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Linking Denitrification and Infiltration Rates during Managed Groundwater Recharge

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 Supporting Information

ABSTRACT: We quantify relations between rates of in situ denitrification and saturated infiltration through shallow, sandy soils during managed groundwater recharge. We used thermal methods to determine time series of point-specific flow rates, and chemical and isotopic methods to assess denitrification progress. Zero order denitrification rates between 3 and 300 $\mu\text{mol L}^{-1} \text{d}^{-1}$ were measured during infiltration. Denitrification was not detected at times and locations where the infiltration rate exceeded a threshold of $0.7 \pm 0.2 \text{ m d}^{-1}$. Pore water profiles of oxygen and nitrate concentration indicated a deepening of the redoxcline at high flow rates, which reduced the thickness of the zone favorable for denitrification. Denitrification rates were positively correlated with infiltration rates below the infiltration threshold, suggesting that for a given set of sediment characteristics, there is an optimal infiltration rate for achieving maximum nitrate load reduction and improvements to water supply during managed groundwater recharge. The extent to which results from this study may be extended to other managed and natural hydrologic settings remains to be determined, but the approach taken in this study should be broadly applicable, and provides a quantitative link between shallow hydrologic and biogeochemical processes.



INTRODUCTION

Global extraction of groundwater for agriculture, municipal, and industrial use has increased dramatically in recent decades, and aquifer overdraft is a common problem throughout the world.^{1,2} In addition, groundwater resources are increasingly threatened by nutrient contamination. Intense global use of nitrogen (N) fertilizers in the last half century has led to widespread nitrate (NO_3^-) contamination of groundwater, particularly in regions of extensive agricultural development.^{3–6} Nitrate contamination in groundwater poses an immediate risk to human health, and can lead to eutrophication of surface water bodies receiving groundwater discharge.⁷

Protecting the quality and quantity of groundwater supplies requires flexible management strategies that promote replenishment of aquifers. Artificial recharge of groundwater using surface water, commonly known as managed aquifer recharge (MAR), is an important management strategy for augmenting supplies⁸ and potentially improving water quality through physical and biogeochemical processes during infiltration and subsurface transport.^{9,10} MAR can use nonpristine water sources such as stormwater runoff, excess irrigation flows, and treated wastewater.^{11,12} Many potential MAR sources have high

concentrations of nutrients, especially nitrate, requiring a better understanding of techniques and conditions that could be used to reduce nutrient loads in infiltrating water.

Denitrification, a microbially mediated process by which nitrate (NO_3^-) is converted to dinitrogen gas (N_2), can remove nitrate during MAR. Denitrification is often carried out by facultative heterotrophic bacteria that utilize nitrate NO_3^- as a terminal electron acceptor when dissolved oxygen (DO), which is energetically favorable, is unavailable.¹³ In recent decades, there has been considerable interest in quantifying denitrification in aquatic systems because this process can help to reduce nitrogen loading, and because incomplete denitrification results in emissions of N_2O which is a powerful greenhouse gas.^{14,15} Denitrification rates in shallow sediments are influenced by redox conditions,¹⁶ nutrient concentration,^{17,18} availability of dissolved and sedimentary organic matter,^{19–22} soil–water content,^{10,23} soil texture,²⁴ mineral composition of the sediments,²⁵ water

