

**DRAINING THE LANDSCAPE:  
HOW DOES THE DROP IN GROUNDWATER LEVEL  
FOLLOWING DAM REMOVAL AFFECT LEACHING OF NITROGEN (N)  
FROM RIPARIAN ZONES?**

by

Evan Lewis

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## ABSTRACT

Dam removals are on the increase, with Pennsylvania currently leading the nation. While most dam removals are driven by aquatic habitat and public safety considerations, we know little about how dam removals impact water quality and riparian zone processes. Dam removals result in a drop in stream water level, which results in drainage or dewatering of the riparian zone. It is hypothesized that this drainage and drying of the riparian soils would increase nitrification (an oxic process) and decrease denitrification (an anoxic process), and thus result in nitrogen (N) leakage from riparian zones. This hypothesis was tested for the 1.5 m high Krady milldam on Chiques Creek, PA which was removed on July 9, 2018. Stream water, soil water, and groundwater was collected from the site and analyzed over two years for nitrogen species. Stream water  $\text{NO}_3\text{-N}$  concentrations varied between 2 -10 mg/L seasonally but did not reveal any long-term decline or increase. Groundwater  $\text{NO}_3\text{-N}$  concentrations remained low and ranged from 0 - 4 mg/L. Shallow soil water  $\text{NO}_3\text{-N}$  concentrations were elevated and ranged between 1- 25 mg/L. Nitrification and denitrification rate measurements on riparian soils indicated that denitrification rates generally exceeded the nitrification values. We speculate that while dam removal and soil drainage have increased the rates of nitrification in surficial riparian soils, denitrification rates in groundwater continue to remain high enough to consume any excess  $\text{NO}_3\text{-N}$ . These results suggest that riparian systems are resilient to changes associated with dam removal or the changes that occur in riparian zone N budgets could take more time beyond the 2-year period of this study. This is the first study that

has investigated the effects of dam removal on riparian groundwater N. Initial results from this study will help watershed managers and agencies make informed decisions with regard to dam removals and their impacts on water quality, particularly as it relates to nitrogen cycling in the riparian zone.

## **Chapter 1**

### **INTRODUCTION**

In the United States, there has been a growing focus on returning streams back to their natural states by removing dams and other impairments (Bellmore et al., 2017). Since 1912, more than 1,490 dams have been removed across the country (American Rivers, 2017). Pennsylvania leads the nation in its abundance of low head milldams as well as dam removals. Since 1916, 311 milldams have been removed in Pennsylvania, 10 in 2016 and 14 in 2017 (American Rivers 2017, Bellmore et al. 2017). Most of these milldams are classified as low head dams with heights less than 7 meters and are typically a relic of colonial and post-colonial era milling activities (Merritts et al., 2011; Walter and Merritts, 2008). Additionally, the number of dam removals is likely seriously underestimated since not all dam removals or dam breaches are recorded. This could be especially relevant in the mid-Atlantic region where thousands of milldams (many undocumented) have existed since the late 1600's and are prone to natural collapse (Walter and Merritts, 2008).

One of the primary reasons milldams have been removed so prolifically in recent years is for reasons of public safety. Low head milldams are often structurally unstable and pose a high risk of drowning under certain circumstances, however they are also being removed to reduce the land owner's financial liability, improve aesthetics/recreational access and/or improve stream habitat for fish (Foley et al 2017,

Hart and Poff 2002, Pohl 2002, Tullos et al 2016). Although it has been established that dam removals improve stream health and water quality, very little follow up research has been conducted after a dam removal in order to observe how streams or riparian zones react to the removal of an in-stream impairment (Bellmore et al., 2017). Instead, the limited body of knowledge has focused dominantly on hydrologic and geomorphological responses to dam removal as opposed to responses concerning water quality (Bellmore et al., 2017, Donovan et al 2015, 2016, Pizzuto 2002, Merritts et al 2011, 2013, Miller et al. 2019).

Considering that dam removals have a high potential to alter stream nutrient exports, it is very surprising how few studies have been performed to evaluate how dam removals may affect short- and long-term water quality, as well as the implications of regulation in streams where milldams have been recently removed. Research shows that dam removals can have strong influences on water quality by not only changing rates of sediment/nutrient and contaminant mobilization and transport but also through the alteration of hydrologic and biogeochemical processes in the riparian zone (Cole et al. 2020, Lowrance et al. 1997, Peterjohn and Correll, 1984, Sweeney et al. 2004). Dam removals, depending on the size of the dam, can cause significant drops in stream water level from less than 1 m to greater than 10 m and this water level drop will have effects which extend great distances upstream (Merritts et al 2011, 2013). Because of the control that dam removals exert on the local water table, a removal can also result in decrease in groundwater elevations in the riparian zone,

particularly in the proximity of the removed dam which could have long lasting ecological repercussions.

Riparian zones are critical to controlling the transport and mitigation of non-point nutrient pollution from uplands in many agricultural watersheds (Lowrance et al., 1997, Cole et al., 2020, Peterjohn and Correll, 1984, Sweeney et al 2004). Riparian zones are considered hotspots of denitrification and typically retain 50% - 90% of total nitrate loadings from upland sources making it incredibly important that riparian zones are functional and their functions are well understood (Lowrance et al. 1997, McClain et al. 2003, Vidon et al. 2010). There are many factors which will influence how a riparian zone will amplify or attenuate nitrate-N concentrations in stream. The ability of a buffer zone to denitrify is dependent on the hydrologic properties of the fluvial system, in particular the method of transport for water traveling above, through, or under the riparian zone to reach the stream (Valkama et al. 2019). Denitrification rates are also controlled by the residence time that water has to interact with the riparian profile as well as the grain size, permeability, and the aerobic state of the riparian zone soils (Valkama et al 2019, Appling et al 2014, Gurwick et al 2008a, b, Hill 2011, Palta et al 2016). The principal agents of nitrate removal from riparian zones include the denitrification of nitrate-N by anaerobic soil microbes and the assimilation of nitrate-N by the roots of plants (Gold et al 1998, Groffman et al 1992, Hill 2019, Lutz et al 2020). These two processes are especially effective when groundwater levels in riparian zone are close to the soil surface and within the root zone. If the riparian zone groundwater elevations drop or decrease following dam removals, it is probable that

the ability of the riparian zone to denitrify could be diminished. Drained riparian zones or riparian soils with deep groundwater levels may also result in soils actively mineralizing and nitrifying nitrogen (Appling et al. 2014, Gurwick et al. 2008a, b, Hill 2011). This could result in nitrate-N leaching from the riparian zone which could undermine their role as nutrient filters or buffers and instead turn them into non-point sources of NO<sub>3</sub> into the fluvial system.

Relatively little is yet known about the role that dam removals may play in affecting the denitrification and nitrification processes in riparian soils and how this affects the concentrations of nitrate-N in the riparian zone. The purpose of this research is to understand the role that dam removals, and by extension localized drops in groundwater, may play in changing a riparian zone's ability to mitigate the leaching of nitrate into the stream and how these changes may affect stream nitrate-N concentrations. In order to address these concerns, the following questions will be assessed:

#### Research Questions

**Question 1:** How do nitrate-N concentrations in riparian groundwater change following dam removal?

**Question 2:** How do denitrification and nitrification rates in riparian soils change with time following dam removal and associated drop in groundwater elevations?

**Question 3:** Does nitrate-N released from nitrification in riparian soils exceed that consumed/removed by denitrification?

**Question 4:** How do riparian concentrations of Nitrate-N in groundwater reflect the soil drainage above the water table at a site with a removed milldam?

Research Hypothesis

**Hypothesis 1:** Nitrate-N concentrations will increase in riparian groundwater following a dam removal because of the decrease in denitrification in the soils and a simultaneous increase in nitrification due to the aerobic conditions of the soil.

**Hypothesis 2:** Denitrification rates will decrease following the removal of a milldam because the resulting drop in groundwater level will cause formerly denitrifying legacy sediment material to be exposed to air and become oxic, limiting the ability of denitrifying anaerobic bacteria in the riparian zone to function. Furthermore, we hypothesize that nitrification rates will increase in riparian soils at this time due to the now oxic riparian zone accommodating nitrifying, aerobic bacteria.

**Hypothesis 3:** Nitrification in newly oxidized near-surface soils will produce nitrate-N in excess of the concentrations of nitrate-N which can be consumed by denitrification at deeper depths in the legacy sediment soil profile.

**Hypothesis 4:** Riparian soil and groundwater nitrate-N concentrations will be directly proportional to the drainage of the soil (depth of groundwater below soil surface).

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## Chapter 2

### LITERATURE REVIEW

#### 2.1 Overview of milldams and motivations for their removal

Milldams in the United States were used as a source of energy from the early 1600's throughout the early 1900's until technological advancements to steam power engines caused milldams to become less viable for the purposes of creating energy (Walter & Merritts, 2008). The purpose of a milldam was to maintain a constant head of water which was then directed through a mill by the raceway in order to power machinery. In the eastern US, milldams were used to run iron forges and furnaces and conduct mining operations but most commonly were used to mill grains (Walter & Merritts, 2008).

Low-head milldams are typically rock or concrete stream impoundments defined as being, < 7 m in height, and their primary functions include milling, irrigation and hydropower (Bruce & Tschantz, 2014). Low head milldams are particularly prevalent in the mid-Atlantic Piedmont region due to the region's ideal stream gradients and close proximity to major ports of shipping (e.g., Philadelphia, Pennsylvania; Baltimore, Maryland; Wilmington, Delaware) (Walter & Merritts, 2008).

In the United States and elsewhere, milldams continue to be removed or breached at ever increasing rates as the momentum fueling river restoration has increased (Dams, 2000). To date, nearly 1,700 dams have been removed in the US since 1912, and nearly 1,200 of these dams were removed in the last 20 years (American & Rivers,

2020). As the national focus on dam removal has grown so has the body of literature recording the geomorphic and ecological responses to these removals (Donovan et al., 2015, 2016, Pizzuto 2002, Merritts et al. 2011, 2013, Miller et al. 2019). With that said, the body of literature pertaining to the removal of low-head milldams is still relatively low.

There are many reasons which motivate the removal of milldams in Pennsylvania and the country at large. It has been estimated that about half of the dams in the northeastern United States were built earlier than 1920, furthermore due to their age, many of these dams are non-compliant with safety regulations (Tonitto & Riha, 2016). Politically, removing milldams is often in the best interest of the state government due to abundant safety, economic and ecological benefits, however the final decision to remove a milldam is often left to the individual land owner (Heinz Center, 2002). It isn't until after the decision has been made by the land owner to remove the structure that the decision to approve the dam removal becomes a public process as determined by state and federal regulations.

Ecologically there are many reasons why a dam removal could be a benefit to stream health. A major consideration is the return of the fluvial system to a pre-dam flow regime which in turn is believed to instigate the return of native species to the system, bolstering the biodiversity of the stream or river (American Rivers, 2017). It has been reported that dam removals can often allow for native, cold water species of fish to return to the fluvial system replacing the species of warm water fish that prefer more still, lake/pond like water regimes (American Rivers, 2017).

Economically, dam removals are an expensive endeavor. The cost of dam removal has been estimated at between \$22,000 – \$30,000 per vertical foot of the dam (Blachy & Uchida, 2017). This cost would be prohibitive to most independent land owners who want to remove a milldam on their own property. Many environmental and government organizations exist however to provide financial support for such undertakings. Some states like Pennsylvania have state run programs which aid landowners with the technical, regulatory and financial matters associated with dam removals. With that said, many low head milldams also fail on their own without being documented, either naturally in a large flow event or due to negligence in maintaining their structural integrity (Brewitt and Colwyn 2019, Magilligan et al. 2017).

In Pennsylvania, the state government and a suite of interdepartmental agencies are all responsible for assuring that any dam removal plan is compliant with federal regulations including regulations established by the Clean Water Act, Rivers and Harbors Act and National Environmental Policy Act (American Rivers, 2007). American Rivers is particularly well established in Pennsylvania as a charitable organization which is supported financially by the federal government as well as by the general public and they are well established as a leader at organizing, planning and carrying out dam removal projects.

## **2.2 Effects of dam removals on water quality**

### **2.2.1 Retention time, dissolved oxygen, and temperature**

There is a plethora of ways in which a dam removal may have long term effects on water quality upstream and downstream of the site of the removed dam. In terms of processes being affected within the stream, a dam drastically decreases the upstream flow velocity of the channel which in turn also increases the retention time (Maavara et al 2020). This increase in retention time, as well as the nature of the dam as a barrier to flow, causes a buildup and increased retention of carbon, sediment and nutrients, all of which have the potential to alter the instream biogeochemical processes which take place and be a hinderance to overall water quality of the system (Ecke et al. 2017, Maavara et al. 2020). These processes can have noticeable effects on water quality parameters such as dissolved oxygen and nutrients, temperature, dissolved organic carbon, total suspended solids, conductivity and pH (Almeida et al. 2019, Burchsted et al. 2010, Van Cappellen and Maavara, 2016, Csiki and Rhoads, 2010, Gold et al. 2016, Lazar et al. 2015, Maavara et al. 2020, Riggsbee et al. 2007, Stanley and Doyle 2002). Furthermore, the presence of a dam causes the temperature gradient behind the dam to stratify with cooler water sinking to the bottom while a thin layer of warmer water sits up top (American Rivers, 2017). After a dam removal, it has been observed that water temperature recorded at or downstream of the site of the removed dam is often found to be significantly cooler than before, a result of decreasing the retention time of the system (American Rivers, 2017). By removing a dam, increasing flow velocity, increasing dissolved oxygen and decreasing the

temperature of the fluvial system the stream will now be better suited to support a wide variety of native species of fish (American Rivers, 2017).

### **2.2.2 Nutrient Cycling**

Milldams also have a drastic influence on in stream nutrient cycling processes as well. A milldam, acting as a barrier to flow will decrease flow velocity in turn decreasing the sediment carrying capacity of the system resulting in accelerated accumulation of sediment behind the dam. This phenomenon is often made abundantly clear during a dam removal when this material gets “flushed” downstream after dam breach. One result of quickly accumulating sediment behind a dam is that this material can bury nutrients and organics very quickly, effectively eliminating them from being able to interact dynamically with the fluvial system (Maavara et al., 2020). These nutrients (particularly nitrogen and phosphorus) can also be eliminated from behind a milldam by means of off-gassing into the atmosphere (Maavara et al., 2020). For fluvial systems impacted by a milldam, nutrient elimination is generally calculated as follows:

$$E = \frac{F_{in} - F_{out}}{F_{in}}$$

In the above equation, E represents the fraction of the eliminated nutrient while  $F_{in}$  is the influx of the nutrient into the reservoir and  $F_{out}$  is the efflux out of the reservoir

through the dam (Maavara et al., 2020). As a result of a milldam increasing the longevity of the systems hydraulic residence time, the biogeochemically available nutrients in the system have a longer duration during which they can be immobilized or eliminated from the system. It has been estimated that for the average damned headwater – coast river continuum, approximately 19% of total nitrogen may be eliminated by means of burial in damned reservoirs while nearly 30% may be eliminated by denitrification behind the dam (Maavara et al., 2020). Comparatively, that number increases drastically when considering total phosphorus which it was estimated nearly 44% would be removed via. burial behind dams, no doubt a byproduct of phosphorus' tendency to undergo sorption with small fluvial particles such as sand, clay, bentonite and hematite (Ball 2003, Maavara et al. 2020).

Furthermore, it has been documented that when a dam is built it causes a shift from a riverine lotic system to a lake like lentic system. In this case the riverine system is being classified as being dominated by primarily heterotrophic, benthic biota while in the case of a lake dominated system it is instead being primarily dominated by autotrophic algae (Laurel et al., 2001). This shift from a heterotrophic to autotrophic dominated system has major implications for nutrient cycling within the channel. It has been documented that autotrophic lake like flow regimes allow for accelerated fixation of inorganic nutrients by means of algal growth and consumption (Wang et al. 2018). Additionally, the capacity for the system to sequester and retain dissolved organic carbon in the system is also believed to increase due to the photosynthetic nature of autotrophic organisms such as algae in the channel (Wang et al., 2018).

### **2.2.3 Sedimentation and Erosion**

The removal of a milldam can also have drastic effects on channel morphology and sedimentation/erosion in the system. Due to the backwater effect that milldams generate and the creation of a low flow velocity millpond, sedimentation behind a dam is typically high. The exact factors which determine the rate which sediment accumulates are a complex web of basin and channel characteristics such as sediment yield off the landscape, sediment type, the presence and proximity of agricultural practices, the geometry of the reservoir and the hydraulics of the fluvial system (Wang et al. 2018). In many cases, organic material such as leaf litter and or phytoplankton/algal biomass can also contribute to organic sedimentation behind a dam depending on the biome in which the fluvial system exists (Wang et al. 2018). Logically, Sediment which is captured behind a milldam will no longer be able to flow downstream. The reduction in sedimentation downstream of a millpond reservoir is estimated to be upwards of 75% and studies conducted in the late 60's estimated that the magnitude of suspended sediment being transported from headwaters to oceans were in the range of 9.8 – 58 Gt yr<sup>-1</sup> while more recent studies (1980 – 2006) have estimated that this flux is likely far greater in the range of 15 -20 Gt yr<sup>-1</sup> (Wang et al., 2018). This drastic reduction in global sediment flux to the ocean is believed to be the result of increased storage capacity generated across the globe in the form of artificial reservoirs like millponds (Wang et al., 2018).

With that said, although massive accumulation and sedimentation of material can be expected upstream of a milldam, this phenomenon has the potential to reduce the storage capacity of the reservoir over time leading to increased flow velocity and decreased sedimentation downstream of the dam which can lead to scouring of the channel bed, erosion and habitat loss in the downstream reaches (Wang et al. 2018). If a dam has been removed then the unconsolidated material left behind the dam will be mobilized and allowed to flow freely. This is of particular interest and concern in the mid-Atlantic region where valley bottoms were extensively dammed for mill power resulting in massive accumulation of unconsolidated legacy sediment material in valley bottoms (Merritts et al. 2013; Walter & Merritts 2008). Particularly in this region, the erosional effects of milldam removal may be particularly drastic. It has been documented that the removal of a milldam can lead to accelerated rates of incision, bank erosion and increased loading of suspended sediments, furthermore this was found to be the case regardless of the upland land use present at the time of the study (Merritts et al. 2013). The processes by which a milldam removal can accelerate erosion in a fluvial system are as follows. The lowering of stream level after the removal of a milldam causes the banks of the stream or river to be exposed to the atmosphere, in turn subaerial processes and seasonal fluctuations in temperature can cause freezing/thawing and or wetting/drying of the material making up the stream banks of the channel and instigate bank erosion (Merritts et al. 2013). Furthermore, rapid drops in stream level can cause the banks of a channel to develop unstable angles

of repose which can lead to episodes of mass wasting (Merritts et al. 2013, Walter & Merritts 2008).

### **2.3 Effects of dam removal on the riparian zone**

The removal of a milldam can have long lasting effects on the dynamics of systems functioning outside the channel corridor itself. A dam removal has effects on the riparian zone beyond accelerating the rate at which the riparian sediments erode and are flushed downstream, in particular it can have drastic effects on the riparian zone flora and the biotic processes within it (Shafroth et al. 2002). When a dam is built, it alters the hydraulic gradient of the stream and surrounding riparian groundwater by artificially raising the hydraulic head above where it would rest in a naturally functioning fluvial system. By increasing the hydraulic head artificially, a milldam can have long lasting effects on the hydraulic gradient flowing throughout the riparian zone as well as the proximity of the groundwater to the surface of the riparian soil (Hill and Duval 2009, Lautz et al. 2006). The combination of a shallower groundwater table and an increased hydraulic gradient will result in growing conditions that are more favorable towards particular species of plant (Shafroth et al. 2002). When that dam is removed, its hydraulic gradient and water table depth will decrease in a short period of time which may allow for native species of plant to repopulate the riparian zone and alter the biotic functions of the riparian soil (Shafroth

et al. 2002) Furthermore, after a dam has been removed and the local water table as dropped, deposits of sub-aqueous sediment may become exposed to air.

