

# Process and Controls on Rapid Nutrient Removal During Managed Aquifer Recharge

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## Introduction

Managed aquifer recharge (MAR) is used to augment water supplies and limit the adverse impacts of groundwater overdraft. However, as demands on groundwater continue to grow and MAR projects become more common, it is increasingly difficult to secure high-quality water sources for MAR. Instead, resource managers must explore options for using MAR sources such as stormwater runoff, treated wastewater, and supplies influenced by agricultural activity. Many such sources are impaired by elevated nutrient concentrations; thus there is a need to understand the conditions under which the quality of managed recharge can be improved. We are studying processes controlling recharge rates and the impacts of MAR on water quality,

with a focus on reducing the nitrate load reaching underlying aquifers.

The central coast region of California (Figure 1) depends heavily on groundwater for agricultural and municipal uses. Overdrafted aquifers are common in this region, resulting in seawater intrusion and other undesirable conditions and processes. To augment the regional freshwater supply and decrease pumping in the coastal zone, the Pajaro Valley Water Management Agency (PVWMA) operates a MAR project as part of a broader effort to improve groundwater conditions in the basin. Surface water is diverted from Harkins Slough during winter (rainy) months when there is sufficient flow in the slough. Diverted water is filtered and pumped into a pond (a modified natural depression) overlying unsaturated eolian and fluvial sand deposits.

Recharge water creates a local mound above a clay layer about 30 m below the base of the pond, then is recovered by dedicated wells that encircle the pond for distribution to local growers. As a result of agricultural and other activities in the basin, diverted slough water is often rich in nitrate (historical values as high as 4 mM); similarly high nitrate values have been measured in water from underlying aquifers.

## Methods

Prior to the Water Year 2008 MAR operational season, we instrumented the Harkins Slough recharge pond to quantify seepage rates and sample infiltrating water beneath the base of the pond. Whole-pond mass balance and infiltration rates were quantified based on a detailed topographic survey of the pond and continuous records of inflows, water level, pond area, precipitation, and evaporation. Nutrients and major ion chemistry were monitored weekly during MAR operation in wells surrounding the recharge pond and in piezometers screened in the shallow subsurface beneath the pond (Figure 1). The stable isotopic composition of nitrate in recharge pond and piezometer water samples was analyzed to investigate whether microbial denitrification (a process which converts nitrate to di-nitrogen gas) could be a mechanism of nitrate removal during recharge. All isotopic data are reported using standard delta notation:

$$\delta (\%) = (R_{\text{sample}} - R_{\text{standard}}) / R_{\text{standard}} \times 1000$$

where  $R_{\text{sample}}$  is the ratio of the heavy to light isotope of a sample and  $R_{\text{standard}}$  is the ratio of the heavy to light isotope of the standard. Nitrogen and oxygen

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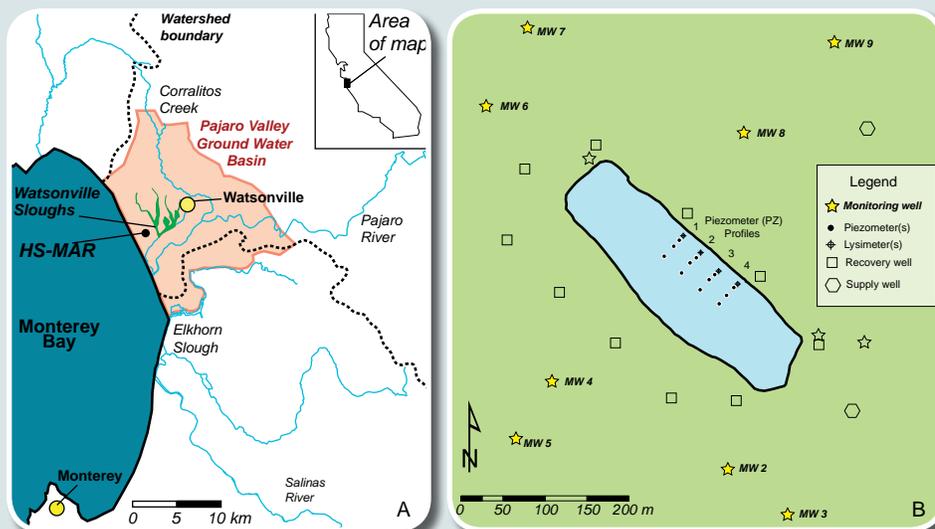


