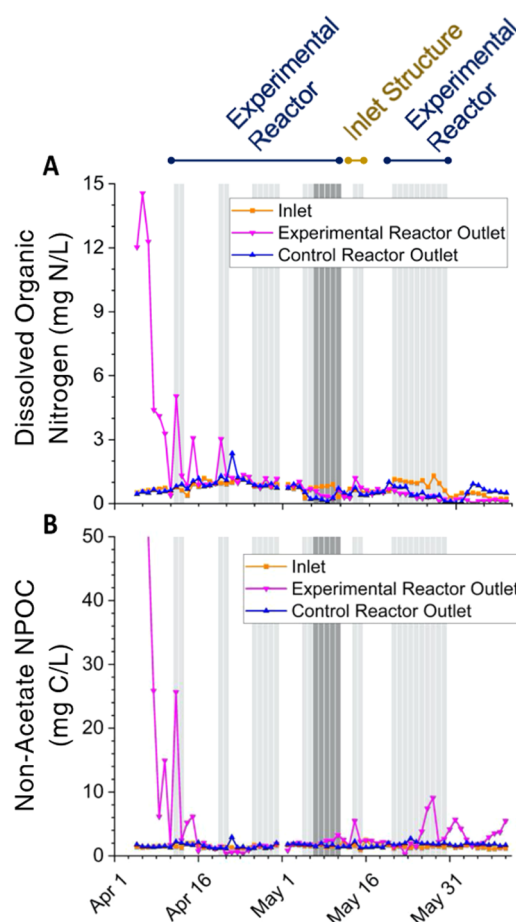
Figure 5. Influent and effluent concentrations of (A) DON and (B) nonacetate DOC. Gray bars show days on which acetate dosing occurred, and blue and gold lines at the top of the figure indicate dosing into the experimental reactor only or into both reactors through the inlet structure.

significant release of nonacetate DOC (Figure 5B). Taken together, these results are consistent with the sloughing of biofilms and/or extracellular polymeric substances (EPS) during and after the storm event. There was an additional significant release of nonacetate DOC, but not DON, in late May. Both of these releases of DON and/or nonacetate DOC occurred only in the experimental reactor, indicating that they were the result of acetate dosing. The event in early April may be attributed to delayed impacts of pilot carbon dosing performed in the previous summer of 2022. Outside of these two events, nonacetate DOC was similar in the experimental and control reactors and ranged from roughly 1−3 mg C/L, consistent with commonly observed levels of woodchip-derived DOC released from WBRs.[13,36]

Carbon dosing increased sulfate removal in the experimental reactor compared to the control, but this was significant only in the dosing period beginning on May 22, when acetate was inadvertently dosed at a greater-than-intended level (Figure S13A). Sulfate reduction occurred in both the experimental and control reactor when flows declined <0.05 L/s. NH_4^+ was detected very infrequently in isolated samples (Figure S13B), so there was no systematic evidence for DNRA leading to the release of NH_4^+ from the reactor.

Techno-Economic Assessment. Operation and maintenance costs ($C_{O\&M}$) of the real-time acetate dosing approach

Table 2. Summary of Exogenous Carbon Dosing in Woodchip Bioreactors

study	duration	setting	temp (°C)	dosed C/N ratio (kg C/kg N)	benefits	adverse impacts
Hartz et al.[17]	52 days	field	13−17 °C	approx. 1.4	completely removed 57−184 mg/L Inlet NO_3^-−N	DOC concentration in the outlet was approximately 10 mg C/L higher than inlet
Roser et al.[18]	34 weeks	lab	5.5 °C	2	14, 15 and 30-fold increase in NRR under 1.5 h-, 8 h- and 12 h-HRT	DOC concentration in the outlet was approximately 30 mg C/L
Feyereisen et al.[19]	4 seasons	field	6−14 °C	2.16	3-fold increase in NRR	reactor biofouling
Moghaddam et al.[41]	∼500 days	lab	∼20 °C	1.48	4-fold increase in NRR	increased sulfate reduction rate; release of methanol in effluent
Moghaddam et al.[42] and Moghaddam et al.[21]	2020: 44 days 2021: 65 days	field	12−18 °C	2020: 1.48−342 2021: 0.34−171	8-fold increase in NRR in 2020; 5-fold increase in 2021	decrease in hydraulic conductivity consistent with biofouling of the woodchip matrix; release of methanol at concentrations >30 mg C/L
this study	∼10 weeks	field	6−12 °C	0.9−2.2	2−5-fold increase in NRR; N load reduction increased from 0.8 to 1.7 kg N	approx. 50% of dosed acetate released in reactor effluent; release of DON during storm event