In addition to altering the abundance and variety of riparian vegetation, a dam removal will likely affect the soil moisture conditions and oxygen availability of the riparian soil profile. In the event that a dam is removed, dewatering will result in the lowering and dropping of the water table which will in turn dry out the upper most levels of the riparian zone, particularly at legacy sediment milldam sites where the height of the post-dam riparian soil profile is controlled by the water level in the stream. At sites such as these, it is probable that the upper most layers of the riparian soil profile will become much drier shortly following a dam removal and it's probable that this will have a drastic effect on the availability of nutrients within that soil profile (Cavagnaro 2016). Furthermore, it has been observed that soil moisture itself is a crucial variable in the productivity of soil nutrient availability and plant growth (Cavagnaro 2016).

#### **2.4 Nitrogen Cycling in soils:**

Nitrogen is a crucially important element for the development and growth of living things as it is crucial for the development of proteins and nucleic acids in organisms (Kuypers et al. 2018). It is well known that nitrogen gas makes up nearly 78% of earth's atmosphere, however only a very large, albeit rare assemblage of nitrogen fixing micro-organisms can utilize this pool of nitrogen. Most other forms of

life must instead utilize biologically available, more reactive species of nitrogen including nitrate, nitrite and ammonium (Kuypers et al., 2018). Nitrate and ammonium, unlike nitrogen gas, are far more rare in our ecosystems and their principal mechanism of generation are dominated by microbes which alter the oxidation state of nitrogen in order to produce more reactive and bioavailable species which can then be utilized by flora and fauna (Kuypers et al. 2018). With that said, anthropogenic sources of bioavailable nitrogen exist in the form of plant fertilizers which are being used with an ever-increasing abundance and frequency due to our modern agricultural practices. It has been estimated that anthropogenic nitrogen has doubled the amount of bioavailable nitrogen being made available to the worlds terrestrial and marine ecosystems (Kuypers et al. 2018).

Generally, the microorganisms responsible for nitrate cycling are designated by the role they play in the nitrogen cycle. Those roles are broadly categorized as nitrifiers, denitrifiers, nitrogen fixers, assimilators, ammonifiers as well as those that facilitate the anammox process under particular circumstances (Tomaszewski et al. 2017, Gao et al. 2018). The nitrogen cycle can be thought to begin with atmospheric dinitrogen gas. Before this pool of nitrogen can become biologically available it must first be fixed by soil bacteria which will assimilate dinitrogen in the atmosphere into a variety of organic compounds and amino acids. Further biological processing and oxidation will result in the fixation of dinitrogen in the atmosphere into ammonia/ammonium within the soil profile (Stein & Klotz 2016)

From this point a two-step series takes place involving nitrifying soil bacteria. If not for these buried nitrifying microbes this oxidized ammonia would likely escape the soil profile and be removed from the system by means of off-gassing back into the atmosphere (Stein & Klotz 2016). Instead, it is further oxidized by a rapid succession of bacterial oxidation. The ammonia is first nitrified by *Nitrosomonas*, a ubiquitous nitrifying soil microbe, into nitrite which is for the most part not yet biologically available. Instead of being allowed to accumulate in the soil, nitrite is instead rapidly converted into nitrate by means of another bacterial oxidation process, this time the result of *Nitrobacter* (Stein & Klotz 2016).

At this point nitrate has been produced and is stable in the soil profile and will constitute the majority of bioavailable nitrogen that will be assimilated by plants in order to grow. It should be noted however that nitrate assimilated by plants in this way has not necessarily been removed from the system. When that organism decays, the available pool of nitrogen species will then be oxidized by aerobic and anaerobic bacteria and fungi present in the soil (Stein & Klotz 2016). This process will then reintroduce simple proteins and amino acids back into the soil profile which can in turn be ammonified reintegrating that pool of nitrogen back into the system.

After the oxidation of ammonia into nitrite and nitrate, it is possible for environmental conditions to subject these byproducts to anaerobic conditions. When this happens denitrification can occur. Denitrification, due to the anoxic soil microbes which fuel the process, occurs primarily in wet soils (Stein & Klotz 2016). Although it should be noted that the process can occur in dry soils as well as long as anoxia is

induced. Under these conditions, a broad spectrum of anaerobic soil microbes will utilize the oxygen found within the chemical structure of nitrates and nitrites found in the soil and reduce them in order to fuel their metabolic processes (Stein & Klotz 2016). This process will ultimately release dinitrogen gas back into the atmosphere completing the cycle.

The bacterial process of anammox is an abbreviation referencing the process of anaerobic ammonium oxidation. Anammox is a unique bacterial and chemical process found in environments with high concentrations of nitrogen and low organic carbon availability, as well as at a limited range of temperature and pH (Tomaszewski et al. 2017). Anammox is the process through which ammonium is oxidized in an anaerobic environment using nitrite as an electron acceptor (Tomaszewski et al. 2017). The byproduct of this process is inert molecular nitrogen, making this method of inorganic nitrogen oxidation favorable for treating nitrogen pollution in high nitrogen, low carbon environments. The process of anammox has been found to occur in anoxic marine and freshwater sediments as well as in some terrestrial ecosystems and unique anthropogenic environments such as petroleum reservoirs and sewage treatment plants (Hu et al. 2011). Our current understanding of anammox processes suggests that anaerobic ammonium oxidation in marine environments is responsible for approximately 50% of global dinitrogen production (Hu et al. 2011). With that said the contribution of the anammox process to terrestrial and freshwater systems is not yet fully understood, however it is speculated that its effects in these environments may be greater than previously believed.

Dissimilatory nitrate reduction to ammonium (DNRA) is the process by which nitrate is reduced to nitrite and then ammonium under low oxygen, anoxic conditions (Rütting et al. 2011). This process is the result of anaerobic microbial respiration using nitrate as an electron acceptor and it is believed to be performed by a broad selection of soil microbes (Rütting et al. 2011). One crucial effect of the DNRA process is that, unlike denitrification which produces inert dinitrogen gas as a byproduct, DNRA converts nitrate into ammonium, another mineral form of nitrogen, which can then linger in an environment conserving the pool of nitrogen in the system (Rütting et al. 2011). This phenomenon may be crucially important to those concerned with ecological nitrate loadings due to the fact that without close observation, the reduction of nitrate by means of denitrification can appear similar to the reduction of nitrate by means of DNRA effectively skewing our perceptions on whether nitrate has been removed from, or stored in a dynamic system. When comparing DNRA to denitrification it should be known that the potential free energy of both reactions favor denitrification over DNRA in most situations,  $-2669 \text{ kJ mol}^{-1}$  vs.  $-1796 \text{ kJ mol}^{-1}$  respectively (Rütting et al. 2011). However, it is currently believed that under conditions that are anoxic and severely nitrate limiting, microbial respiration will be hindered by the scarcity of available nitrate to use as an electron acceptor (Rütting et al. 2011). Under these conditions, as well as with an abundance of electron donating carbons, DNRA is believed to be the preferred method of microbial nitrate reduction.

## **2.5 Riparian Zones and nitrogen cycles**

The riparian zone is home to a complex web of biological systems effecting nitrogen attenuation and expansion. The process of nitrification in tandem with ammonification are the primary mechanisms by which organic nitrogen inputs from the environment are converted into bioavailable forms of inorganic nitrogen. However, nitrification in the riparian zone is often overlooked. Studies have shown that nitrification and mineralization rates in soils are influenced heavily by the systems oxic conditions, temperature, moisture and depth (Macduff et al. 1985). Some studies have found that the process of nitrification in soil profiles are typically limited by the available pool of ammonia, and found that in these situations the rates of nitrification were never less than the rate of ammonification (Macduff et al. 1985). Furthermore, temperature has been found to have an effect on the ability of soils to nitrify. It has been found that high and low temperatures, of approximately 35°C and 2°C respectively, both have inhibiting effects on nitrate and ammonium oxidizing bacterial processes (Macduff et al. 1985, Tan et al. 2018). With that said, temperature appears to have a greater limiting influence on the process of nitrification in soils than it does the process of ammonification. Soil moisture, being one of the primary controls on the soil profiles oxic state, has a profound influence on the process of nitrification. Its effects on mineralization are also prominent. Mineralization rates have been known to increase in soils with the presence of soil moisture, however they can still be notably elevated even in soils at or below the permanent wilting point of the soil (De Neve & Hofman 2002; Kladivko & Keeney 1987). Lastly, the presence or absence of carbon is

a crucial ingredient which facilitates the redox reactions dominating nitrification and mineralization processes. In an environment with a high C:N ratio, soil microbes can actively assimilate supplies of soil nitrogen while in soils with C:N ratios below microbial demands, net mineralization followed by nitrification will be facilitated (Pinay et al. 2018).

Denitrification, unlike the microbial biochemical processes of mineralization and nitrification functions most productively in soils with considerable moisture (Ha et al. 2015). Studies have shown that the optimum soil characteristics to facilitate the denitrification process are to have high soil moisture in the range of >60% pore space filled with water, a temperature in the range of 25°C and a pH of approximately 7 (Ha et al. 2015). Under these conditions, should the soil be anoxic and rich with organic carbon, the denitrification process will be supported. In the riparian zone, soil moisture and temperature are often seasonally controlled, however labile organic carbon is typically found closer to the surface where leaf litter and other biological products accumulate. On that note unique conditions of the riparian soil may affect gradients in soil moisture, grain size and organic material. The spatial distribution of these controlling factors within the riparian zone may generate pockets or lenses within the riparian profile where the process of denitrification is more easily facilitated than others. Lastly for denitrification to occur, there must be a bountiful supply of nitrate to be used as an electron acceptor in tandem with organic carbon to be utilized as an electron donor, all this under anoxic conditions (Ha et al. 2015)

The fixation of molecular nitrogen into bioavailable mineral nitrogen species is performed by a wide variety of bacteria species within the riparian soil profile (Ha et al. 2015). Many of these bacteria are autotrophs and heterotrophs which live freely throughout the soil profile however some species form symbiotic relationships with legumes and rhizobium utilizing the anoxic conditions present within the root nodules (Ha et al. 2015). Nitrogen fixation is an important component at facilitating plant growth at shallower depths in the riparian zone as well as at introducing organic nitrogen compounds to the riparian corridor. Nitrogen assimilation, unlike nitrogen fixation, is a process that affects inorganic nitrogen species as opposed to molecular or organic forms of nitrogen. Assimilation is the term given to the “consumption” of inorganic nitrogen by plants to develop organic compounds, amino acids and DNA. In the riparian zone, assimilation is dominated by the type and quantity of riparian vegetation established at the site which can vary widely.

## **2.6 Pollution Control and Riparian Best Management Practices:**

A TMDL (total maximum daily load) is a method of addressing pollution and water quality concerns which affect streams and rivers across the entire United States (USEPA. 2018). A TMDL is a metric of how much of any particular pollutant can be allowed within a body of water in order for that body of water to meet established water quality goals. If a river or stream has been identified as an impaired waterway under section 303(d) of the clean water act, then the state with jurisdiction over that

waterway must develop TMDLs according to which stream or river poses the greatest environmental concern (USEPA. 2018). Typically, a TMDL will be developed by a state in order to meet water quality targets for a system then that TMDL will be submitted to the EPA in order to be approved (USEPA. 2018). In order for a TMDL to be successful, it must take into account all inputs of a pollutant, whether they be point source or nonpoint source and appropriately budget the ideal loadings from each source in order to meet established water quality targets for the system (USEPA 2018). In order to do this, a TMDL may suggest implementing a variety of BMPs (Serra et al. 2018) throughout a watershed in order to meet these reduction targets.

BMPs can be categorized as being a point or nonpoint source control measure, and many different types of BMP exists to mitigate various forms of nutrient pollution. One of the most common BMPs used to mitigate upland nutrient transport into a fluvial system would be the establishment of a riparian forest buffer. Riparian forest buffers are used primarily to filter out or otherwise consume nutrient pollution, pesticides and animal waste from upland sources before it is capable of mixing and interacting with channel flow (USDA 2020). Typically, a riparian buffer is composed of trees and shrublike plants which act to further stabilize stream banks and prevent erosion, filter out sediment runoff, as well as provide habitat, food and shade to local species of aquatic organism (USDA 2020). In terms of upland nitrate pollution, it is believed that the riparian zone plays a critical role in preventing upland sources of nitrate-N from flowing into the stream. Nitrogen transport in this way is dominated by overland flow and shallow groundwater flow mechanisms. In the event that the

groundwater table should drop, as has been observed to occur after the removal of a milldam, then nitrate-N flowing via shallow groundwater flow may be too deep below the shallow riparian surface to be mitigated effectively.

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## **Chapter 3**

### **SITE DESCRIPTION AND METHODS**

In order to address the questions and goals of this study a series of experiments and monitoring campaigns were performed at the Krady dam site where a milldam was removed on July 9, 2018. The groundwater and stream water at the site were regularly sampled for nitrate-N and continuously monitored in order to see if stream/groundwater concentrations changed in the months/years following dam removal. We also closely monitored stream/groundwater elevations and total stream discharge in order to understand hydrologic changes to the river. Soil sampling and analysis was also performed to assess in-situ changes in denitrification and nitrification rates in soils following the drop in groundwater levels. Lastly, a macrocosm experiment was also conducted. The purpose of this experiment was to estimate nitrification and denitrification for soils from the study site under oxic and anoxic conditions, respectively.

#### **3.1 Site Description**

The Krady milldam was located on Chiques Creek in Rapho and West Hempfield Townships, Lancaster County, PA (Google Coordinates 40.068944, -76.499639) and only 5 km upstream from where it feeds into the Susquehanna River. The catchment area which drains into the Krady milldam study site is approximately 159 km<sup>2</sup> and approximately 68% agricultural, 13% forested, 11% residential and 7%

grassland by area. The soils in the catchment and riparian zone are predominantly silt loams, examples of which include the Newark silt loam, Nolin silt loam and the Hagerstown silty clay loam all of which are found in abundance within a close proximity to the site of the removed dam (Soil Survey 2020). The study site is located just south of the PA ridge and valley province and the upstream extent of the contributing drainage area has a relatively minor slope and elevation gradient. The topography is dominated by rolling hills, and meandering fluvial channels. The geology of the upstream contributing drainage area is composed predominantly of dolomite/limestone (40%) shale (30%) and lesser degrees of arkosic sandstones, quartzites, conglomerates, phylites and diabase intrusions (30%) (DCNR 2020). The study site is situated in the ledger formation, a light grey medium – coarse crystalline massive dolomite (DCNR 2020).

The Krady milldam itself, originally named “J Risser's G & S Mill”, had been built in the late 1800’s for the purpose of supplying power to an immediately adjacent grist and saw mill. Although the shape and size of the dam may have been modified since it was first built, it stood approximately 1.5 m tall and 30 m wide before it was removed on July 9, 2018 by American Rivers. The project opened up 2.9 miles of dam impacted stream and allowed it to return to precedent flow conditions and in the process improved habitat for resident/migratory fish while also removing a potentially dangerous piece of degrading infrastructure (Thomas-Blate, 2018).

After the Krady milldam was removed, dewatering caused large swaths of riparian bank soils, which had previously been submerged, to be exposed to air. This

effect was seen most clearly at the site of the removed dam, but could also be witnessed thousands of meters upstream. In the process of dewatering, large blocks of in stream sediment and debris were deposited and then promptly flushed downstream in the coming months (Figure 3.1).



Figure 3.1: Stream water level before and after dam removal at the site of the Krady milldam

### **3.2 Hydrologic monitoring for streamflow, riparian groundwater, and soil water**

In order to monitor how groundwater elevations and nitrate concentrations changed over time following dam removal, a series of groundwater wells were installed at the site. Five groundwater wells (W1-W5) were installed over a seven-month period between October 2018 and April 2019. Two additional duplicate wells (Well 1B near W1 and well 3B near W3) were installed at a later date in November of 2019. Two wells, well 1 and well 2, were installed on the north bank of the stream immediately upstream of the former dam (Figure 3.2). Three more wells; well 3, well 4 and well 5, were installed on the south bank 130 m upstream of the site of the dam on a meter-thick legacy sediment terrace (Figure 3.2). All wells were augured to approximately 2 meters in depth. Each of the wells had soil sample collected at regular depths of 0.3 meters. Each well was constructed of perforated PVC tubing of 5 cm diameter. Water level sensors (U20L HOBO) were placed at known depths within each of the groundwater wells in order to measure the height of the groundwater table every 30 minutes for the duration of the study. A RTK GPS unit was used in order to record the exact elevations and locations at the soil surface of each of the wells. Groundwater elevations measured by the water level sensors were then related to the measured elevations to allow for comparison of well values against each other. Similarly, groundwater depths from the soil surface were also computed.

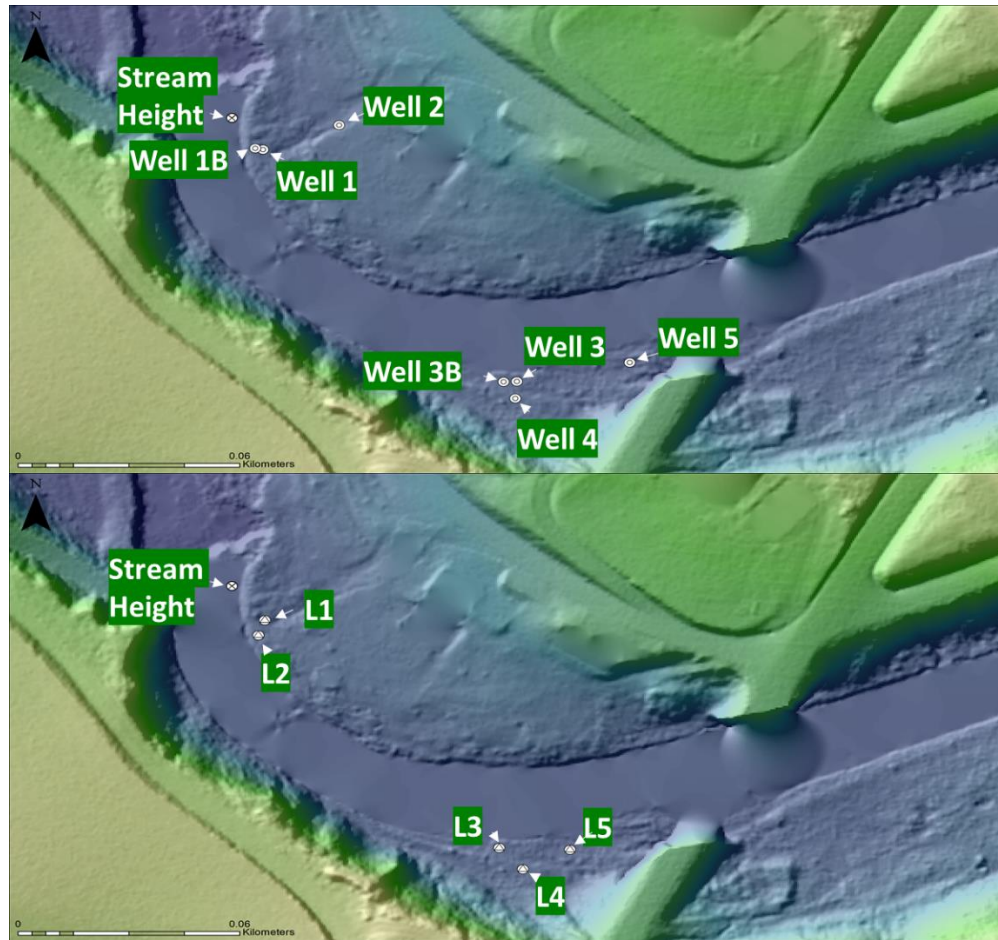


Figure 3.2 Locations of groundwater wells and shallow soil lysimeters installed at the Krady milldam site

Stream velocity measurements for determining discharge were periodically performed downstream of the former dam using a Flowtracker 2 velocity probe. Measurements were collected using a standard 0.6 method for calculating discharge from shallow streams and a mean section discharge equation was applied to these measurements. Using the measured streamflow depths and discharge, a relationship was developed between discharge and stream height (Figure 3.3). This relationship

was then extended to the depths measured every 30 minutes by the Hobo streamflow sensor to compute Chiques discharge at the dam site.