Figure 1. (A) Location of the field area in central coastal California. The MAR project is located adjacent to Harkins Slough, part of a large wetland system draining southern Santa Cruz county. (B) Site map of Harkins Slough managed aquifer recharge pond, adjacent monitoring wells, and piezometer installations.

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isotope ratios are reported relative to atmosphere and Vienna Standard Mean Ocean Water, respectively.

Results and Discussion

MAR totaled  $6.0 \times 10^6 \text{ m}^3$  (810 ac-ft) in 2008, with diversions occurring from January to May. Diversion was stopped periodically due to variable water quality and slowing percolation rates. The peak recharge rate of 1.5 to  $2.0 \times 10^4 \text{ m}^3/\text{day}$  (12 to 16 ac-ft/day) was maintained for nearly 30 days (Figure 2). The greatest pond-wide specific infiltration rate of 1 m/d was achieved within 10 days of filling the pond. Infiltration rates decreased after about 30 days of MAR, eventually becoming nearly stagnant after 50 days.

After delivery of  $3 \times 10^5 \text{ m}^3$  (about 240 acre-feet), mounding of recharge water became apparent in monitoring wells located 300 to 600 meters from the pond (Figure 2). Prior to filling the recharge pond, head measurements suggest that groundwater in the underlying aquifer flowed mainly to the southwest. The formation of a local mound eventually reversed the head gradients north of the pond. Wells south of the pond showed the greatest response to recharge water, with head increases of 4.5 to 5 meters.

The chemistry of water in the shallow aquifer comprises a mixture of natural recharge from precipitation, MAR water, and irrigation returns from surrounding agricultural fields.