were determined as the cost of acetate. This was estimated to be 86 USD per additional kg of N removed with acetate dosing, based on the ratio of total dosed acetate to additional NO_3^- removal of 5.1 kg C/kg N determined by comparing the experimental reactor data to the model-based "baseline" estimate for N removal. The annualized capital cost (without $C_{O\&M}$) was determined to be 1,524 USD using the equipment used in our 2023 field study (Table S1). However, because model-based predictions of effluent NO_3^- can be used in place of sensing for dosing decisions (Figure S8), we estimate that this can be reduced to 199 USD by excluding the cost of the NO_3^- sensor and using a lower-cost microcontroller (Table S2). To provide a rough estimate of the N-normalized capital cost, we can assume a representative influent NO_3^- load to the bioreactor from May to November of 30 kg N and a typical cumulative load reduction of ∼20%.[15] If the real-time acetate dosing were able to double the cumulative N load reduction, as was achieved in this study, an additional NO_3^- removal of 6 kg of N could be achieved, for an annualized capital cost of 26 USD/kg of N (without the NO_3^- sensor). This assessment suggests that the cost of acetate will be the key driver of the overall cost of the real-time acetate dosing approach, particularly since economies of scale achievable with large bioreactors[37] and high influent N loads that could decrease N-normalized capital costs will not affect N-normalized acetate costs since C dosing is responsive to discharge and influent N loads.

DISCUSSION

Effects of Exogenous Carbon Dosing in Woodchip Bioreactors. Woodchip bioreactor performance is typically poor during cold periods or storm events,[15,18,21,38−40] and here we evaluated the use of biostimulation of microbial denitrification with exogenous carbon to improve NO_3^- removal during these critical times.[19,21,22] Several studies on exogenous carbon dosing of WBRs have been performed in recent years (Table 2) and have shown that C dosing is effective at increasing NRR. Our results confirm the potential of C dosing to increase NRR up to 5-fold relative to "baseline" conditions, and we quantified an improvement in cumulative N load reduction from 11.3% (under a model-based "baseline" scenario) to 24.1%. Because we performed active carbon dosing during only 28 days of this 67-day experimental campaign, it is likely that greater improvements in cumulative N load reductions are readily achievable. We also acknowledge

that this 2-month field experiment was relatively short, and factors including adaptation of the microbial community to acetate could impact the effectiveness of exogenous carbon dosing and/or release of unmetabolized acetate over longer time scales. Prior field-based studies did not include process modeling to predict bioreactor performance, so an important contribution of this study is the use of process modeling to quantify additional N removal achieved due to carbon dosing beyond "baseline" performance of the bioreactor.

Similar to earlier studies, we also observed the release of unmetabolized C from the reactors. While earlier studies did not quantitatively track their C mass balances, our co-injection of Br^- tracer and monitoring of effluent acetate allowed us to determine that 51.5% of the acetate was not utilized in the reactor. We did not measure the hydraulic conductivity in the reactor and so were not able to assess potential bioclogging of the reactor,[19,21] but higher protein concentrations in experimental reactor woodchips along with release of significant DON and nonacetate DOC in April suggests that C dosing increased biomass on woodchip surfaces and may have contributed to biofilm sloughing events.

A key distinction between these earlier studies and the current investigation is that we used real-time sensing of bioreactor discharge to dose acetate, allowing dosing rates to respond to variability in bioreactor discharge and maintain constant C concentrations of either 7.5 or 15 mg C/L. Constant dosing rates in earlier field studies led to C concentrations and C/N ratios that varied widely with changes in discharge and N loading.[21] Our targeting of relatively low C/N ratios was intended to overcome kinetic limitations to denitrification. Dosing at a relatively low acetate level of 7.5 mg C/L, or a C/N mass ratio of 0.9, effectively stimulated NRR by a factor of 2 to 5 relative to "baseline" performance (Figure S6). This stimulation of NRR was similar to that in earlier studies, which typically employed higher C/N ratios (Table 2), suggesting that lower levels of C dosing can be effective at overcoming kinetic limits to denitrification while minimizing risks of unmetabolized C release.

Notably, the NRR in the experimental reactor was consistently elevated compared to the "baseline" scenario, even when C dosing was not occurring (Figure S6). This was likely due to higher biomass concentrations on experimental reactor woodchips (Figure S7), which we partly attribute to the pilot C dosing that occurred in 2022. These results highlight long-term changes to woodchip properties caused by

C dosing, which may impact performance long after active dosing ends.