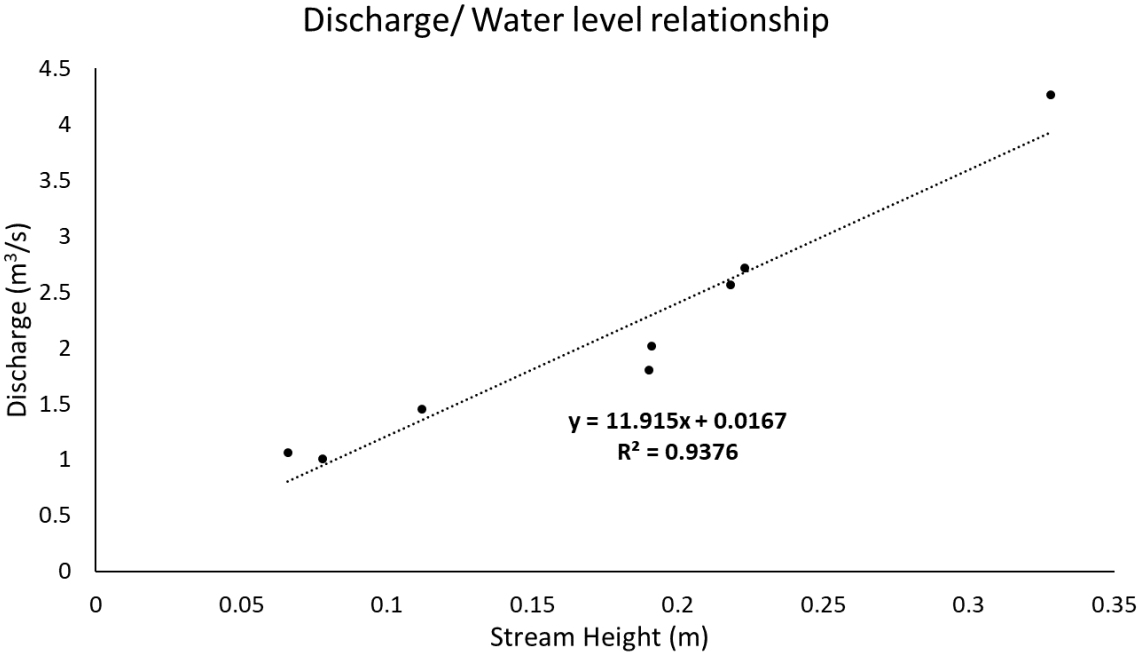


Figure 3.3: Cross-plot of discrete discharge measurements taken in the field; cross plotted against measured stream height. This figure illustrates the linear relationship between discharge and stream height in low flow conditions of the fluvial system

Using georeferenced stream and groundwater elevations, hydraulic gradients were calculated by dividing the difference in stream and groundwater elevations by the linear distance in meters to the edge of the stream bank. Furthermore, the depth of the drained soil profile at each groundwater well was also determined by computing the

groundwater depth below the soil surface (depth of sensor from the soil surface minus the measured head of water above the sensor).

To compare groundwater responses among wells, average, maximum and minimum values were computed. When compiling these statistics, periods of no data, where water levels dropped below the depth of the water level sensor, were not used.

Lastly, five shallow soil lysimeters were also installed at the site in October of 2019. All lysimeters were installed within a close proximity of their corresponding well number apart from lysimeter 2, which was placed at the well 1 site in addition to lysimeter 1. Each lysimeter was buried in the upper 30 cm of the riparian soil at an angle of 45 degrees. Using a portable hand pump, each lysimeter chamber was pressurized to the ~ 50 psi. Water sample was collected from each lysimeter using a standard plastic syringe connected to a short length of tubing. Sample was drawn from all lysimeters which captured water on a biweekly basis and all remaining sample was evacuated from each sample container before being repressurized.

### **3.3 Water grab sampling**

On a biweekly basis groundwater was sampled from all wells. Groundwater wells were sampled using a battery powered electric pump to draw sample up the wells into clean, 250 mL polythene bottles. Each bottle was field rinsed twice with sample water before sampling and care was taken to follow proper field sampling procedures to ensure sample quality. Stream water samples were collected by manual

grab sampling using the same methods to ensure sample quality. All samples collected in this way were transported from the field site on ice to minimize transient nitrogen cycling within the sample container.

### **3.4 Water quality and monitoring**

All water samples were filtered through a 0.7  $\mu\text{m}$  glass filter using standard vacuum filtration techniques within 48 hours of having been sampled then immediately refrigerated. All groundwater samples were initially analyzed for nitrate-N using a S::CAN Spectrolyzer. Six nitrate standards, ranging between 0-10 mg/L nitrate-N were run at the beginning of each analysis to assure quality control for these initial tests. Each sample was then also processed by the University of Delaware Soils Laboratory to determine concentrations for nitrate-N, ammonium-N, dissolved organic carbon and Total-N. Nitrate-N and ammonium-N were measured calorimetrically using a Bran&Luebbe Autoanalyzer 3 (Bran& Luebbe, Buffalo Grove, IL). Total bound nitrogen-N was measured directly by combustion and total dissolved organic carbon was calculated by difference using an Elementar Vario-Cube TOC Analyzer (Elementar Americas, Mt. Holly, NJ). These Nitrate-N values were then compared with the results of the in-house S::CAN Spectrolyzer results in order to assure quality control. Remaining sample was then refrigerated for the rest of the study period. These analytes were then plotted against each other as a scatterplot time series. Minimum, maximum and average concentrations of these analytes were calculated however these

statistics only represent the groundwater conditions of the site at periods where there were detectable levels of water observable in the groundwater wells.

Apart from wells, lysimeters were also installed in the shallow soil across the study site. Some weeks yielded shallow soil water which could be sampled from all lysimeters and others were dryer yielding captured soil water in fewer sample chambers. The period of observation for all lysimeters installed at the site was between November 2019 and February 2020. The shallow soil water captured in this way was subsampled and delivered to the University of Delaware Soils Laboratory to be analyzed for Nitrate-N and Ammonium-N calorimetrically using a Bran&Luebbe Autoanalyzer 3 and these values were verified by comparing the results with an in house S::CAN Spectrolyzer. These results were illustrated as a time series as well as cross plotted against the precedent drained profile depths at each respective lysimeter over the preceding 7-day period. The preceding 7-day drained profile was calculated by averaging the depth of the drained soil profile across this 7-day period not accounting for periods where the drained profile could not be calculated due to groundwater being below levels of detection.

A comparison between the height of the drained profile and the concentration of nitrate-N in shallow soil water was made by cross plotting each individual lysimeter samples concentration of nitrate-N against the average 7-day precedent drained profile depths at each lysimeter's corresponding groundwater well. This generated a time series illustrating the depth from the surface of the terrace to the height of the water table. The 7-day average precedent conditions were calculated from this data set by

taking the average of all drained profile depth measurements within the precedent 7-day window of time excluding instances where groundwater was below detectable levels of observation.

Lastly, for nitrate-N measured across the study site in both stream, groundwater and shallow soil water, a T-test was applied to discern whether significant differences existed between the concentration of nitrate-N observed and the locality where the sample was taken. Statistical analysis which yielded a  $p < 0.05$  were considered to be significant.

### **3.5 Soil Sampling and elemental analysis**

In November of 2018, soil samples were taken from the legacy sediment terrace at the well 3 site. Samples were collected from the legacy sediment terrace by using a soil auger to extract 5 sediment cores in 0.3 m increments below the surface down to a depth of 1.8 m. Almost five months later, a second series of soil cores were extracted from the Krady mill site. In April of 2019, two sediment samples were collected at depths of 0.3 m and 0.6 m for well 1, well 2 and well 3. At well 4 and well 5, 5 soil samples were collected from the legacy sediment terrace at 0.3 m intervals in depth at this time.

Then, in August of 2019 soil samples were collected again from well 1, well 4 and well 5 at depths of 0.3 m and 0.6 m. At well 3 soil samples were collected at the

surface of the legacy sediment terrace as well as at depths of 0.3 m and 0.6 m below the surface. Samples were also collected at well 3 by auguring laterally into the shallow subsurface of an immediately adjacent streambank at depths of 0.6 m, 1.1 m and 1.8 m.

In November of 2019, two additional groundwater wells were installed at the site to substitute for wells 1 and 3 during periods of low groundwater elevations. These wells were installed at greater depths of 2.8 meters each and samples were collected from them both at 0.3-meter intervals. Lastly, in July of 2020, two soil profiles were augured at wells 1 and 5 and soil samples were collected at 0.3 m intervals for a depth of 2 meters each.

All soil samples collected from the site during this period were transported from the site on ice and analyzed for TN, TOC, nitrate-N, ammonium-N and N process rates (denitrification, nitrification, and mineralization) as described below.

### **3.6 Denitrification enzyme assays (DEA), nitrification and mineralization analysis**

DEA, nitrification and mineralization analysis was performed by the University of Rhode Island Watershed Hydrology Laboratory. DEA samples were processed for unamended field conditions as well as amended conditions. DEA analyses were performed by homogenizing the mixed soil sample with DI water and sodium nitrate ( $\text{NaNO}_3$ ), purging the sample container with helium and acetylene gas in order to induce anoxia and to prevent the conversion of  $\text{N}_2\text{O}$  to  $\text{N}_2$  gas. In the case of amended

DEA assays, glucose was added to prevent soil enzyme activity from being carbon limited. Headspace gas was then sampled from the sample container and analyzed using gas chromatography in order to quantify the denitrification product ( $\text{N}_2\text{O}$ ) gas in  $\mu\text{g}/\text{kg}/\text{h}$ .

Net nitrification and mineralization incubations were also performed by the University of Rhode Island Watershed Hydrology Laboratory using a week-long incubation in the laboratory. Total N, nitrate-N and ammonium-N for the soil samples was determined at the start of the incubation. Soils were incubated at  $25^\circ\text{C}$  for a week and a measured amount of water was added to maintain constant soil/sample weight. The N concentrations are determined at the end of the incubation. The difference in ammonium-N and nitrate-N concentrations pre- and post-incubation provided the net ammonification and nitrification rates, respectively and all results were collected and reported in units of  $\mu\text{g}/\text{kg}/\text{h}$  as to allow comparison with each other.

### **3.7 Laboratory macrocosm experiment Sampling**

The intent of this rudimentary laboratory/greenhouse experiment was to determine if nitrate-N is leached/released from oxic, dewatered riparian sediment, and in contrast, if nitrate-N is consumed/denitrified under anoxic conditions. To accomplish this, thirty riparian soil samples were collected at the study site. These samples were collected from the legacy sediment terrace located 130 m upstream of the removed dam. These samples consisted of twelve surficial soil samples which were collected in batches of 6

from 2 groundwater wells (Wells 3 & 5) (Figure 3.4). The surficial samples were collected in sets of two, in triplicate, from wells 3 and 5 for a total of 6 surficial samples per groundwater well (Figure 3.4). All surface samples were collected by removing the top organic layer of soil with a trowel before extracting a 10 cm depth sample. Attention was given to maintain the soil integrity to the best of our ability during the extraction process. Each sample was then labeled and stored in gardening pots of known mass.

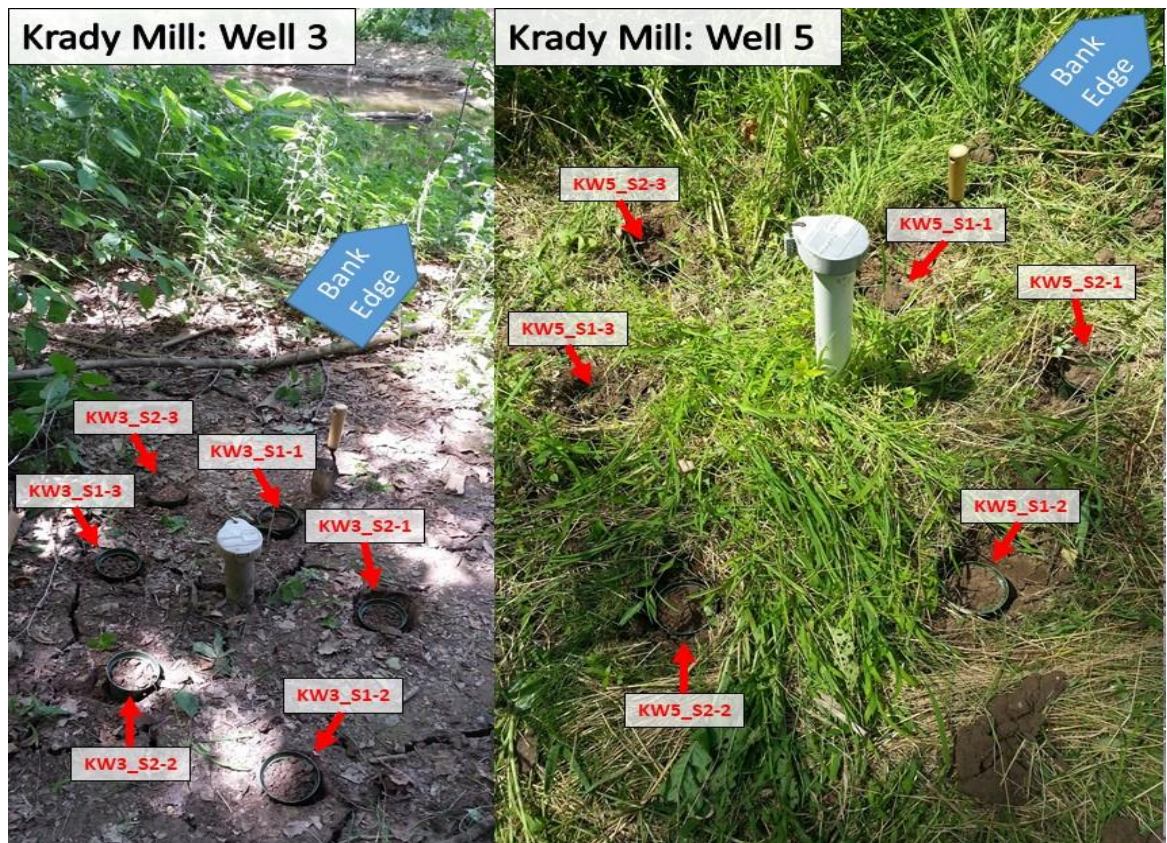


Figure 3.4: Location of macrocosm samples taken from wells 3 & 5. The relative locations of the six surficial samples collected from each of the 3 groundwater wells are identified above.

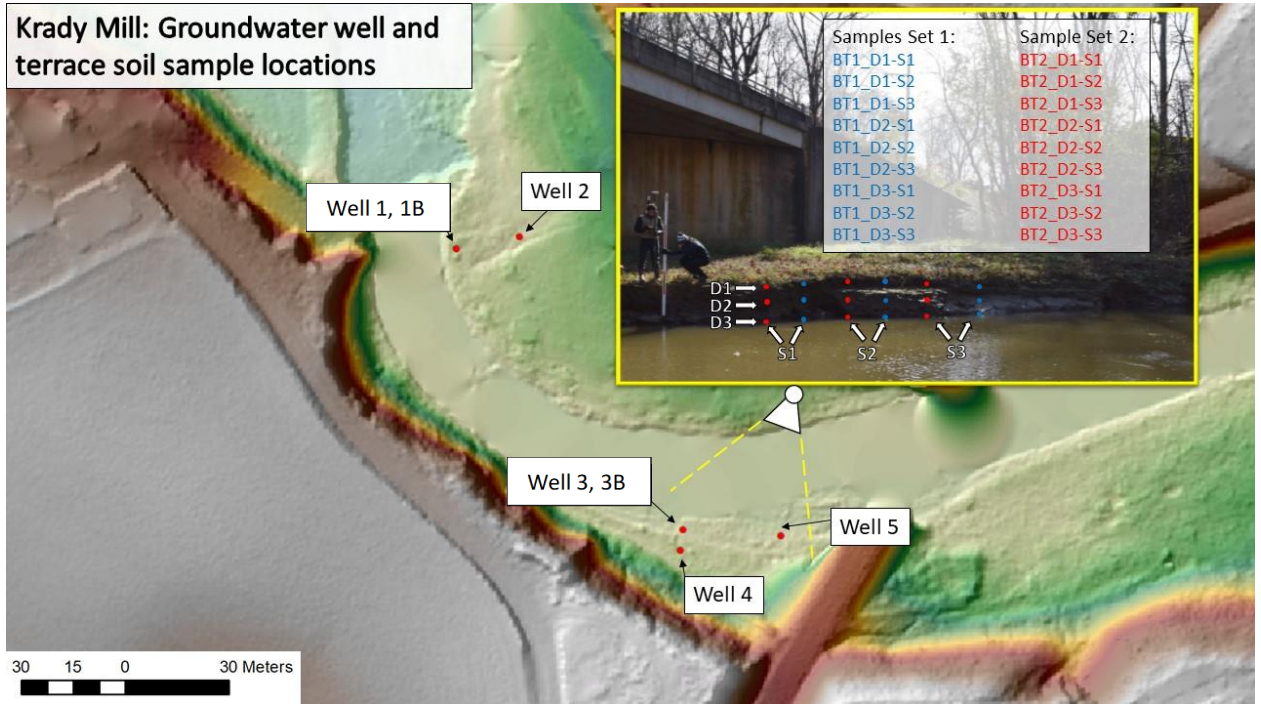


Figure 3.5: A DEM image of the Krady milldam site. Locations of wells 1-5, as well as the locations of terrace depth macrocosm samples. Samples processed for the macrocosm experiment were removed from between wells 3 and 5 and are indicated above.

Eighteen samples were collected from the bank of the Krady mill legacy sediment terrace in order to capture the behavior of the soil at depths in the terrace profile (Figure 3.5). Two sets of samples were extracted from the terrace. Each of the two sets consisted of samples taken at three depths and were sampled in triplicate across the surface of the terrace. The samples taken at depth were taken from right above the water line at a depth of 5' (1.5 m), halfway up the bank profile at a depth of 2.5' (0.76 m) and at the surface of the terrace at a depth of 5" (0.13m). These 18

samples were extracted from the terrace using a trowel to scrape the top layer of organic material off of the surface, then by digging out a 10 cm core from the bank laterally (Figure 3.6). These samples were then stored in gardening pots of known mass.