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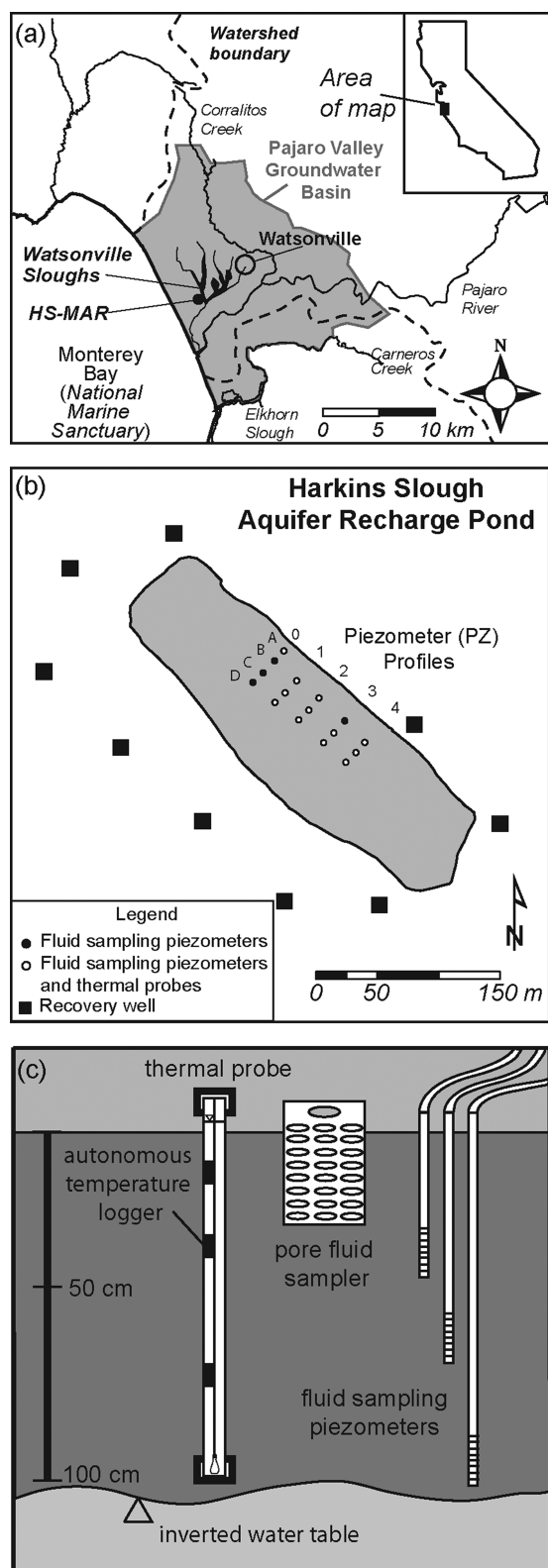


Figure 1. Maps and diagrams showing field site and methods used in this study. (a) Regional map showing the Pajaro Valley Groundwater Basin and the location of the recharge pond (labeled HS-MAR). Inset shows location of site in central coastal California, U.S.A. (b) Detailed site map showing instrument locations within the Harkins Slough artificial recharge pond. (c) Schematic illustration showing a cluster of instruments for thermal measurement and fluid sampling in shallow soils below the base of the infiltration pond.

temperature,²⁶ and fluid residence time.²⁷ However, the effects of fluid flow on denitrification rates remain poorly understood in many settings, in part because of the difficulty of making contemporaneous, in situ measurements of both processes. Studies conducted at the mesocosm scale have limited ability to capture spatial and temporal heterogeneity in fluid flow, and studies conducted at larger scales generally use spatially averaged fluid flow rates, obscuring functional relationships. Laboratory studies also may not be representative of field conditions. For example, Smith et al.²⁸ estimated denitrification rates that were up to 26 times higher in incubation experiments using cores of aquifer material than rates determined in situ in the same aquifer. Similarly, laboratory experiments using intact stream sediment cores found denitrification rates of 100–400 mg N m⁻² d⁻¹, whereas studies completed at the reach scale detected no denitrification once dilution of the stream by groundwater was taken into account.²⁹

The primary objective of this study was to link the spatial and temporal dynamics of fluid flow and denitrification. We accomplished this goal by combining pore-fluid nitrate concentration and isotopic data with point-specific infiltration rates. Fieldwork was completed within an operating MAR system, which has uniquely strong experimental control at a field scale, with accurate accounting of fluid and nutrient storage and fluxes. An earlier study at this field site showed that the nutrient load delivered to the aquifer during MAR is 30–60% less than that in water entering the recharge pond, based on an assessment of whole-system infiltration rates and changes to local nitrate concentrations in shallow sediment pore fluids.³⁰ In this study, we combine newly developed methods to measure infiltration rates with contemporaneous and collocated determination of denitrification rates to relate the dynamics of shallow hydrologic and biogeochemical processes to nitrate load reduction.