Fate of Dosed Acetate in the Woodchip Bioreactor. 51.5% of the dosed acetate was not consumed in the reactor. This release of unmetabolized acetate in the bioreactor effluent is a form of "pollution swapping"[19,21,42] and was the primary drawback of our approach. Improving the efficiency of acetate utilization is essential for minimizing both pollution swapping and for improving the cost-effectiveness of the C dosing approach since the cost of acetate was a major cost driver. One factor that likely led to low acetate utilization was incomplete mixing of dosed acetate (and Br^-) in the reactor (Figure S9). A short period of carbon dosing into the inlet structure rather than in screened wells in the woodchip matrix was used to test the effects of enhanced mixing, but the results were inconclusive, partly because of residual acetate and bromide in the reactor from earlier C dosing. The observation of greater acetate utilization at higher temperatures (Figure S9) also suggests that acetate utilization efficiencies could be higher during warmer times of the year.

The ratio of dosed C to additional N removal was 2.5 kg of C/kg of N, using the model-based "baseline" scenario to estimate additional N removal. The theoretical C/N mass ratio for denitrification with acetate as electron donor is 1.49[34] and sorption to woodchips was low (Figure S12), so a substantial fraction of acetate was consumed by microbial processes other than denitrification. Acetate oxidation by O_2 was probably an important sink for acetate since dissolved O_2 ranged from 2 to 8 mg/L at a location 1.7 m upstream of the acetate injection gallery (Figure S4) and it is plausible that there was residual dissolved O_2 in the water at the wells where acetate was injected. The likely role of O_2 as a sink for acetate also means that efforts to improve mixing of the acetate solution by dosing directly into the inlet structure, where DO concentrations are typically high, will cause a larger fraction of the acetate to be consumed by O_2, decreasing the ratio of metabolized C to N removed. Finally, while acetate dosing did enhance SO_4^{2-} reduction this only occurred in late May when reactor discharge and SO_4^{2-} loads were small (Figure S13A), so SO_4^{2-} reduction represented a relatively small sink for acetate. Acetate production via fermentation in the reactor was likely negligible for most of the experimental study since the presence of NO_3^- throughout the reactor led to high redox potentials (Figure S5), though it is possible that acetate or other fermentation products were released from the reactor as residence times increased and redox potentials dropped at the end of May and early June. Fermentation products could have contributed to the nonacetate NPOC released from the experimental reactor in late May and early June, when higher-than-expected levels of carbon dosing stimulated SO_4^{2-} reduction and the onset of more deeply reducing conditions.

Environmental Implications. Exogenous C dosing into woodchip bioreactors is effective at stimulating NO_3^- removal rates and substantially improving NO_3^- load reductions during cool spring weather when NO_3^- removal in passive treatment systems is poor. Real-time control of C dosing allowed acetate to be dosed at different discharge-dependent rates and to maintain steady C/N ratios. Our results showed that the relatively low C/N ratio of 0.9 kg of C/kg of N was effective at overcoming kinetic limitations to denitrification, indicating that the marginal benefits of targeting stoichiometric C/N ratios of 1.5 to 2 may be small while increasing costs and risks of pollution swapping. Nonetheless, even with this lower C/N

ratio, a significant fraction of the dosed acetate was not metabolized in the reactor. We also caution that this approach was designed for our specific site, and a different control logic may be warranted for WBRs with different characteristics (e.g., with higher or more variable influent NO_3^- concentrations).

The economic cost of N loading to coastal waters is estimated to range from 12 USD to 56 USD/kg N,[43−45] while we determined the cost of acetate alone to be 86 USD/kg N. The costs per kg N removed must therefore be reduced for the C dosing approach to become cost-effective. This analysis underscores the importance of improving acetate utilization efficiency in reactors. We recommend injecting acetate through a subsurface manifold system in the woodchip matrix in order to improve mixing of the dosed C solution while avoiding acetate consumption by O_2 which would occur if acetate is dosed into the inlet structure. The manifold would be located some distance downstream of the reactor inlet, allowing residual dissolved O_2 to be removed before acetate was introduced. The use of low-value labile carbon in liquid forms that could be readily injected via dosing pumps, potentially including a sodium acetate-based ice melt, would also improve cost-effectiveness. It is also possible that acetate dosing could lengthen the lifetime of woodchip beds by providing a non-woodchip carbon source, potentially offsetting costs associated with media recharge. This research has identified a number of opportunities to improve the cost-effectiveness of exogenous carbon dosing that can be pursued in future research. Further study into other lower-cost methods to improve C bioavailability in WBRs (e.g., deliberate drying and reflooding of woodchip media to stimulate release of labile C from woodchip biomass[13,46,47]) is also warranted.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestengg.4c00020.

> Additional methodological details on woodchip characterization, determination of theoretical C/N ratios, biokinetic modeling, and the techno-economic assessment; summarizing costs of real-time control approach; and visualizing sensor data, cumulative acetate dosing, stimulation of nitrate removal rates, and other additional results (PDF)

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