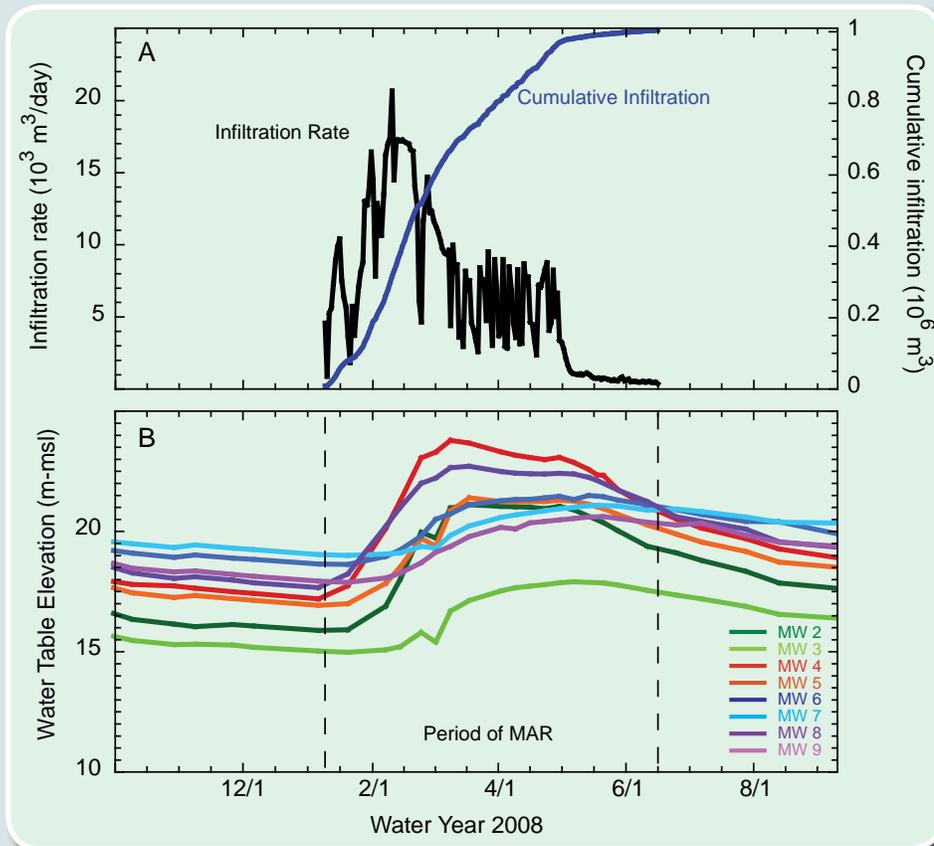


Figure 2. (A) Record of daily infiltration rate and cumulative infiltration from the Harkins Slough recharge pond in the 2008 water year. Daily infiltration rates are based on a pond mass balance calculation derived from measurements of inflows (slough diversions), precipitation, evaporation and storage. (B) Water table elevation in monitoring wells surrounding the recharge pond. The formation of a local groundwater mound is apparent two weeks after the start of MAR.

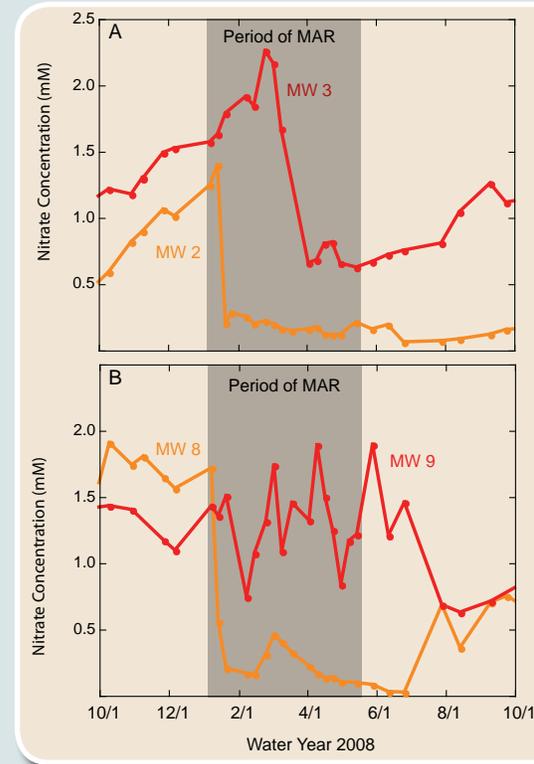


Figure 3. (A) Concentration of nitrate in monitoring wells MW 2 and MW 3 located downgradient from the recharge pond. (B) Concentration of nitrate in MW 8 and MW 9 located upgradient from the pond. While the arrival of MAR water can be seen at MW 2, 3 and 8, MW 9 appears to be minimally impacted by MAR despite being a similar distance away from the pond as MW 3.

Changes in the groundwater chemistry showed the arrival of MAR water within days of filling the pond, much faster than would be predicted based on whole-pond infiltration rates. In 2008, the concentration of nitrate in the underlying aquifer was significantly diluted by the addition of low-nitrate MAR water. The composition of the groundwater observed in downgradient monitoring wells MW 2 and MW 3 showed a greater proportion of recharge water than those north of the pond (MW 8 and MW 9), where the local groundwater mound reversed the flow direction in the aquifer (figure 3). Although the arrival of low-nitrate