EXPERIMENTAL SITE AND METHODS

Field Site. Field work was completed using the Harkins Slough managed aquifer recharge system (HS-MAR), located in the Pajaro Valley of central coastal California (Figure 1). The HS-MAR system is a three hectare infiltration pond that occupies a modified natural depression having a maximum depth of 6 m. Water is diverted to the recharge pond from nearby Harkins Slough (a wetland draining part of the 3400 km² Pajaro River watershed) during the winter rainy season when flows are sufficiently high. As infiltration proceeds during each operating year (typically 100 days between January to May), a wetting front and inverted water table are driven downward into soils underlying the pond, eventually forming a 1–2 m thick saturated layer. Infiltrating water passes through a 20–30 m thick vadose zone and creates a local water table mound in the underlying perched aquifer within eolian, fluvial, and alluvial sediments.³¹ Diversions from Harkins Slough to the infiltration pond continue each year until the rate of infiltration below the pond is greatly reduced because of a reduction in hydraulic conductivity.³² At the end of each operating season when the pond is dry, shallow soils are scraped and tilled in preparation for future MAR. Artificial recharge water is recovered from the shallow aquifer using dedicated wells that encircle the pond, blended with water from elsewhere in basin, and distributed to local growers for use in irrigation.

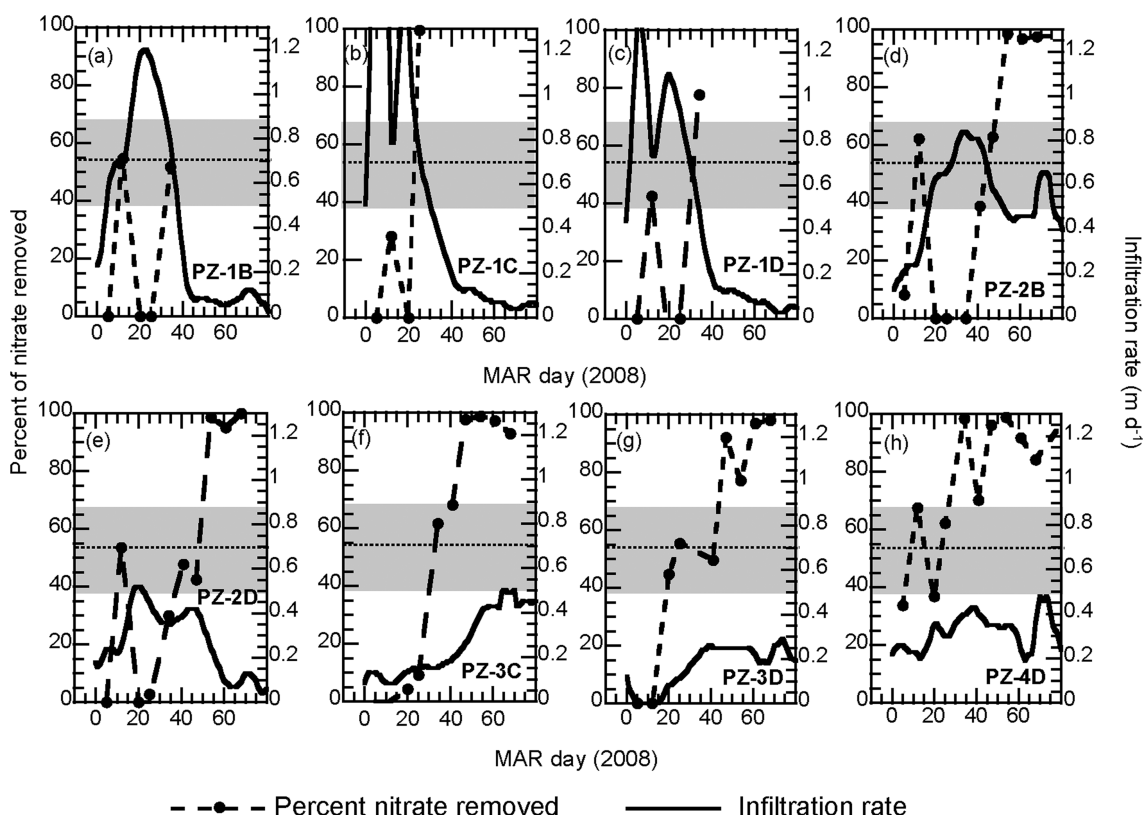


Figure 2. Infiltration rate and the percentage of initial nitrate concentration removed during 2008 operations at eight piezometer where collocated measurements were made. Water samples were collected at piezometers screened at 0.5 m depth beneath the base of the pond.

Point Measurements of Infiltration Rate. Point-specific infiltration rates during MAR were determined using heat as a tracer, applying time-series analysis to subsurface thermal data.^{32–34} Temperature was recorded at 15-min intervals with a resolution of 0.02 °C using autonomous thermal loggers suspended on cables inside water-filled, 3.8 cm diameter polyvinyl chloride (PVC) tubes (Figure 1b,c). Tubes were installed in holes excavated with a hand auger, and the annulus around the tubes was backfilled with bentonite and native soil (2008), or silica slurry (2009), to ensure a good thermal contact with the surrounding soil. Time-series records of temperature were filtered to extract daily temperature fluctuations, and pairs of subsurface sensors were analyzed to resolve the amplitude reduction of this diurnal temperature signal with depth. These values were used to solve for fluid infiltration rates based on a one-dimensional (vertical) conservation of heat equation.³⁴ This method yields daily values of the vertical component of infiltration representative of the interval between sensors pairs. Infiltration rates were interpreted only when soils surrounding the sensors were saturated,³² which corresponds to times when shallow piezometers were used to recover pore water samples.