Figure 3.6: The relative locations of the Krady milldam terrace depth samples. Sample Identification can be understood as follows (BT1\_D2-3 / Bridge terrace sample set 1, depth 2, subsample 3). BT2\_D(1,2&3)3 not visible in the above image due to the angle of the photo.

### 3.8 Macrocosm Experiment Sample Analysis Procedures

After the sample collection process, all 36 samples had their mass' calculated in the lab accounting for the known mass of the sample container. All samples had material removed until the final sample mass was within the range of 250 g - 260 g to

maintain consistency across all samples. The average sample mass was recorded to be 254 g for all 36 samples and the standard deviation between sample masses was calculated to be 1.74 g.

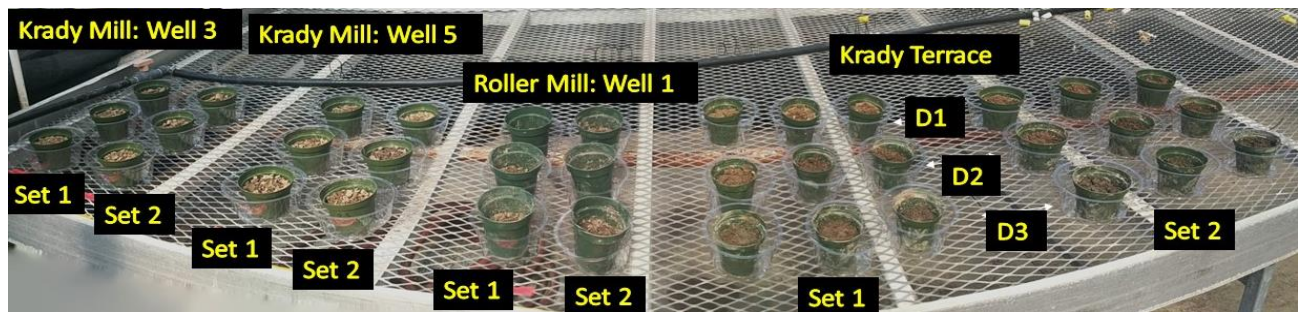


Figure 3.7: The layout of well 3, well 5, RMW1 and all Krady Terrace samples for the macrocosm experiment. Sample set 1 is kept in a constant state of anoxia while sample set 2 is kept under oxic conditions before being flushed with DI water and sampled. Samples from the RMW1 sample set reflect samples collected from an additional study site and served as a metric to compare between. For the purposes of this study, the results of the RMW1 sample set have been omitted.

All 36 samples were then stored in a temperature-controlled greenhouse. The eighteen samples from sample set 1, were placed in dishes allowing them to be continuously saturated throughout the length of the experiment when inundated with stream water collected from the site. The eighteen samples from sample set 2 were placed in identical dishes, but were left to dry for two weeks before having 150 ml of DI water added to them (Figure 3.7).

Stream water from the site, was sampled every two weeks in bulk directly from the dam site. On a biweekly basis this water would have its nitrate-N concentrations

measured using an absorbance based (S::CAN, inc.) spectrolyzer. At the beginning of each iteration of the experiment 500 ml of this water was poured into the dish of each sample in sample series 1 so that each sample became fully hydrated. The same was done with two empty dishes which were used as standards in order to track naturally occurring background shifts in nitrate-N concentrations throughout the duration of the experiment in order to account for any ambient shifts in  $\text{NO}_3\text{-N}$ .

Over the duration of each experiment period, sample series 1 was subsampled at the end of every week. The total volume of water remaining and nitrate-N concentrations for each sample was measured. Each sample tray was then dumped, cleaned and had 500 ml of fresh Chiques water added to it to refresh the experiment. A nitrate-N concentration mass balance was performed comparing before and after nitrate-N concentrations accounting for evaporation. This procedure produced a weekly series of data over the course of our observational period exhibiting any nitrate-N loss which had occurred.

Simultaneously, the samples from sample set 2 were left for the entire two-week sample duration without water in a climate-controlled greenhouse to fully air dry. At the end of the two-week period 150 ml of de-ionized water was then measured and added to each of the samples in sample set 2. This water was allowed to percolate through the sample and collect in a tray beneath the sample container. The water which had passed through the sample was then immediately analyzed for nitrate using a S::CAN Spectrolyzer. This experiment generated a bi-weekly series of data over the course of our observational period illustrating nitrate--N which had been added.

All samples which were collected for both sample sets were refrigerated for the duration of the study. In order to confirm the accuracy and reliability of the data collected from the S::CAN Spectrolyzer, 100 samples were subsampled before being refrigerated and stored. These subsamples were then delivered to the University of Delaware Soils Laboratory to be analyzed for nitrate-N.

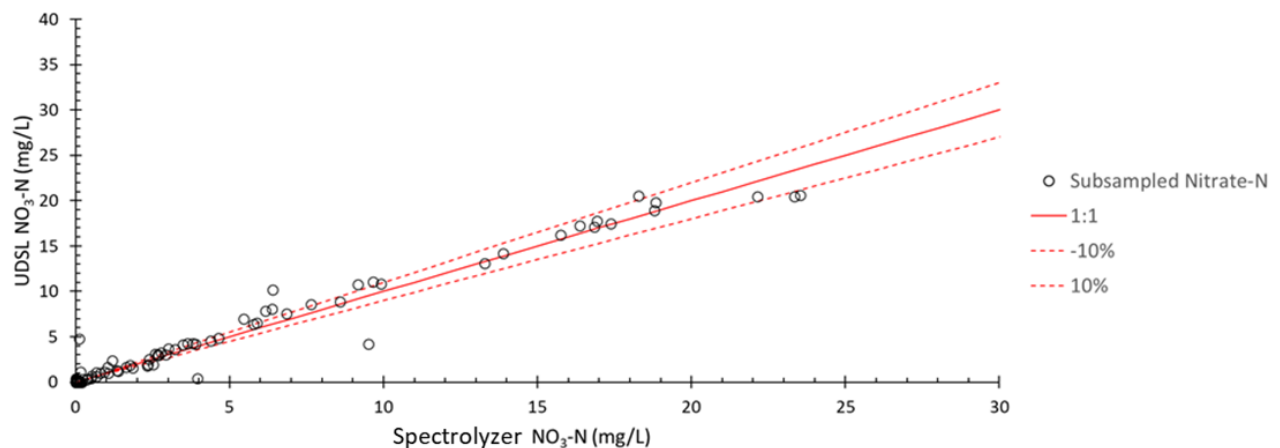


Figure 3.8: This cross plot represents the 1:1 relationship observed between nitrate-N measured on the in-house S::CAN Spectrolyzer vs. the nitrate-N measured by the University of Delaware Soils Laboratory.

In figure 3.8, the relationship between these two methods of measuring nitrate-N is illustrated (Figure 3.8). This linear 1:1 relationship between results taken from the two analytical methods illustrate that the results gathered from using the S::CAN Spectrolyzer method are similar to the results gathered from the University of Delaware Soils Lab. Due to this, each individual result of the nearly 700 macrocosm subsamples analyzed in this way can be regarded with a level of reliability.

After the macrocosm experiment had been operating for 8 iterations (between July 2019 and September 2019) it was observed that nearly 100% of the starting nitrate-N concentration in all samples in sample set 1 was being removed. The intent of this experiment to simulate conditions these soils may experience in the field, however after noticing this the experimental procedures were adjusted to limit each of these samples' exposure to sunlight in an attempt to minimize any photosynthetic algal activity that may have been occurring in the sample container. For this reason, between the 8<sup>th</sup> and 9<sup>th</sup> iteration of the anoxic experiment, a thick tarp was placed over the experiment functionally limiting photosynthesis from occurring at detectable levels in the experiment. From this point forward, 100% removal of nitrate-N in the sample containers was far less common and only detectable when initial concentrations of nitrate-N in the stream water were low.

## REFERENCES

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## Chapter 4

### RESULTS

#### 4.1 Stream water level, flow, and groundwater elevations

Average stream water level at the Chiques creek over the duration of the study was 82.8 m above sea level, with a maximum and minimum of 83.8 m and 82.5 m respectively (Figure 4.1). The average discharge over the study was 2.11 m<sup>3</sup>/s (Figure 4.2). Streamflows were generally elevated during winter and spring and lower in late summer and early autumn (September-October).

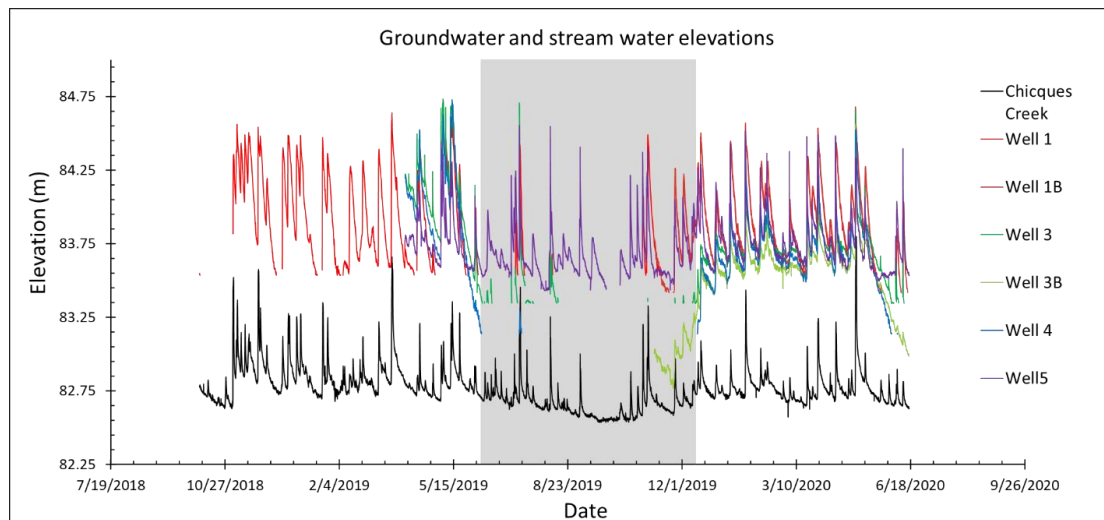


Figure 4.1: Timeseries depicting rising and falling water levels found in the stream channel and at all groundwater wells. Periods of no data are the result of dry weather conditions where the water level was below the maximum depth of the water level sensor. The grey region in the figure illustrates the driest period of time when sampling was most limited across all wells.

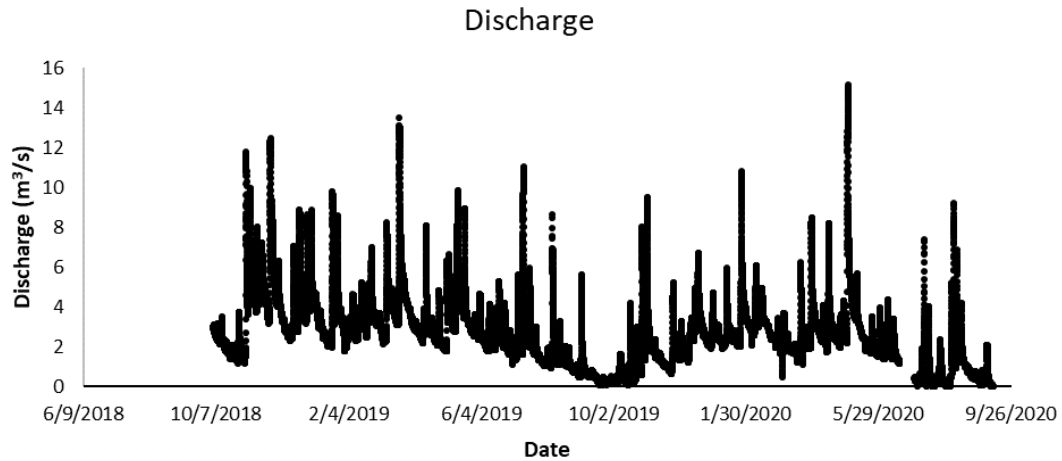


Figure 4.2: Time series illustrating discharge measured for the Chiques Creek over the duration of the observational period

Groundwater elevations were generally greater than the stream water levels (Figure 4.1). Well 1 recorded an average groundwater elevation of 83.9 m, with a minimum and maximum of 83.5 m and 84.7 m respectively (Figure 4.1), whereas the adjoining well 1B recorded an average, minimum and maximum of 83.9 m, 83.4 m and 84.6 m, respectively (Figure 4.1). Well 2, which was furthest north from the stream channel and at a higher soil elevation went dry as early as May 2019. Well 3 had an average, minimum and maximum groundwater elevation measured to be 83.8 m, 83.4 m and 84.7 m respectively while well 3B measured 83.5 m, 82.8 m and 84.6 m respectively (Figure 4.1). Lastly, well 4, which was upslope of well 3, measured an average, minimum and maximum of 83.7 m, 83.1 m and 84.7 m. The elevation of groundwater at well 5, which was closest to the stream, measured 83.7 m, 83.4 m, and

84.6 m (Figure 4.1). Overall, the elevations recorded from groundwater wells across the site show that the level of the groundwater table was above the level of stream flow by approximately 1 m (Figure 4.1).

While stream water level was measured throughout the duration of the study period, groundwater elevations in many wells dropped below the sensor depth during dry periods in the summer and fall. All groundwater wells, apart from well 5, recorded water levels below the level of the sensor between June 2019 and December 2019. Well 5, which was closest to the stream on the south terrace, on the other hand was not influenced as heavily by this dry season and for this reason is the only groundwater well which did not go dry for any length of time during the study period (Figure 4.1). Overall, stream and groundwater levels did not show any long-term increasing or decreasing trend since water level monitoring began in November, 2018 and such temporal changes were not expected.

The unsaturated soil profile above the groundwater level, referred to here as the “drained soil profile,” varied considerably across the riparian zone. The average, maximum, minimum, and the range of the unsaturated thickness for all well locations is reported in Table 4.1 and temporal patterns of these values are presented in Figure 4.3. The average drained soil profile, for well 1 was 1.26 m, smaller than that of well 1B which was 1.62 m (Figure 4.3, Table 4.1). The smaller value for well 1 was likely because of the groundwater falling below the sensor and the sensor not being able to record the deeper depths (well 1B sensor was located at greater depth than well 1 and likely recorded greater depths). Groundwater wells 3 and 3B both recorded an average

drained profile thickness equal to 0.85 m and 1.15 m, respectively. According to these measurements, each well can be categorized by how wet it is compared with each other. Across the duration of the study, well 5 was by far the wettest well followed by well 3B, well 3 and well 4 with wells 1 and 1B, which were closest to the former dam, being the driest wells that were measured. Although there was considerable variation over the study period, it was noted that the unsaturated depth was typically the greatest in the fall between August and December with the shallowest drained depths measured in wetter seasons between April and June.

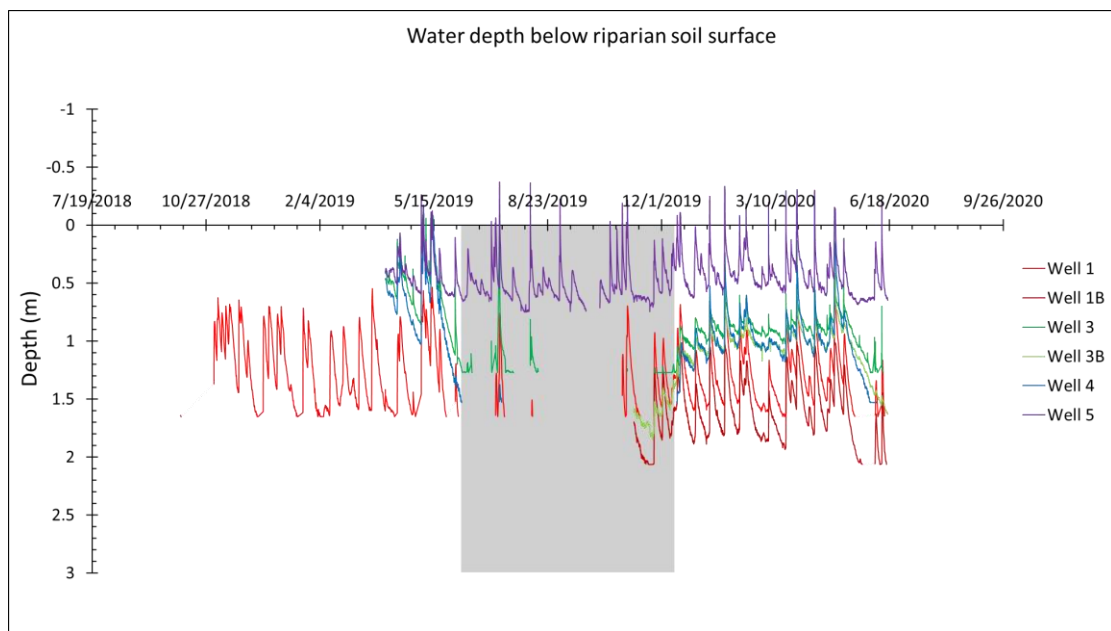


Figure 4.3: Timeseries illustrating the GW depth below the riparian soil surface for each groundwater well. The grey region in the figure illustrates the driest period of time when sampling was most limited across all wells.

Lastly, wells 4 and 5 both measured average drained profile thicknesses of 0.93 m and 0.46 m respectively (Figure 4.3, Table 4.1). When the thickness of the drained profile at wells located closest to the site of the removed dam (wells 1 & 1B) are observed and compared with the thickness of the drained profile at well sites furthest upstream (well 5) what becomes clear is that the thickness of the drained profile above the water table increases as distance from site of the dam decreases. For most wells the range of thickness (maximum – minimum thickness of the drained profile) was found to be similar with wells 1, 1B and 5 demonstrating a range of 1.12 m - 1.15 m and wells 3, 3B and 4 demonstrating ranges from 1.23 m – 1.59 m (Figure 4.3, Table 4.1).

Table Table 4.1: Minimum, maximum, mean and range of values for the unsaturated or drained soil profile (depth from soil surface to groundwater) for the GW well locations.

| Location | Minimum Drained Profile (m) | Maximum Drained Profile (m) | Mean Drained Profile (m) | Range of depth (m) |
|----------|-----------------------------|-----------------------------|--------------------------|--------------------|
| Well 1   | 0.51                        | 1.65                        | 1.26                     | 1.14               |
| Well 1B  | 0.91                        | 2.06                        | 1.62                     | 1.15               |
| Well 3   | -0.12                       | 1.27                        | 0.85                     | 1.39               |
| Well 3B  | 0.06                        | 1.85                        | 1.15                     | 1.79               |
| Well 4   | -0.06                       | 1.53                        | 0.93                     | 1.59               |
| Well 5   | -0.37                       | 0.75                        | 0.46                     | 1.12               |

## **4.2 Riparian to stream hydraulic gradients**

Hydraulic gradients from the well to the stream water surface were found to be comparable among the wells. Wells 1 and 1B measured average hydraulic gradients of 0.08 m/m and 0.07 m/m respectively while wells 3 and 3B measured averages of 0.07 m/m and 0.05 m/m (Figure 4.4). Wells 4 and 5, being located furthest upstream from the site of the removed milldam recorded average hydraulic gradients similar to those recorded elsewhere throughout the study site of 0.05 m/m and 0.07 m/m respectively (Figure 4.4). Across the site, hydraulic gradients ranged from -0.01 m/m to 0.14 m/m with a sitewide average being equal to 0.08 m/m. Although all wells behaved similarly to each other with hydraulic gradients responding to the same temporal patterns, wells 3 and 5 typically measured the highest hydraulic gradients while well 4 definitively measured the lowest with a maximum of 0.09 m/m. Although peaks were measured at all times of year due to storms and high flow events, the hydraulic gradients measured across the site were typically highest in April through June. Except for one unique and brief period of measurement in July of 2019, all wells recorded positive hydraulic gradients greater than zero (Figure 4.4). With that said, it is crucial to note that during extended periods of dry conditions when the groundwater levels were very low and below the sensor the hydraulic gradients were likely negative, indicating flow from the stream to the riparian zone.

