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Dissimilatory Nitrate Reduction to Ammonium (DNRA) Can Undermine Nitrogen Removal Effectiveness of Persistently Reducing Riparian Sediments

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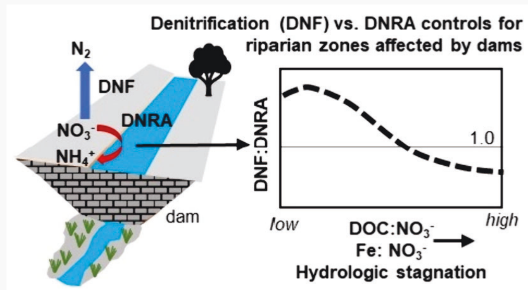

ABSTRACT: Denitrification (DNF) and dissimilatory nitrate reduction to ammonium (DNRA) compete in reducing sediment conditions where DNF permanently removes nitrogen (N), while DNRA retains N with the conversion of nitrate (NO_3^-) to ammonium (NH_4^+). Thus, an increase in the level of DNRA can undermine permanent N removal. We investigated the relative magnitude and controls of these two processes at two milldam-affected riparian sites. DNRA (5.2−37.6 μg L^{-1} h^{-1}) accounted for 10−79% of total NO_3^- reduction and was highest in riparian sediments with higher iron (Fe) and sodium (Na^+) in groundwater. DNF was the primary mechanism for NO_3^- reduction when Fe and Na^+ concentrations were low but when NO_3^- was elevated. DNRA rates were higher for treatments with higher dissolved organic carbon (DOC):NO_3^- and Fe:NO_3^- ratios, indicating the stimulation of both heterotrophic and Fe^{2+} driven autotrophic DNRA. DNF and DNRA rates and their microbial functional genes decreased with increasing sediment depths. These findings imply that hydrologically stagnant and persistently reducing conditions associated with relict milldams and similar anthropogenic structures may enhance DNRA at the expense of DNF and undermine permanent N removal in riparian zones. Thus, the effects of such structures need to be accounted for in watershed N management strategies.

KEYWORDS: *Riparian zones, groundwater, nitrogen, denitrification, DNRA*

1. INTRODUCTION

Human activities have substantially increased the amount of reactive nitrogen (N) in our environment contributing to eutrophication, harmful algal blooms, and contamination of our drinking water supplies.[1,2] One key management practice to mitigate excess N in surface and groundwaters is riparian zones that can permanently remove N from soils through natural processes like denitrification (DNF).[3−5] DNF typically occurs under wet and reducing riparian soil conditions.[6] However, reducing soil conditions also support dissimilatory nitrate (NO_3^-) reduction to ammonium (DNRA), another microbially driven process that competes with DNF and converts NO_3^- to ammonium (NH_4^+)[7,8] and thus retains biologically available N in the system. The natural hydrologic, redox, and biogeochemical regime of riparian ecosystems can, however, be altered by anthropogenic structures like dams[9−11] with potential consequences for reductive N processes. Here, we investigate how mill-dam-driven reducing riparian soil conditions affect the efficacy of N removal by altering the balance between DNF and DNRA.

While both DNF and DNRA typically occur in anaerobic soil environments, there are important hydrologic and biogeochemical differences that can affect the occurrence and rates of DNF and DNRA.[12,13] DNF is facilitated by facultative anaerobes that persist in both oxic and anoxic soil environments while DNRA is performed by obligate anaerobes that require anoxic environments.[8,14] Dynamic hydrologic conditions that facilitate redox fluctuations tend to promote DNF,[15−17] while DNRA is generally greater in persistently reducing and less variable hydrologic conditions.[18−22] In addition, different electron donor to acceptor ratios may also affect the relative rates of DNF and DNRA depending on whether heterotrophic or autotrophic pathways dominate.[23]

For heterotrophic pathways, the relative dominance of the two processes has been found to be significantly influenced by the concentrations and ratios of organic carbon (OC) and NO_3^--N (OC:NO_3^-).[12,24−26] DNF generates more energy per unit of OC and thus is dominant under low OC concentrations, while DNRA yields more energy per mole of

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