Fluid Sampling and Nitrate Measurements. Synoptic water samples were collected from the infiltration pond itself and from nests of piezometers screened beneath the base of the pond (Figure 1b,c). Twelve piezometer nests were installed along four transects during the 2008 operating season, with screen depths of 50 and 100 cm beneath the base of the pond. An additional profile was added in 2009 and fluid sampling piezometers were screened at depths of 30, 60, and 90 cm to improve vertical resolution. Data presented in this study are from piezometers

collocated with eight thermal probes in 2008 and three thermal probes in 2009. Fluid sampling piezometers were constructed from 1-cm diameter polycarbonate tubing, perforated at the base and wrapped with a fine mesh nylon screen. Piezometer holes were bored with a hand auger when the pond was dry, and a coarse sand filter (grain diameter = 0.7–1.7 mm, well rounded, >97% silica) was installed around the screen and capped with a 10 cm bentonite seal. The annulus of each borehole was back-filled with native soil, and a second bentonite seal was placed at the ground surface to prevent water from flowing down the piezometer tubing. Piezometers were developed after installation to ensure a good connection with the formation by saturating the sand filter and soil around the screens, then flushing water back and forth through the piezometer screen using a peristaltic pump.

Fluid samples from piezometers were collected with nylon tubing that extended to the edge of the pond, allowing access throughout MAR operations. Additionally, pore water samples were collected throughout the season using dialysis samplers (peepers).³⁵ Peepers were submerged in a container filled with deionized water and bubbled with N₂ for a minimum of 10 days, then deployed in the base of the pond as it was being filled. Peepers were left deployed in the base of the pond for at least 14 days, then they were recovered sequentially at different times during the MAR season, providing samples that are most representative of conditions for ~24 h preceding recovery.³⁶

Water samples were field filtered with 0.45 μmol cellulose acetate filters into acid washed polyethylene bottles. A subset of samples was filtered through 0.22 μmol cellulose acetate filters for nitrate isotopic analysis. All samples were placed on ice immediately and returned to the lab. Samples collected for