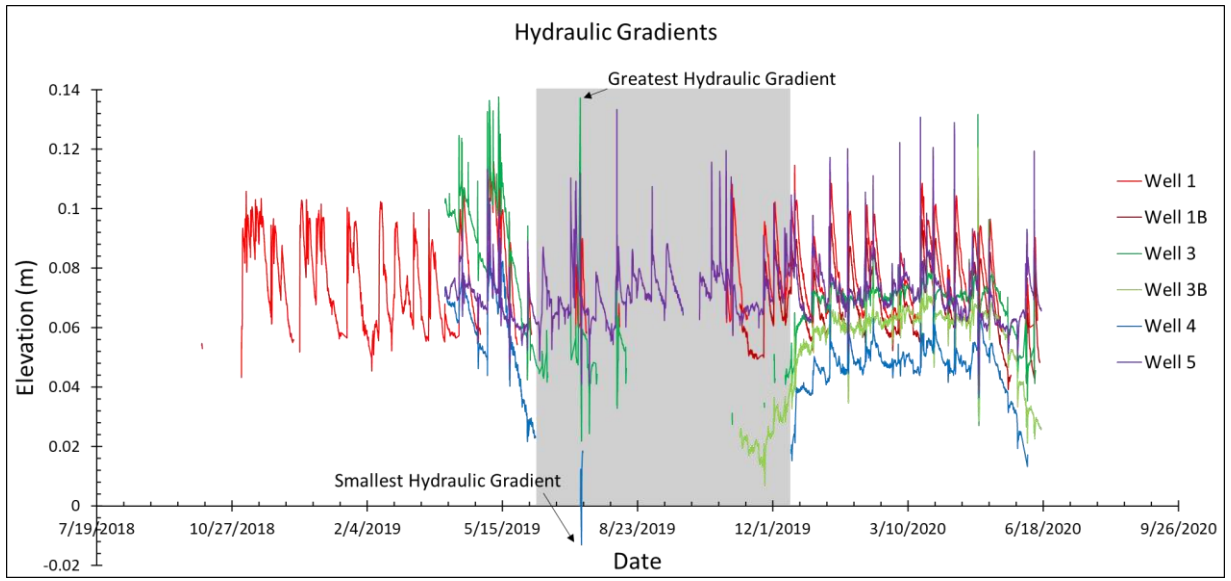


Figure 4.4: Hydraulic gradients calculated from each groundwater well. Periods of no data are the result of dry field conditions during which time hydraulic gradients are unknown. The grey region in the figure illustrates the driest period of time when sampling was most limited across all wells.

### 4.3 Nitrogen concentrations in ground, soil, and stream water

The lowest and highest recorded stream nitrate-N values observed were 2.06 mg/L in October and 9.10 mg/L in September, respectively, with the average stream nitrate-N equal to 7.13 mg/L (Figure 4.5, Table 4.2). Across the duration of the study, stream nitrate concentrations remained elevated at about 7 mg/L and showed no increasing or decreasing trends with time since dam removal. Typically, the highest concentrations of stream nitrate-N were observed in the spring after the winter thaw between February and March with the lowest observed concentrations occurring in mid to late fall between October and November. In comparison, nitrate-N in

groundwater was found to be much lower than the concentrations of nitrate-N observed in stream water (Figure 4.5).

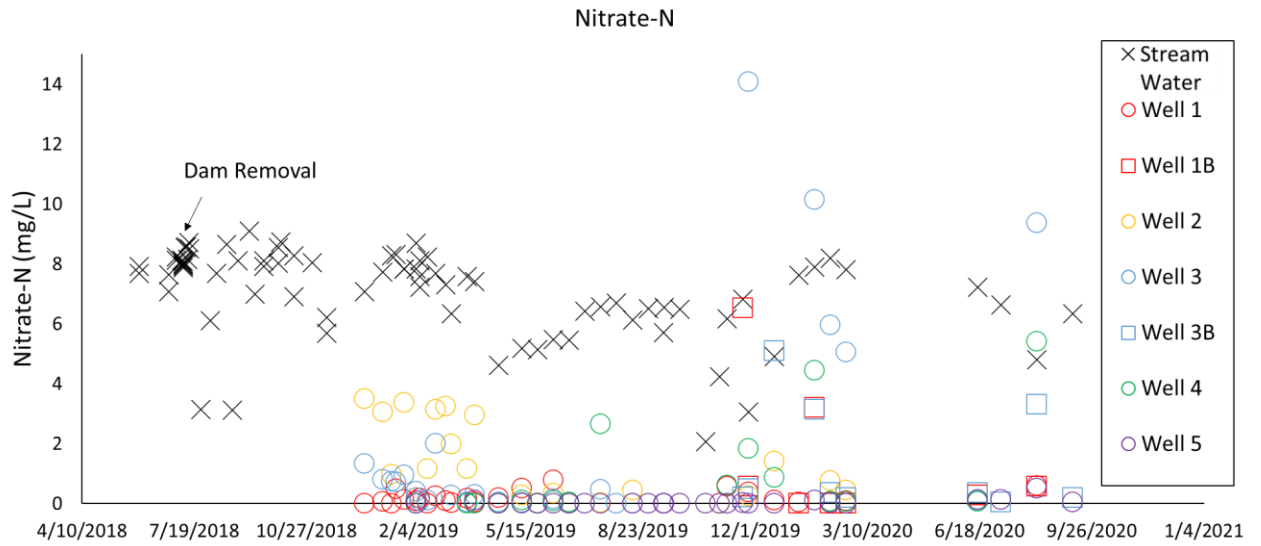


Figure 4.5: Time series of nitrate-N concentrations in stream and groundwater wells over the study period (July 2018 – September 2020).

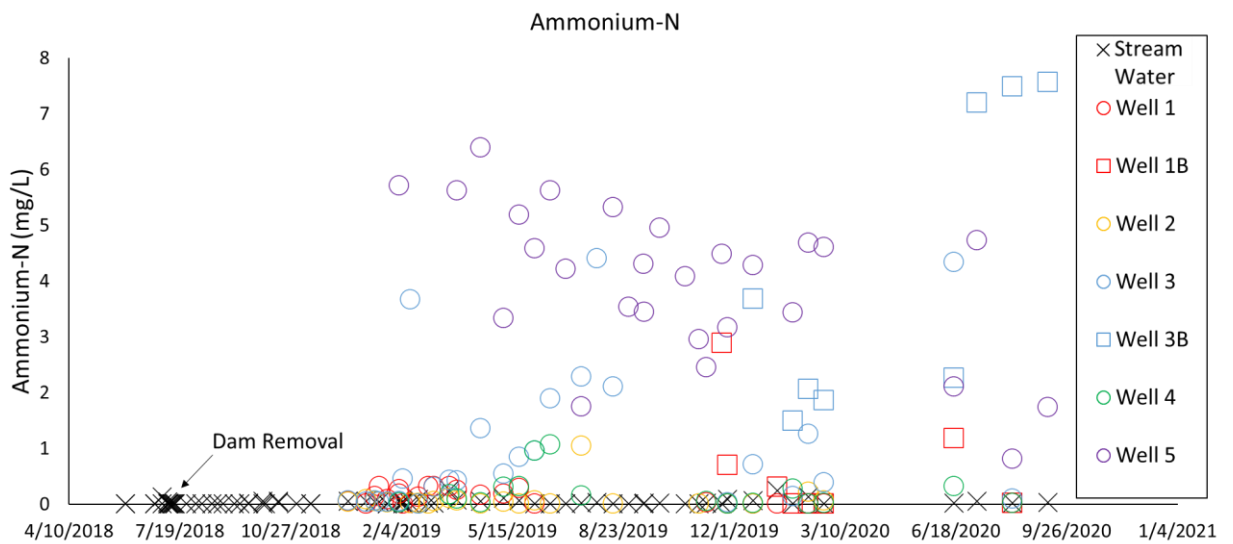


Figure 4.6: Time series of Ammonium-N concentrations in stream and groundwater wells over the study period (July 2018 – September 2020).

Wells 1 and 1B recorded average concentrations of nitrate-N in groundwater to be equal to 0.18 mg/L and 1.72 mg/L, respectively. Further upstream, wells 3 and 3B had average groundwater nitrate-N concentrations of 2.43 mg/L and 1.59 mg/L, respectively (Figure 4.5, Table 4.2). Well 4 had an average nitrate-N concentration of 0.72 mg/L while well 5 had an average nitrate-N concentration of 0.02 mg/L (Figure 4.5, Table 4.2). Ammonium-N was measured to be below 1 mg/L for all groundwater wells apart from wells 3B and 5, which recorded average ammonium concentrations of 4.75 mg/L and 4.27 mg/L respectively (Figure 4.6, Table 4.2). In contrast to groundwater wells 3B and 5, stream water ammonium-N concentrations were very low and close to detection levels (Figure 4.6). Again, no long-term increase or decrease was apparent for ammonium-N for stream and groundwaters.

Total nitrogen varied considerably from  $>1$  mg/L to 12 mg/L in both stream and ground water with no discernable long-term trends (Figure 4.7). For stream water the nitrate-N composed 93% of TN while for groundwater averaged to be 24%. Similar to the variability for TN, DOC displayed high variability, however, concentrations of DOC were consistently found to be greater in well samples ( $>0$  mg/L – 45 mg/L) than in stream water ( $> 0$  mg/L – 15 mg/L). However, no long-term

increasing or decreasing trends were observed for TN and DOC since dam removal

(Figure 4.8).

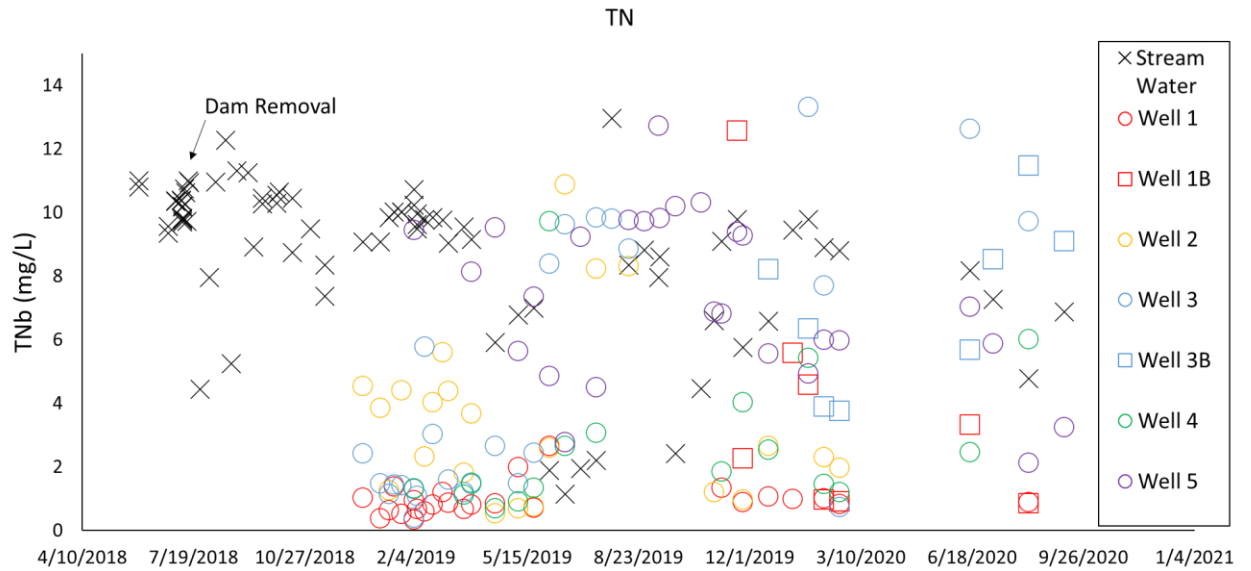


Figure 4.7: Time series of TN concentrations in stream and groundwater wells over the study period (July 2018 – September 2020).

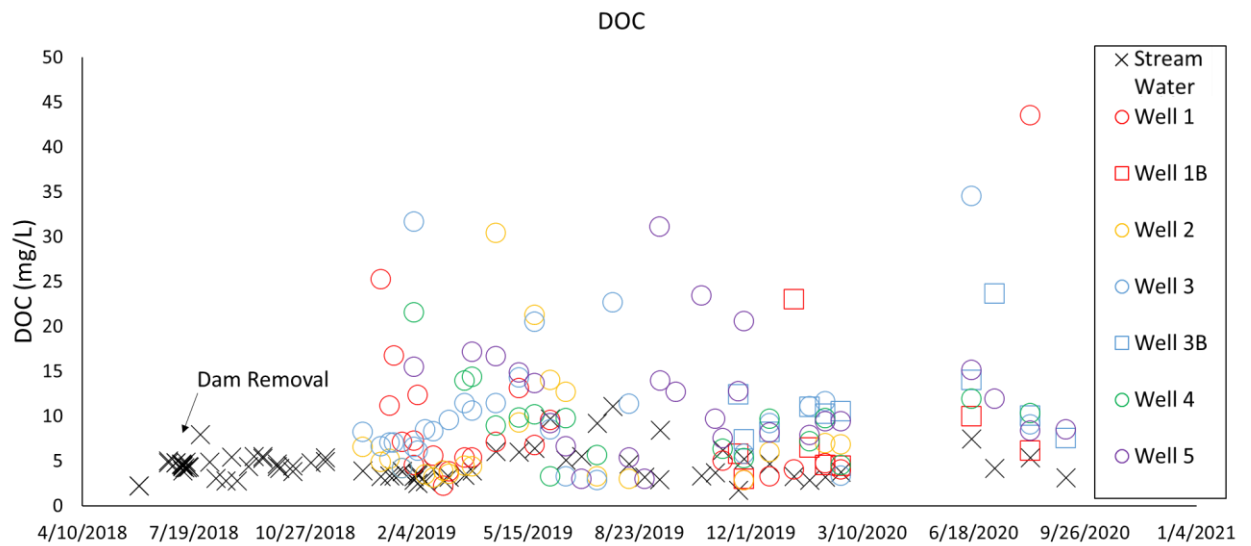


Figure 4.8: Time series of DOC concentrations in stream and groundwater wells over the study period (July 2018 – September 2020).

Table Table 4.2: Mean and range of concentrations for dissolved organic carbon (DOC), total nitrogen (TN), ammonium-N (NH<sub>4</sub>-N) and nitrate-N (NO<sub>3</sub>-N) for stream, ground, and soil waters.

| <b>Location</b>    | <b>DOC (mg/L)</b>               | <b>TN (mg/L)</b>               | <b>NH<sub>4</sub>-N (mg/L)</b> | <b>NO<sub>3</sub>-N (mg/L)</b> |
|--------------------|---------------------------------|--------------------------------|--------------------------------|--------------------------------|
| <b>Stream</b>      | <b>7.52</b><br>(1.70 – 241.86)  | <b>8.88</b><br>(1.14.12.97)    | <b>0.03</b><br>(0.01 – 0.25)   | <b>7.13</b><br>(2.06 – 9.10)   |
| <b>Well 1</b>      | <b>16.27</b><br>(2.22 – 172.52) | <b>0.96</b><br>(0.32 – 2.65)   | <b>0.13</b><br>(0.01- 0.32)    | <b>0.18</b><br>(0.00 – 0.78)   |
| <b>Well 1B</b>     | <b>7.85</b><br>(2.97 – 23.02)   | <b>4.47</b><br>(0.89 – 12.56)  | <b>0.65</b><br>(0.01 – 2.89)   | <b>1.72</b><br>(0.01 – 6.53)   |
| <b>Well 2</b>      | <b>12.06</b><br>(2.86 – 105.67) | <b>3.49</b><br>(0.52 – 10.88)  | <b>0.09</b><br>(0.01 – 1.04)   | <b>1.30</b><br>(0.01 – 3.50)   |
| <b>Well 3</b>      | <b>10.04</b><br>(2.80 – 31.68)  | <b>5.82</b><br>(0.39 – 30.79)  | <b>0.87</b><br>(0.01 – 4.41)   | <b>2.43</b><br>(0.01 – 19.28)  |
| <b>Well 3B</b>     | <b>9.96</b><br>(7.39 – 12.41)   | <b>10.77</b><br>(3.75 – 21.96) | <b>4.75</b><br>(1.49 – 10.82)  | <b>1.59</b><br>(0.20 – 5.10)   |
| <b>Well 4</b>      | <b>9.32</b><br>(3.24 – 21.51)   | <b>2.58</b><br>(0.68 – 9.71)   | <b>0.23</b><br>(0.01 – 1.06)   | <b>0.72</b><br>(0.01 – 4.45)   |
| <b>Well 5</b>      | <b>19.12</b><br>(2.96 – 168.74) | <b>7.77</b><br>(2.77 – 12.72)  | <b>4.27</b><br>(1.75 – 6.39)   | <b>0.02</b><br>(0.01 – 0.11)   |
| <b>Lysimeter 1</b> | NA                              | NA                             | <b>0.03</b><br>(0.01 – 0.11)   | <b>5.19</b><br>(4.10 – 6.41)   |
| <b>Lysimeter 2</b> | NA                              | NA                             | <b>0.12</b><br>(0.01 – 0.33)   | <b>2.78</b><br>(1.65 – 4.22)   |

|                        |    |    |                              |                                |
|------------------------|----|----|------------------------------|--------------------------------|
| <b>Lysimeter<br/>3</b> | NA | NA | <b>0.13</b><br>(0.01 – 0.37) | <b>18.52</b><br>(9.97 – 24.13) |
| <b>Lysimeter<br/>4</b> | NA | NA | <b>0.05</b><br>(0.01 – 0.16) | <b>11.45</b><br>(4.09 – 17.33) |
| <b>Lysimeter<br/>5</b> | NA | NA | <b>0.05</b><br>(0.01 – 0.13) | <b>3.47</b><br>(1.23 – 5.87)   |

Across the board, all soil water lysimeters had higher concentrations of nitrate-N compared to the co-located groundwater wells (Figure 4.9). For lysimeters 1 through 5, the average concentration of nitrate-N was 5.19 mg/L, 2.78 mg/L, 18.52 mg/L, 11.45 mg/L and 3.47 mg/L, respectively with a range between 1.23 mg/L and 24.12 mg/L (Figures 4.9 – Figure 4.10). For the same length of time (Nov 2019 – Feb 2020) during which lysimeters were deployed in the field, the average concentration of nitrate-N measured in the shallow soil was 7.38 mg/L compared to 1.35 mg/L measured in the groundwater. The average ammonium-N measured was low for all lysimeters ranging from 0.03 mg/L to 0.13 mg/L.

The results of the t-test statistical analysis illustrated that there was no statistically significant difference between the concentration of nitrate-N measured in stream and lysimeter samples (Figure 4.9). However, samples collected from stream and lysimeters were significantly different from the well samples (well 1, well 3, well 4, well 5). Among the well samples, well 5 typically measured low concentrations of nitrate-N and was significantly different than wells 1 – 4 (Figure 4.9). Lastly well, 3 typically had higher concentrations of nitrate-N than wells 1 and 4, however this

difference was found to only be statistically significant when the results from well 3 were compared with the results taken from well 1 ( $p=0.02$ ). Well 3 and 4 on the other hand were not found to be just statistically different from each other ( $p = 0.11$ ).