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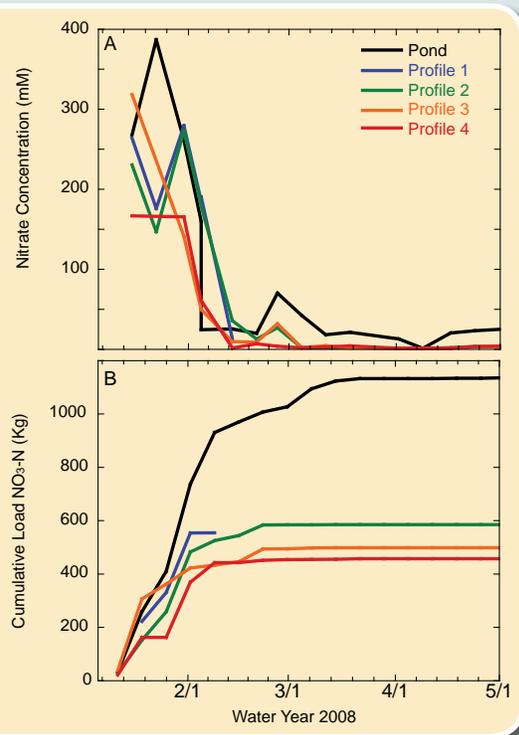


Figure 4. (A) Comparison of the concentration of nitrate in the recharge pond and piezometers screened 0.5 m beneath the pond in instrument profiles 1, 2, 3, 4. (B) Apparent cumulative load of nitrate-nitrogen in the recharge water and piezometers. Load calculations are based on weekly infiltration volumes for the whole pond and weekly measurement of nitrate concentration in a given piezometer profile. This calculation compares potential load reductions if the behavior at that profile is applied to the whole pond infiltration.

MAR water was observed at MW 2 within days of filling the recharge pond, it was several weeks before MAR chemistry was detected at MW 3. To the north of the pond, which is upgradient prior to development of the local mound, the composition of groundwater quickly approached that of the diversion water at the closest well, MW 8, but MAR had minimal influence on the groundwater chemistry observed at MW 9 (Figure 3b). Variations in water level and chemistry around the

recharge pond suggest heterogeneous recharge and flow within the perched aquifer.

Nitrate concentrations were lowered in the underlying aquifer during MAR primarily from dilution, but substantial reduction in nitrate concentrations was also observed during shallow infiltration. The concentration of nitrate in diverted slough water was reduced by 10 to 98% during the first meter of infiltration throughout recharge operations in 2008 (Figure 4a). The greatest reductions of concentration occurred at lower nitrate concentrations and slower infiltration rates, but load reductions were significant at higher recharge rates as well, even though removal efficiencies were lower. Observations of nitrate concentrations and recharge rates suggest that the cumulative removal of nitrate after the 40th day of the recharge season was on the order of 600 kg nitrate-N, or more

than 50% of the nitrate mass diverted from the slough into the MAR pond (Figure 4b).

Potential mechanisms for the nitrate removal during infiltration include assimilation by plants and microbial denitrification. Microbial denitrification is a process by which nitrate is converted to di-nitrogen gas during the oxidation of organic carbon, generally within a low oxygen environment. Whereas assimilation by plants comprises a temporary sink for nitrate, denitrification represents a true removal of nitrogen from the aquatic environment. Denitrification is well documented in many environments such as rivers and wetlands, but the extent and controls on denitrification during recharge are not well understood (Böhlke et al., 1995).

Stable isotopes of nitrate are useful for identifying denitrification because

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this process is known to enrich the residual nitrate pool in the heavier isotopes of nitrogen and oxygen (higher  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  values) in a characteristic ratio of 1:2 (Böttcher et al., 1990). In shallow sediments below the Harkins Slough recharge pond, the ratio of  $\delta^{18}\text{O}$  to  $\delta^{15}\text{N}$  in nitrate of infiltrating water was consistently enriched with respect to the nitrate in diversion water. The isotopic enrichment proceeded along a ratio of 1:2 in a plot of  $\delta^{18}\text{O}$  versus  $\delta^{15}\text{N}$  in nitrate, suggesting that denitrification is the likely mechanism of removal (Figure 5). Interestingly, diverted slough water had  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  values that were relatively high when compared with typical values of fertilizers ( $\delta^{15}\text{N}$  -5‰ to +10‰) and soil nitrogen ( $\delta^{15}\text{N}$  +3‰ to +7‰) (Kendall, 2008), suggesting that some denitrification may also have occurred in the slough before diversion to the recharge pond. Denitrification in this system of rapid infiltration does not appear to be limited by the supply of carbon, as organic carbon concentrations in infiltrating water remain high throughout the recharge season. A significant finding of this research is that conditions in the shallow subsurface of the pond can support microbial denitrification, even at infiltration rates as high as 1 m/d, when it might be expected that dissolved oxygen levels would be too high for denitrification to operate efficiently.