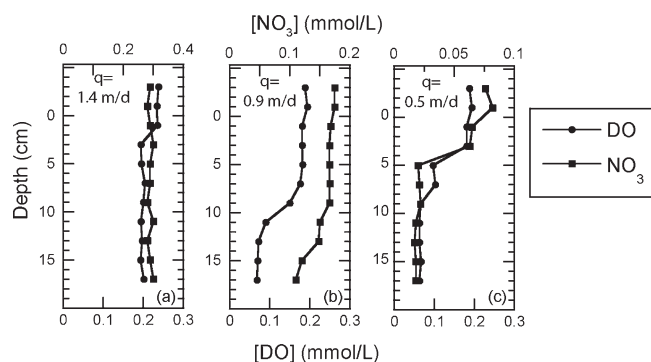


Figure 3. Porewater concentrations of DO and NO_3^- at three different infiltration rates at location 0B. (a) 1.4 m d^{-1} on MAR day 10 (b) 0.9 m d^{-1} on MAR day 21 and (c) 0.5 m d^{-1} , on MAR day 30.

nutrient analysis were stored at 4°C and samples collected for isotopic analysis were frozen until analyzed. Dissolved and total nutrient concentrations were determined within one week of collection by colorimetric flow injection analysis on a Lachat Instrument QuickChem 800, with accuracy (based on field and lab blanks, spikes, and standards) of 2–5%. The $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate (relative to air and VSMOW, respectively) were measured at the UCSC Stable Isotope Facility using a procedure modified from McIlvin and Altabet (2005). Absolute accuracy for NO_3^- isotopic analyses was 0.2‰ and 0.3‰ for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, respectively.

Identifying Denitrification and Quantifying its Rate. We used the difference between $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate in pond surface water and residual nitrate in pore fluids to identify the occurrence of net denitrification. Isotopic fractionation during microbial denitrification causes residual nitrate to become progressively enriched in $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$, with a typical fractionation ratio ($\Delta\delta^{18}\text{O}:\Delta\delta^{15}\text{N}$) around 0.6.^{37,38} At times and subsurface locations where this characteristic enrichment of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of nitrate was observed, we used the gradient in NO_3^- concentration to quantify the extent of net denitrification during infiltration. Denitrification rates (r) were determined as follows:

$$r = \{[\text{NO}_3^-]_{\text{initial}} - [\text{NO}_3^-]_{\text{piezometer}}\}/t \quad (1)$$

where initial refers to samples collected in pond surface water, piezometer refers to porewater sampled from piezometers screened in the saturated sediments beneath the pond, and t is the mean travel time between the bottom of the pond and the piezometer screen. The dominant flow direction through shallow, saturated soil below the pond is vertically downward (the pond is much wider than deep, and vertical head gradients are considerably larger than horizontal gradients),³² so the mean travel time from the pond to subsurface piezometer screens, and between screens, is approximated as a function of infiltration rate and spacing between sampling points. Water samples from the pond and piezometers were collected on the same day due to rapid rates of infiltration relative to the spacing between sample depths, and the comparatively slow rate of change of nitrate concentration in the pond.

RESULTS

Infiltration Rates. Point measurements of daily infiltration rate indicate considerable temporal and spatial variability in the rate of infiltration through the base of the pond. Infiltration rates

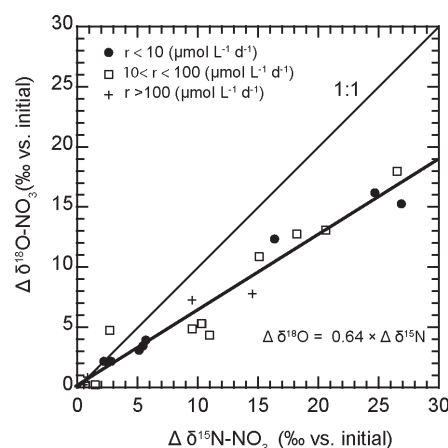


Figure 4. Change in $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of NO_3^- during infiltration in 2008 for the same locations shown in Figure 2. $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values of nitrate in pond surface water represented initial nitrate isotopic compositions. The linear relationship and ratio of isotopic enrichment $\Delta\delta^{18}\text{O}:\Delta\delta^{15}\text{N}$ of 0.64 ($r^2 = 0.96$) suggest that net denitrification occurred in the saturated zone beneath the recharge pond. Samples are grouped according to denitrification rate (r), to show that a consistent relationship between denitrification rate and the magnitude of $\Delta\delta^{15}\text{N}$ and $\Delta\delta^{18}\text{O}$ was not observed in this study (Table S1, Supporting Information).