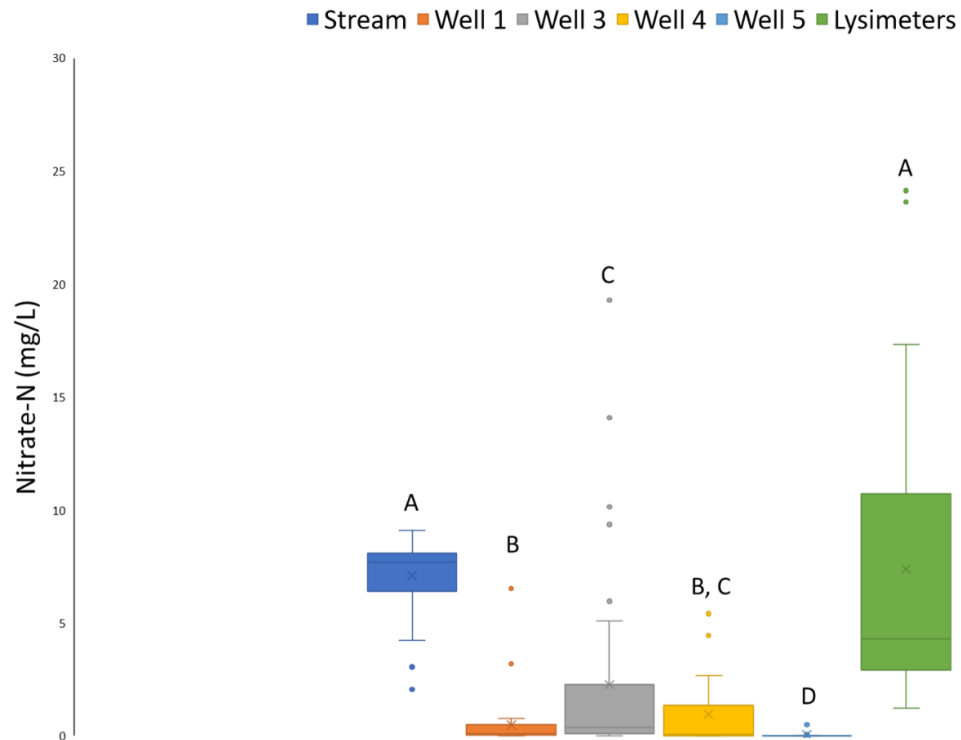


Figure 4.9: Stream water nitrate-N compared with nitrate-N from groundwater wells and soil water lysimeters. The letters above each sample set characterize which sets are statistically significant from each other. Samples with the same letter are not significantly different from each other while those with different letters are significantly different.

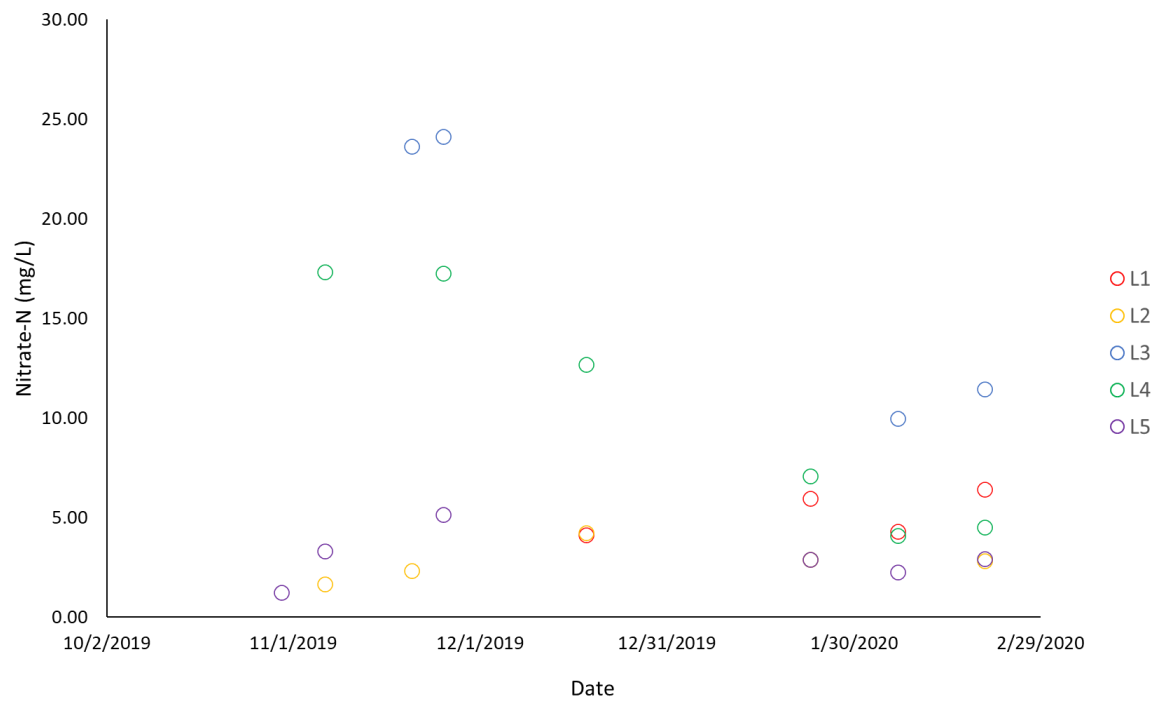


Figure 4.10: Nitrate-N concentrations for shallow soil lysimeters L1-L5. In all lysimeters, the maximum nitrate-N value recorded was 24.1 mg/L in well 3. The minimum value was 1.2 mg/L in well 5 and the average calculated from all lysimeter measurements was 7.6 mg/L



2.8 mg/L and 6.4 mg/L. The highest lysimeter nitrate-N concentrations and the broadest range of values (5-25 mg/L) were observed for lysimeters (L3 and L4) which had intermediate groundwater depths (0.8 – 1.2 m). This pattern appeared to suggest that there was an optimal groundwater depth in the vicinity of 1 m that provided ideal moisture and oxygenated conditions for the production of nitrate-N in the soil profile.

#### 4.5 Soil nitrate-N and ammonium-N concentrations at groundwater well locations

Soil nitrate-N concentrations for well locations varied with depth, typically in the range of >0 mg/kg to 25 mg/kg, with well 5 exhibiting slightly higher concentrations of 40 mg/kg nitrate-N in the shallower samples collected (Figure 4.12).

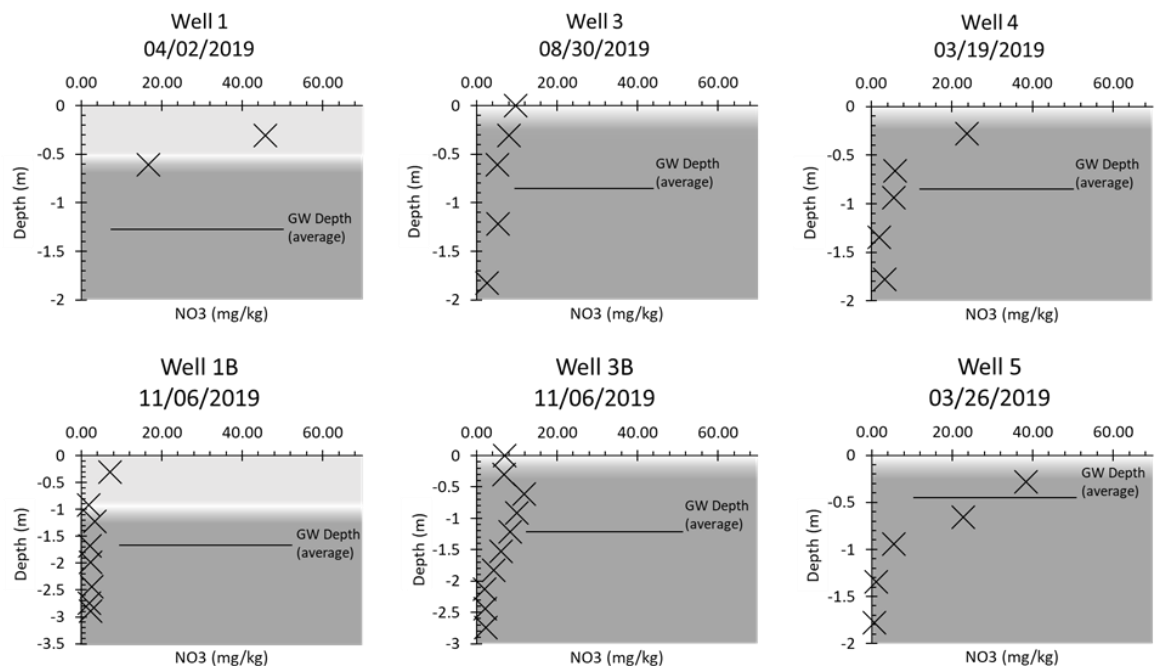


Figure 4.12: Scatterplots illustrating the concentrations of nitrate-N in soil samples collected from various depths at groundwater wells. The light grey shaded region represents the depth of riparian soil that was above the water table for the entire study duration. The dark grey shaded region represents the depth of riparian soil that was below the highest recorded groundwater elevation. Each well's average groundwater depth over the course of the entire study is indicated with text for each well.

Across most wells, the samples with the highest concentration of nitrate-N were typically collected from shallow depth at or slightly above the average depth of the water table (Figure 4.12). Conversely, the concentration of nitrate-N declined rapidly with depth below the depth of the water table.

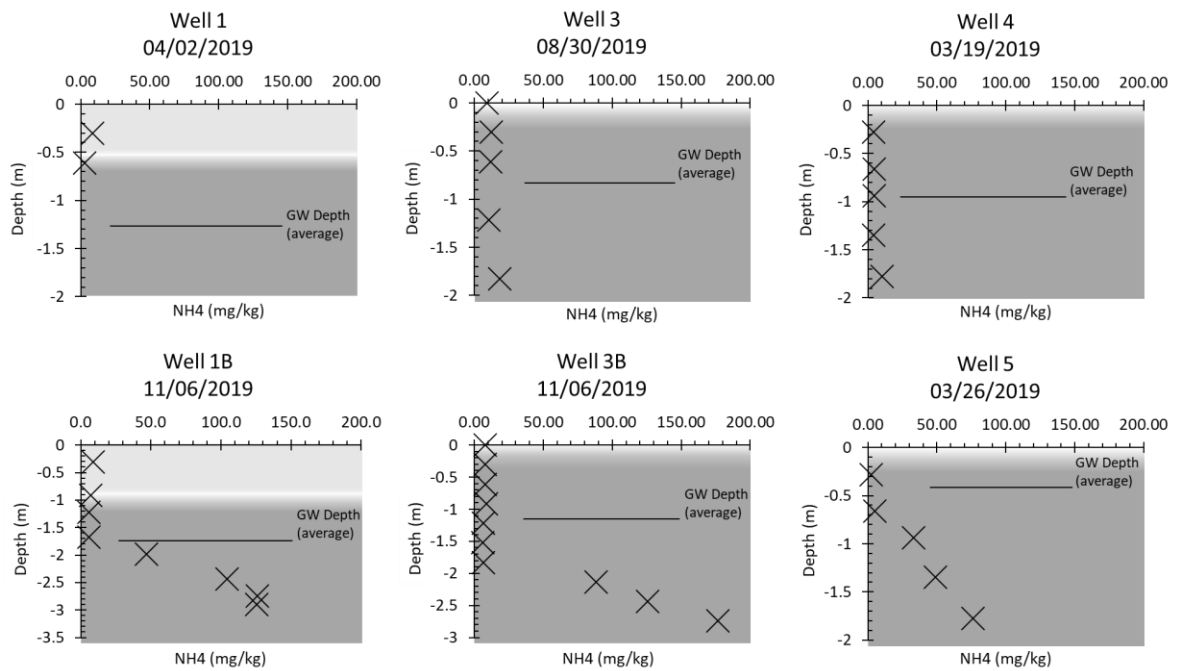


Figure 4.13: Scatterplots illustrating the concentrations of Ammonium-N for soils collected from various depth at the groundwater wells. The light grey shaded region represents the depth of riparian soil that was above the water table for the entire study duration. The dark grey shaded region represents the depth of riparian soil that was below the highest recorded groundwater elevation. The average groundwater depth for the wells over the course of the entire study is indicated with text.

In contrast to nitrate-N, an opposite relationship was observed for ammonium-N concentrations, with lower concentrations for shallow soils above the water table and higher concentrations for soils below the surface of the water table (Figure 4.13). In the case of wells 1B, 3B and 5, it can be seen that the concentration of ammonium begins to spike considerably at about about the same depth as the average groundwater elevation measured for each well. The maximum concentration of ammonium-N for all three wells is recorded for the lowermost soil depth.

#### **4.6 Denitrification enzyme assay (DEA), Nitrification, and Mineralization of riparian soils**

Amended denitrification potentials ( $\mu\text{g}/\text{kg}/\text{h}$ ) were highest in shallow soils (Figure 4.14) and then declined rapidly with soil depth.

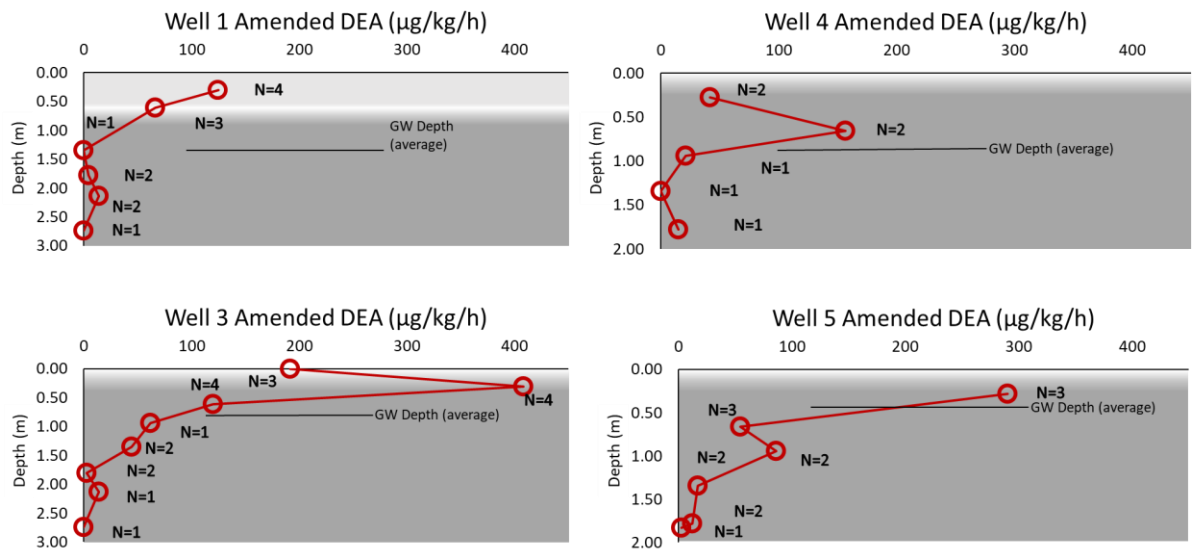


Figure 4.14: Scatterplots illustrating average DEA measurements taken from each field locality plotted by depth. In the above illustrations, the maximum water elevation is designated by the uppermost extent of the dark grey area and soils that were never below the water table are represented by the light grey area while the average groundwater depth is denoted on each figure with text.

Typically, DEA values from the shallow depths above the average groundwater level ranged between 50 µg/kg/h – 400 µg/kg/h (Figure 4.14). At depths below the average water table, DEA dropped rapidly never measuring greater than 100 µg/kg/h.

Unamended DEA measurements generally followed the same trend with depth as those observed for amended DEA values. Unlike with the amended DEA results however, the unamended DEA values were always considerably less. (Figure 4.15).

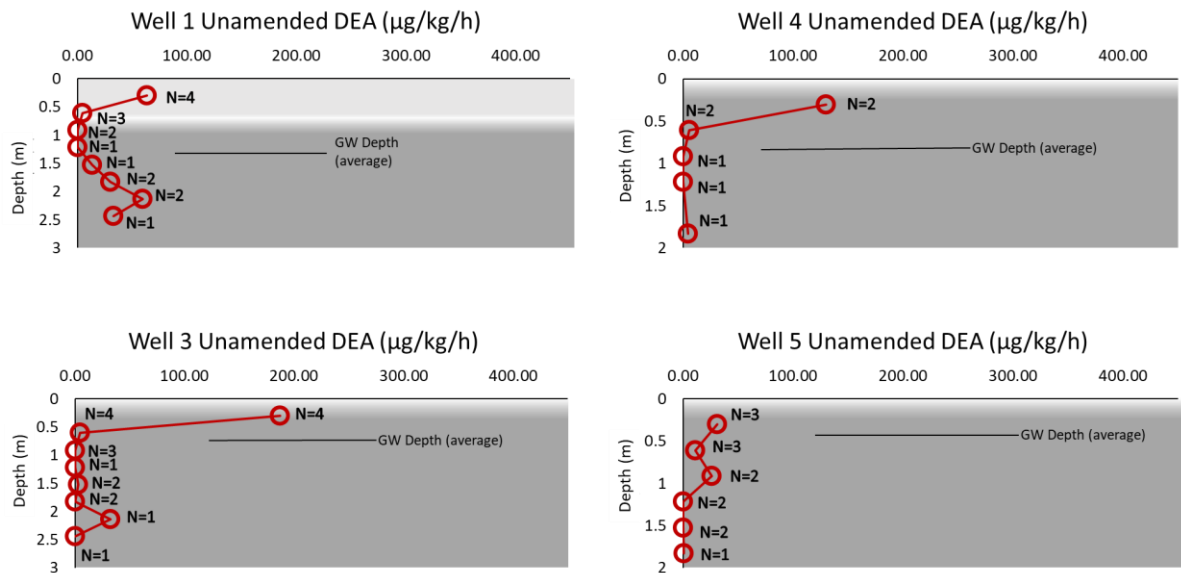


Figure 4.15: Scatterplots illustrating average unamended DEA measurements taken from each field locality plotted by depth. In the above illustrations, the maximum water elevation is designated by the uppermost extent of the dark grey area and soils that were never below the water table are represented by the light grey area while the average groundwater depth is denoted on each figure with text. The “N” value indicates the number of duplicates averaged at each particular point in the depth profile to create that points average.

Lastly, amended DEA measurements collected for soils at different times over the study duration indicated strong seasonal variability but did not reveal any consistent long-term increasing or decreasing trends with time (Figure 4.16). DEA measurements for April 2019 yielded the highest values over the study period suggesting influence of wet spring conditions on these measurements. DEA measurements conducted over the summer (August 2019) generated the lowest values (Figure 4.16).