## Conclusions

MAR can lead to significant changes in groundwater chemistry. Combined studies of physical and chemical hydrogeology help to resolve water and solute flow paths, reaction, and fate. Groundwater mounding and chemistry below the Harkins Slough MAR pond suggest that recharge, flow, and reactions occur heterogeneously. Nitrate concentrations decrease consistently within the shallow subsurface below the recharge pond, and stable isotopes

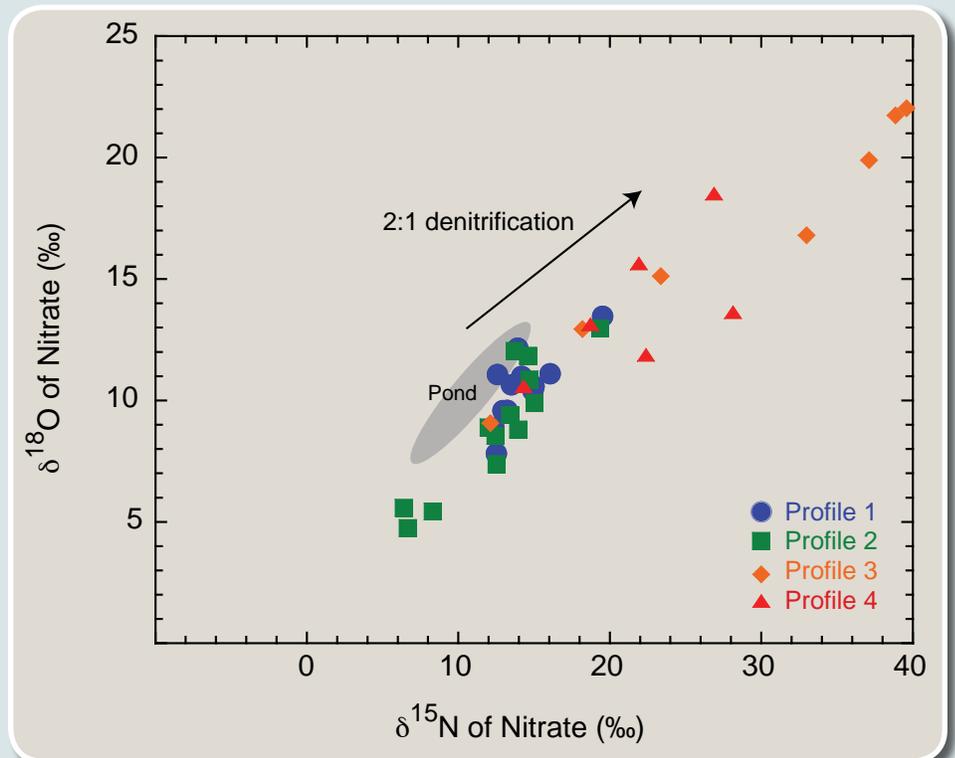


Figure 5.  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of nitrate in water samples collected from the recharge pond and piezometers screened at 0.5 and 1 meter beneath the pond (Figure 1).

of nitrate collected from shallow piezometers suggest that denitrification is an important process in nitrate removal from this system. Although there are differences in the extent and rate of nitrate removal across the pond, about 50% of the nitrate load applied in diverted slough water was removed during the first two months of MAR operation. Denitrification appears to be an efficient method of nitrate removal within this MAR system even at high rates of infiltration and initial nitrate concentration.

## References

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