ranged from <0.1 to 4.4 m d^{-1} . The highest rates of infiltration occurred at piezometers located in Profiles 0, 1, and 2 (Figures 2a–e, and S1 in Supporting Information). In this portion of the pond, infiltration rates were higher for the first 40 days of operations, followed by a rapid decline. In contrast, infiltration rates measured in piezometers in profiles 3 and 4 ranged from <0.1 to 0.2 m d^{-1} when the pond was first filled. In this portion of the pond, infiltration rates gradually rose throughout the MAR operating season, but never exceeded 0.5 m d^{-1} (Figures 2f–h).

Denitrification During Infiltration. Nitrate was the dominant form of inorganic nitrogen in pond water during this study. The concentration of nitrate in the pond ranged from $650 \mu\text{mol L}^{-1} \text{NO}_3^-$ when the pond was first filled to $20 \mu\text{mol L}^{-1} \text{NO}_3^-$ at the end of the season, with changes occurring relatively smoothly and systematically throughout the two operating seasons (Figure S2, Supporting Information). Nitrate concentration in the pond declined over time due to flushing of the slough by winter rain, with nitrate concentration generally $<100 \mu\text{mol L}^{-1}$ after the first 40 days of operations. Ammonium was present in the pond water at concentrations typically less than $5 \mu\text{mol L}^{-1} \text{NH}_4^+$. The concentration of dissolved organic carbon in the pond was considerably higher than that of nitrate, ranging from 0.5 to $2 \text{ mmol L}^{-1} \text{C}$.

DO and NO_3^- concentration profiles in pore water were determined with dialysis samplers at several locations collected when infiltration rates were between 0.5 to 1.4 m d^{-1} (Figure 3). These data show that the zone of oxygen penetration into the subsurface deepened at higher flow rates. Oxidic conditions persisted to $>15 \text{ cm}$ when the infiltration rate was above 1 m d^{-1} , but shallowed to 5 cm at an infiltration rate of 0.5 m d^{-1} . The depth at which NO_3^- removal was initiated was also shallower at lower flow rates. At the resolution of the dialysis samplers (2 cm), the reduction of $[\text{DO}]$ and $[\text{NO}_3^-]$ was collocated when infiltration rates were $<0.9 \text{ m d}^{-1}$.

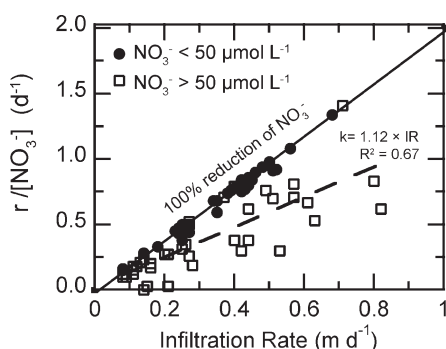


Figure 5. Cross plot of denitrification rate, r , normalized by initial nitrate concentration $[\text{NO}_3^-]$ versus infiltration rate into the saturated zone beneath the pond. Samples with initially higher and lower values of $[\text{NO}_3^-]$ show different, but internally consistent, trends.