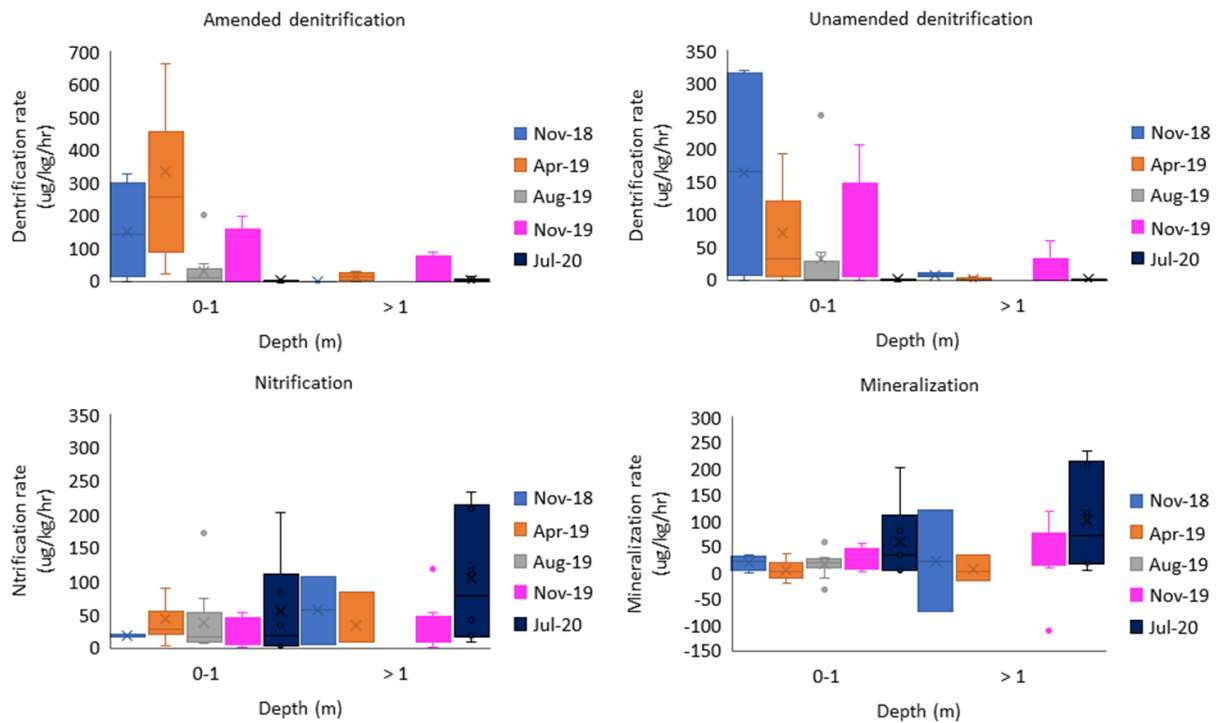


Figure 4.16: Temporal variability in amended and unamended DEA, nitrification and mineralization values averaged across all wells over the study period. The y axis illustrates the rate at which each process was occurring while the color of the box and whisker plot illustrates the time of year/seasonality of each observation. Depth is categorized across the x axis in groups ranging from between 0-1 m and >1 m.

Nitrification rates varied considerably with soil depth and sampling location (Figure 4.17). Except for well 5, nitrification rates were generally higher for near-surface soils and declined with depth (Figure 4.17). For well 5, higher nitrification rates were observed for deeper soil layers. When denitrification and nitrification rates

are compared (Figure 4.16 versus 4.17), nitrification rates were lower than denitrification values for all locations except well 5.

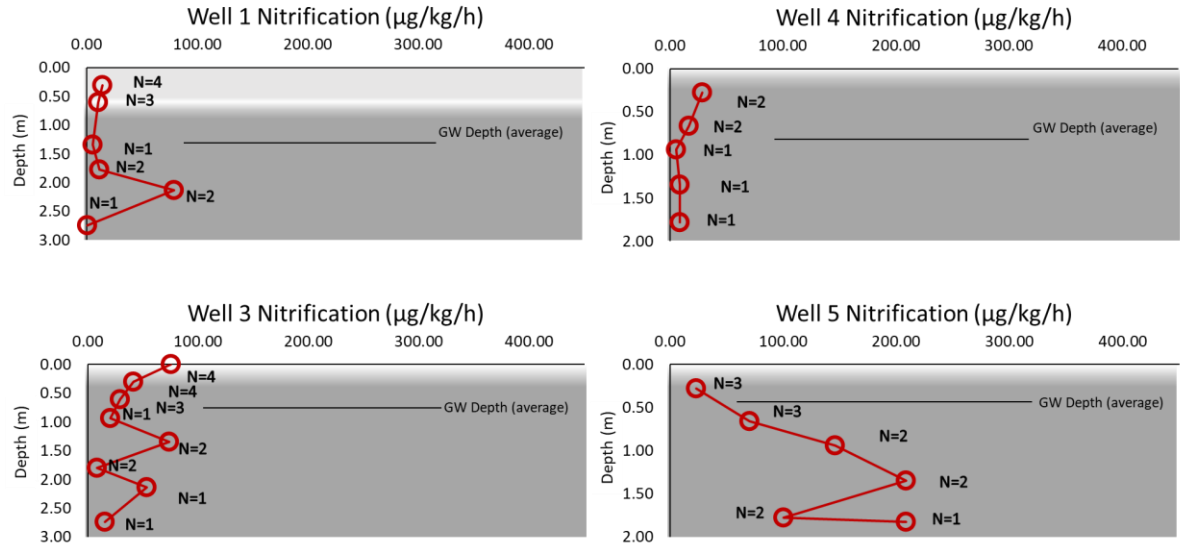
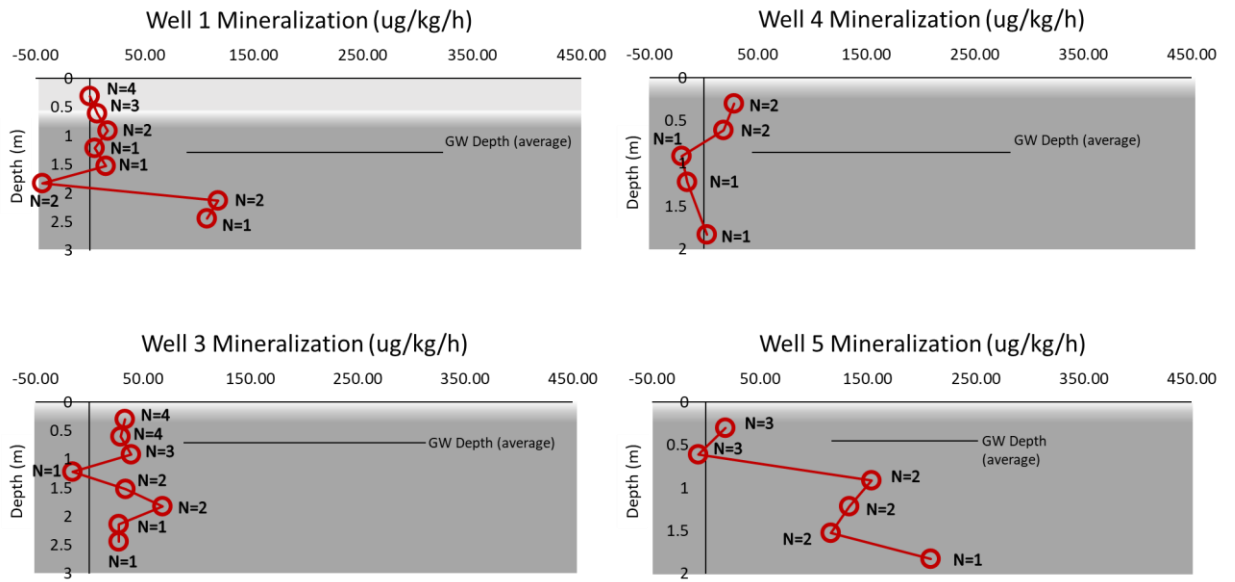


Figure 4.17: Scatterplots illustrating average nitrification measurements taken from each field locality plotted by depth. In the above illustrations, the maximum water elevation is designated by the uppermost extent of the dark grey area and soils that were never below the water table are represented by the light grey area while the average groundwater depth is denoted on each figure with text.

Well 5, similar to the majority of other wells observed did show increased rates of nitrification in samples collected from depth below the average water level, however well 5 had nitrification measured at rates much higher than all other wells observed ranging from approximately 0 µg/kg/h – 200 µg/kg/h (Figure 4.17). Above the average water table, nitrification was low however it was found to increase immediately below this point. Nitrification rates were found to increase with depth

below the average elevation of the groundwater table (Figure 4.17). The largest exception to this can be found from the observations made at well 4. At well 4, unlike other wells, nitrification rates were measured to be greater in the shallow surface soil. These rates would decrease as the depth of the sample approached the average groundwater table, but then did not increase below the water table as has been observed in many other sample sets and wells at the site (Figure 4.17).

Mineralization rates with soil depth matched the general trends in nitrification (Figure 4.18). Mineralization for wells 1, 3 and 4 typically ranged between 0  $\mu\text{g}/\text{kg}/\text{h}$  – 50  $\mu\text{g}/\text{kg}/\text{h}$  occasionally dropping into low negative values (indicating N immobilization/consumption) at depths below 1 meter (Figure 4.18). Well 5 on the other hand exhibited far greater rates of mineralization than other wells, with a profile similar to that of the nitrification depth profile for well 5 (Figure 4.18). Well 5 was the only well to exhibit mineralization results at a rate close to 250  $\mu\text{g}/\text{kg}/\text{h}$  at any depth. Other than those measured for well 5, mineralization rates were generally lower than nitrification and denitrification rates.



4.18: Scatterplots illustrating average mineralization measurements taken from each field locality plotted by depth. In the above illustrations, the maximum water elevation is designated by the uppermost extent of the dark grey area and soils that were never below the water table are represented by the light grey area while the average groundwater depth is denoted on each figure with text.

#### 4.7 Macrocosm experiment: Anoxic and oxic soil treatments and changes in soil N species

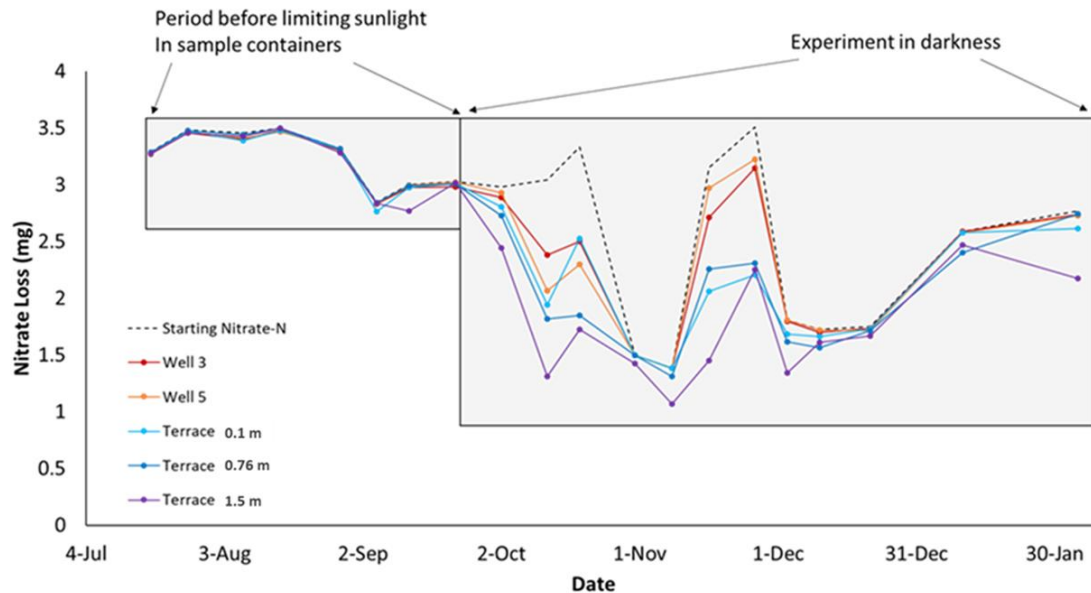


Figure 4.19: The starting (dashed line) and ending nitrate-N concentrations for various anoxic treatments. Each iteration lasted for approximately 10 days before the iteration was ended and the next iteration was started.

Early (Iterations 1-8) portions of the anoxic macrocosm incubation experiment which were conducted in open/sunlight (without cover) indicated near complete consumption of nitrate-N in soil solution (Figure 4.19). This suggested nitrate-N in soil solution was being consumed likely by photosynthetic algae. Moving forward (since iteration 9 beginning in October), the experiment was performed in darkness (treatments covered with a tarp) to better simulate buried soil conditions not exposed to sunlight. After performing 12 iterations of the anoxic incubations in darkness, it was found that 50% to 100% of the nitrate-N in our sample containers was consumed over the course of

each experiment iteration (Figure 4.19). If the dark portion of the experiment is considered, wide variation in nitrate-N consumption for the treatments can be seen as well as elevated N losses for the surficial soils' samples from well locations 3 and 5.

For oxic treatments, nitrate-N concentrations (ranging from 1.15 mg/L – 32.3 mg/L) were measured in all treatments throughout the course of the experiment suggesting nitrification and leaching of nitrate-N from the soils. The mass of nitrate-N released is presented in Figure 4.20. Generally, soil samples collected from shallower depths (W3, W5 and Terrace 0.1 m) yielded higher concentrations of nitrate-N compared to soil samples from greater depths (Terrace 0.76 m and Terrace 1.5 m).

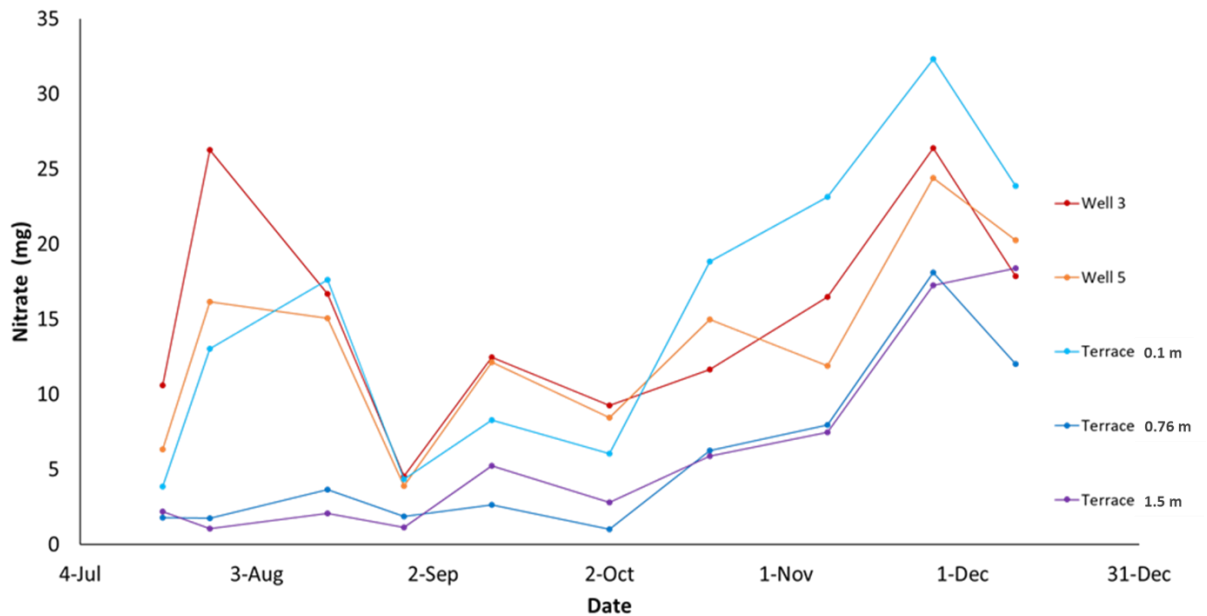


Figure 4.20: Nitrate-N concentrations in soil solution recorded for the oxic treatment. Each line represents the concentration of nitrate-N recorded from the DI water passed through each sample container after each experiment iteration

When pre-incubation and post-incubation values of %N and  $\delta^{15}\text{N}$  for the soils are compared a consistent increasing or decreasing trend is not observed (Figure 4.21). However, for a majority of the soil samples (terrace at 1.5 m being the exception),  $\delta^{15}\text{N}$  appears to have increased or enriched in both the oxic and anoxic samples since the beginning of the macrocosm experiment (Figure 4.21). The greatest positive shift in  $\delta^{15}\text{N}$ , however, was typically for the anoxic incubation, particularly wells 3 and 5 (Figure 4.21).

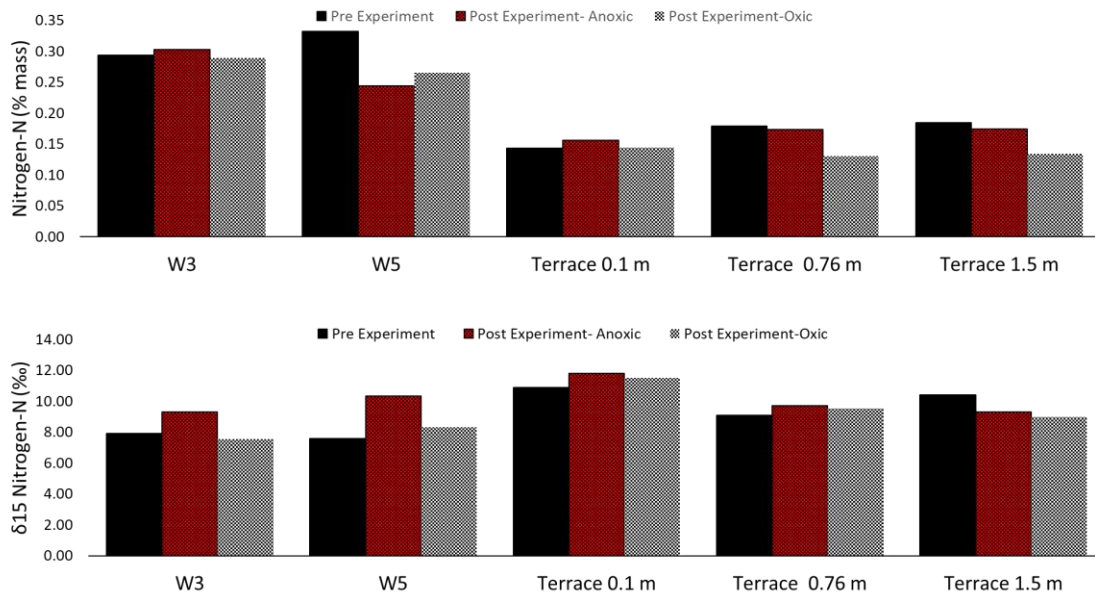


Figure 4.21: Percent N and  $\delta^{15}\text{N}$  for anoxic and oxic soil treatments. From this it can be seen that a slight enrichment of  $\delta^{15}\text{N}$  can be observed for most samples between the anoxic and pre-experiment samples observed.

## Chapter 5

### DISCUSSION

The results presented in the previous chapter provided important insights into how N process rates and concentrations varied in time and space following milldam removal and subsequent dewatering of riparian soils. These results are discussed and evaluated below in light of the key questions and primary hypotheses (Figure 5.1). The key questions were: (1) How do nitrate-N concentrations in riparian groundwater change following dam removal? (2) How do denitrification and nitrification rates in riparian soils change with time following dam removal and associated drop in groundwater elevations? (3) Does nitrate-N released from nitrification in riparian soils exceed that consumed/removed by denitrification? (4) How do riparian concentrations of Nitrate-N in groundwater reflect the soil drainage above the water table at a site with a removed milldam.

Question 1: How do nitrate-N concentrations in riparian groundwater change following dam removal?

One of the principal questions we set out to answer with this research was how nitrate-N concentrations in groundwater responded to the removal of a milldam and the resultant drop on local groundwater level in the riparian corridor. We expected to observe increasing concentrations of nitrate-N in groundwater following the Krady milldam removal, as the newly oxidized shallow riparian terrace experienced an oxic

regime shift and began to actively nitrify. This concept is illustrated in greater detail in Figure 5.1.