Nitrate concentrations in the saturated zone beneath the pond were lower than in pond surface water at times and locations where and when infiltration rates were less than $0.7 \pm 0.2 \text{ m d}^{-1}$ (Figure 2). At locations where infiltration rates were consistently less than $0.7 \pm 0.2 \text{ m d}^{-1}$ (e.g., PZ-3D and PZ-4D), the percentage of nitrate removed in the subsurface increased with time of MAR operations, and a 60% decrease from the initial nitrate concentration was common. The threshold infiltration rate above which denitrification was not observed varied somewhat between sampling locations. For example, nitrate removal was not observed at infiltration rates above 0.5 m d^{-1} at piezometers in Profile 2, whereas nitrate removal was observed at infiltration rates up to 0.8 m d^{-1} at PZ-1C (Figure 2).

The isotopic composition of nitrate in water diverted to the pond changed over the time, with both the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate in the pond decreasing during the operational season (Table S1, Supporting Information). Figure 4 shows the change in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ ($\Delta\delta^{15}\text{N}$, $\Delta\delta^{18}\text{O}$) between pond water and residual nitrate in pore waters sampled on the same day at times and locations where NO_3^- concentrations decreased during infiltration. In many locations both $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ increased by more than 15 ‰ in the first 50 cm of infiltration, but values at individual locations vary considerably. The absolute magnitude of the change in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate varied over time and between sample locations, and we did not observe a relationship between denitrification rate and isotopic enrichment. However, despite variability in the magnitude of $\Delta\delta^{15}\text{N}$ and $\Delta\delta^{18}\text{O}$ we observed a relatively consistent ratio of $\Delta\delta^{18}\text{O}$: $\Delta\delta^{15}\text{N} = 0.64$ (Figure 4).

Zero order denitrification rates in the saturated zone beneath the pond ranged from 3 to $300 \mu\text{mol L}^{-1} \text{ d}^{-1}$. The highest rates of denitrification occurred when $[\text{NO}_3^-]$ in the pond was $>100 \mu\text{mol L}^{-1}$, and denitrification rates generally decreased with pond nitrate concentration, consistent with a first-order behavior. When $[\text{NO}_3^-]$ was less than $50 \mu\text{mol L}^{-1}$, near complete removal of NO_3^- during shallow infiltration was common. Because denitrification rates decreased with the pond nitrate concentration, it is useful to normalize by initial nitrate concentration when comparing denitrification rates between locations and sampling dates. There was a positive correlation between infiltration rate and first order denitrification rate at all locations monitored in 2008 and 2009 (Figure 5).

DISCUSSION

Reductions in nitrate concentration and dual enrichment of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of residual nitrate were observed in the sediments beneath the recharge pond, consistent with microbial denitrification occurring during infiltration. Denitrification in the saturated zone below the infiltration pond occurred when infiltration rates were between 0.01 m d^{-1} and 0.9 m d^{-1} . At locations in Profiles 0, 1, 2, where infiltration rates tended to be greatest, there was no measurable denitrification in the upper 1 m of soil when infiltration rates were above $0.7 \pm 0.2 \text{ m d}^{-1}$. When the rate of infiltration was below the maximum threshold, denitrification rate was positively correlated with infiltration rate. This observation suggests that the higher flux of NO_3^- into the subsurface may have stimulated denitrification. This interpretation is consistent with laboratory experiments during which increased fluid flow enhanced uptake of DO and NO_3^- by stimulating facultative aerobes which rapidly switch to NO_3^- once [DO] is lowered.^{39,40}

The ability of the soil microbial community to denitrify available nitrate at higher infiltration rates was likely limited by deeper penetration of oxygen into the saturated zone (Figure 3). Deepening of the redoxcline reduced the thickness of the saturated zone that was favorable for denitrification. In addition, the residence time of infiltrating water within this zone was reduced at higher infiltration rates, limiting the time available for denitrification processes to occur. From the present study it is not possible to determine if denitrification occurred in the unsaturated zone beneath our sampling points at times when high rates of infiltration caused deeper penetration of oxic conditions. However, no additional denitrification beneath the shallow saturated zone was detected in a prior study of nitrate loading at this site.³⁰ If denitrification does not occur in the unsaturated zone, then denitrification during MAR is limited mainly by the thickness of saturated zone, particularly at high rates of infiltration.

The highest zero-order rate of denitrification observed in this study was $300 \mu\text{mol L}^{-1} \text{ d}^{-1}$, whereas the average rate of denitrification calculated for shallow soils below the MAR pond system was $40 \mu\text{mol L}^{-1} \text{ d}^{-1}$. Denitrification rates in artificial recharge systems are not widely reported, but rates between 40 and $500 \mu\text{mol L}^{-1} \text{ d}^{-1}$ can be inferred from infiltration rates and gradients in nitrate concentrations reported by Greskowiak et al.⁴¹ for a recharge pond near Lake Tengel, Germany. Interestingly, in that system a reduction in nitrate concentration was observed at flow rates as high as 3 m d^{-1} , but significant nitrate removal at 150 cm depth beneath the pond was not achieved until infiltration rates declined to less than 1 m d^{-1} . Zero order denitrification rates calculated in this study and in Greskowiak et al.⁴¹ are within the range of values determined for small streams, lakes, and rivers reported in recent compilations (after converting MAR denitrification rates by volume to rates by area).^{43,46} However, MAR denitrification rates reported here and in Greskowiak et al. are among the highest reported in the groundwater literature, where rates of less than $1 \mu\text{mol L}^{-1} \text{ d}^{-1}$ are more common.^{42,43} Apparent denitrification rates are likely higher in MAR systems due to high flow rates, and because measurements are made over short flow paths that isolate the denitrifying zone. Denitrification rates in the Harkins Slough MAR system may also be comparatively high because there is no limitation on the availability of dissolved carbon as diverted water originates from a local wetland with high carbon content.

It is possible that similarly high rates of denitrification occur in natural groundwater systems where there is an adequate supply of electron donors and solutes migrate into zones of reducing conditions, but these elevated denitrification rates would be difficult to detect in studies conducted over long flow paths. For example Tesoriero et al.⁴⁴ measured denitrification rates of 3.5 to 7 $\mu\text{mol L}^{-1} \text{d}^{-1}$ along an approximately 9 month long groundwater flow path to a creek, but in situ estimates of denitrification across the redoxcline adjacent to the creek were as high as 385 $\mu\text{mol L}^{-1} \text{d}^{-1}$.

The primary uncertainties in the denitrification rates determined in this study result from errors in infiltration rates calculated using thermal methods, and analytical errors associated with fluid sampling, processing and lab analyses. The latter are relatively small based on the methods used in this study, generally <5%, but accurate determination of infiltration rates using thermal methods requires measurement or estimation of soil thermal properties (conductivity, heat capacity, dispersivity) that vary in natural sediments.⁴⁷ For a true infiltration rate of 1 m d^{-1} , errors in calculated values on the order of $\pm 20\%$ are expected based on a reasonable range of sediment properties.³⁴ Errors of this magnitude would have little influence on the relative spatial and temporal trends documented in this study, although they would shift calculated denitrification rates proportionately.

This study illustrates considerable spatial and temporal variability in denitrification rates during infiltration, even within a relatively homogeneous and controlled soil–water system. In addition, at 50% of the locations where point infiltration rate measurements were determined in 2008 and 2009, the rate of infiltration was too high to allow measurable denitrification for periods of 1 day (PZ-2B) to 17 days (PZ-1B). This suggests that limiting infiltration rates during MAR could be beneficial for improving water quality in underlying aquifers.

It remains to be determined how representative our results are for rates of denitrification in other MAR systems, and within a variety of natural hydrologic systems, when there is no limit to available organic carbon and other electron donors. That said, this work shows how quantitative links can be elucidated between hydrologic and biogeochemical processes during soil infiltration. Additional work is needed to determine the nature of microbial populations that are most important for facilitating denitrification in shallow soils during infiltration and recharge, and the extent to which conditions in managed systems can be optimized so as to achieve simultaneous water supply and water quality objectives.

■ ASSOCIATED CONTENT

S Supporting Information. A table (Table S1) of the data presented in Figure 3 and three figures which provide additional experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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