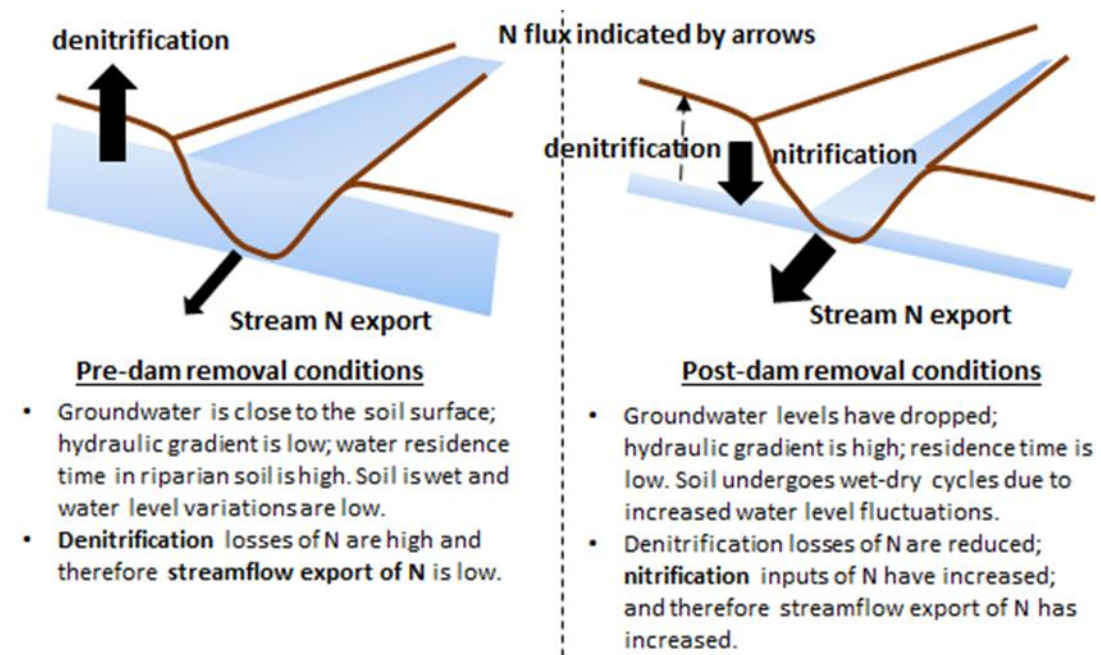


Figure 5.1: Conceptual model/schematic illustrating the primary hypothesis of how groundwater level changes following dam removal affect N transformations and potential stream export of nitrogen.

We hypothesized that as the oxic riparian soil drained following dam removal, rates of nitrification in this soil profile would increase and lead to elevated concentrations of nitrate-N in the local groundwater. This nitrifying behavior has been observed to dominate shallow, oxic, riparian soils such as those at the Krady milldam and can ultimately lead to the leaching of nitrate-N into the surrounding soil and water profile

(Burt and Pinay, 2005, Cirimo and McDonnell 1998, Hefting et al. 2004, Weitzman et al. 2017).

Although we expected to observe increased levels of nitrate-N in riparian groundwater, we were unable to observe any increasing long-term trends following the removal of the Krady milldam in July 2018. It is important to note however that groundwater sampling began four months after the removal of the Krady milldam and precedent groundwater conditions were not recorded for comparison with this data set. For all groundwater wells observed at the Krady milldam site, no long-term increase in nitrate-N was observed. Instead, nitrate-N remained low for all wells in the 0 mg/L – 3 mg/L range.

The results of our DEA surveys and shallow soil lysimeters have shown us that nitrification is very likely to be occurring in these shallow soils as is evident in the considerable concentrations of nitrate-N recorded during our lysimeter sampling campaign which measured concentrations of nitrate-N in the shallow soil much higher than those detected at greater depths (Table 4.2). Seeing as nitrification is likely occurring in these shallow soils, then why is there no evidence of any increase in nitrate-N observed at any of the observation wells installed at the field site and why did the riparian system behave in such a way that contradicts our initial hypothesis?

The excess nitrate-N generated from the drained riparian profile is likely being drained through the riparian zone to deeper depths where the denitrification process can efficiently mitigate the influx. As can be observed from the results of our DEA and nitrification incubations, the rate of denitrification measured in these legacy

sediment terraces typically exceeded the rates of nitrification recorded in the shallow subsurface (Figure. 4.13, Figure 4.16). For this reason, it is likely that the nitrate-N being produced in the oxic riparian zone is being quickly and efficiently mitigated at deeper anoxic regimes in the riparian profile. Furthermore, due to the nature of milldam legacy sediment deposits and their predominance in the study region, buried organic rich soil horizons may be affecting denitrification dynamics observed at the study site. It has been documented that the presence of buried organic rich layers, such as buried milldam deposits or leaf litter mats, can play a significant role in providing a source of labile organic carbon to a riparian system and thus increasing a system's ability to denitrify (Appling et al. 2014, Gurwick et al. 2008, b, Hill 2011).

In the case of groundwater wells 3 and 5, another process may be occurring which could have the effect of reducing the concentration of available nitrate-N in the riparian zone, although unlike with denitrification the process of dissimilatory nitrate reduction to ammonium (DNRA) does not have the effect of removing nitrate-N from the system but instead converts it into another form of inorganic nitrogen, ammonium. In the case of observation wells 3 and 5 the levels of ammonium measured in the groundwater are elevated over those measured in other observation wells (Table 4.2, Figure 4.5). Until recently, elevated rates of ammonium in anoxic groundwater were typically associated with the inhibition of ammonium consumption and the nitrification process in anoxic regimes (Hefting et al. 2004, Hill and Duval 2009). With that said many recent studies have shown that the process of DNRA may in fact be responsible for elevated accumulation of ammonium in anoxic regimes such as the

one observed at the Krady milldam site (Burgin and Hamilton 2007, McPhillips et al. 2015, Pandey et al. 2020, Rutting et al. 2011, Sgouridis et al. 2011). If the process of DNRA is in fact occurring at the field site it could in part account for the rapid consumption of nitrate-N produced in oxic soil regimes, however on a broader landscape scale it is most likely that a combination of accelerated rates of denitrification, assimilation and localized instances of DNRA are responsible the minimal long-term accumulation of groundwater nitrate-N which we observed at the field site.

*Question 2: How do denitrification and nitrification rates in riparian soils change with time following dam removal and associated drop in groundwater elevations?*

In this research we were expecting to observe a gradual shift in the denitrifying and nitrifying ability of the riparian zone with time following the dam removal. Specifically, we expected to observe the denitrifying potential of riparian soils be slowly diminished while also observing the nitrifying ability of shallow riparian soils to gradually increase following the dam removal. With that said, the results of our study show that no noticeable long-term increase or decrease in denitrification or nitrification potential occurred at our field site over the duration of study.

In order to address this question, the principal data used were the results of the DEA and nitrification incubation experiments. For all observation wells, our first suite of samples collected in April 2019 recorded denitrification potentials in the shallow soil far greater than were ever observed again with a maximum DEA potential of 1291

$\mu\text{g}/\text{kg}/\text{h}$  recorded for well 3 and  $664 \mu\text{g}/\text{kg}/\text{h}$  recorded for well 5. After that first initial observational period however, all denitrification potentials measured from all wells at the site measured to be far less hovering in the range of  $0 \mu\text{g}/\text{kg}/\text{h} - 325 \mu\text{g}/\text{kg}/\text{h}$  for shallow riparian soils. At first this could resemble a rapid decrease in denitrification potential following dam removal, however this disparity between high and low DEA measurements is far more likely the result of seasonal controls on temperature, moisture and organic carbon inputs to the riparian system.

Alternatively, when we compare the results of samples collected from well 3, each taken 1 year apart but all collected during the autumn season 11/2018, 08/2019, and 11/2020 respectively, we see very little difference in the rates of DEA recorded with only a slight measured decrease in DEA recorded between the 2018 -2019 observational period (Figure 4.15). For samples collected from well 1 however, no noticeable difference could be discerned between any seasonally similar duplicate samples. Furthermore, the results of the nitrification incubations performed very similar to the results of the DEA experiments which ultimately suggest that no long-term increase or decrease in nitrification or denitrification potential was observed at the study site over the duration of the study period.

Although our results have shown that the riparian zones efficiency at nitrifying or denitrifying has been largely unaffected there are several important caveats to consider. Although the riparian zones nitrate processing efficiency has remained largely unchanged, the effects of dam removal has exposed massive volumes of previously subaqueous legacy sediment material and made it subaerial. Although

nitrification rates themselves do not appear to have been galvanized in the shallow riparian zone, the sheer volume of added oxic riparian material could still potentially generate a considerable amount of additional nitrate-N to the system. With that said, groundwater nitrate-N levels generally did not increase during the course of this study suggesting that any excess nitrification is being mitigated by high rates of denitrification at the site (Figure 4.4).

Another important consideration concerning the results of our monitoring is that our focused observational period at the study site lasted for less than 3 years. Little is yet known about how riparian microbial communities respond to groundwater regime shifts in and it is widely speculated that this process could take considerably longer than the amount of time that was available to study the site. A longer-term monitoring campaign at the Krady milldam site will be needed in order to conclusively determine whether or not denitrification and nitrification rates in riparian soils change significantly after a rapid drop in the local water table.

*Question 3: Does nitrate-N released from nitrification in riparian soils exceed that consumed/removed by denitrification?*

In this study we expected to observe higher rates of nitrification in the shallow riparian soils compared to what we measured. Furthermore, we expected that the rates and total accumulation of nitrate-N in the riparian soils would exceed the denitrification capacity of the soils. This, we hypothesized, would ultimately lead to an

accumulation of elevated nitrate-N concentrations in riparian groundwater. However, our measurements show that this did not occur.

The results of our DEA and nitrification incubations illustrate that, under idealized laboratory conditions, denitrification potential in shallow (0 m-1 m depth) riparian soil is greater than the nitrification potential at those same depths (Figure 4.17, Figure 4.18). Interestingly, when DEA and nitrification rates are compared at depths greater than 1 m below the surface, the potential rates of denitrification appear to be less than the corresponding potential rates of nitrification for those same soil profiles. At a glance, it would appear as if nitrate-N would be accumulating in the riparian zone for these reasons, however this was not observed to be true. The process of nitrification, although potentially more productive in deeper soils is severely inhibited by soil moisture and the presence of groundwater meaning that nitrification cannot function productively at the site at depths greater than 1.5 m – 2.0 m.

On a landscape scale, this means that the window of productivity in the riparian zone which would enable the nitrification process is much narrower than for the process of denitrification, which is occurring at a slower rate, but is enabled over a greater range of the riparian depth profile. Since no accumulation of nitrate-N has been observed in the groundwater at the Krady mill site, yet the process of nitrification is clearly occurring at rates as high as 400  $\mu\text{g}/\text{kg}/\text{h}$  in some lenses, it appears that any nitrate-N generated in this way is being efficiently denitrified by the much larger volume of denitrifying substrate found in the riparian zone.

*Question 4: How do riparian concentrations of Nitrate-N in groundwater reflect the soil drainage above the water table at a site with a removed milldam.*

We had initially hypothesized that a correlation would exist between the concentrations of nitrate-N observed in groundwater and the thickness of the drained riparian soils. In principle we hypothesized that a greater volume of actively nitrifying material would correlate to greater concentrations of nitrate-N detected in each corresponding groundwater well. Instead, no relationship could be established between the depth of the drained profile and groundwater nitrate-N concentrations at any well site. This is likely due to the fact that nitrate-N values recorded in groundwater were very low across all wells, a byproduct of rapid denitrification at depth as has been discussed previously. What we instead observed was a quasi-normal distribution comparing rates of nitrate-N in the shallow soil with the depth of the drained profile (Figure 4.10).

Across the field site, the average thickness of the drained profile was measured to range from 0.46 m to 1.69 m. Furthermore, the thickness of the drained profile was found to be greater at the site of the removed milldam and become thinner further upstream (Figure 4.2). This is likely the result of the thickening of the legacy sediment terrace as it approaches the milldam, a byproduct of legacy sediment terrace deposition, as has been widely documented in the literature (Merritts et al 2011, Walter and Merritts 2008). For all wells observed, the range of minimum and maximum drained profile thicknesses recorded for each well ranged between -0.37 m and 2.06 m. Because each well had a range of depth for the drained profile recorded to

be similar to each other, this is evidence that no groundwater well experienced significantly higher or lower amounts of groundwater flashiness; a factor which is known in the literature as having the potential to galvanize nitrification and or denitrification (Bernard-Jannin et al. 2017, Guo et al. 2014, Peralta et al. 2013, Tomasek et al. 2018, Ye et al. 2017). Since all wells appear to have experienced the same environmental controls on water level and experienced similar stream stage fluctuations it is difficult to compare between them in order to determine if the effects of stream stage flashiness could have resulted in increased denitrification at any particular well. It has been proposed that the nitrogen-N sourcing effects of a drained oxic riparian soil could be offset by the potential increased nitrate-N mitigating behavior of drying/wetting cycles of groundwater elevation in regimes such as this (Gu et al. 2012, Graham et al. 2019, Shi et al. 2019, Ye et al. 2017). With that said, it is uncertain whether or not the apparent nitrate-N mitigating behaviors of this riparian corridor is the result of high rates of denitrification of deep riparian soils or the product of the newly developed wet/dry cycling that the riparian soil could be experiencing. More long-term studies will be necessary in order to discern these particular nuances relating to soil drainage and the potential that these drained profiles have to experience wet/dry cycling.

*Question 5: What are the implications for management and water quality*

With the growing national focus on mitigating nutrient pollution in rivers and streams, the importance of the riparian zone as a tool to accomplish water quality targets has

never been more important here in the United States or across the world (Birgand et al. 2007, Cole et al. 2020, Pinay et al. 2019, Riis et al. 2020). For example, as a testament to the importance of riparian zones as a management tool for water quality the Chesapeake Bay Program has set an annual goal to plant 900 miles of riparian buffers every year as well as established a final goal to develop 14,400 miles of riparian buffer by the year 2025 (Chesapeake Bay Program 2016). The entire process requiring substantial investments through federal, state and local funding sources estimated at hundreds of millions of dollars or greater (Alliance for the Bay 2015). With such considerable investments of money and labor, it is crucially important that riparian development projects are targeted with as much knowledge and understanding as possible to prevent any practices (such as dam removals) which may undercut the effectiveness of riparian buffers. The results of this research have shown that the riparian zones nitrate mitigating potential was not negatively affected in the short term as a consequence of dam removal as was previously hypothesized. Although longer term studies are still needed to understand how dam removals may affect riparian zones, these results show that dam removals in legacy sediment impacted stream corridors did not cause the conversion of the riparian zone into a source of nitrate pollution rather than a sink. This is positive news considering the increasing number of dam removals being implemented in the mid-Atlantic region for fish passage and public safety while also considering the tremendous efforts that are currently being made to meet nitrate-N total maximum daily load (TMDL) reductions within the region.

Apart from these broad implications, there is a more subtle implication that we can pull from this project, and that is the significance of dissimilatory nitrate reduction to

ammonium (DNRA). It has been widely suggested that DNRA could be a major driver of accumulating concentrations of ammonium in anoxic soils, like those observed at observation wells 5 and 3 at the Krady milldam study site (Burgin and Hamilton 2007, McPhillips et al. 2015, Pandey et al. 2020, Rutting et al. 2011, Sgouridis et al. 2011). Furthermore, the process of DNRA is encouraged in localities with high concentrations of dissolved organic carbon (DOC) and low concentrations of nitrate-N (Pandey et al. 2020, Rutting et al. 2011, Sgouridis et al. 2011, Wang et al. 2020). Some evidence has also been found to suggest that the presence of fine soil particles (clays, silts, loess, etc.) may have the potential to further promote DNRA by acting as barriers to flow within the soil profile ultimately contributing towards an optimally reducing environment (Chen et al. 2015, Sgouridis et al. 2011). The combination of these parameters as well as our observations of regularly high concentrations of ammonium found in the groundwater at the study site illustrate to us that DNRA may possibly be playing a more significant role than previously believed or accounted for. With this said, more research, evidence and monitoring of this site will need to be conducted in order determine with any certainty if DNRA is occurring, or if instead these elevated concentrations of ammonium-N are the product of elevated rates of mineralization at depth in the legacy sediment profile. The importance of this from a policy perspective is that unlike denitrification, the process of DNRA does not remove nitrate-N from the system but instead converts it into a less mobile form of inorganic nitrogen which has the potential to be remobilized in the future. In order to meet nitrogen reduction targets and TMDLs in the Chesapeake Bay watershed, it would be optimal to select sites which encourage active denitrification as opposed to DNRA. Further research will need to be done in order to fully understand the scope of DNRA in

riparian zones, whether or not it has played a role at the Krady mill site, its long-term consequences, and its ability to release stored inorganic nitrogen. With that said long-term monitoring of future riparian developments should not fail to pay attention to this subtle nitrogen cycling process.

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## Chapter 6

### CONCLUSIONS AND RECOMMENDATIONS

To our knowledge, this is the first study that has investigated the effects of dam removal on riparian N processing. To date, most dam removal studies have primarily focused on changes in stream geomorphology and hydrology, erosion and transport of sediment and sediment-bound nutrients, and impacts on aquatic habitat. Understanding how dam removals and associated dewatering could impact riparian N processing is critical given that riparian zones are important management practice for nonpoint source pollution control. The key conclusions that can be derived from this study were as follows:

1. Nitrate-N in riparian groundwater did not show any increase in concentrations following the removal of the Krady milldam or the shifting of the surficial riparian soil regime from an anoxic to oxic environment.
2. There was no short-term shift in denitrification and/or nitrification potentials in soils from the riparian zone following dam removal and the shift in the riparian zones to a more oxic state.
3. Although nitrification is likely occurring in the newly oxidized shallow riparian soils, excess nitrate-N has not accumulated to the point where it can surpass the ability of the riparian soils to mitigate the nitrate-N through denitrification.

While observations from this study were limited to 2 years following the removal of the Krady milldam, no increase or decrease in the concentration of nitrogen-N was found in riparian groundwater following dam removal. From this it can be concluded that concerns of a dam removal causing the riparian zone to accumulate nitrate-N and function as a nitrogen source are unlikely to occur, particularly within a 2-year time frame since dam removal. This suggests that riparian ecosystems and their functionality may be resilient against the changes associated with milldam removals. It should be noted though that the Krady dam was a small low-head milldam (1.5 m tall). More research is needed to investigate and understand if the results observed in this study extend to taller milldams.

Furthermore, this project would have greatly benefited from a longer-term observational period, as well as increased monitoring during the pre-dam removal conditions. Future studies which attempt to emulate this approach to monitoring a dam removal would do well to begin monitoring at the site before the removal of the milldam as well as utilize higher frequency automated and in-situ sampling procedures in order to capture changes which occur at the site at a greater temporal resolution.

This study also did not reveal any significant changes in stream water N following dam removal. Nitrate-N concentrations in stream water were however greater than those measured for groundwater and were attributed to the high N loadings in this predominantly agricultural watershed (inputs from cropland fertilizer and animal waste). It is likely that in developed watersheds, the effects of a single dam removal on stream water N may not be very apparent and could be masked by elevated

N loadings and concentrations from many agricultural and urban sources throughout the watershed.